

NMR Investigation of the Dihydrogen-Bonding and Proton-Transfer Equilibria between the Hydrido Carbonyl Anion $[\text{HRe}_2(\text{CO})_9]^-$ and Fluorinated Alcohols

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Abstract: The interaction of fluorinated alcohols with the anionic hydrido complex $[\text{HRe}_2(\text{CO})_9]^-$ (**1**) has been investigated by NMR spectroscopy. According to the acidic strength of the alcohols, the interaction may result not only in the formation of dihydrogen-bonded $\text{ROH}\cdots[\text{HRe}_2(\text{CO})_9]^-$ adducts **2**, but also in proton transfer to give the neutral species $[\text{H}_2\text{Re}_2(\text{CO})_9]$ (**3**). With the weaker acid trifluoroethanol (TFE) evidence for the occurrence of the dihydrogen-bonding equilibrium was obtained by 2D ^1H NOESY. The dependence of the hydride chemical shift on TFE concentration at different temperatures provided values for the constants of this equilibrium, from

which the thermodynamic parameters were evaluated as $\Delta H^\circ = -2.6(2)$ kcal mol⁻¹, $\Delta S^\circ = -9.3(2)$ cal mol⁻¹ K⁻¹. This corresponds to a rather low basicity factor ($E_b = 0.64$). Variable-temperature T_1 measurements allowed the proton-hydride distance in adduct **2a** to be estimated (1.80 Å). In the presence of hexafluoroisopropyl alcohol (HFIP) simultaneous occurrence of both dihydrogen-bonding and proton-transfer equilibria was observed, and the equilibria shifted versus the protonated

product **3** with increasing HFIP concentration and decreasing temperature. Reversible proton transfer between the alcohol and the hydrido complex occurs on the NMR timescale, as revealed by a 2D ^1H EXSY experiment at 240 K. For the more acidic perfluoro-*tert*-butyl alcohol (PFTB) the protonation equilibrium was further shifted to the right. Thermal instability of **3** prevented the acquisition of accurate thermodynamic data for these equilibria. The occurrence of the proton-transfer processes (in spite of the unfavorable pK_a values) can be explained by the formation of homoconjugated $\text{RO}\cdots\text{HOR}^-$ pairs which stabilize the alcoholate anions.

Keywords: hydride ligands • hydrogen bonding • NMR spectroscopy • protonation • rhenium

Introduction

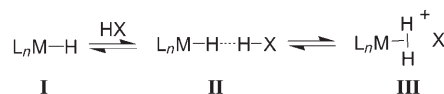
Since the discovery of the unconventional M–H \cdots H–X hydrogen bond (H-bond), in which a metal hydride acts as the electron donor (or H-bond acceptor) with respect to a positively polarized hydrogen atom,^[1] a number of studies have been devoted to understanding the nature of this interaction, its spectroscopic features, and its chemical significance.^[2] Well-defined spectroscopic (mainly IR and NMR) methodologies have been developed for identifying the presence of this interaction,^[3] for which the term “dihydrogen bond” has been coined.^[4] This proton-hydride interaction

can be fairly strong (up to 7.0 kcal mol⁻¹) and affect stereochemistry, dynamics, and reactivity of the involved species. Although the first examples concerned proton donors belonging to ligands bound to the metal center carrying the hydrido ligand,^[1] a number of intermolecular H \cdots H interactions were soon evidenced in solution,^[5–7] and it has been suggested (and experimentally verified) that they are the first step in the protonation pathway to a dihydrogen complex (Scheme 1),^[8,9] as well as intermediates along the pathway to heterolytic splitting of dihydrogen.^[10]

In several cases, the simultaneous presence of the three species **I–III** depicted in Scheme 1 has been detected,^[6] and information on the two equilibria—dihydrogen bond forma-

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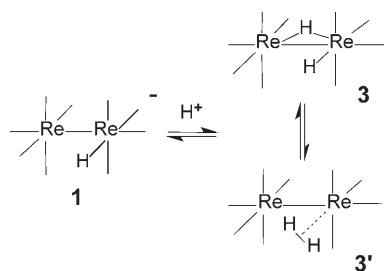
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Scheme 1.

tion and subsequent proton transfer to the hydride—has been obtained by a suitable combination of IR and NMR approaches.

All cases so far investigated involved neutral mononuclear complexes bearing a substantial number of donor ligands (phosphanes or cyclopentadienyl groups) that increased the negative polarization of the hydrido ligand. We wondered whether the hydricity of a transition metal hydride bearing only carbonyl ligands was high enough to allow the onset of dihydrogen bonding. A few preliminary experiments showed that the Re–H bond of the neutral complex $[\text{HRe}(\text{CO})_5]$ does show some H-bond-acceptor capability, but too low to be accurately characterized by the usual spectroscopic methods.^[11] We considered therefore the dinuclear anionic complex $[\text{HRe}_2(\text{CO})_9]^-$ (**1**, Scheme 2). Some of us recently



Scheme 2.

showed^[12] that low-temperature protonation of this anion by strong acids (e.g., $\text{CF}_3\text{SO}_3\text{H}$, HBF_4) gives the neutral species $[\text{H}_2\text{Re}_2(\text{CO})_9]$ (**3**, Scheme 2), which contains one terminal and one bridging hydride ligand, in fast exchange via $\eta^2\text{-H}_2$ tautomer **3'** as a relatively high energy (3 kcal mol^{-1}) intermediate. This tautomer is probably involved both in the irreversible H_2 elimination that occurs at $T > 240 \text{ K}$, and in the formation of the neutral species by protonation of the anion **1** (protonation at the hydridic site is kinetically preferred with respect to the metal).^[13]

We have now investigated the interaction of **1** with weaker proton donors, such as fluorinated alcohols, and we have obtained clear evidence for the formation of dihydrogen-bonded adducts $\text{ROH} \cdots [\text{HRe}_2(\text{CO})_9]^-$ (**2**). Moreover, we have shown that, depending on the acidic strength of the proton donor, these adducts **2** may be in equilibrium with the protonation product $[\text{H}_2\text{Re}_2(\text{CO})_9]$.

As proton donors the alcohols $\text{CF}_3\text{CH}_2\text{OH}$ (2,2,2-trifluoroethanol, TFE), $(\text{CF}_3)_2\text{CHOH}$ (1,1,1,3,3,3-hexafluoropropan-2-ol, HFIP), and $(\text{CF}_3)_3\text{COH}$ (perfluoro-*tert*-butyl alcohol, PFTB) were used, because they span a range of Brønsted and hydrogen-bond acidities^[14–16] which usually fits well with the corresponding basicities of hydrido complexes and thus provides the opportunity of observing dihydrogen bonding and/or proton-transfer reactions. Moreover, these alcohols have been extensively used by other groups that have investigated dihydrogen-bonding equilibria, and this gives the possibility of comparing the behavior of **1** with that of other transition-metal hydrides.

Results and Discussion

Previous thorough studies have shown that intermolecular proton–hydride interactions can be best characterized by a combination of variable-temperature IR and NMR methods.^[3,5,6]

It is well known that formation of H-bonds causes a shift to lower frequency and a broadening of the ν_{HX} absorption of the proton donor.^[17] These effects have been widely exploited to estimate the strength (ΔH°) of intermolecular dihydrogen bonds by use of empirical correlations, such as Jørgensen's equations.^[3] Moreover, IR spectroscopy, due to its short timescale, allows the detection of separate absorptions for the hydride **I** and H-bonded adduct **II** of Scheme 1 (e.g., in the ν_{CO} region). Therefore (at least in favorable cases corresponding to the presence of a single CO or NO resonance) the direct quantification of the two species **I** and **II** may be possible, and then the determination of the constants ruling the association equilibria. From this point of view, the NMR data are less informative, because on the NMR timescale **I** and **II** are always in fast exchange that results in averaged NMR parameters (chemical shift, relaxation times, and so on), and extraction of the necessary information from the observed data is more laborious.

In the case of the anion $[\text{HRe}_2(\text{CO})_9]^-$ (**1**) the ν_{CO} region of the IR spectrum is rather complex (five absorptions) and did not allow the observation of separate bands for **1** and the H-bonded adduct. Therefore, most of the investigation had to be performed by NMR spectroscopy. Indeed, valuable information about this kind of unconventional interaction can also be obtained from the averaged NMR data. In particular, comparison of the chemical shift and of the relaxation time of the hydrido ligand in the presence or absence of the alcohol allow estimates of K for the association equilibrium and of the $\text{H} \cdots \text{H}$ distance in the dihydrogen-bonded adduct.^[5a,b]

The choice of the solvent was problematic. Indeed no solvent able to accept H-bond (ethers, ketones, or any compound containing O or N atoms) could be used, because it would compete (successfully) with the hydrido complex for hydrogen bonding. On the other hand, salts of anion **1** are insoluble in apolar solvents such as hydrocarbons. Finally, the use of halogenated solvents should be avoided, because hydride/halogen exchange has been observed for **1**,^[18] as is often the case with transition metal hydrides. This would have practically excluded any solvent. However, since H/Cl exchange in CH_2Cl_2 is catalyzed by light and becomes very slow at low temperature, we chose CH_2Cl_2 as solvent, taking care to keep the samples in the dark and at low temperature.

Interaction of $[\text{NET}_4][\text{HRe}_2(\text{CO})_9]$ with TFE: The addition of $[\text{NET}_4]\text{-I}$ ^[19] (up to 0.1 M) to CH_2Cl_2 solutions of TFE (0.02 M) at room temperature did not cause any appreciable change in the ν_{OH} region of the IR spectrum, at variance with what was previously observed for many neutral hydrido complexes.^[5a,6f,6k] An analogous room-temperature experi-

ment with an excess of TFE ($[\text{NEt}_4]\text{-1}$ 6×10^{-3} M, TFE 0.1 M) did not show any change in the ν_{CO} region. This indicated that the proton-hydride interaction was either absent or weaker than in these previous cases. Instead, clear evidence of the presence of the dihydrogen bond in solution was provided by NMR analysis at low temperatures.

Indeed, progressive additions of TFE to a CD_2Cl_2 solution of $[\text{NEt}_4]\text{-1}$ at 202–235 K caused a significant upfield shift of the hydride resonance (Figure 1). The same effect was ob-

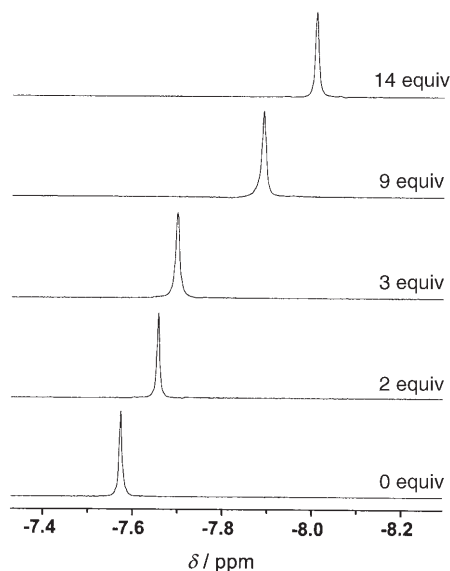


Figure 1. Hydride region of ^1H NMR spectra of $[\text{NEt}_4][\text{HRe}_2(\text{CO})_9]$ (7×10^{-3} M, CD_2Cl_2 , 212 K) in the presence of different amounts of TFE.

served on lowering the temperature at constant alcohol concentration (Figure 2). This behavior is attributable to the occurrence of an equilibrium [Eq. (1)] which is fast on the NMR timescale and therefore leads to an averaged hydride signal.

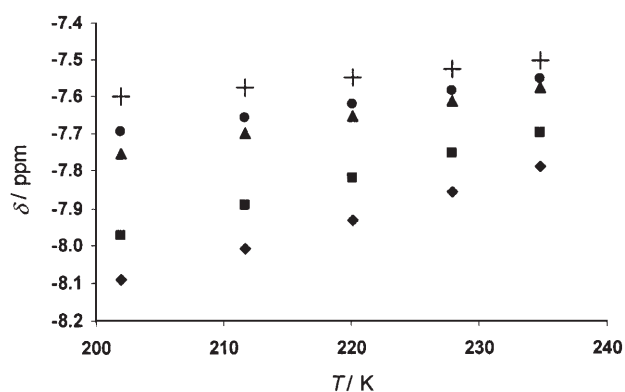
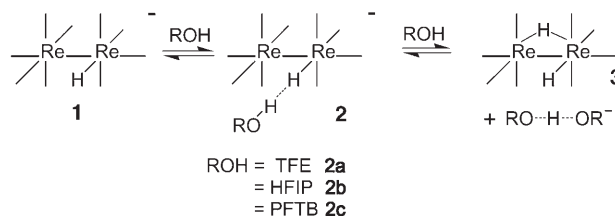


Figure 2. Variation of the chemical shift of the hydride resonance of **1**+**2a** with the temperature in the presence of different TFE concentrations (7×10^{-3} M, CD_2Cl_2): + **1** alone, ● 2 equiv of TFE, ▲ 3 equiv of TFE, ■ 9 equiv of TFE, ◆ 14 equiv of TFE.



The position of the averaged signal depends on the chemical shift and on the molar fraction x_2 of hydrogen-bonded $\text{ROH} \cdots [\text{HRe}_2(\text{CO})_9]^-$ adduct **2a** (ROH = TFE, see Scheme 3), according to Equation (2). It has already been



Scheme 3.

established that the resonance of a hydride undergoing a dihydrogen-bonding interaction is shifted upfield,^[5a] making $\delta_2 < \delta_1$.

$$\delta_{\text{obs}} = x_1 \delta_1 + x_2 \delta_2 \quad (2)$$

The molar fraction x_2 is expected to increase on lowering the temperature (due to the increase in the equilibrium constants typical of associative processes), and on increasing the concentration of the proton donor ROH. A relationship between the molar fractions and the equilibrium constant K can be easily determined (see Experimental Section).^[5a,b] Fitting of the experimental δ_{obs} at each temperature in the presence of different ROH concentrations provided estimates of the values of the two unknown parameters K and δ_2 (see Table 1). From the values of K at different temperatures, the thermodynamic parameters of equilibrium (1) were estimated through the van't Hoff relationship: $\Delta H^\circ = -2.6(2)$ kcal mol $^{-1}$, $\Delta S^\circ = -9.3(2)$ cal mol $^{-1}$ K $^{-1}$.

Table 1. Values of the equilibrium constants K and of the chemical shifts δ_2 of adduct **2a** obtained by two different types of nonlinear fitting of the experimental variable-temperature data for the interaction of **1** with TFE.

T [K]	$K^{[a]}$ [M $^{-1}$]	$\delta_2^{[a]}$ [ppm]	$S^{2[c]}$	$K^{[b]}$ [M $^{-1}$]	$\delta_2^{[b]}$ [ppm]	$S^{2[c]}$
201.9	7.37	-8.77	5.6×10^{-5}	7.56	-8.75	1.0×10^{-4}
211.7	5.86	-8.75	8.1×10^{-5}	5.80	-8.76	1.0×10^{-4}
220.1	4.39	-8.80	9.0×10^{-5}	4.26	-8.83	1.1×10^{-4}
227.9	3.49	-8.80	7.8×10^{-5}	3.17	-8.83	9.1×10^{-5}
234.8	2.91	-8.76	8.0×10^{-5}	2.79	-8.80	9.1×10^{-5}

[a] Obtained by fitting of the data to Equation (8). [b] Obtained by fitting of the data to Equation (11). [c] Goodness of fit, corresponding to the sum of the squares of the difference between experimental and calculated δ (case a) or between the two members of Equation (11) (case b).

The intermolecular proton-hydride interaction was confirmed by a 2D NOESY experiment at 221 K, which showed a cross-peak between the hydride signal (at -7.90 ppm) and

the OH resonance (at 2.95 ppm; Figure S1, Supporting Information).

The proton–hydride distance was estimated through measurement of the longitudinal relaxation times T_1 of hydride **1**, alone and in the presence of 1 equiv of TFE. As shown in Figure 3, the T_1 values obtained in the latter case were sig-

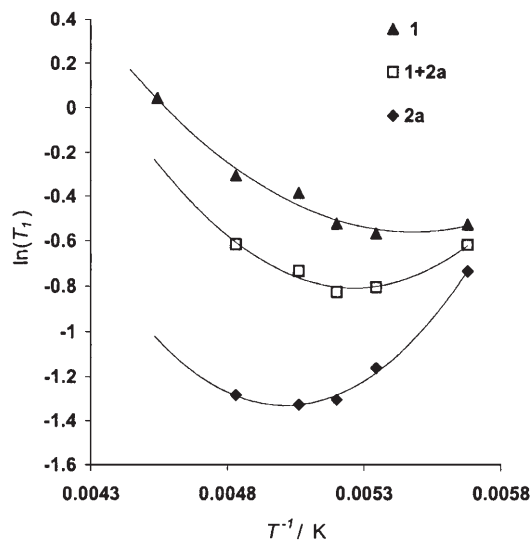


Figure 3. ^1H relaxation times T_1 measured for $[\text{HRe}_2(\text{CO})_9]^-$ (**1**) alone (\blacktriangle) and in the presence of 1 equiv of TFE (averaged signal for **1** and **2a**, \square) (CD_2Cl_2 , 11.7 T). The symbol \blacklozenge marks the values computed for the adduct **2a**. Lines are drawn as a visual aid only.

nificantly shorter, as the observed relaxation rate ($R_1 = 1/T_1$) is the weighted average of those of **1** and **2a** [Eq. (3)]. Indeed in **2a** the presence of a hydrogen atom in close proximity to the hydride contributes to its relaxation by dipolar interaction, strongly shortening its T_1 .^[8c,20,21] From the knowledge of this contribution it is possible to extract the value of the H...H distance $r_{\text{H-H}}$ through Equation (4), where ν is the Larmor frequency of the proton at the experimental magnetic field, and $(\Delta R_1)_{\text{min}}$ the difference between the relaxation rate of the hydride in **2a** at the minimum and that of **1** at the corresponding temperature.^[22]

$$(R_1)_{\text{measured}} = x_1(R_1)_1 + x_{2a}(R_1)_{2a} \quad (3)$$

$$r_{\text{H-H}} = 5.817[\nu(\Delta R_1)_{\text{min}}]^{-1/6} \quad (4)$$

The molar fractions at the temperatures of the inversion recovery experiments were calculated from the equilibrium constants, and from these the actual values of $(R_1)_{2a}$ reported in Figure 3 as diamonds.^[23] Thus, a proton–hydride distance of 1.80 Å was calculated, a value in the range of those previously estimated for other hydride complexes.^[3]

The NMR data unambiguously demonstrated that a fraction of the alcohol molecules interacts with the hydridic site. However, these data cannot rule out that other TFE molecules interact with the oxygen atoms of the carbonyl ligands.

In this hypothesis, some ν_{CO} band should exhibit a red shift due to weakening of the C–O bond.^[24] On the contrary, an IR spectrum of **1** acquired at 223 K in CH_2Cl_2 in the presence of a high TFE concentration (30 equiv) showed ν_{CO} bands somewhat broadened and slightly blue shifted with respect to those of **1** alone (Figure S2, Supporting Information). This fits with the hypothesis that the observed ν_{CO} IR spectrum arises from the overlap of the bands of **1** and **2a**, the latter shifted to higher frequencies due to the decreased π backdonation caused by the interaction of **1** with an electrophile. The absence of bands at lower frequency indicates that the interaction of the alcohol with the carbonyl ligands of **1** is negligible.

An empirical rule [Eq. (5)] correlates the enthalpy variation ΔH° on H-bond formation with the acidic and basic properties of the species involved in the interaction.^[25] This rule allows the “basicity factor” E_j of each H-bond acceptor to be determined from the knowledge of the “acidity factor” P_i of the proton donor and the enthalpy variation ΔH_s° measured in the same solvent for a standard H-bond adduct, namely, phenol–diethyl ether.

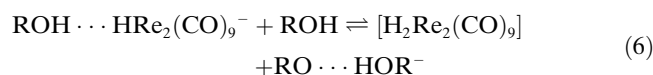
$$E_j = \Delta H_{ij}^\circ / (\Delta H_s^\circ P_i) \quad (5)$$

In the present case we evaluated^[26] an E_j value of 0.64(6). This indicates that the H-bond-accepting capability of hydride **1** is lower than that reported for most neutral complexes containing stronger donor ligands than CO^[2a,3] (ranging from 1.67 for $[\text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3]\text{OsH}_2$ ^[5g] to 0.91 for $[\text{WH}(\text{CO})_2(\text{NO})(\text{PR}_3)_2]$ ^[5a]) and is comparable with the values (0.68–0.79) found for the neutral rhenium dihydrides $[\text{ReH}_2(\text{NO})(\text{CO})(\text{PR}_3)_2]$.^[6e]

Interaction of $[\text{NET}_4][\text{HRe}_2(\text{CO})_9]$ with HFIP: Addition of HFIP to CD_2Cl_2 solutions of $[\text{NET}_4]\text{-1}$ caused not only the expected upfield shift of the hydride resonance of **1**, due to the formation of **2b**,^[27] but also the formation of variable amounts of the neutral complex $[\text{H}_2\text{Re}_2(\text{CO})_9]$ (**3**, $\delta = -10.7$ ppm). Proton transfer, with formation of the RO^- anion, most likely affords initially the $\eta^2\text{-H}_2$ tautomer, which is in fast exchange with the more stable isomer containing a terminal and a bridging hydride ligand (Scheme 2).^[12]

In the protonation of neutral metal hydrides leading to $\eta^2\text{-H}_2$ cationic complexes, it is usually assumed that, in non-polar solvents, the conjugate base of the protonating agent remains hydrogen-bonded to the acidic atoms of the dihydrogen ligand in a tight ion pair, which can subsequently transform into a solvent-separated ion pair and then free ions.^[6fj,9] The anionic charge on our hydridic complex makes the situation very different here. The protonated product **3** is neutral, and we can confidently rule out the involvement of its hydrido ligands in H-bonding with the alcoholate, because the position of the hydride resonance ($\delta = -10.7$ ppm, averaged signal for bridging and terminal hydrides)^[12] did not change on varying the nature of the alcohol. We think that in the present case (excess of free alcohol and aprotic, slightly polar solvent) the RO^- anion is mainly stabilized by

interaction with a second alcohol molecule [Eq. (6)]. In fact, a proton donor which is able to interact with the unconventional H-bond acceptor **1** is expected to establish a much stronger conventional H-bond with an OR⁻ anion. The formation of homoconjugate A...H...A^{-/+} pairs (A = OTf,^[28,29] CF₃COO,^[6f] *p*-NO₂-PhOH,^[6f] PhNH₂^[30]) in the protonation/deprotonation of organometallic complexes has been previously observed, and their role in stabilizing the charged species and then assisting/promoting proton transfer has been theoretically investigated.^[5h,6j,6l,9]



The proton in the RO...HOR⁻ anions is expected to have a very positive chemical shift, due to the strength of the H-bond involved.^[31] Therefore, the strong downfield shift (>2.5 ppm at 220 K) undergone by the (averaged) proton resonance of HFIP in the presence of 1 equiv of **1** supports the formation of the homoconjugated pair. Indeed, this shift cannot be attributed solely to formation of the Re₂H...HOR⁻ dihydrogen bond, because for TFE, which under analogous conditions is not able to protonate **1**, the observed downfield shift was much smaller (ca. 0.4 ppm).

The invariant relative intensities of the resonances of reactants and products of Equation (6) with time indicated attainment of equilibrium. The reversibility of the protonation reaction is in line with the previous observation that **3** can be deprotonated in [D₈]THF, even by relatively weak bases such as PMe₂Ph (pK_a = 6.50).^[12]

The equilibrium was further confirmed by the observation that the amount of **3** increased with increasing alcohol concentration, in accordance with the mass action rule (Figure 4) and that the ratio between the (averaged) signal of **1+2b** and the signal of **3** slightly and reversibly (at *T* < 230 K, see below) increased with increasing the temperature (Figure 5).

Proton transfer in both directions is fast enough to allow the onset, in a 2D EXSY map recorded at 240 K (Figure 6), of exchange cross-peaks between the signal of **3** (δ =

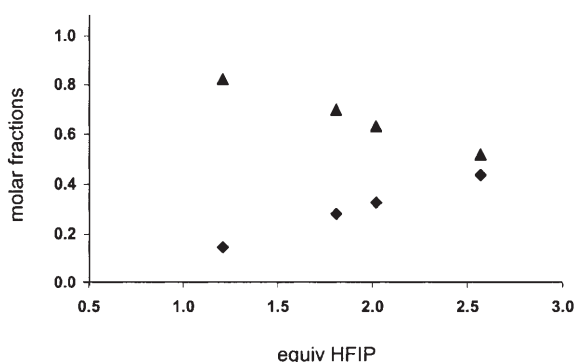


Figure 4. Dependence of the molar fractions of [HRe₂(CO)₉]⁻ (free and H-bonded, **1+2b**, ▲) and of [H₂Re₂(CO)₉] (**3**, ◆) on the relative HFIP concentration (CD₂Cl₂, 211 K).

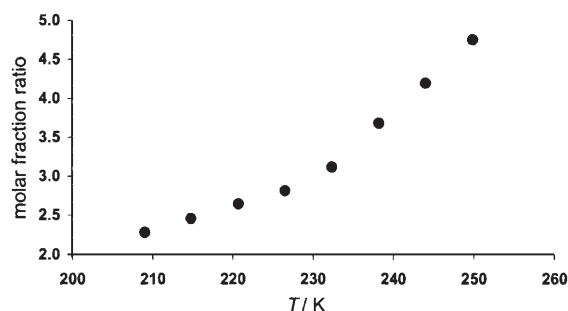


Figure 5. Ratio between the molar fractions of [HRe₂(CO)₉]⁻ (**1+2b**) and [H₂Re₂(CO)₉] (**3**), as observed on increasing the temperature in CD₂Cl₂ solution, with [**1**] = 0.04 M and [HFIP] = 0.08 M.

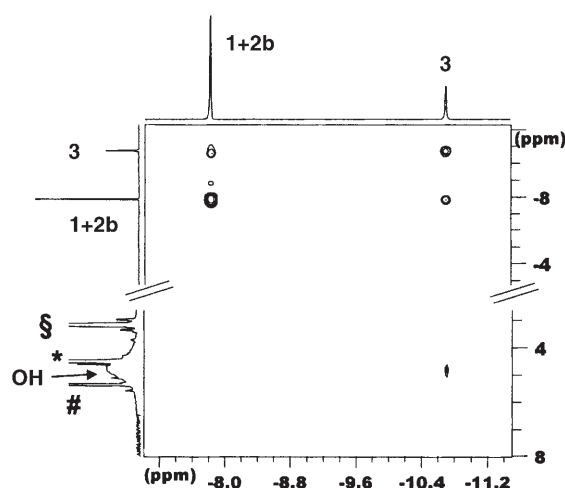
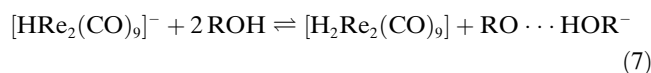


Figure 6. ¹H,¹H EXSY on a mixture of **1** and HFIP ([**1**] = 0.012 M, [HFIP] = 0.030 M, CD₂Cl₂, 240 K, τ_m = 0.25 s). In the bottom panel, the intensity of the 2D map has been magnified by 4, and the F1 trace by 16. # marks the solvent, * the CH resonance of HFIP, and § the CH₂ resonance of NEt₄⁺.

-10.71 ppm) and those at δ = -7.83 ppm (averaged **1+2b**) and at δ = 4.79 ppm (the broad OH signal).

The (slight) shift towards the left side of the protonation equilibrium (6) with increasing temperature indicates that the overall reaction (7) is exothermic, but cannot provide certain information about the sign of Δ*H*^o for proton-transfer step (6), since the formation of H-bonded adduct **2** in the preceding step (1) is certainly exothermic. The proton transfer step has been shown to be predominantly exothermic,^[2a] but an endothermic process has also been reported.^[6a]



By using very high alcohol concentrations, we succeeded in driving equilibrium (7) to the right even for the weaker acid TFE: in the presence of 0.44 mol L⁻¹ of TFE (corresponding to 65 equiv) we observed formation of a small amount (ca. 9%) of the protonated species **3** at 223 K. This

corresponds to $K=9\times 10^{-4}$ for the overall equilibrium (7) and 2×10^{-4} for equilibrium (6), on using the previously estimated $K=4$ for equilibrium (1). At higher TFE concentrations, phase separation between TFE and CD_2Cl_2 prevented any more accurate evaluation of the equilibrium constants.

In the case of HFIP, the estimation of the constants ruling the formation of the dihydrogen-bonded adduct [Eq. (1)] and the subsequent proton-transfer step was problematical. First, the presence of the simultaneous proton-transfer equilibrium introduced various uncertainties in the optimization procedure used to evaluate K of equilibrium (1), as discussed in the Experimental Section. Moreover, the neutral species **3** is thermally unstable and irreversibly loses H_2 at temperatures higher than about 240 K to give several decomposition products, only partly identified.^[32] Although we investigated the interaction of **1** with HFIP below 240 K, variable amounts of decomposition products usually formed in the mixtures, due to the slight unavoidable warming during the transfer of the NMR tubes in and out the spectrometer. In our **1**/HFIP mixtures, besides all the previously observed species,^[32] we recognized the presence also of the tetranuclear anion $[(\text{CO})_9\text{Re}_2(\mu\text{-H})\text{Re}_2(\text{CO})_9]^-$ (**4**),^[33] which was the main decomposition product. Its formation is due to the fact that here, at variance with the previous study,^[12] the decomposition of **3** occurred in the presence of unconverted $[\text{HRe}_2(\text{CO})_9]^-$, which can act as σ -donor ligand toward the coordinatively unsaturated fragment $[\text{Re}_2(\text{CO})_9]$ to afford **4**.

The presence of this variety of byproducts, particularly when their nature or the stoichiometry of their formation is not well defined, made the optimization procedures used to obtain the K values infeasible. Attempts to analyze data from variable-temperature experiments with small amounts of byproducts provided ΔH° values which, even if not unreasonable (taking into account that the acidity factor P_i of HFIP is about 1.2 times that of TFE^[6k] and that the ratio between the corresponding α_2 parameters is 1.35),^[14] were too variable in different experiments (-2.9 to -3.8 kcal mol⁻¹) to accurately characterize the strength of the dihydrogen bond. The lack of reliable data for the first step hampered any quantitative characterization of the second equilibrium, that is, proton transfer.

Interaction of $[\text{NEt}_4][\text{HRe}_2(\text{CO})_9]$ with PFTB: With this alcohol the protonation equilibrium (7) was much more shifted to the right than with HFIP, in agreement with the higher Brønsted acidity of PFTB. Indeed, low-temperature titration experiments showed that upon addition of more than three equivalents of PFTB, **1** was completely transformed into **3** (and its decomposition products). Interestingly, at intermediate stages of the titration, the hydride resonance of unconsumed **1** was only slightly shifted with respect to that of **1** alone ($\Delta\delta=0.03$ ppm on addition of 1.5 equivalents of PFTB at 220 K, whereas shifts on the order of tenths of a ppm were observed for TFE and HFIP under analogous conditions), that is, a very small fraction of H-bonded adduct **2c** was present in solution. Since PFTB is known to be a better H-bond donor than TFE or HFIP,^[14] this implies

that the remaining concentration of free alcohol was very low and therefore provides a further indirect evidence that the RO^- anions act as scavengers of ROH molecules by forming $\text{RO}\cdots\text{HOR}^-$ anions or even higher aggregates.^[34]

Thermodynamic and kinetic considerations: Reliable thermodynamic data were only obtained for the dihydrogen bonding equilibrium involving TFE. These data (favorable ΔH° , unfavorable ΔS° , see above) correspond to a ΔG° of -0.54 kcal mol⁻¹ at 225 K. For this alcohol, the subsequent proton transfer is unfavorable, and indeed from the K evaluated in the presence of a large excess of alcohol, a ΔG° of about $+4$ kcal mol⁻¹ can be estimated for this step (Figure 7). In this figure the dihydrogen complex **3'** of Scheme 2 is also shown, as the kinetic product, about 3 kcal mol⁻¹ less stable than its classical tautomer **3**.^[12]

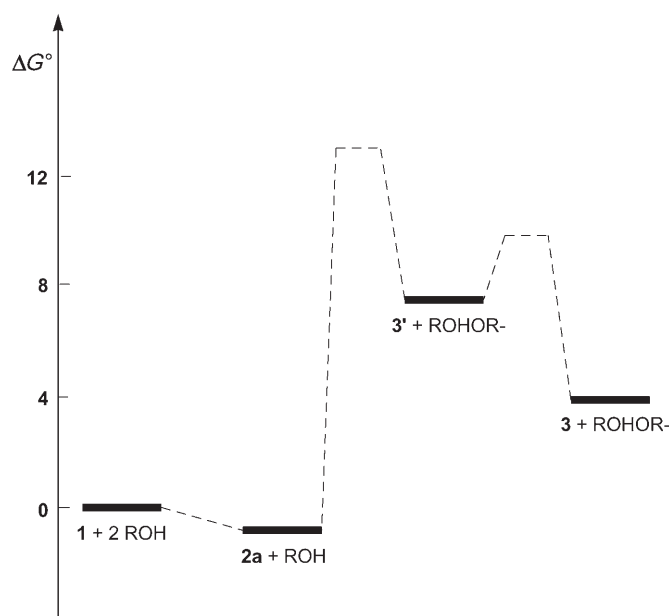


Figure 7. Semi-quantitative free-energy profile of the interaction between $[\text{HRe}_2(\text{CO})_9]^-$ (**1**) and TFE (at 225 K).

From the kinetic point of view, the dihydrogen-bond equilibrium is fast on the NMR timescale (a sharp averaged signal is always observed for the hydride and its adduct with the alcohol), in agreement with the fact that the formation of the H-bonded adduct is usually viewed as a diffusion-controlled step^[6g] (accordingly, no barrier is depicted in Figure 7 for this step). On the contrary, the proton transfer equilibrium is slow on the NMR timescale: separate sharp signals for the hydride **1** and its protonated derivative **3** are observed, and this sets the upper limit for the rate constants at about 5 s^{-1} , because higher values would affect the bandwidth of the signals. On the other hand, the proton-transfer equilibrium was always attained in the few minutes between the addition of the proton donor and the acquisition of the spectra. These considerations set the proton-transfer rate within rather narrow limits, corresponding to ΔG^\ddagger in the range 13–15 kcal mol⁻¹.^[35] This agrees not only with litera-

ture data,^[2a,6d,6f,6g] but also with the value estimated from the 2D EXSY experiment at 240 K for the interaction of **1** with HFIP (Figure 6). The free-energy profile of Figure 7 can therefore be drawn on the basis of the above considerations.

The protonation equilibrium involving PFTB is well shifted to the right, and hence K is greater than 10^2 . Thus, for PFTB ΔG° between the reactants and the products of equilibrium (7) is negative, with an absolute value greater than 2 kcal mol^{-1} . In the case of HFIP, the observation of comparable amounts of reactants **1**+**2b** and product **3** in the presence of a slight excess of alcohol indicates that for this proton donor the ΔG° value of equilibrium (7), either positive or negative, should be close to 0.

Therefore, the free-energy profile of the proton-transfer reaction for the three alcohols can be qualitatively sketched as in Figure 8, where the starting energies have been arbi-

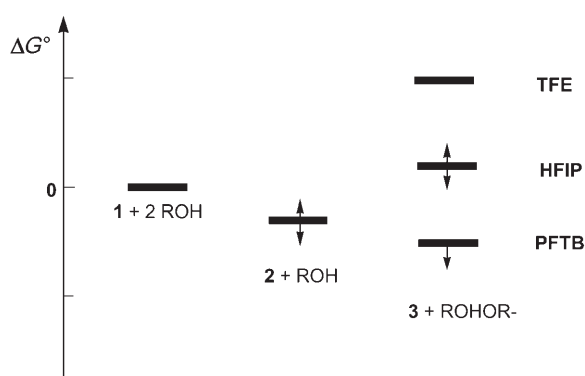


Figure 8. Qualitative free-energy profile of the interaction between $[\text{HRe}_2(\text{CO})_9]^-$ (**1**) and the three fluorinated alcohols TFE, HFIP, and PFTB. The arrows indicate the uncertainty.

trarily placed at the same level to evidence the different free-energy variations. Indeed, the scheme has the sole purpose of showing that, in the reasonable hypothesis of formation of homoconjugated pairs, the different positions of the protonation equilibria for the three alcohols are attributable, all other species being identical, to the different relative stabilities of the $\text{RO}\cdots\text{HOR}^-$ anions with respect to two moles of free alcohol.

Conclusion

The interaction of electrophiles with transition metal carbonyl hydride anions often occurs with the oxygen atoms of the carbonyl ligands.^[36] The data reported here demonstrate that in this case the protons of the alcohols interact with the hydridic site rather than with the surface of negatively polarized oxygen atoms surrounding the $[\text{HRe}_2(\text{CO})_9]^-$ ion. This witnesses the strength of the dihydrogen bonding interaction.

Such strength is demonstrated also by the observation that even a neutral hydrido complex containing only π -acidic ligands, such as $[\text{HRe}(\text{CO})_5]$, has some (very weak)

propensity for acting as a hydrogen-bond acceptor.^[37] The replacement of a carbonyl ligand of $[\text{HRe}(\text{CO})_5]$ by pentacarbonylrhenate $[\text{Re}(\text{CO})_5]^-$ affords the $[\text{HRe}_2(\text{CO})_9]^-$ ion,^[38] in which the negative charge obviously increases the H-bond-accepting capability of the hydride.

Dihydrogen bonds involving anionic transition metal hydrides have been so far observed only in ion pairs in which the counteranion is the H-bond donor (typically the NH moiety of potassium(aza-crown) cations).^[7] The paucity of reports concerning anionic hydrides is likely due to the strongly hydridic character usually associated with the negative charge, which results in easy protonation, followed by H_2 elimination.^[36] The large number of carbonyl ligands in **1** drastically lowers the hydricity of the H ligand, as evidenced by the basicity factor, which is at the lower limit of the range of factors determined for the other (neutral) hydrides. This suggests that, for increasing the hydricity of an H ligand, ligands with higher donor capability than carbonyl may be more effective than the negative charge (which in this case is, in fact, delocalized over two metal centers).

Although the complexity of the system hampered the acquisition of quantitative data for all the alcohols, the qualitative picture is very clear and nicely illustrates the effects of the different acidities on the reaction pathway.^[39,40]

With TFE (moderate H-bond donor, $\alpha_2=0.57$, poor Brønsted acid, $\text{p}K_a=12.4$)^[14] the interaction usually stops at the level of dihydrogen bonding: in solution comparable amounts of the adduct **2a** and of the free hydride **1** are present, in fast equilibrium, and the relative amount of hydrogen-bonded adduct increases with decreasing temperature and increasing TFE concentration. With the strongest acid PFTB ($\alpha_2=0.86$, $\text{p}K_a=5.4$)^[14] in contrast, the interaction results essentially in proton transfer.

The acidity of HFIP, intermediate between those of TFE and PFTB ($\alpha_2=0.77$, $\text{p}K_a=9.3$)^[14] provides the opportunity of observing both the dihydrogen-bonding and the proton-transfer equilibria. Although the thermal instability of the protonation product $[\text{Re}_2\text{H}_2(\text{CO})_9]$ hampered complete characterization of the thermodynamics of the system, the reversible proton transfer between the alcohol and the hydrido complex, occurring on the NMR timescale, was clearly photographed by 2D exchange spectroscopy.

The occurrence of such proton transfer is rather surprising, both on the basis of the low basicity factor of **1** (to our knowledge, this is the first case in which proton transfer by weak acids is observed for a transition metal hydride with $E_f < 0.8$)^[3] and of the poor Brønsted acidity of HFIP ($\text{p}K_a=9.3$)^[14] whereas **3** is a stronger acid than PMe_2Ph , which has $\text{p}K_a=6.5$ ^[12].^[41] We think that a key factor for explaining this, as well as a protonation equilibrium with PFTB substantially driven to the right, is stabilization of the alcoholate anion by H-bonding with the excess of alcohol. Therefore, the position of the protonation equilibrium under these conditions (slightly polar aprotic solvent, excess of protonating agent) depends on the stability of the homoconjugate $\text{RO}\cdots\text{HOR}^-$ pairs with respect to two moles of ROH (Figure 8), rather than on the thermodynamic acidity of the

involved proton donors. From another point of view, even if the dihydrogen-bonded $\text{Re}_2\text{H}\cdots\text{HOR}^-$ adduct is really the intermediate in protonation of the hydride, the assistance of a stronger, “conventional” $\text{RO}\cdots\text{HOR}^-$ hydrogen bond is necessary to drive the protonation equilibrium to the right.^[5h,6j,6l,9]

Experimental Section

All manipulations were performed under N_2 using oven-dried Schlenk-type glassware. CD_2Cl_2 (C.I.L.) was dried over activated molecular sieves. $[\text{HRe}(\text{CO})_5]$ ^[42] and $[\text{NEt}_4][\text{HRe}_2(\text{CO})_9]$ ^[43] were prepared by literature procedures. TFE, HFIP, and PFTB were used as received (Aldrich). Exposure of samples containing anion **1** to direct sunlight or to standard fluorescent lighting was strictly avoided.

All spectra were acquired on a Bruker AVANCE DRX-300 equipped with a 5 mm QNP probe and a DRX-400 equipped with a 5 mm BBI probe; T_1 measurements were performed on a Bruker AVANCE DRX-500 equipped with a 5 mm QNP probe. The temperature was calibrated with standard $\text{CH}_3\text{OH}/\text{CD}_3\text{OD}$ solution.^[44]

Interaction between $[\text{HRe}(\text{CO})_5]$ and fluoroalcohols: A solution of $[\text{HRe}(\text{CO})_5]$ in CD_2Cl_2 (0.025 M) was treated with 4.5 equivalents of HFIP. The NMR spectrum at 223 K showed an upfield shift of the hydride resonance of 0.012 ppm. The experiment was repeated with PFTB (5.5 equiv), which gave an upfield shift of 0.028 ppm. The addition of further PFTB (up to 10 equiv) caused phase separation. An analogous experiment in which the solution of $[\text{HRe}(\text{CO})_5]$ was treated with a base (NEt_3 , 5 equiv) under the same conditions did not show any shift of the hydride signal.

Interaction between $[\text{NEt}_4][\text{HRe}_2(\text{CO})_9]$ and fluoroalcohols: A typical experiment for measuring the chemical shifts at different temperatures and alcohol concentrations was as follows: A solution of $[\text{NEt}_4][\text{HRe}_2(\text{CO})_9]$ (3 mL, ca. 0.007 M) in CD_2Cl_2 was prepared in the dark and then transferred under nitrogen atmosphere into five NMR tubes, and the amount of solution in each tube was weighed. Different amounts of alcohol were then added at 193 K to four of these tubes by a 10 μL microsyringe. The concentration of alcohol was usually maintained below 0.1 M to avoid self-association. To assure strictly constant temperature, the spectra of the five samples were acquired in sequence at each temperature. In the intervals between the measurements at different temperatures the samples were maintained in a bath at 193 K. The lower temperature limit for the experiments was set by the necessity of avoiding separation of the alcohol phase from CD_2Cl_2 , which was observed at progressively higher temperatures with increasing $[\text{ROH}]$. The upper limit was set both by the decreased concentration of adduct **2** on increasing the temperature and, in the case of HFIP, by the thermal instability of **3**.

Equilibrium analysis: The results of the above experiments were used to estimate K of equilibrium (1) as follows: By expressing the molar fractions x in Equation (2) as a function of the equilibrium constant K , Equation (8) is easily obtained,^[5a,b] where C_{ReH} and C_{ROH} are the starting concentrations of the hydride and the alcohol, respectively, and δ_1 and δ_2 are the chemical shifts of the free hydride (known) and of the H-bonded adduct (unknown), respectively. The values of the two unknown parameters K and δ_2 were provided by nonlinear fitting of the experimental δ values using the Levenberg–Marquardt algorithm (the computations were performed by Matlab).

$$\delta_{\text{calcd}} = \delta_1 + (\delta_2 - \delta_1) \frac{1}{2C_{\text{ReH}}} (C_{\text{ReH}} + C_{\text{ROH}} + 1/K) - \sqrt{(C_{\text{ReH}} + C_{\text{ROH}} + 1/K)^2 - 4C_{\text{ReH}}C_{\text{ROH}}} \quad (8)$$

In the case of HFIP, C_{ReH} and C_{ROH} did not correspond to the amounts introduced into solution (due to the simultaneous occurrence of the pro-

tonation reaction) and had to be substituted by the residual concentrations C'_{ReH} and C'_{ROH} , obtained from the mass balances [Eqs. (9) and (10)]

$$C_{\text{ReH}} = C'_{\text{ReH}} + [\mathbf{3}] + 2[\mathbf{4}] + \sum [\mathbf{1}]_{\text{consumed}} \quad (9)$$

$$C_{\text{ROH}} = C'_{\text{ROH}} + 2[\mathbf{3}] + 2[\mathbf{4}] + \sum [\text{ROH}]_{\text{consumed}} \quad (10)$$

where $\Sigma[\mathbf{1}]_{\text{consumed}}$ and $\Sigma[\text{ROH}]_{\text{consumed}}$ represent the overall amounts of **1** and ROH, respectively, consumed by the formation of decomposition products different from **4**. These terms cannot be evaluated when the nature of the products or the stoichiometry of the reaction responsible for their formation is not well defined. The factor of 2 that multiplies **3** in Equation (10) accounts for the formation of the $\text{RO}\cdots\text{HOR}^-$ pairs [see Eqs. (6) and (7)]. The actual concentrations of the known hydride species were easily evaluated from the ratio between the integrated intensity of the hydride signals and those of the NEt_4^+ cation.

A different manipulation of the same relationships led to Equation (11).^[45]

$$K = \frac{\delta_{\text{obs}} - \delta_1}{(\delta_2 - \delta_{\text{obs}})(C_{\text{ROH}} - \frac{\delta_{\text{obs}} - \delta_1}{\delta_2 - \delta_1} C_{\text{ReH}})} \quad (11)$$

Minimization of the difference between the two members of the equation by the same Levenberg–Marquardt algorithm provided values of K and δ_2 almost identical to those obtained by the previous approach (see Table 1).

Measurements of T_1 of $[\text{NEt}_4][\text{HRe}_2(\text{CO})_9]$ in the presence of TFE: A 0.05 M solution of $[\text{NEt}_4][\text{HRe}_2(\text{CO})_9]$ in CD_2Cl_2 was prepared and transferred into two NMR tubes. To one of these one equivalent of TFE was added. Both tubes were degassed and then used for inversion recovery T_1 NMR measurements. The T_1 values were calculated with the nonlinear three-parameter fitting routine of the Bruker WIN1D program.

^1H EXSY experiment on a mixture of **1, **2b**, and **3**:** A 2D ^1H EXSY experiment on a sample of **1** (0.012 M) in the presence of 2.5 equiv of HFIP at 240 K showed that the signal of **3** ($\delta = -10.71$ ppm) had exchange cross-peaks with the averaged signal of **1** and **2b** ($\delta = -7.83$ ppm) and the very broad OH resonance at $\delta = 4.79$ ppm. An estimate of the exchange rate constant between **3** and **2b** from the volume analysis of the 2D EXSY requires the knowledge of the relative population of the two sites. In the absence of a reliable value for the equilibrium constant of reaction (1), the amount of **2b** in the mixture was calculated from the experimental averaged chemical shift by assuming two limit values for the chemical shift of adduct **2b** ($\delta = -8.75$ and -8.35 ppm, respectively, determined on the base of the fitting analysis previously described). The $k_{2b,3}$ rate constants calculated accordingly ranged from 3.6 to 2.2 s^{-1} , and these set ΔG^\ddagger in the range 13.2–13.4 kcal mol^{-1} .

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- [1] a) J. C. Lee, A. L. Rheingold, B. Muller, P. S. Pregosin, R. H. Crabtree, *J. Chem. Soc. Chem. Commun.* **1994**, 1021; b) A. J. Lough, S. Park, R. Ramachandran, R. H. Morris, *J. Am. Chem. Soc.* **1994**, *116*, 8356.

- [2] For reviews on dihydrogen bonding, see: a) N. V. Belkova, E. S. Shubina, L. M. Epstein, *Acc. Chem. Res.* **2005**, *38*, 624; b) L. M. Epstein, E. S. Shubina, *Coord. Chem. Rev.* **2002**, *231*, 165; c) R. Custelcean, J. E. Jackson, *Chem. Rev.* **2001**, *101*, 1963; d) M. J. Calhorda, *Chem. Commun.* **2000**, 801; e) I. Alkorta; I. Rozas, J. Elguero, *Chem. Soc. Rev.* **1998**, *27*, 163; f) R. H. Crabtree, *J. Organomet. Chem.* **1998**, *577*, 111; g) R. H. Crabtree, O. Eisenstein, G. Sini, E. Peris, *J. Organomet. Chem.* **1998**, *567*, 7; h) R. H. Crabtree, P. E. M. Siegbahn, O. Eisenstein, A. L. Rheingold, T. F. Koetzle, *Acc. Chem. Res.* **1996**, *29*, 348.
- [3] L. M. Epstein, N. V. Belkova, E. S. Shubina in *Recent Advances in Hydrides Chemistry* (Eds.: M. Peruzzini, R. Poli), Elsevier, Amsterdam, **2001**, p. 391.
- [4] T. R. Richardson, S. Gala, R. H. Crabtree, P. E. M. Siegbahn, *J. Am. Chem. Soc.* **1996**, *118*, 12875.
- [5] a) E. S. Shubina, N. V. Belkova, A. N. Krylov, E. V. Vorontsov, L. M. Epstein, D. G. Gusev, M. Niedermann, H. Berke, *J. Am. Chem. Soc.* **1996**, *118*, 1105; b) N. V. Belkova, E. S. Shubina, A. V. Ionidis, L. M. Epstein, H. Jacobsen, A. Messner, H. Berke, *Inorg. Chem.* **1997**, *36*, 1522; c) J. A. Ayllon, S. S. Sabo-Etienne, B. Chaudret, S. Ulrich, H.-H. Limbach, *Inorg. Chim. Acta* **1997**, *259*, 1; d) A. Messner, H. Jacobsen, H. Berke, *Chem. Eur. J.* **1999**, *11*, 3341; e) P. Desmurs, K. Kavallieratos, W. Yao, R. H. Crabtree, *New J. Chem.* **1999**, *23*, 1111; f) A. Albinati, V. I. Bakhmutov, N. V. Belkova, C. Bianchini, I. de los Rios, L. M. Epstein, E. I. Gustul, L. Marvelli, M. Peruzzini, R. Rossi, E. S. Shubina, E. V. Vorontsov, F. Zanobini, *Eur. J. Inorg. Chem.* **2002**, 1530; g) E. I. Gustul, N. V. Belkova, M. S. Sverdlov, L. M. Epstein, E. S. Shubina, V. I. Bakhmutov, T. N. Gribanova, R. M. Minyaev, C. Bianchini, M. Peruzzini, F. Zanobini, *Chem. Eur. J.* **2003**, *9*, 2219; h) E. V. Bakhmutova, V. I. Bakhmutov, N. V. Belkova, M. Besora, L. M. Epstein, A. Lledos, G. I. Nikonov, E. S. Shubina, J. Tomàs, E. V. Vorontsov, *Chem. Eur. J.* **2004**, *10*, 661.
- [6] a) J. A. Ayllon, C. Gervaux, S. Sabo-Etienne, B. Chaudret, *Organometallics* **1997**, *16*, 2000; b) E. S. Shubina, N. V. Belkova, E. V. Bakhmutova, E. V. Vorontsov, V. I. Bakhmutov, A. V. Ionidis, C. Bianchini, L. Marvelli, M. Peruzzini, L. M. Epstein, *Inorg. Chim. Acta* **1998**, *280*, 302; c) S. Gründemann, S. Ulrich, H. H. Limbach, N. S. Golubev, G. S. Denisov, L. M. Epstein, S. Sabo-Etienne, B. Chaudret, *Inorg. Chem.* **1999**, *38*, 2550; d) N. V. Belkova, E. V. Bakhmutova, E. S. Shubina, C. Bianchini, M. Peruzzini, V. I. Bakhmutov, L. M. Epstein, *Eur. J. Inorg. Chem.* **2000**, 2163; e) N. V. Belkova, E. S. Shubina, E. I. Gustul, L. M. Epstein, I. L. Eremenko, S. E. Nefedov, *J. Organomet. Chem.* **2000**, *610*, 58; f) N. V. Belkova, A. V. Ionidis, L. M. Epstein, E. S. Shubina, S. Gruendemann, N. S. Golubev, H. H. Limbach, *Eur. J. Inorg. Chem.* **2001**, 1753; g) V. I. Bakhmutov, E. V. Bakhmutova, N. V. Belkova, C. Bianchini, L. M. Epstein, D. Masi, M. Peruzzini, E. S. Shubina, E. V. Vorontsov, F. Zanobini, *Can. J. Chem.* **2001**, *79*, 479; h) E. I. Gustul, N. V. Belkova, G. M. Babakina, L. M. Epstein, E. S. Shubina, C. Bianchini, M. Peruzzini, F. Zanobini, *Russ. Chem. Bull. Int. Ed.* **2003**, *52*, 1204; i) J. Andrieu, N. V. Belkova, M. Besora, E. Collange, L. M. Epstein, A. Lledos, R. Poli, P. O. Revin, E. S. Shubina, E. V. Vorontsov, *Russ. Chem. Bull. Int. Ed.* **2003**, *52*, 2679; j) N. V. Belkova, M. Besora, L. M. Epstein, A. Lledos, F. Maseras, E. S. Shubina, *J. Am. Chem. Soc.* **2003**, *125*, 7715; k) N. V. Belkova, P. O. Revin, L. M. Epstein, E. V. Vorontsov, V. I. Bakhmutov, E. S. Shubina, E. Collange, R. Poli, *J. Am. Chem. Soc.* **2003**, *125*, 11106; l) N. V. Belkova, E. Collange, P. Dub, D. A. Lemenovskii, A. Lledos, O. Maresca, F. Maseras, R. Poli, P. O. Revin, E. S. Shubina, E. V. Vorontsov, *Chem. Eur. J.* **2005**, *11*, 873.
- [7] a) S. E. Landau, K. E. Groh, A. J. Lough, R. H. Morris, *Inorg. Chem.* **2002**, *41*, 2995; b) K. Abdur-Rashid, A. J. Lough, R. H. Morris, *Can. J. Chem.* **2001**, *79*, 964; c) K. Abdur-Rashid, D. G. Gusev, A. J. Lough, R. H. Morris, *Organometallics* **2000**, *19*, 834; d) D. G. Gusev, A. J. Lough, R. H. Morris, *J. Am. Chem. Soc.* **1998**, *120*, 13138; e) K. Abdur-Rashid, D. G. Gusev, S. E. Landau, A. J. Lough, R. H. Morris, *J. Am. Chem. Soc.* **1998**, *120*, 11826.
- [8] a) S. Feracin, T. Bürgi, V. I. Bakhmutov, I. Eremenko, E. V. Vorontsov, A. B. Vimenits, H. Berke, *Organometallics* **1994**, *13*, 4194; b) E. S. Shubina, A. N. Krylov, N. V. Belkova, L. M. Epstein, A. P. Borisov, V. D. Mahaev, *J. Organomet. Chem.* **1995**, *493*, 275; c) R. H. Morris, *Can. J. Chem.* **1996**, *74*, 1907.
- [9] V. I. Bakhmutov, *Eur. J. Inorg. Chem.* **2005**, 245.
- [10] R. H. Morris in *Recent Advances in Hydrides Chemistry* (Eds.: M. Peruzzini, R. Poli), Elsevier, Amsterdam, **2001**, p. 1.
- [11] The addition of fluoroalcohols to solutions of $[\text{HRe}(\text{CO})_5]$ in CD_2Cl_2 caused an upfield shift of its hydride signal, but the shift was too small (even at low temperature and with relatively high alcohol concentrations) to allow a reliable investigation (see Experimental Section).
- [12] M. Bergamo, T. Beringhelli, G. D'Alfonso, P. Mercandelli, A. Sironi, *J. Am. Chem. Soc.* **2002**, *124*, 5117.
- [13] E. T. Papish, M. P. Magee, J. R. Norton in *Recent Advances in Hydrides Chemistry* (Eds.: M. Peruzzini, R. Poli), Elsevier, Amsterdam, **2001**, p. 39.
- [14] In principle, the proton-transfer acidity is different from the hydrogen-bond acidity, which measures the ability of a molecule to act as hydrogen-bond donor.^[15] A scale based on $\lg K$ values for complexation in CCl_4 has been constructed to quantify the latter ability for protic solutes.^[16] The values of the derived α_2 parameters for the fluorinated alcohol here used are: TFE 0.567, HFIP 0.771, PFTB 0.862. This order qualitatively follows that of Brønsted acidity in aqueous solution ($\text{p}K_a=12.39$ for TFE, 9.3 for HFIP, 5.4 for PFTB), although this is by no means a general feature.^[16]
- [15] M. H. Abraham, R. M. Doherty, M. J. Kamlet, R. W. Taft, *Chem. Br.* **1986**, 551.
- [16] M. A. Abraham, P. L. Grellier, D. V. Prior, P. P. Duce, J. J. Morris, P. J. Taylor, *J. Chem. Soc. Perkin Trans. 2* **1989**, 699.
- [17] G. A. Jeffrey, *An Introduction to Hydrogen Bonding*, Oxford University Press, Oxford, **1997**.
- [18] T. Beringhelli, G. D'Alfonso, unpublished data.
- [19] The NEt_4^+ salt was used all through this study, because this cation is not expected to give any specific interaction with the anion in the ion-pair present in CD_2Cl_2 solution.
- [20] A. Abragam, *The Principles of Nuclear Magnetism*, Oxford University Press, Oxford, **1973**, Chapter 8.
- [21] G. D. Hamilton, R. H. Crabtree, *J. Am. Chem. Soc.* **1988**, *110*, 4126.
- [22] The relaxation time of adduct **2** is dominated by hydrogen-hydrogen dipole-dipole interaction; at the minimum of T_1 it is possible to obtain τ_c according to the relationship $\omega\tau_c=0.62$.
- [23] As expected, the minimum relaxation time for **2a** occurs at temperatures higher than for **1**. Indeed, for the latter compound the relaxation of the hydride is entirely attributable to the rhenium-hydrogen dipolar interaction, the minimum of which is observed when $\omega\tau_c=0.926$. T. Beringhelli, G. D'Alfonso, M. Freni, A. P. Minoja, *Inorg. Chem.* **1992**, *31*, 848.
- [24] B. V. Lokshin, S. G. Kazarian, A. J. Ginzburg, *J. Mol. Struct.* **1988**, *174*, 29.
- [25] See E. S. Shubina, N. V. Belkova, L. M. Epstein, *J. Organomet. Chem.* **1997**, *536-537*, 17 and references therein.
- [26] The following values were used for the computations: $\Delta H_s^\ddagger = -4.6 \text{ kcal mol}^{-1}$ (CH_2Cl_2), $P_s=0.90$ for TFE.^[6k]
- [27] At 198 K the expected NOE cross-peak between the hydride resonance (**1+2b**) and the OH proton of the alcohol is observed.
- [28] R. M. Bullock, J.-S. Song, D. J. Szalda, *Organometallics* **1996**, *15*, 2504.
- [29] T. P. Fong, C. E. Forde, A. J. Lough, R. H. Morris, P. Rigo, E. Rocchini, T. Stephan, *J. Chem. Soc. Dalton Trans.* **1999**, 4475.
- [30] E. T. Papish, F. C. Rix, N. Spetseris, J. R. Norton, R. D. Williams, *J. Am. Chem. Soc.* **2000**, *122*, 12235.
- [31] F. Hibbert, J. Emsley, *Adv. Phys. Org. Chem.* **1990**, *26*, 255.
- [32] Previous studies^[12] have shown that the decomposition of **3** in CD_2Cl_2 affords a variety of hydridic species: among these, only $[\text{HRe}_3(\text{CO})_4]$ and $[\text{HRe}(\text{CO})_5]$ have so far been identified.
- [33] M. Bergamo, T. Beringhelli, G. D'Alfonso, P. Mercandelli, M. Moret, A. Sironi, *Organometallics* **1997**, *16*, 4129.
- [34] The acquisition of quantitative data on the position of the equilibria involving PFTB was further hampered by the formation of a precipi-

- tate, likely the $[\text{NEt}_4][\text{ROHOR}]$ salt, since it contained both the NEt_4^+ ion and alcohol molecules.
- [35] These values must be decreased by about 0.5–1.5 kcal in the hypothesis that a molecule of ROH is involved in the rate-determining step, and therefore k_{obs} is proportional to ROH concentration.^{19]}
- [36] M. Y. Darensbourg, C. E. Ash, *Adv. Organomet. Chem.* **1987**, 27, 1.
- [37] This propensity, in spite of its weakness, seems higher than that for behaving as H-bond donor, since the presence of an H-bond acceptor such as NEt_3 did not cause any shift of the hydride signal.
- [38] This is not a formal relationship only, but a true method for synthesizing the anion **1**: M. Bergamo, T. Beringhelli, G. D'Alfonso, G. Ciani, M. Moret, A. Sironi, *Organometallics* **1996**, 15, 1637.
- [39] G. Orlova, S. Scheiner, *J. Phys. Chem. A* **1998**, 102, 4813.
- [40] H. S. Chu, Z. Xu, S. M. Ng, C. P. Lau, Z. Lin, *Eur. J. Inorg. Chem.* **2000**, 993.
- [41] On passing from water to CD_2Cl_2 we would expect a marked decrease in the acidity of ROH (due to the loss of stabilization of RO^- by the protic solvent water), stronger than that concerning the cationic acid $[\text{HPMe}_2\text{Ph}]^+$.
- [42] M. A. Urbancic, J. R. Shapley, *Inorg. Synth.* **1990**, 28, 165.
- [43] T. Beringhelli, G. D'Alfonso, L. Ghidorsi, G. Ciani, A. Sironi, H. Molinari, *Organometallics* **1987**, 6, 1365.
- [44] A. L. Van Geet, *Anal. Chem.* **1970**, 42, 679.
- [45] F. L. Slejko, R. S. Drago, D. G. Brown, *J. Am. Chem. Soc.* **1972**, 94, 9210.

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