First Investigation of Non-Classical Dihydrogen Bonding between an Early Transition-Metal Hydride and Alcohols: IR, NMR, and DFT Approach

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Abstract: The interaction of [$NbCp_2H_3$] with fluorinated alcohols to give dihydrogen-bonded complexes was studied by a combination of IR, NMR and DFT methods. IR spectra were examined in the range from 200–295 K, affording a clear picture of dihydrogen-bond formation when [$NbCp_2H_3$]/HOR_f mixtures (HOR_f = hexafluoroisopropanol (HFIP) or perfluoro-*tert*-butanol (PFTB)) were quickly cooled to 200 K. Through examination of the OH region, the dihydrogen-bond energetics were determined to be 4.5 ± 0.3 kcal mol^{-1} for TFE (TFE = trifluoroethanol) and 5.7 ± 0.3 kcal mol^{-1} for HFIP. ^1H NMR studies of solutions of [$NbCp_2H_2^BH^A$] and HFIP in [D_8]toluene revealed high-field shifts of the hydrides H^A and H^B, characteristic of dihydrogen-bond formation, upon addition of alcohol. The magnitude of signal shifts and T_1 relaxation time measurements show preferential coordination of the alcohol to the central hydride H^A, but are also consistent with a bifurcated character of the dihydrogen bonding. Estimations of hydride–proton distances based on T_1 data are in good accord with the results of DFT calculations. DFT calculations for the interaction of [$NbCp_2H_3$] with a series of non-fluorinated (MeOH, CH_3COOH) and fluorinated (CF_3OH, TFE, HFIP, PFTB and CF_3COOH) proton donors of different strengths showed dihydrogen-bond formation, with binding energies ranging from -5.7 to -12.3 kcal mol^{-1}, depending on the proton donor strength. Coordination of proton donors occurs both to the central and to the lateral hydrides of [$NbCp_2H_3$], the former interaction being of bifurcated type and energetically slightly more favourable. In the case of the strong acid H_3O^+, the proton transfer occurs without any barrier, and no dihydrogen-bonded intermediates are found. Proton transfer to [$NbCp_2H_3$] gives bis(dihydrogen) [$NbCp_2(\eta^2\text{-}H_2)_2$]$^+$ and dihydride(dihydrogen) complexes [$NbCp_2(H)_2(\eta^2\text{-}H_2)$]$^+$ (with lateral hydrides and central dihydrogen), the former product being slightly more stable. When two molecules of TFA were included in the calculations, in addition to the dihydrogen-bonded adduct, an ionic pair formed by the cationic bis(dihydrogen) complex [$NbCp_2(\eta^2\text{-}H_2)_2$]$^+$ and the homoconjugated anion pair ($CF_3COO\cdots H\cdots OOCCF_3$)$^-$ was found as a minimum. It is very likely that these ionic pairs may be intermediates in the H/D exchange between the hydride ligands and the OD group observed with the more acidic alcohols in the NMR studies.

Keywords: ab initio calculations · hydrides · hydrogen bonds · IR spectroscopy · NMR spectroscopy

Introduction

The basicity of transition-metal hydrides is a well documented phenomenon, manifesting in, for example, various hydride-transfer processes and in hydride-bridged structure formation.[1] One major recent achievement in this area was the discovery of non-classical hydrogen bonds between transition-metal hydrides and proton donors, also called a "dihy-

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drogen bond".[2–5] Having small interaction enthalpy, hydrogen bonding usually results only in small perturbations of the electronic structures of participating molecules. Nevertheless, it modifies their properties, giving the opportunity to fine-tune the properties of an organometallic complex.[6] For example, the alteration of quantum exchange couplings[7] in polyhydride compounds upon dihydrogen-bond formation has been observed.[8] All these studies have been performed for metals from the late and middle parts of the transition series, but no example for early transition-metal complexes has been reported. This is surprising in view of the fact that in a comparable ligand environment, the more electropositive early transition metal renders the hydride more basic and, hence, a stronger dihydrogen bond would be expected.

Abstract in Catalan: *La interacció del [$NbCp_2H_3$] amb alcohols fluorats per donar complexos amb enllaços de dihidrogen ha estat estudiada combinant els mètodes IR, RMN i DFT. S'ha examinat l'espectre IR en l'interval 200–295 K. S'hi observen senyals clars de formació d'enllaç de dihidrogen quan les barreges [$NbCp_2H_3$]/HOR_f (HOR_f = hexafluoroisopropanol (HFIP) o perfluoro-tert-butanol (PFTB)) són ràpidament refredades fins a 200 K. A partir de ĺestudi de la regió OH s'ha determinat que les energies de l'enllaç de dihidrogen són 4.5 ± 0.3 kcal mol^{-1} per al TFE (TFE = trifluoroetanol) i 5.7 ± 0.3 kcal mol^{-1} per al HFIP. Els estudis mitjançant mètodes ^1H RMN de solucions de [$NbCp_2H^B_2H^A$] i HFIP en d_8-tolué revelen uns desplaçaments cap a camp alt dels hidrurs H^A i H^B després de l'addició de l'alcohol, signe caracteristic de la formació d'enllaç d'hidrogen. La magnitud dels desplaçaments químics i dels temps de relaxació T_1 mostra una preferència per la coordinació de l'alcohol a l'hidrur central H^A, que és consistent amb un caràcter bifurcat de l'enllaç de dihidrogen. Les estimacions de les distàncies hidrur–protó a partir de dades T_1 estan en concordança amb els resultats dels càlculs DFT. Aquests càlculs mostren la formació de l'enllaç de dihidrogen entre el [$NbCp_2H_3$] i series de donadors de protons de diferent força, no fluorats (MeOH, CH_3COOH) i fluorats (CF_3OH, TFE, HFIP, PFTB i CF_3COOH). Aquests enllaços tenen energies entre 5.7 i 12.3 kcal mol^{-1}, segons la força del donador. El donador de protons es pot coordinar tant a l'hidrur central del [$NbCp_2H_3$] com als laterals, la interacció sobre l'hidrogen central és de tipus bifurcat i és energèticament una mica més favorable que la lateral. En el cas d'un acid fort H_3O^+, la tranferència protònica es dóna sense barrera, i no es troben intermedis amb enllaços dihidrogen. De la transferència protònica al [$NbCp_2H_3$] en resulten els complexos bis(dihidrogen) [$NbCp_2(\eta^2\text{-}H_2)_2$]$^+$ i dihidrur(dihidrogen) [$NbCp_2(H)_2(\eta^2\text{-}H_2)$]$^+$ (amb els hidrurs laterals i el dihidrogen central). Dels dos productes, el bis(dihidrogen) és una mica més estable que el dihidrur(dihidrogen). Quan s'inclouen dues molècules de TFA en els càlculs, a més a més de l'adducte amb enllaç dihidrogen es troba el mínim parell iònic, format pel complex catiònic bis(dihidrogen) [$NbCp_2(\eta^2\text{-}H_2)_2$]$^+$ i el parell aniònic homoconjugat ($CF_3COO\cdots H\cdots OOCCF_3$)$^-$. Aquests parells iònics poden ser intermedis en l'intercanvi H/D entre els lligands hidrur i el grup OD observat en els estudis de RMN amb els alcohols més acids.*

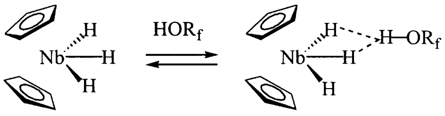
Some of us have previously showed that basic metal–hydride bonds of 18-electron Group 5 metallocene trihydrides undergo direct reactions with Group 14 and 15 Lewis acids.[9] Analogous coordination of Group 13 Lewis acids to the same system was studied by quantum mechanical calculations.[10] [$NbCp_2H_3$][11] appears to be a perfect candidate with which to study the phenomenon of dihydrogen bonding in the early transition-metal hydrides, because this compound has basic hydrides, but no coordination vacancy or lone pairs on the metal or any other site of the complex, thus providing a very clear "picture" of the hydride and proton interactions. In addition, the structural and spectroscopic properties of this compound have previously been thoroughly studied experimentally by X-ray[12] and NMR relaxation techniques,[13] and computationally by DFT calculations.[14]

Here we report a comprehensive investigation of the interaction of [$NbCp_2H_3$] with proton donors by a combination of IR, NMR and DFT methods.

Results and Discussion

IR studies: Infrared spectroscopy has proved itself to be the most informative and useful method by which to investigate hydrogen-bond phenomena in solutions and solids.[15] Study of the M–H stretching region provides identification and assignment of the dihydrogen-bond formation, whereas the OH stretching region in the IR spectrum provides strong evidence of hydrogen bonding and allows one to obtain quantitative information about the energetics of interaction. Given our previous experience in this field,[2b,d,5] we set out to study the hydrogen bonding of [$NbCp_2H_3$] with several proton donors of different strengths: perfluoro-*tert*-butanol (PFTB), hexafluoroisopropanol (HFIP) and trifluoroethanol (TFE).

IR spectra of the [$NbCp_2H_3$]/ROH systems in the ν_{OH} region show a typical picture of hydrogen-bond formation (Scheme 1), exhibited by proton donors in the presence of hydrides. We carried out the IR measurements at low ROH concentrations to avoid self association at room temperature. The intensities of free ν_{OH} bands decrease and new, broad, low-frequency bands of the bonded group (ν_{OH}^{bonded}) appear. The ν_{OH} band shift ($\Delta\nu_{OH} = \nu_{OH}^{free} - \nu_{OH}^{bonded}$) depends on the strength of proton donors (Table 1).



HOR_f = fluorinated alcohols

Scheme 1. Hydrogen-bond formation in [$NbCp_2H_3$]/ROH systems.

Table 1. IR spectral characteristics of the hydrogen-bonded adducts of $[NbCp_2H_3]$ (**1**) with alcohols.

	$\nu_{OH\,free}$ $[cm^{-1}]$	$\nu_{OH\,bonded}$ $[cm^{-1}]$	$\Delta\nu_{OH}$ $[cm^{-1}]$	$-\Delta H$ $[kcal\,mol^{-1}]$	$E_j^{[a]}$
TFE	3628	3380	248	4.6	0.91
HFIP	3621 3585	3270	333[b]	5.7	0.95

[a] The basicity factor as defined in Equation (2). [b] Medium value of two $\nu_{OH\,free}$ bands was used for $\Delta\nu_{OH}$ calculation.

It is known that a new low-frequency ligand stretching vibration band (such as ν_{CO}, ν_{NO}, $\nu_{M\text{–}Cl}$, $\nu_{M\text{–}H}$) indicates that this ligand is a proton-accepting site. The bands of the ligands not participating in the hydrogen bonding shift upwards.[2d] IR study of $[NbCp_2H_3]$ is straightforward in that only hydride ligands can be the site of proton attack. Two types of nonequivalent hydrides—one central (H^A) and two lateral (H^B)—in the bisecting plane of the niobocene moiety are present in the molecule of $[NbCp_2H_3]$. Since the symmetry of the molecule is C_{2v}, three fundamental M–H stretching vibrations ($2a_1+b_1$) should, in principle, be observed in the IR spectra.[16] Being very close to each other,[16] however, in methylcyclohexane they give only an average band ν_{NbH} of medium intensity at 1724 cm^{-1}. A decrease in the temperature leads to a steady decrease in the intensity of this band, due to a fall in solubility.

Abstract in Russian: Взаимодействие $[NbCp_2H_3]$ со фторированными спиртами, приводящее к образованию комплексов с «диводородной» связью, было изучено методами ИК, ЯМР и ТФП (DFT). ИК спектры, измеренные в диапазоне 200–295 К, четко показывают образование диводородной связи в случае быстро охлажденной смеси $[NbCp_2H_3]/HOR_f$ (HOR_f = гексафтор-2-пропанол (HFIP) или перфтор-трет-бутанол (PFTB)). Энтальпии образования диводородной связи (ΔH) определены по области валентных колебаний OH-групп и составляют –4.5±0.3 ккал моль$^{-1}$ для TFE (TFE= трифторэтанол) и –5.7±0.3 ккал моль$^{-1}$ для HFIP. ^1H ЯМР исследования растворов $[NbCp_2H^B{}_2H^A]$ и HFIP в толуоле-d_8 показывают смещение H^A и H^B гидридных сигналов в сильное поле при добавлении спирта, что является характерной чертой образования диводородной связи. Относительная величина сдвига сигналов и измерение времен релаксации T_1 указывают на предпочтительную координацию спирта по центральному гидриду H^A, однако также согласуются и с бифуркатным характером диводородной связи. Оценка расстояния гидрид-протон, основанная на данных T_1, хорошо согласуется с результатами расчетов ТФП. Расчеты ТФП взаимодействия $[NbCp_2H_3]$ с серией нефторированных (MeOH, CH_3COOH) и фторированных (CF_3OH, TFE, HFIP, PFTB и CF_3COOH) протонодоноров различной силы показывают образование диводородной связи с энергией взаимодействия от –5.7 до –12.3 ккал моль$^{-1}$ в зависимости от силы протонодонора. Координация протонодоноров происходит как по центральному, так и по боковому гидридам $[NbCp_2H_3]$, причем первое взаимодействие является бифуркатным и энергетически немного более выгодным. В случае сильной кислоты H_3O^+ перенос протона происходит без барьера, и диводородно-связанные интермедиаты не образуются. Протонирование $[NbCp_2H_3]$ приводит к бис-диводородному $[NbCp_2(\eta^2\text{-}H_2)_2]^+$ и диводород-дигидридному комплексам $[NbCp_2(H)_2(\eta^2\text{-}H_2)]^+$ (с боковыми гидридами и молекулой диводорода в центральном положении), причем первый продукт немного более стабилен. Когда две молекулы CF_3COOH были включены в расчет, в дополнение к диводородно-связанному аддукту был найден минимум, принадлежащий ионной паре, образованной катионным бис-диводородным комплексом $[NbCp_2(\eta^2\text{-}H_2)_2]^+$ и гомосопряженным анионом $(CF_3COO\cdots H\cdots OOCCF_3)^-$. Такие ионные пары, весьма вероятно, могут быть интермедиатами H/D обмена между гидридными лигандами и OD-группой, который наблюдался в экмпериментах ЯМР с использованием более кислых спиртов.

Addition of HFIP and PFTB to a *saturated* solution of $[NbCp_2H_3]$ in methylcyclohexane at room temperature results in an approximately twofold decrease in the ν_{NbH} band intensity (Figure 1). The band broadens and its half-width ($\Delta\nu_{1/2MH}$) increases to 45 and 60 cm^{-1} in the presence of HFIP and PFTB, correspondingly (the initial $\Delta\nu_{1/2MH}$ is 32 cm^{-1}). The appearance of high- and low-frequency shoulders on the $\nu_{Nb\text{–}H}$ band (band broadening) indicates H···H complex formation. A steady decrease in the temperature to 200 K leads to a drastic decrease and broadening of the band. This trend is opposite to what would be expected on the basis of an equilibrium between the hydrogen-bonded and the free hydride, which should favour the formation of the complexed species at low temperature. The most likely cause of this trend is the precipitation of the initial hydride due to a drastic fall in solubility.

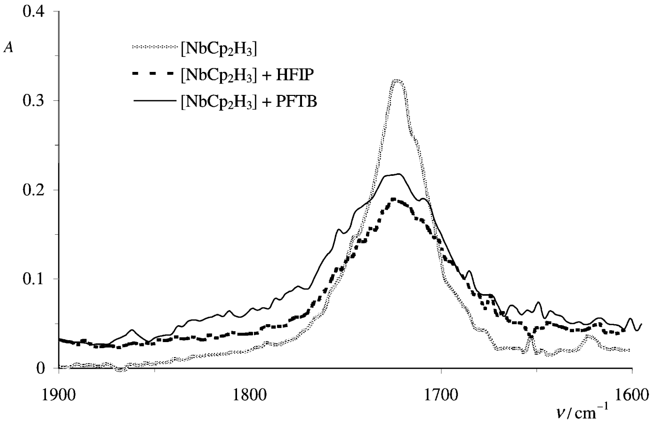


Figure 1. Room temperature IR spectra of $[NbCp_2H_3]$ (**1**) in the presence of HFIP and PFTB.

In contrast, rapid cooling of mixtures of $[NbCp_2H_3]$ with PFTB and HFIP in methylcyclohexane to 200 K results in a dramatically different picture. IR spectra recorded immediately after preparation of the mixtures show a sharp increase in the integral intensity and the formation of two new bands (Figure 2). The intensity of the ν_{NbH} band of the starting trihydride decreases in the presence of HFIP (c = 0.05 M) and practically disappears in the presence of PFTB (c = 0.05 M), while new, low- and high-frequency bands appear. The low-frequency shifted band ($\Delta\nu$ = –30–35 cm^{-1}) can be assigned to a ν_{NbH} stretching mode of the hydride ligand bonded to alcohol. The high-frequency bands at 1751–1746 cm^{-1} ($\Delta\nu$ = +22–27 cm^{-1}) are attributable to ν_{NbH} of the terminal NbH

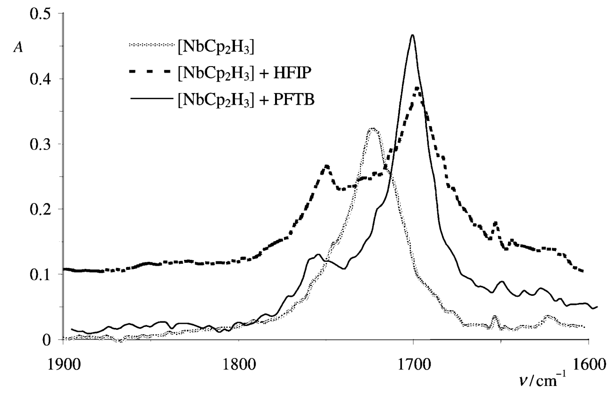


Figure 2. IR spectra of $[NbCp_2H_3]$ (**1**) in the presence of HFIP or PFTB at 200 K.

group of complexes with dihydrogen bonding. Comparison of the IR spectra of $[NbCp_2H_3]$ in the presence of HFIP and PFTB shows that the equilibrium between the dihydrogen-bonded complexes and starting trihydride shifts further to the right in the case of a stronger proton donor. IR spectra taken after rapid cooling to 230–270 K show formation of only one broad band of high intensity, while repeated recording of spectra from the same sample at any temperature between 200 and 270 K shows a steady decrease in this band. Further heating to room temperature restores the intensity of the band to the values obtained when the reactants are mixed at room temperature. These observations suggest that rapid cooling of the sample and immediate recording of the low-temperature IR spectra allow us to overcome the problem of the low solubility of $[NbCp_2H_3]$ at low temperatures and to show the shift of the equilibrium to the dihydrogen-bond formation on cooling.

Strength of the NbH···HO hydrogen bond: The hydrogen-bonding enthalpy ($-\Delta H^0$) of the NbH···HO bond was determined from the empirical correlation $-\Delta H^0$ versus $\Delta\nu_{OH}$ [Eq. (1)] proposed by Iogansen for organic systems[15a] and employed by some of us[2d,5] for dihydrogen bonds.

$$-\Delta H^0 = \frac{18\Delta\nu_{OH}}{\Delta\nu_{OH} + 720} \tag{1}$$

So far this has been used as a very simple and convenient method to determine the hydrogen-bond strength. Here it turned out to be the only method available, because we could not exactly determine the concentration of the trihydride $[NbCp_2H_3]$ due to its partial precipitation from the solution at low temperatures.

Calculations performed with Equation (1) showed that the dihydrogen bonds NbH···HOR in the $[NbCp_2H_3]$/HOR system are of medium strength, namely $-\Delta H^0 = 4.5 \pm 0.3\,\text{kcal}\,\text{mol}^{-1}$ for TFE and $5.7 \pm 0.3\,\text{kcal}\,\text{mol}^{-1}$ for HFIP. The E_j basicity factor[2d] value [Eq. (2)] of 0.93 shows that

$$E_j = \frac{\Delta H_{ij}}{\Delta H_{11} P_i} \tag{2}$$

this hydride is indeed quite basic and that its proton-accepting properties are comparable with those of hydride ligands in $[ReH\{CH_3C(CH_2PPh_2)_3\}(CO)_2]$ (0.97)[5f] and $[WH(CO)_2(NO)(PMe_3)_2]$ (0.91).[5a]

NMR studies: The formation of intermolecular dihydrogen bonds between transition-metal hydride complexes and Brønsted acids can be readily identified by ^1H NMR techniques.[17] It has been shown that dihydrogen bonding affects two NMR parameters: the hydride chemical shift and the T_1 relaxation time. Upon complexation with a proton donor the hydride signal shifts to high field, which is typical for a hydride occupying a bridging position, whereas the T_1 relaxation time diminishes because a proton in the vicinity of a hydride provides an additional source of relaxation.

^1H NMR and ^1H T_1 relaxation studies of dihydrogen bonding between $[NbCp_2H^AH^B_2]$ (**1**) and HFIP have been performed in $[D_8]$toluene. In full accord with previous results,[13] the variable-temperature ^1H NMR spectra of free **1** show that the chemical shifts of the hydride ligands are only slightly dependent on the temperature. Both hydride resonances undergo insignificant low-field shifts (H^A and H^B by 0.10 and 0.05 ppm, respectively) on cooling in the 295–230 K temperature region. Also in agreement with related studies,[13] the hydride ligands in **1** show ^1H $T_{1(min)}$ times of 0.109 and 0.133 s for the H^A (central) and H^B (lateral) protons, respectively (190 K, 400 MHz). In addition, the $T_{1(min)}$ time of the Cp protons is measured as 1.024 s. The addition of an equivalent of HFIP to the solution of **1** results in a high-field shift of the H^A hydride resonance from −2.38 to −3.67 ppm at 230 K. On cooling to 180 K this resonance appears at −4.03 ppm (Figure 3). The effect of the presence of HFIP on the chemical shift of H^B is less pronounced (Figure 3). Nevertheless, the H^B resonance also undergoes a high-field shift on addition of HFIP, from −3.40 to −3.81 ppm at 230 K. As a result, both signals overlap at about 210 K. An increase in the concentration of HFIP magnifies this trend and at a ratio of **1** to HFIP of 1:2 the overlap is already observed at 250 K. These data can be interpreted well in terms of the formation of dihydrogen bonds with the participation of both hydride ligands, with the pref-

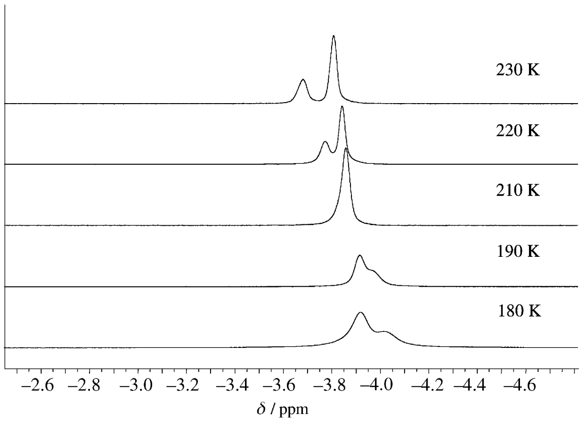


Figure 3. ^1H NMR spectra for the interaction of **1** with HFIP.

erential formation of a dihydrogen bond to the central ligand (H^A). These results are also consistent with a bifurcated character of this dihydrogen bonding (see DFT calculations). In support of the occurrence of dihydrogen bonding, we have measured the variable-temperature ^1H T_1 times from the solution containing an equivalent of HFIP. The main feature of the data collected is the fact that the T_1 time of the CH proton of the alcohol goes through a minimum (0.136 s) at 210 K, very close to the temperature of minimal relaxation times for all the resonances of [$NbCp_2H_3$] (200 K). Taking the small inertia moment of the free alcohol into account, such behaviour provides good evidence for intermolecular interactions between **1** and HFIP. Unfortunately, the T_1 times of the hydride ligands, measured in the presence of an equivalent of HFIP, show minimum values when the two hydride resonances overlap, whereas the addition of 5–10 equivalents of HFIP to **1** results in rapid decomposition into unidentified products, apparently because of complete proton transfer. The overlapped hydride signals show a ^1H $T_{1(min)}$ time of 0.106 s (200 K). Taking into account the twofold difference in the integral intensities of H^A and H^B, this relaxation time characterises the H^B resonance. In the absence of HFIP, the $T_{1(min)}(H^B)$ time was determined as 0.133 s. Thus HFIP causes a shortening of $T_{1(min)}(H^B)$, usually attributed to additional dipole–dipole interactions due to hydride–proton contacts.[17] This proton–hydride relaxation contribution is calculated as 1.91 s^{-1} (0.106^{-1}–0.133^{-1}) and translates into a $H^B \cdots HO$ distance of 1.92 Å by a standard treatment.[17] The overlap of resonances H^A and H^B does not provide a direct measurement of $T_{1(min)}(H^A)$. At higher temperatures (higher than the temperature of the recording of the minimal relaxation time by 20, 30 and 40 K), however, resonances H^A and H^B are observed separately, providing the relaxation measurements (Table 2). Comparison of these data with the T_1 times, collected in a solution of **1** in [D_8]toluene, shows that HFIP shortens the T_1 times of both hydride resonances. On the basis of the trend in Table 2 one can estimate $T_{1(min)}(H^A)$ as 0.086 s. In turn, the proton–hydride dipolar contribution is calculated as 2.46 s^{-1}, corresponding to a $H^A \cdots HO$ distance of 1.84 Å. The distance estimations are semiquantitative, because they are based on the assumption of a complete shift of the equilibrium towards the hydrogen-bonded complexes. In spite of this, the $H^A \cdots HO$ and $H^B \cdots HO$ distances correspond well to the results of DFT calculations, discussed in the next section.

Table 2. The ^1H T_1 relaxation times (in [D_8]toluene) of **1**, **1**/HFIP (1:1) and **1**/[D_1]HFIP (1:1), measured for ligands H^A and H^B at temperatures higher than the temperatures of observations of minimal times (min) by 10, 20, 30 and 40 K.

δT [K]	**1**		**1**/HFIP = 1:1		**1**/[D_1]HFIP = 1:1		
	$T_1(H^A)$	$T_1(H^B)$	$T_1(H^A)$	$T_1(H^B)$	$T_1(H^A)$	$T_1(H^A)$[b]	$T_1(H^B)$[c]
min	0.109	0.132	0.086[a]	0.106	0.108	[d]	0.142
10	0.116	0.146	[e]	0.120	0.147	0.182	0.211
20	0.167	0.221	0.125	0.167	0.190	0.239	0.291
30	0.253	0.345	0.149	0.222	0.272	0.311	0.401
40	0.367	0.500	0.221	0.333			

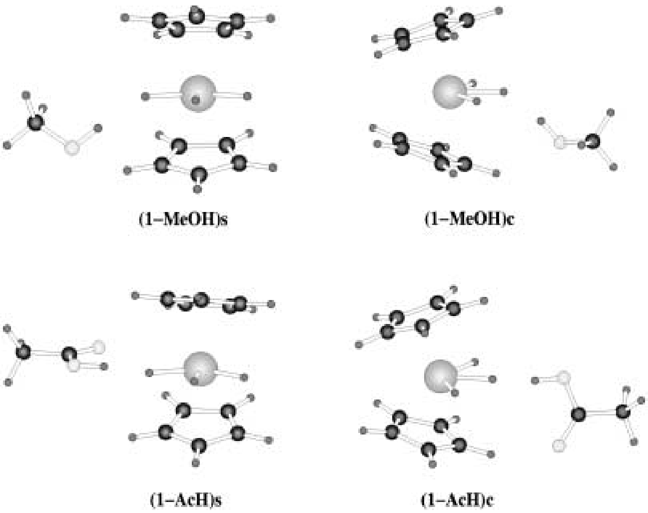
[a] Estimated value. [b] Data for isotopomer [$NbCp_2H^BD^BH^A$]. [c] Data for the composite resonance of the H^B ligands in the isotopic mixture. [d] The H^A signals of [$NbCp_2H^BH^BH^A$] and [$NbCp_2H^BD^BH^A$] overlap. [e] The signals of H^A and H^B overlap.

To verify the above conclusions experimentally, we attempted the $T_{1(min)}$ measurements for a Nb–H⋯DOR dihydrogen-bond complex. The low-temperature addition of an equivalent of [D_1]HFIP to a solution of **1** in toluene showed the expected high-field shifts of hydride resonances H^A and H^B with decreasing temperature. Unfortunately, the NMR spectra also revealed a very fast isotopic exchange between **1** and [D_1]HFIP, resulting in the formation of a mixture of isotopomers [$NbCp_2H_3$], [$NbCp_2D^BH^BH^A$] and [$NbCp_2H^BH^BD^A$]. In good agreement with the high-field isotope shifts,[13] the H^A ligands in [$NbCp_2H^B_2H^A$] and [$NbCp_2D^BH^BH^A$] give the resonances at −3.78 and −3.82 ppm with an integral intensity ratio of 3:1 at 240 K. Poorly resolved H^B signals of the isotopomers are observed at −3.86 ppm. It is evident that the H/D exchange reduces the probability of the formation of Nb–$H^A \cdots$DOR bonds in relation to Nb–$H^A \cdots$HOR complexes. Nevertheless, taking account of the 3:1 ratio described above, the probability of the Nb–$H^A \cdots$DOR formation is significantly higher. Table 2 provides data from the ^1H T_1 measurements for this isotopomeric mixture, leading to the following conclusions. Firstly, the T_1 times practically do not differ from those previously reported for the same isotopomeric mixture except in the absence of [D_1]HFIP.[13] According to reference [13] the increase in T_1 on going from [$NbCp_2H^BH^BH^A$] to the D isomers is explained in terms of reduction of H^A–H^B dipole–dipole interactions. Secondly, the $T_1(H^A)$ times in the presence of [D_1]HFIP are remarkably elongated with respect to those measured for **1**:HFIP. This effect clearly demonstrates the decrease in the hydride–proton dipole–dipole interactions in the Nb–$H^A \cdots$DOR pairs. Thirdly, the $T_{1(min)}(H^A)$ times in free **1** and in the Nb–$H^A \cdots$DOR complex are practically identical. This strongly supports the above estimation of the relaxation contribution due to the $H^A \cdots$HO contacts. Finally, it is very likely that this H/D exchange between the hydride ligands and OD group of the alcohol may proceed through the dihydrogen complexes found in the DFT calculations described below.

DFT study of the dihydrogen bonding

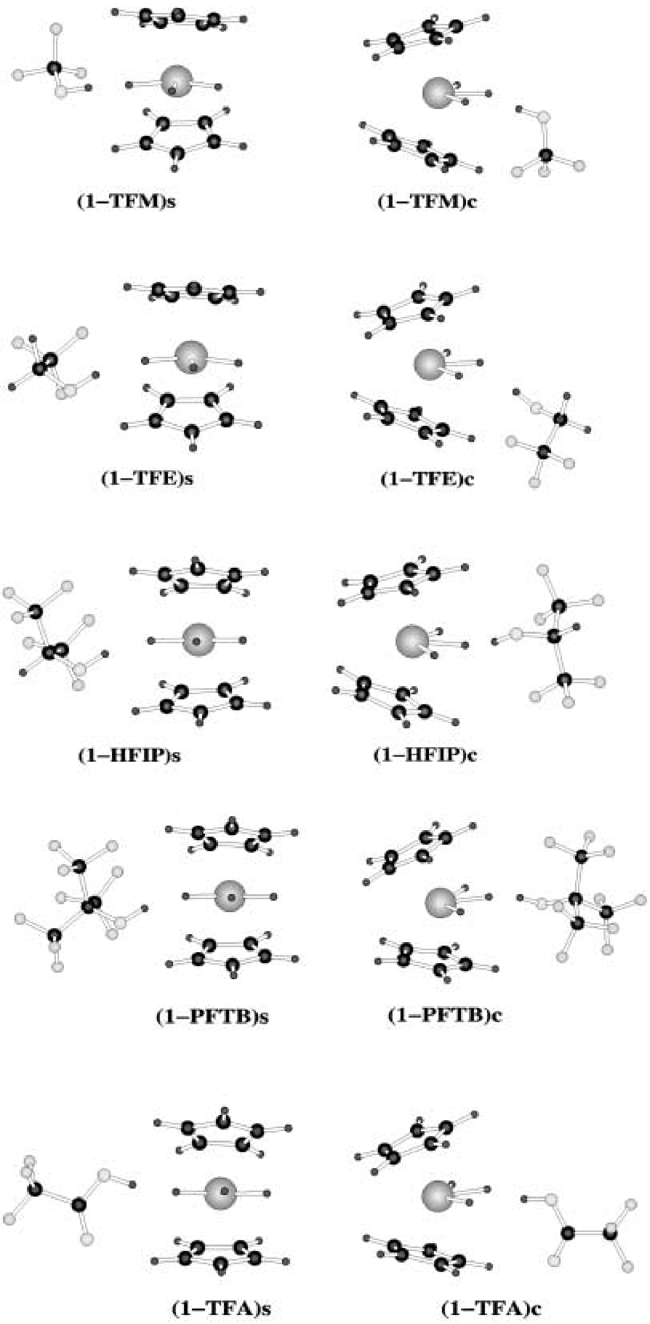
Structure and binding energy of the NbH⋯HOR complexes: The interaction of [$NbCp_2H_3$] (**1**) with a series of proton donors of weak and medium strengths [CH_3OH (MeOH), CH_3COOH (AcH), CF_3OH (TFM), CF_3CH_2OH (TFE), $(CF_3)_2HCOH$ (HFIP), $(CF_3)_3COH$ (PFTB) and CF_3COOH

(TFA)] was studied by DFT calculations. In all cases the formation of a dihydrogen-bonded adduct was observed. Because **1** has two basic sites, the central H^A and lateral H^B hydrides, two coordination isomers are possible and for each of the proton donors considered; both forms, labelled as **c** (central) and **s** (side), were found as true minima on the potential-energy surface. The optimised structures with the non-fluorinated proton donors are shown in Figure 4 and those with the fluorinated ones in Figure 5. The main structural parameters and the interaction energies are collected in Table 3. The formation of the dihydrogen bond is reflected in the lengthening of the Nb–H and O–H bond lengths from their values in the isolated compounds. The hydrogen-bond energies span a range between 5 and 12 kcal mol^{-1}. After correction of the basis set superposition error (BSSE) the adducts are still stable, with interaction energies between 3 and 8 kcal mol^{-1} (Table 3). These values compare well with the calculated values reported in the literature for this kind of interaction,[3,18] although it has been shown that theoretical values obtained in the gas phase overestimate the strength of the H···H interaction.[19] From the structural and energetic values the hydrogen bonds in this series of $[NbCp_2H_3]\cdot HOR$ adducts can be classified as moderate.[20]


(1–MeOH)s (1–MeOH)c

(1–AcH)s (1–AcH)c

Figure 4. Optimised structures for the lateral (**s**) and central (**c**) adducts of **1** with MeOH and AcH.


(1–TFM)s (1–TFM)c

(1–TFE)s (1–TFE)c

(1–HFIP)s (1–HFIP)c

(1–PFTB)s (1–PFTB)c

(1–TFA)s (1–TFA)c

Figure 5. Optimised structures for the lateral (**s**) and central (**c**) adducts of **1** with TFM, TFE, HFIP, PFTB and TFA.

In agreement with the experimentally obtained results, the formation of the central adduct to the hydride H^A is favoured in almost all the systems, although for a given proton donor the energy differences between adducts of the central (H^A) and lateral (H^B) hydrides are small (less than 1.5 kcal mol^{-1}). This behaviour can be attributed to the higher hydridic character of H^A. In $[NbCp_2H_3]$ the Nb–H^A bond is significantly longer (0.014 Å) than the two Nb–H^B bonds, suggesting less efficient electron donation in this site and thus a more hydridic character for H^A. However, a fast exchange of the ROH molecule between the A and B sites can be expected from the low energy difference found between the two isomers. At high concentrations of the acid both positions could be occupied. The magnitude of the H···H interaction, reflected both in the H···H distance and in the ΔE of interaction correlates with the proton donor strength. Although the trihydride–alcohol interaction is stronger in the central adducts, for a given proton donor the H···H distance is shorter in the lateral adduct than in the central one. This apparent contradiction is explained by the bifurcated nature of the central dihydrogen-bond complexes. The proton is further away from H^A in **c** than from H^B in **s**, but in **c** there is an additional short proton···H_B distance (see Table 3). As a result, the Nb–H_B bond length corresponding to the hydride H^B closest to the proton is slightly elongated. The (Nb)H-H-O and Nb-H-H(O) angles also confirm the bifurcated nature of these hydrogen bonds.

Table 3. Main geometrical parameters [distances in Å and angles in degrees] and binding energies ΔE [kcal mol^{-1}] of the lateral (**s**) and central (**c**) dihydrogen-bonded complexes **1**·HOR.

	Nb–H^A	Nb–H^{B}[a]	Nb–$H^{B'}$	H–OR[b]	H···HOR	(Nb)H-H-O	Nb-H-H(O)	ΔE[d]
[$NbCp_2H_3$] (**1**)	1.751	1.737	1.737					
(**1**-MeOH)**s**	1.752	1.749	1.733	0.972(0.965)	1.781	159.7	150.4	−5.7(−3.3)
(**1**-MeOH)**c**	1.759	1.738	1.736	0.972	1.792[c]/2.593[a]	160.6	133.4	−6.7(−4.1)
(**1**-AcH)**s**	1.752	1.752	1.732	0.988(0.972)	1.668	164.0	128.8	−8.3(−4.8)
(**1**-AcH)**c**	1.759	1.741	1.734	0.986	1.707[c]/2.191[a]	60.1	130.6	−8.6(−5.8)
(**1**-TFE)**s**	1.752	1.753	1.731	0.979(0.967)	1.677	163.6	147.4	−8.7(−4.8)
(**1**-TFE)**c**	1.763	1.737	1.734	0.979	1.646[c]/2.802[a]	170.1	139.6	−8.7(−5.9)
(**1**-HFIP)**s**	1.751	1.753	1.730	0.986(0.969)	1.583	164.1	152.8	−10.2(−3.8)
(**1**-HFIP)**c**	1.750	1.741	1.730	0.985	1.635[c]/2.074[a]	164.3	126.0	−9.5(−4.5)
(**1**-PFTB)**s**	1.751	1.755	1.728	0.992(0.969)	1.510	165.7	155.9	−10.9(−5.1)
(**1**-PFTB)**c**	1.755	1.740	1.731	0.990	1.589[c]/2.054[a]	165.3	125.6	−11.1(−6.4)
(**1**-TFA)**s**	1.750	1.756	1.729	1.001(0.973)	1.467	170.9	148.7	−10.0(−7.5)
(**1**-TFA)**c**	1.764	1.742	1.733	0.996	1.587[c]/2.086[a]	161.4	128.6	−11.3(−8.7)
(**1**-TFM)**s**	1.751	1.762	1.728	0.997(0.968)	1.503	174.5	134.0	−11.9(−6.7)
(**1**-TFM)**c**	1.764	1.741	1.734	0.990	1.670[c]/1.961[a]	159.0	121.9	−12.3(−8.0)

[a] Hydride H^B closest to the proton. [b] Values in brackets are O–H bond lengths in free alcohols ROH. [c] Hydride H^A. [d] BSSE-corrected binding energies in brackets.

While the former angle has similar values in the central and lateral adducts (between 160 and 170°), the latter is much more closed in the central complexes. The values of the Nb-H^A-H(O) angle (about 125°) place the proton not very far from the hydride H^B (at about 2 Å) in the central adducts. Additional interactions between the fluorine substituents and the H atoms of the Cp rings (in TFM, TFE, HFIP and PFTB) or between the carbonyl oxygen and the H atoms of the Cp rings (in AcH and TFA) further contribute to the stabilisation of the adducts. The shortest distances between the hydrogen atoms of the Cp rings and the F or O atoms are about 2.3–2.4 Å.

The binding energies of the fluorinated proton donors are higher than those of the non-fluorinated ones. The weakest dihydrogen bond is formed with MeOH, and the strongest with TFA and TFM. The order of the [$NbCp_2H_3$]·HOR interactions is: MeOH < AcH ≈ TFE < HFIP < PFTB ≈ TFA < TFM. When the BSSE is corrected the binding energies are considerably reduced, but the order is little affected. The only exception occurs with the HFIP adducts. Without consideration of the HFIP adducts, the mean percentage of the BSSE in the calculated binding energy is 42.4 % for the side adducts and 34.3 % for the central ones. Correction for the larger BSSE found in the HFIP adducts [62.6 % in $(1\text{-HFIP})_s$ and 52.3 % in $(1\text{-HFIP})_c$] places HFIP between MeOH and AcH in the ordering of the proton donors by their binding energies.

The presence of the proton donor breaks the pseudo C_{2v} symmetry of the trihydride niobocene. Now the two lateral hydrides H_B are no longer equivalent. The Nb–H bond lengths already show this nonequivalence, but the main consequences are to be found in the $H^A \cdots H^B$ distances. Because of the C_{2v} symmetry of the isolated [$NbCp_2H_3$], its two lateral hydrides H^B are equidistant from H^A ($H^A \cdots H^B$ = 1.776 Å). In the central adducts with proton donors the central hydride H^A interacting with the proton moves away from the H^B closest to the proton and approaches the second noninteracting hydride H^B ($H^{B'}$). For instance, in $([NbCp_2H_3]\cdot TFA)_c$ the $H^A \cdots H^B$ separation is 1.901 Å and the $H^A \cdots H^{B'}$ distance is 1.738 Å. Similarly, in the lateral adducts the H^B–proton interaction induces a remarkable shortening of the $H^A \cdots H^{B'}$ distance. For instance, in $([NbCp_2H_3]\cdot TFA)_s$ the $H^A \cdots H^B$ separation is 1.808 Å, whereas the $H^A \cdots H^{B'}$ distance is 1.722 Å. These structural changes can be understood by regarding these hydrogen bonds as incipient proton-transfer reactions.[20] At the limit, increasing dihydrogen bonds should lead to a complete transfer of the proton on the hydride and result in the formation of a η^2-dihydrogen ligand. Indeed, there is mounting evidence that the H···H dihydrogen-bond complexes constitute important intermediates of transition-metal hydride protonation.[2–5,19] Protonation at H^A should give a H^A–H dihydrogen ligand and so the central adducts could be intermediates in the formation of a dihydrogen–dihydride product. Protonation at H^B produces a H^B–H dihydrogen ligand. The formation of this π-acceptor ligand in the coordination sphere of niobium could induce the formation of a second dihydrogen ligand through the approach of H^A to $H^{B'}$. The decrease in the $H^A \cdots H^{B'}$ distances in the lateral adducts indicates that these dihydrogen-bonded complexes could be intermediates in the formation of a bis(dihydrogen) product. The same behaviour was found in a theoretical study of the trihydride niobocene with Lewis acids.[10] The decrease in the electron density around the metal caused by the interaction between the lateral hydride H^B and the proton induces the incipient formation of a $H^A \cdots H^{B'}$ bond.

We have tried to obtain the proton-transfer products—namely, the ion pairs composed of the Nb–dihydrogen cation and the RO anion—but all attempts to optimise such structures have ended up in the initial hydride–proton adducts. The protonation of a transition-metal hydride in the gas phase appears to be a difficult process with the weak or moderate proton donors considered above. The reaction energies ΔE (+168.4, +131.5, +105.4, +144.7, +125.4, +107.4 and +103.8 kcal mol^{-1}) were calculated in the gas phase for the proton-transfer reactions with MeOH, AcH, TFM, TFE, HFIP, PFTB and TFA, respectively. Looking at the thermodynamics of the proton transfer from R–OH to [$NbCp_2H_3$], it is clear that this reaction in the gas phase is highly unfavourable. This is an expected result, in view of the fact that this process entails the creation of two net charges (+ and −) from two initially neutral species. The final products could only be obtained if a polar solvent were to assist the charge-separation process by solvolysis of the ions. The enthalpies of protonation in solution must be much lower. For technical reasons relating to the size of the systems it was not possible to calculate the solution values of these energies. However, we think that the obtained ΔE values should be usable to classify this series of RO–H proton donors according to their tendency to protonate [$NbCp_2H_3$]. It is worth mentioning that the protonation energies follow the same trend as the magnitude of the H···H interactions, reinforcing the assumption of dihydrogen-bond formation as incipient proton-transfer reactions.

Proton transfer from H_3O^+ to [$NbCp_2H_3$]: We have also studied the interaction of a strong acid, modelled as H_3O^+, with [$NbCp_2H_3$]. In this case no dihydrogen-bonded species was obtained as a minimum. With this strong acid a proton transfer to the hydride occurs without any barrier, leading to dihydrogen complexes (Figure 6). The process ($\mathbf{1}+H_3O^+ \rightarrow [NbCp_2(\eta^2\text{-}H_2)_2]^+ + H_2O$) is very exothermic in the gas phase ($\Delta E = -58.9\ \mathrm{kcal\,mol^{-1}}$).

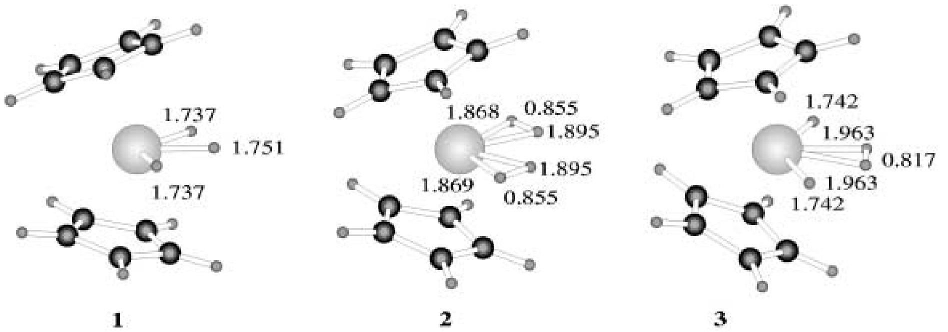


Figure 6. The optimised structures of **1** and the protonation products [$NbCp_2(\eta^2\text{-}H_2)_2$]$^+$ (**2**) and [$NbCp_2H_2(\eta^2\text{-}H_2)$]$^+$ (**3**).

As for the other proton donors, two isomers corresponding to the protonation of H^A and H^B result. The protonation at the lateral hydride H^B gives the compound **2** shown in Figure 6. Compound **2** is a bis(dihydrogen) complex [$NbCp_2(\eta^2\text{-}H_2)_2$]$^+$. In this compound, as a result of the formation of the H^BH dihydrogen ligand, the two remaining hydrogen atoms approach in such a way that another dihydrogen ligand $H^AH^{B'}$ is formed. In **2** there are some differences in the bonding parameters of the two M–H_2 units and the two M–H distances of each coordinated H_2 are slightly different.

The formation of the bis(dihydrogen) complex **2** can be compared with what happens when a π-acceptor ligand is present in a [MCp_2H_2L]$^+$ system:[21] namely, the π-acceptor ligand stabilises the dihydrogen form. The d^2 [MCp_2LH] complexes behave as Lewis bases and they can therefore be protonated by acids at room temperature to give the corresponding cationic complexes. When L is a π-acceptor ligand, the dihydrogen complex can be prepared.[22] Compounds such as [$NbCp'_2(\eta^2\text{-}H_2)(CO)$]$^+$ and [$NbCp'_2(\eta^2\text{-}H_2)(CNR)$]$^+$ have been thoroughly studied both experimentally and computationally. In **2**, one of the dihydrogen ligands can be regarded as playing the role of a π-acceptor ligand L, and such behaviour has previously been observed in other systems.[23]

In [MCp_2H_2L]$^+$ there is a possibility of finding two stereoisomers, depending on whether the two hydrides are *cis* (*cisoid*) or whether L is placed between them (*transoid*). In addition to the *cisoid*-isomer **2**, in which the two *cis*-hydrides approach to form a dihydrogen molecule, we have also found the *transoid*-isomer, actually a dihydrogen–dihydride structure (**3**) (Figure 6), the product of protonation of the central hydride H^A in **1**. Structure **3** lies only 1.7 $\mathrm{kcal\,mol^{-1}}$ above the bis(dihydrogen) form **2**. The short H–H distance (0.817 Å) and long M–H distances (1.963 Å) in the Nb-η^2-H_2 unit of **3** suggest that a very easy H_2 release can take place in this compound.

These results clearly show that the dihydrogen species are formed from the interaction of **1** with strong acids. Previously, protonation of metallocene hydrides had been experimentally addressed in the case of [MCp_2H_2] (M = Mo, W). It was shown that protonation by HCl occurs through dihydrogen intermediates.[24]

Influence of homoconjugated anionic species [RO···H···OR]$^-$ on the protonation: The importance of the homoconjugate pairs formed by the acid and its conjugate base in the protonation processes of transition-metal hydrides is becoming recognised.[25] The production of such species has been regarded as the driving force of the protonation reaction with not very strong acids. The involvement of two alcohol molecules and the formation of a homoconjugate pair in the protonation of [$RuCp(H)(CO)(PCy)_3$][19a,b] and [$FeCp^*(dppe)H$][19c] has been demonstrated recently. It has also been reported that treatment of [$TaCp'_2H_3$] ($Cp' = \eta^5\text{-}t\mathrm{Bu}C_5H_4$) with excess trifluoroacetic acid leads to the formation of the dicarboxylate tantalum(v) complex [$TaCp'_2(H)(OCOCF_3)_2$], with evolution of H_2.[26] Protonation of the trihydride by TFA has been proposed as the first step of the reaction. We have theoretically addressed this possibility in the niobocene trihydride complex, by considering the participation of two molecules of TFA.

There are multiple possibilities for hydrogen bonding in a system composed of the trihydride **1** and two molecules of TFA. As we are interested in the formation of [ROHOR]$^-$ ion, we did not perform a systematic search of all the minima, but have taken as a starting point the optimised geometry of **1**–TFA (vide supra) and placed a new molecule of the acid so that it would form a hydrogen bond with the carbonyl oxygen of the former. In this way we found the dihydrogen-bonded complex **1**–2TFA, in which both the H···H and the O···H hydrogen bonds are present (Figure 7). In this

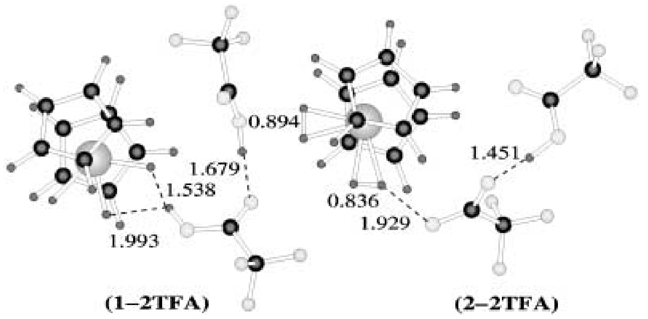


Figure 7. The optimised structures of the adducts of **1** with two molecules of TFA: $[NbCp_2H_3]\cdot(TFA)_2$ (**1**–2TFA) and $[NbCp_2(\eta^2\text{-}H_2)_2]^+\cdot(OOCCF_3\cdots HOOCCF_3)^-$ (**2**–2TFA).

structure a bifurcated dihydrogen bond is found, with the proton interacting both with the central and with one of the lateral hydrides. The dihydrogen-bonded complex is found 24.2 kcal mol^{-1} below the reactants. The extra stabilisation, of more than 10 kcal mol^{-1} with respect to the monomer case, is mainly due to the hydrogen bond between the two TFA molecules. If the sum of the energies of **1** and of the $(CF_3COOH)_2$ dimer is taken as the origin of the energy, the interaction energy is only 5.3 kcal mol^{-1}. This low value is the result of the destabilisation introduced for the rupture of one strong O–H···O interaction present in the bifurcated $(TFA)_2$ dimer, partly compensated for by the new Nb–H···H–O interaction.

The most important point in consideration of the dimeric acid species is that the ion pair **2**–2TFA formed by the cationic bis(dihydrogen) complex $[NbCp_2(\eta^2\text{-}H_2)_2]^+$ and the dimeric counteranion is now found as a minimum, even in the gas phase. Starting from **2** and $(CF_3COO\cdots H\cdots OOCCF_3)^-$, optimisation does not return to the dihydrogen-bonded complex **1**–2TFA, but ends up in the ion pair **2**–2TFA (Figure 7). In this intermediate, one η^2-H_2 ligand acts as a proton donor to one of the oxygen atoms of the incoming base CF_3COO^-, while the hydroxy proton of the second TFA molecule forms a strong hydrogen bond with the second oxygen of the carboxylate group. Such an ionic pair intermediate has been already found in the protonation of a Ru–H hydride with TFA.[19] As a consequence of the hydrogen-bond formation, the Nb–H distances in the dihydrogen ligand interacting with OR$^-$ are not equivalent and the dihydrogen is tilted.

Two effects account for the influence of the [ROHOR]$^-$ homoconjugated ion on stabilizing the dihydrogen complex. On one hand, the reduced basicity of [ROHOR]$^-$ relative to RO$^-$ prevents abstraction of the proton from the dihydrogen complex and allows it to be a stable species. On the other hand, the presence of a strong [RO···H···OR]$^-$ hydrogen bond introduces an additional factor at work, which stabilises the proton-transfer product through the delocalisation of the negative charge. As a result of the two effects, the bis(dihydrogen) complex **2**–2TFA is found only 9.1 kcal mol^{-1} above the dihydrogen-bonded complex **1**–2TFA. However, even with the introduction of an additional TFA molecule, the charge-separation process leading from the ion pair to the solvent-separated ions is extremely energy-consuming. The gas-phase ΔE for the hydride protonation with TFA is reduced from 103.8 kcal mol^{-1} to 66.5 kcal mol^{-1} when the participation of the second TFA molecule is taken into account, but this value is still too much higher to justify the existence of **2** as a product of the protonation with ROH acids. It has been shown in a study of the protonation of $[RuCp(H)(CO)(PCy)_3]$ that solvent plays a major role in assisting the charge-separation step.[19]

The finding of energetically accessible $[NbCp_2(\eta^2\text{-}H_2)_2]^+\cdot[RO\cdots H\cdots OR]^-$ ion pairs strongly supports our proposal of the participation of dihydrogen complexes in the observed H/D exchange between the hydride ligands of $[NbCp_2H_3]$ and the OD groups of the more acidic alcohols and also accounts for decomposition of $[NbCp_2H_3]$ in the presence of excess proton donors, such as HFIP, in nonpolar solvents.

Conclusions

Although early transition-metal hydrides are usually formed by metals in high oxidation states, thanks to the highly electropositive nature of the early metals they can exhibit a distinctive hydridic character. In this work the basic nature of an early transition-metal hydride such as $[NbCp_2H_3]$ has been demonstrated by study of the phenomenon of dihydrogen-bond formation with perfluorinated alcohols by IR, NMR and DFT studies. In spite of the formal oxidation state (v) of the niobium in this complex, the energetics of the dihydrogen bonds NbH···HOR determined by IR spectroscopy are medium in strength, being 4.5(3) kcal mol^{-1} for trifluoroethanol and 5.7(3) kcal mol^{-1} for hexafluoroisopropanol. The DFT study provides important details on the dihydrogen bonding: namely, 1) both nonequivalent hydride sites of $[NbCp_2H_3]$ form dihydrogen bonds, the central hydride being the preferential position and 2) coordination of the protons to the lateral hydride is normal, whereas bonding to the central hydride is bifurcated. From the DFT study the strength of the $[NbCp_2H_3]\cdots HOR$ dihydrogen bond follows the trend: MeOH < AcH ≈ TFE < HFIP < PFTB ≈ TFA < TFM. Proton transfer on $[NbCp_2H_3]$ occurs with excess alcohol or when stronger acids are used. DFT calculations showed that the proton transfer products are bis(dihydrogen) and dihydride(dihydrogen) complexes, the former being slightly more stable. Acids as strong as H_3O^+ afford proton transfer without intermediate formation of dihydrogen bonds. According to the DFT study, medium strength acids such as trifluoroacetic acid can give proton-transfer products as a consequence of the stabilizing effect of the homoconjugate anions [RO···H···OR]$^-$.

Experimental Section

All operations were carried out under dry argon with use of standard Schlenk techniques. Methylcyclohexane was dried over Na/K alloy and distilled before use. The $[NbCp_2H_3]$ complex was prepared by the literature method[27] and recrystallised from diethyl ether. HFIP, TFE and PFTB were purchased from commercial sources. *O*-Deuterated HFIP was prepared by deprotonation of HFIP by BuLi with subsequent addition of weak D_2SO_4 in D_2O, followed by separation and distillation. IR studies were carried out as described previously.[5]

NMR studies: All NMR studies were carried out by standard techniques in NMR tubes sealed under vacuum. [D$_8$]Toluene was dried and deoxygenated by conventional procedures. NMR data were collected on Bruker AC 200 and AMX 400 spectrometers. The conventional inversion-recovery method (180–τ–90)[28] was used to determine T_1. T_{1sel} and T_{1bis} relaxation times were measured by application of selective 180° pulses provided by the decoupler systems of the spectrometers. The duration and power of the 180° selective pulses (180 $_{sel}$–τ–90) were regulated to excite only one or two NMR resonances. The calculation of relaxation times was made by use of the nonlinear three-parameter fitting routine of spectrometers. In each experiment, the waiting period was 5 times longer than the expected relaxation time and 16–20 variable delays were employed. The duration of pulses was controlled at every temperature. The errors in T_1 determinations were lower than 4%. The details of relaxation theory are given in reference [13].

Computational details: Calculations were performed by use of the Gaussian 98 series of programs.[29] Density functional theory (DFT) was applied with the B3LYP functional.[30] An effective core potential (ECP)[31] and its associated double-ξ LANL2DZ basis set[29] were used for the niobium atom. The C, O and hydride and hydroxyl H atoms were represented by use of the 6–31 G(d,p) basis set, whereas the 6–31 G basis set was employed for the F and the rest of the H atoms.[32] All the geometry optimisations were full, with no restrictions. The basis set superposition error (BSSE) was computed by the counterpoise method,[33] through the use of the MASSAGE keyword in the Gaussian program.[29]

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