Probing Regioselective Intermolecular Hydrogen Bonding to $[Re(CO)H_2(NO)(PR_3)_2]$ Complexes by NMR Titration and Equilibrium NMR Methodologies

Andreas Messmer, Heiko Jacobsen, and Heinz Berke*[a]

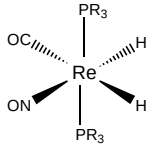
Abstract: The hydrogen-bonding interaction of rhenium hydrides $[Re(CO)H_2(NO)(PR_3)_2]$ (R = Me **1a**, Et **1b**, iPr **1c**) with two different proton donors (hexafluoro-2-propanol (HFIP) and perfluoro-2-methyl-2-propanol (PFTB)) was studied in solution using variable-temperature (VT) NMR spectroscopy. As a novel feature, $ReH\cdots HX$ intermolecular hydrogen bonding was observed to be dependent on R, the HX acid strength, the HX concentration, temperature and solvent type. The regioselectivity of these interactions could be verified. Hydrogen bonding occurs preferably with the hydride H_a *trans* to NO, but also with the hydride H_b *trans* to CO, and with the O_{NO} atom. These interactions show similar dependencies on the steric requirements of the phosphanes and the chemical nature of the acidic substrates. NMR equilibrium constants and thermodynamic data ($-\Delta H = 2.3-6.2$ kcal mol^{-1}) are reported for the hydrogen-bonded complexes in solution. Difference NOE measurements for **1a** and **1b** allowed us to confirm the regioselectivity of the hydrogen bonding to H_a and H_b, with the major interaction to H_a. From the NMR relaxation time measurements of the hydrides, hydrogen bond lengths were obtained (1.78 – 1.94 Å). A solvent effect was established with considerably smaller K and $-\Delta H$ values in toluene than in methylcyclohexane, which could be related to 'aromatic' hydrogen bonding between the fluorinated alcohols and toluene.

Keywords: alcohols · hydrogen bonds · NMR spectroscopy · rhenium · solvent effects

Introduction

The discovery of dihydrogen complexes by Kubas et al. in 1984[1] initiated quite a large number of studies, which concerned their synthetic development, structural investigations and explorations of their physical properties.[2–8] The most common method for the generation of dihydrogen complexes is the protonation of transition metal hydrides.[2–7] It was proposed that unique species of the type $MH\cdots HX$ with hydrogen bonding to a metal-bound hydrogen atom ("dihydrogen bond") are intermediates in such processes.[9, 10] The idea that such "dihydrogen bonding" might occur prior to the proton transfer to transition metal hydrides has recently been verified experimentally.[11, 12] Dihydrogen bonding can indeed be observed intra-[11–18] or intermolecularly.[19–25] Intermolecular interactions were described with weak proton donors for ruthenium, tungsten and rhenium hydride ligands either in the solid state[20, 21] or in solution.[11, 19, 22–25] Presumably most of the hydrides, which display a high propensity for the formation of dihydrogen bonds, have a $M^{\delta+}-H^{\delta-}$ bond,[26] which has a relatively strong hydridic polarization. This polarization in turn provides sufficient electrostatic attraction in the hydrogen-bonding process.[27]

For the rhenium hydrides **1a** and **1c**, the existence of dihydrogen complexes has been demonstrated by low-temperature NMR spectroscopy.[9] In order to further substantiate the above proposal that hydrogen bonding might occur prior to proton transfer, we have carried out variable-temperature (VT) IR studies on the interaction of **1a–c** with perfluoro-*tert*-butylalcohol (PFTB).[22] This work revealed a phosphane-dependent competition between the $M-H\cdots HO$ and $M-NO\cdots HO$ adducts.



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R = Me **a**, Et **b**, *i*Pr **c**

In the present paper, we would like to deepen our understanding of this secondary type of binding phenomenon of the hydrides **1a–c**. With the use of two substrates of different acidity, namely hexafluoroisopropylalcohol (HFIP) and

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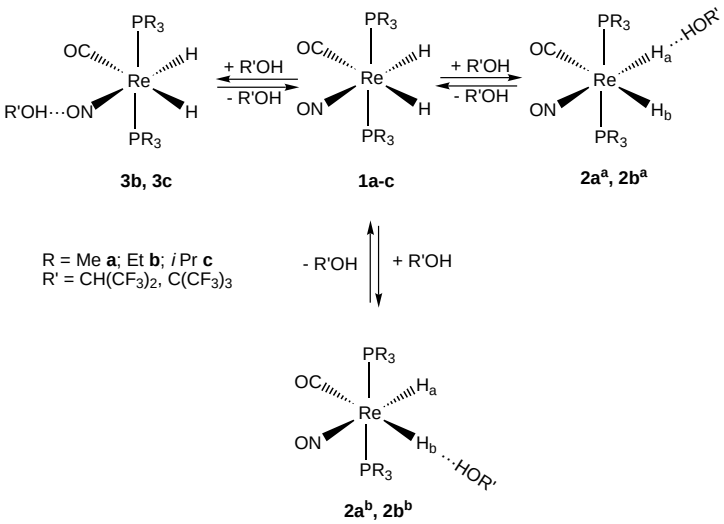
PFTB, and by varying their concentrations, we expect to obtain a comprehensive picture revealing chemical factors like binding strength and site selectivity of the binding. The method of choice is VT-equilibrium NMR spectroscopy,[28] which provides detailed information about the hydrogen-bonding process and about valuable geometrical parameters.[19]

Results and Discussion

Structural studies: The interaction between **1a–c** and acidic alcohols might take place at different sites of the transition metal complex. Either a hydride ligand or the O_{NO} atom might be involved in dihydrogen bonding (Scheme 1). We have to further differentiate between the two different hydride ligands; either H_a (*trans* to NO) or H_b (*trans* to CO) might be the preferred site. Our previous studies[22] have shown that interaction with O_{CO} is not likely to occur. We will exclude this particular interaction from our discussion.

It is expected that ^{1}H NMR spectroscopy will be especially suitable for tracing the hydrogen bonding to the hydride ligands and for specifically probing the regioselectivity of this interaction. Thus, the NMR method should provide evidence for the attack at either H_a or H_b of **1a–c**. We investigated the effect of the interaction in **1a–c** by VT titrations with PFTB and HFIP. For practical reasons, [D_8]toluene had to be used as the least polar and most easily available VT NMR solvent. The use of toluene meant that the alcohols were sufficiently soluble at low temperature.



Scheme 1.

Useful information was obtained from the determination of the chemical shift changes $\Delta\delta$ ($\Delta\delta = \delta(\mathbf{2}) - \delta(\mathbf{1})$), from the T_1(min) values and from NOE effects[19] of the metal-bound hydrogen atoms. It should be emphasized that due to the relatively small ΔH for hydrogen-bonding interactions, it was expected that the NMR analysis would be determined by equilibration processes, which are rapid on the NMR time-scale. This should lead to an averaging of the signals of the free complexes **1a–c** and of the **1a–c**$\cdots$HOR′ adducts **2a**,**b** or **3b,c**. Under these conditions, we anticipated that the observed NMR effects do not only depend on temperature, but also that they depend on the position of the respective equilibrium or equilibria, that is they are concentration dependent.

This is clearly demonstrated by the chemical shift behaviour of the hydride resonances in the presence of PFTB or HFIP. We found that if these acidic substrates are in contact with the hydride ligands, the resonances move significantly upfield ($\Delta\delta < 0$) when the alcohol concentration is increased or the temperature is lowered. If there is an interaction with the O_{NO} atom, a lowfield shift ($\Delta\delta > 0$) is observed under the same conditions. It should be mentioned that in principle the type of interaction cannot be established from such chemical shift observations. However, in connection with the results from previous IR studies[22] and other NMR experiments (vide infra), it is reasonable to assume that the observed effects are indeed due to hydrogen bonding. Apparently, the **1a–c**$\cdots$HOR′ adducts with the hydrides possess higher chemical shifts for H_a and H_b, whereas adducts with O_{NO} lead to lower shifts for H_a. Naturally, with higher alcohol concentrations and at lower temperatures, the adduct equilibrium concentrations increase. Such dependencies are typical of associative equilibria, which are generally disfavoured by entropy. As proposed above, our NMR experiments not only enable us to resolve the H/O_{NO} regioselectivity of the hydrogen bonding, but also to differentiate between the binding to H_a and H_b (Scheme 1).

For **1a** in the presence of PFTB or HFIP, one finds remarkable negative $\Delta\delta$ changes for H_a (Figure 1 and

Abstract in German: *Die Wechselwirkung über Wasserstoffbrückenbindungen der Rheniumhydride $Re(CO)H_2(NO)(PR_3)_2$, R = Me **1a**, Et **1b**, iPr **1c** wurden in Lösung bei verschiedenen Temperaturen mit zwei Protonendonatoren (Hexafluorisopropanol (HFIP) und Perfluor-2-methyl-2-propanol (PFTB)) durch NMR-Spektroskopie untersucht. Als neues Phänomen wurden ReH$\cdots$HX-Wechselwirkungen beobachtet, welche Abhängigkeiten vom Rest R, der Säurestärke von HX und ihrer Konzentration, der Temperatur und dem Lösungsmitteltypus zeigten. Diese Wechselwirkungen waren ausserdem regioselektiv, wobei vorzugsweise Interaktion mit H_a trans zu NO stattfand, aber auch mit H_b trans zu CO und dem O_{NO}-Atom. Alle diese Gleichgewichte haben ungefähr gleiche Abhängigkeiten vom sterischen Anspruch der Phosphan-Liganden und von der Art der Säure. Ferner wurden NMR-Gleichgewichtskonstanten und thermodynamische Daten ($-\Delta H = 2.3–6.2$ kcal mol^{-1}) erhalten. Differenz-NOE-Messungen für **1a** und **1b** bestätigen schliesslich das erhaltene Bild der Regioselektivität bei der Ausbildung von Wasserstoffbrückenbindungen zu H_a und H_b, wobei diejenige zu H_a bevorzugt gebildet wird. Aus NMR-Relaxationszeitmessung für die Hydride wurden Wasserstoffbrückenbindungsabstände erhalten (1.78–1.94 Å). Ein Lösungsmitteleffekt zeigte beträchtlich kleinere K- und $-\Delta H$-Werte in Toluol als in Methylcyclohexan, welche auf die Ausbildung von konkurrierenden „aromatischen Wasserstoffbrückenbindungen“ zwischen Toluol und den fluorierten Alkoholen zurückgeführt wird.*

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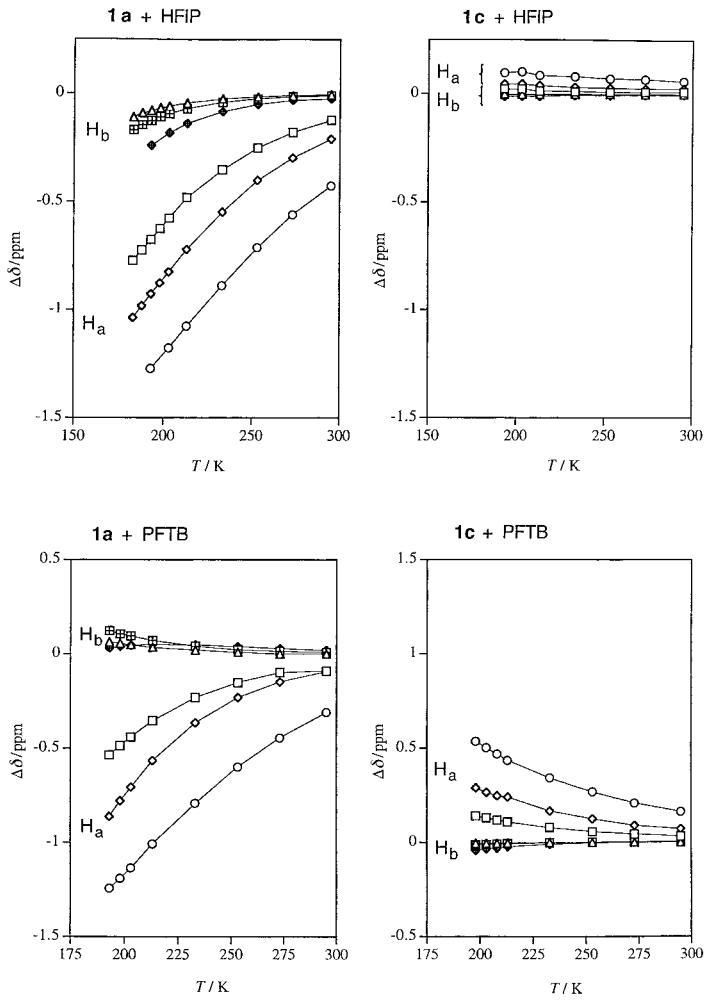

Figure 1. Chemical shift change ($\Delta\delta$) [ppm] vs T [K] of the ^{1}H hydride resonances of **1a** and **1c** (0.05 mol L^{-1}) in the presence of HFIP (above) and PFTB (below). □, △: **1a**, **1c**: HFIP, PFTB = 1:1; ◇ ▽: **1a**, **1c**: HFIP, PFTB = 1:2; O, ◆: **1a**, **1c**: HFIP, PFTB = 1:5.

Table 1. Selected chemical shift differences $\Delta\delta$ (δ(**2**) – δ(**1**)) [ppm] for the hydrides H_a and H_b of **1a–c** (0.05 mol L^{-1}) in the presence of HFIP or PFTB (ratio 1:5) at various temperatures.

	T [K]	$\Delta\delta$ H_a		H_b	
		HFIP	PFTB	HFIP	PFTB
1a	295	– 0.43	– 0.31	– 0.02	0.02
	273	– 0.56	– 0.44	– 0.03	0.03
	253	– 0.71	– 0.60	– 0.05	0.03
	233	– 0.89	– 0.79	– 0.08	0.03
	213	– 1.08	– 1.01	– 0.14	0.02
	193	– 1.27	– 1.24	– 0.24	– 0.04
1b	295	– 0.10	0.05	0.02	0.01
	273	– 0.16	0.05	0.03	0.02
	253	– 0.24	0.04	0.03	0.01
	233	– 0.36	0.01	0.04	0.02
	213	– 0.51	– 0.03	0.06	0.01
	193	– 0.72	– 0.10	0.06	– 0.03
1c	295	0.06	0.16	0.00	0.00
	273	0.07	0.20	0.00	0.00
	253	0.07	0.26	– 0.01	0.00
	233	0.08	0.33	– 0.01	– 0.01
	213	0.08	0.43	– 0.01	– 0.02
	193	0.10	0.51	– 0.01	– 0.02

Table 1). This can be interpreted in terms of the fairly large involvement of H_a in hydrogen-bonding interactions. The δ values of the H_b atom of **1a** are practically not affected by the addition of PFTB at temperatures down to 213 K. Only at the very low temperature of 193 K, one might sense that H_b starts to become involved ($\Delta\delta = -0.04$, Table 1). The addition of HFIP influences the chemical shift of H_b to a much more pronounced extent. Thus, it displays qualitatively the same trends in the concentration and temperature dependencies as H_a of **1a** (Figure 1). Apparently PFTB possesses a high selectivity for the attachment to H_a and HFIP also shows a significant preference for the binding to this ligand. However, in a less selective manner, it noticeably interacts with H_b as well. This difference in the behaviour of the alcohols cannot only originate from a difference in the steric environments of both hydride positions, which are indeed quite similar. It should rather be associated with differences in their electronic properties, that is "hydridicity".[26a] One would expect that PFTB with higher interaction energies (vide infra) would bind more selectively to one of the hydrogen atoms. Furthermore, it is worth mentioning that the chemical shift data do not provide evidence that O_{NO} of **1a** gets involved in hydrogen bonding with any of the alcohols used.

For **1c** in the presence of PFTB, positive $\Delta\delta$ values, which correspond to lowfield shifts, are obtained for H_a (Figure 1 and Table 1). These are interpreted in terms of an interaction with the O_{NO} atom (**3c**) and thus contact with H_a is less plausible. Therefore, a molecule of type **2c** with $ReH\cdots HOC(CF_3)_3$ bound to it presumably does not exist. This is in full agreement with our previous IR studies,[22] which allowed us to conclude that **1c** undergoes hydrogen bonding exclusively with O_{NO}. HFIP shows similar behaviour but smaller chemical shift differences are observed, which suggests a weaker interaction with the O_{NO} atom. It was quite surprising to see a relatively wide spread of chemical shifts for H_a, especially for **1c**/PFTB mixtures. These shifts appear even though they originate from hydrogen bonding to a fairly remote site. We believe that this cannot solely be caused by differences in any steric changes occurring upon hydrogen bonding. Rather we assume an effective electronic mechanism, by which the hydrogen bonding of the O_{NO} atom is communicated to H_a. The chemical shifts of H_b of **1c** are practically not altered by the addition of PFTB or HFIP. This suggests that in both cases there is no $H_b\cdots HOR'$ contact.

At a first glance, the results of the HFIP and PFTB attachment to H_a of **1b** seemed to be difficult to analyze. While the chemical shifts of H_a of **1a** and **1c** showed parallel trends in their concentration and temperature dependencies for a given alcohol, those of mixtures with **1b** did not behave uniformly. HFIP always caused small negative $\Delta\delta$ values, but PFTB for instance, in the region of 1:1 to 1:5 **1b**/PFTB ratios, gave rise to small negative $\Delta\delta$ values at lower temperatures, which then changed into positive ones at high temperatures (Table 1). Both data series could ultimately be interpreted in an unified manner with the assumption that there is an overlay of positive (lowfield) and negative (highfield) chemical shift increments, which give rise to the resulting $\Delta\delta$ values. This can be explained by NMR averaging of the **2b**^{a} ⇌ **1b** ⇌ **3b** equilibria. For the HFIP adducts, it is suggested that the

$H_a \cdots HOR'$ binding of **2b**[a] prevails at all temperatures and alcohol concentrations. For hydrogen bonding with PFTB, $H_a \cdots HOR'$ attachment apparently dominates at higher temperatures, whereas at low temperatures there is a preference for $R'OH \cdots ON$ binding. Thus, it might even happen that both shift increments accidentally cancel each other out, which can be found for the **1b**/PFTB 1:2 and 1:5 mixtures; for the latter this is at around 230 K. In the presence of PFTB, H_b of **1b** shows very minor effects. This indicates only marginal involvement of H_b in the hydrogen-bonding process. For HFIP, a slight chemical shift influence can be seen on H_b, which leads us to the conclusion that HFIP does attack **1b** to form **2b**[b], however, this is not the preferred reaction. In this case, three simultaneous associations, $H_a \cdots HOR'$ of **2b**[a], $R'OH \cdots ON$ of **3b** and $H_b \cdots HOR'$ of **2b**[b] (Scheme 1), exist and their K values decrease in the given order.

All this demonstrates that the chemical shift effects on H_a and H_b already allow us to establish a fairly comprehensive picture of the hydrogen bonding to $[Re(CO)H_2(NO)(PR_3)_2]$ complexes. Furthermore, it was possible to extract quantitative equilibrium data from the given changes in δ. In the cases where the NMR experiments indicate that only one major 1:1 adduct is formed, as is the case for the association of **1a** with PFTB and of **1c** with HFIP or PFTB, only one association reaction was considered in the analysis. From Equations (1) and (2), formation constants K could be established for corresponding equilibria (compare Scheme 1). In Equation (1), c(add), c(ReH) and c(alc) are the equilibrium concentrations of **2** or **3**, **1** and the alcohols, respectively and K is the equilibrium constant.

$$K = c(\text{add})/[c(\text{ReH}) \times c(\text{alc})] \quad (1)$$

$$\delta(\text{eq}) = \delta(\text{ReH}) + [\delta(\text{add}) - \delta(\text{ReH})]X(\text{add}) \quad (2)$$

δ(eq) is the averaged equilibrium chemical shift of δ(ReH) and δ(add); δ(ReH) and δ(add) are the chemical shifts of **1** and **2**, and **3**, respectively; c_t(ReH) and c_t(alc) are the initial concentrations of **1** and the alcohols. $X(\text{add}) = (0.5/c_t(\text{ReH}))(c_t(\text{ReH}) + c_t(\text{alc}) + 1/K - ((c_t(\text{ReH}) + c_t(\text{alc}) + 1/K)^2 - 4c_t(\text{ReH})c_t(\text{alc}))^{1/2})$ is the mole fraction of **2** and **3**, which is obtained from the solution of Equation (1).

Equation (2) represents the 'equilibrium NMR' methodology,[19, 28] which can be solved by computer fitting of the curves of δ(eq) vs. the initial alcohol concentrations c_t(alc). In this way, the association constants K and the δ(add) values for the hydrogen-bonding adducts could be obtained for different temperatures (Table 2 and Supporting Information). A definite treatment of the chemical shift data of **1b** in the presence of PFTB and HFIP could not be achieved, since for the two or three parallel equilibria to **2b**[a], **2b**[b] and **3b** a fit of at least four independent parameters out of one available data set for H_a would be required.

In our previous comparative study of dihydrogen bonding to the related tungsten complexes $[WH(NO)(CO)_2(PR_3)_2]$,[19] the NMR-derived K values, obtained from measurements in $[D_8]$toluene, showed comparable trends to those obtained from IR measurements in hexane. However, the NMR-derived K values were significantly smaller than the IR-derived K values. A solvent effect was considered as a possible explanation for this phenomenon. In the present work, we tried to analyze this effect in more detail. To this end, we carried out exemplary NMR measurements of the adduct formation of PFTB with **1a** in $[D_{14}]$methylcyclohexane. Experimentally this turned out to be limited by the low solubility of PFTB at low temperature, so that a temperature range for the titrations comparable to that for the $[D_8]$toluene experiments could not be established. However, we were able to determine the equilibrium constants in this solvent in the temperature range of 313 – 273 K. The obtained K values are almost up to one hundred times larger than those in toluene (for instance $K = 1.9\ \text{L mol}^{-1}$ in toluene and $180.6\ \text{L mol}^{-1}$ in methylcyclohexane at 273 K, compare Table 2). Thus, solvent dependency of the K values could indeed be verified experimentally. We will return to the influence of the solvent at a later point in our discussion.

The analysis of the K values confirmed the regioselectivity of the hydrogen bonding to the hydrides of **1a**, with generally stronger involvement of H_a; the hydride ligand is *trans* to the NO group. In the case of the interaction of HFIP with **1a**, where significant binding also to H_b takes place, two sets of data could be extracted from two sets of chemical shift values, which correspond to the equilibria with H_a and H_b. For an appropriate treatment, it was necessary to apply a modified curve-fitting procedure to allow for coupling of both equilibria shown in Scheme 1. This treatment was based on the reasonable assumptions that only 1:1 adducts are formed under the experimental conditions and that the influences of association at H_b are neglegible for the chemical shift of H_a, and vice versa. Remarkably the K values for the attachment of HFIP to H_a of **1a** are larger than those of PFTB (Table 2) even though the interaction strength of PFTB generally exceeds that of HFIP (vide infra). Consequently we have to assume that the binding of PFTB is associated with more positive $T\Delta S$ increments, which contribute to ΔG. In contrast

Table 2. NMR-derived selected K, ΔH and ΔS values for the hydrogen bonding adducts **2a** and **3c**. K values at T of T_1(min) obtained from extrapolations of the van't Hoff plots, as well as T_1(min) data and calculated hydrogen bonding lengths.[10, 19, 29, 30]

	K [L mol] at 213 K	K [L mol^{-1}] at 273 K	ΔH[a] [kcal mol^{-1}]	ΔS[a] [eu]	K [L mol^{-1}] (T [K]) of T_1(min)	T_1(min)(add) [ms] of $H_{a/b}$	r(H···H) [Å]
2a[a](PFTB)[b]		181	-6.2 ± 0.4	-12.4 ± 1.4			
2a[a](PFTB)[c]	8.9	1.9	-3.1 ± 0.02	-10.0 ± 0.1	17.1 (196)	135	1.78
2a[a](HFIP)[c]	14.0	4.7	-2.1 ± 0.04	-4.7 ± 0.1	22.0 (196)	141	1.80
2a[b](HFIP)[c]	3.3	1.0	-1.7 ± 0.15	-5.5 ± 0.6	4.4 (194)	178	1.94
3c(PFTB)[c]	3.4	1.6	-1.4 ± 0.06	-4.1 ± 0.2			
3c(HFIP)[c]	3.0	1.7	-1.3 ± 0.1	-3.2 ± 0.5			

[a] Errors obtained from linear regression. [b] Measured in $[D_{14}]$methylcyclohexane. [c] Measured in $[D_8]$toluene.

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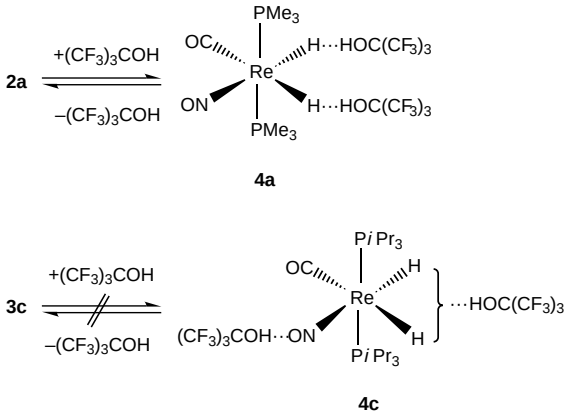
to the diverging behaviour of HFIP and PFTB in the presence of **1a**, both alcohols show similar *K* values for the attachment to the O_{NO} location of **1c**. Presumably this has to do with a diminished steric hindrance for the interaction at O_{NO}, which means there is less discrimination when hydrogen bonds are formed with both proton donors.

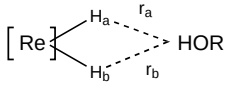
At this point, we have to keep in mind that the simultaneous contact of HFIP to H_a and H_b could also be matched with other mechanistic alternatives. Likewise, the signal-averaged NMR data would to a certain extent be consistent with the formation of doubly hydrogen-bonded adducts of type **4a** in consecutive steps (Scheme 2).



Scheme 2.

This however, seems to be less plausible for the HFIP adducts, since experiments with the **1a**/HFIP mixture in a 1:1 molar ratio indicated, despite the low alcohol concentration, contact between HFIP and both hydrides H_a and H_b. For consecutive equilibrium steps generating doubly hydrogen-bonded species, one would rather expect NMR evidence of stepwise associations expressed in terms of dependence on the alcohol concentration or temperature. Unfortunately, the interaction of **1a** with PFTB might indeed be a stepwise double adduct formation process, which occurs only at relatively high **1a**/PFTB ratios $\geq$1:5 and at quite low temperatures with significantly greater $\Delta\delta$ values for H_b. However, such a condition is at the experimental limits imposed by the solvent toluene. From the NMR data for the **1a** systems, we cannot establish with certainty, whether, in a high alcohol concentration regime, the parallel equilibria of Scheme 1 or the consecutive ones of Scheme 1 and 2 would better fit reality. The same is valid for the T_1(min) experiments analyzed below. However, the IR experiments carried out in hexane[22] allowed us to apply higher PFTB/**1** concentration ratios at lower absolute concentration levels and their results were indeed in favour of the formation of doubly hydrogen-bonded adducts of type **4a**. Furthermore, our analyses of the chemical shift data in [D_8]toluene did not indicate that the doubly bonded species **4c** would exist, since even at PFTB concentration ratios $>$1:5 H_a or H_b did not show any respective chemical shift response.

For the hydrogen bonding of HFIP to **1a** and **1b**, there is still another conceivable structural arrangement, which involves an asymmetric hydrogen bonding bridging mode. This structure would agree with the requirement for simultaneous contact between HFIP and the hydrides H_a and H_b. However, this bonding type should be associated with only one hydrogen-bonding equilibrium, which can definitely be ruled out from the results of the above analysis.



In further support of the results of the chemical shift measurements, we then sought to trace the contacts between H_a or H_b of **1a–c** with HFIP and PFTB by the determination of the temperature-dependent minima of the T_1 relaxation times (T_1(min)).[10, 29, 30] In monohydride complexes, these minimum relaxation times are generally relatively long for the metal-bound hydrogen atoms, because there are usually no significant dipolar interactions to assist the relaxation process. These interactions originate from magnetically polarizing nuclei in close vicinity. In $Re(H)_2$ complexes, these relaxation times are somewhat shorter, since both the hydrides have an influence.[31] The contact between an OH proton and the hydrides is expected to assist the relaxation process of the hydrides further.[10, 11, 19, 29, 30] For example, it is shown in Figure 2, how for **1a** the T_1 relaxation times of H_a and H_b develop with temperature, in the presence and in the absence of HFIP. The minima of the parabolas move with added HFIP

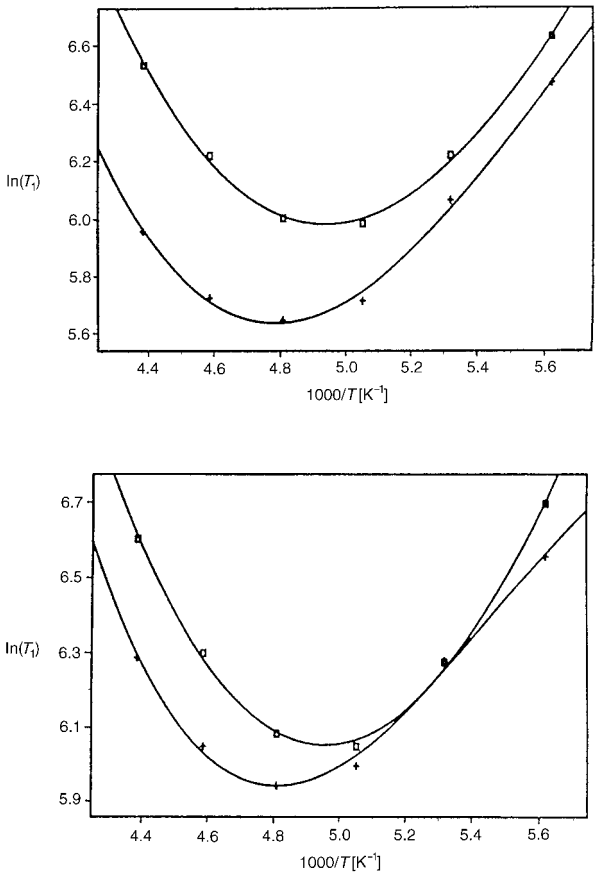


Figure 2. Plots of ln (T_1) (500 MHz) vs 1/*T* for the hydrides H_a (above) and H_b (below) of **1a** (0.05 mol L^{-1}) (□) and in the presence of HFIP (0.1 mol L^{-1}) in toluene[D_8] (+).

to higher temperatures and to shorter relaxation times. As expected, this occurs for H_b to a smaller extent.

In Table 3, the changes in T_1(min) (300 MHz) of the hydrides H_a and H_b are compiled for complexes **1a–c**, with

Table 3. Temperature-dependent minimum relaxation times T_1(min) of the hydride atoms H_a and H_b of **1a–c** (0.05 mol L^{-1}) and those with HFIP or PFTB present (ratio 1:5, 1:8 for PFTB) in [D_8]toluene at 300 MHz.

	T_1(min)[ms]				
			H_a		
	without	with HFIP	Δ	with PFTB	Δ
1a	236[a]	145	91	147	89
1a (1:8)	236[a]			145	91
1b	208	167	41	176	32
1c	174	170	4	171	3
			H_b		
1a	243[a]	206	37	221	22
1a (1:8)	243[a]			217	26
1b	215	202	13	217	−2
1c	167	167	0	173	−6

[a] T_1(min) extrapolated

and without added HFIP or PFTB. The quite sizeable reduction of the minimum relaxation times for H_a of **1a** and **1b** in the presence of HFIP or PFTB again supports the idea that the respective hydride ligands of these complexes are in noticeable contact to protons of HFIP or PFTB. For **1c**, there is only a negligible ΔT_1(min) for H_a and also for H_b, which implies that, for this compound, there is no such hydride contact. This observation is fully consistent with the conclusions reached from the chemical shift and the IR experiments.[22] As mentioned before, PFTB in contact with H_a of **1a** or **1b** shows strong effects and the quite comparable sizes of ΔT_1(min) for HFIP make it clear that it is mainly the dipolar interaction of the HO proton, which assists the relaxation of the hydrides. From Table 3 it can also be seen that the T_1(min) values of the H_a atoms of **1a** and **1b** decrease to a greater extent than those of the respective H_b nuclei. This implies that H_a undergoes a stronger interaction with the proton donor. The weak contact of H_b of **1a** as indicated in the presence of PFTB at the temperature of T_1(min) (192 K) is in agreement with the chemical shift results, where the H_b interaction sets in at around 190 K. Furthermore, one finds a decrease in ΔT_1(min) for H_a and H_b from **1a** to **1b**, which means that the contact between HFIP or PFTB and the hydride ligands gets looser in this order. The tendency to contact the hydrides (**1a** > **1b** > **1c**) contrasts with an anticipated increase in their "hydridicity", which in turn originates from the enhanced ability to donate electron density ($PiPr_3 > PEt_3 > PMe_3$).[32] Instead, this trend correlates with an inverse order of the steric bulk of these ligands.

From the determined T_1(min) values for the hydrides of **1a** and subsequently from their excess relaxation rates ΔR_1(min), the lengths to the $OH_{HFIP,PFTB}$ protons were calculated.[19, 29, 30] The required entity T_1(min)(add) of complexes **2** could not be determined directly, but had to be calculated from the averaging Equation (3), which is related to Equation (2).

$$T_1(\mathrm{min})(\mathrm{add}) = (T_1(\mathrm{min})(\mathrm{eq}) - (X(\mathrm{ReH}) \times T_1(\mathrm{ReH})))/X(\mathrm{add}) \quad (3)$$

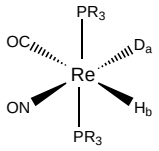
T_1(min)(eq) is the equilibrium-averaged temperature-dependent minimum relaxation time; T_1(ReH) is the relaxation time of **1** at the temperature of T_1(min)(eq); T_1(min)(add) and T_1(min)(ReH) are the temperature-dependent minimum relaxation times of the hydride ligands of **2** and **1**, respectively. X(ReH) and X(add) are the mole fractions of complexes **1** and **2** at the temperature of T_1(min)(eq).

The lengths $r(\mathrm{H}\cdots\mathrm{H})$ in [Å] were then obtained from Equation (4).[19, 37]

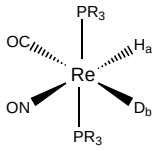
$$r(\mathrm{H}\cdots\mathrm{H}) = 5.817(\tilde{\nu} \times \Delta R_1(\mathrm{min}))^{-1/6} \quad (4)$$

$\tilde{\nu}$ is the NMR frequency in MHz and $\Delta R_1(\mathrm{min}) = 1/T_1(\mathrm{min})(\mathrm{add}) - 1/T_1(\mathrm{min})(\mathrm{ReH})$. The values obtained are 1.78 Å for the contact between PFTB and H_a (**2a^a**) and 1.80 Å and 1.94 Å for the H_a (**2a^a**) and H_b (**2a^b**) hydrogen-bonding lengths to HFIP, respectively (Table 2). They fall into the range determined for other such interactions.[10, 19] The 1.78 Å length of **2a^a** is on the short side of the scale and confirms the relatively strong hydrogen bonding in this case. It is important to recognize that in the **2a**/(HFIP) system we quite reasonably obtained a shorter contact to H_a than to H_b (in the ratio of about 0.93). This is not far from the ratio calculated from the NOE experiments, which we will describe in more detail.

NOE effects from the OH proton of HFIP and PFTB to H_a and H_b of **1a–c** provide more evidence that the OH proton of HFIP or PFTB is involved in hydrogen bonding. In order to show the distinction between the interactions of HFIP with H_a and H_b more clearly, a 1:1 mixture of the D isotopomers **1a,b^{Da}** and **1a,b^{Db}** was prepared. In this way, polarization transfer by the "other" hydride ligand could be excluded and the effects were expected to be more pronounced . The results of these measurements are collected in Table 4.



(1a, b)^{Da}



(1a, b)^{Db}

Due to the exchange of H_a and H_b at higher temperatures and a zero NOE at around −70 °C, measurements for **1b** had to be carried out at −90 °C, which meant that there was a

Table 4. Difference NOE measurements of a 1:1 mixture of the Re(CO)DH(NO)$(PR_3)_2$ isotopomers **1^{Da,Db}** and of **1c** (0.05 mol L^{-1}) in the presence of HFIP (0.1 mol L^{-1}) (1:2 ratio) in [D_8]toluene at −60 °C (**1a, 1c**) and −90 °C (**1b**) and of **1a–c** (0.05 mol L^{-1}) in the presence of PFTB (1:2 ratio) in [D_8]toluene at 295 K. H_{HOR} was irradiated. The values for r_a/r_b are the $H_b\cdots HOR'/H_a\cdots HOR'$ length ratios calculated from $(\eta(H_b)/\eta(H_a))^{1/6}$.

	$\eta(H_a)$	$\eta(H_b)$	r_a/r_b
1a/HFIP	9.1×10^{-2}	4.3×10^{-2}	0.87
1b/HFIP	-1.5×10^{-1}	-4.4×10^{-2}	0.82
1c/HFIP		no effect	
1a/PFTB	-2.8×10^{-1}	no effect	
1b/PFTB	-4×10^{-2}	no effect	
1c/PFTB		no effect	

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negative NOE effect with decreasing NOE intensities $\left(\text{NOE effect } \eta = \frac{I - I_0}{I_0}\right)$. From $\eta(H_a)$ and $\eta(H_b)$, it was possible to calculate approximate length ratios r_a/r_b of the hydride/HO separations.[29, 33] The ratios for **1a** were in reasonable agreement with those of the T_1(min) measurements (compare Table 3). The quite sizeable NOE responses in the **1a,b**^{Da,Db}/HFIP systems again make the $H_{a,b}\cdots HOR'$ hydrogen-bonding contacts of **1a,b** quite evident. For **1c**, we were not able to prepare the isotopomeric mixture of **1c**^{Da,Db}. Instead the parent complex **1c** was used in the NOE experiments with HFIP. Since practically no effect was found, one can quite confidently rule out any hydrogen bonding of the hydrides of **1c** at reasonable distances. Comparable results were obtained from room-temperature NOE experiments of **1a–c** with PFTB. In the case of **1c**, there was no detectable NOE response of H_a and H_b. In contrast to the measurements in the presence of HFIP, no effect was found for H_b of **1a** and **1b**, which confirms that PFTB has a strong preference for binding to H_a.

The results from our NMR experiments present a clear picture of the nature of hydrogen bonding between **1a–c** and proton donors. The hydride ligands of **1a** and **1b** are able to establish notable contacts with the fluorinated alcohols. For **1c**, the hydride ligands do not interact with the proton donors, or they interact just to a very minor extent. In this case, the O_{NO} atom is involved in hydrogen bonding instead. Furthermore, the NMR studies provided evidence for the regioselectivity of the contacts to the hydrides. This regioselectivity depends on the alcohol used. PFTB shows a preference for binding to H_a and the O_{NO} atom, while HFIP can, in a less selective manner, additionally bind to H_b. The general preference of both alcohols for the attachment to H_a presumably arises from the higher "hydridicity" of H_a,[26a] which in turn may be interpreted as a consequence of the strong *trans* influence of the nitrosyl group. The equilibrium NMR data finally allowed us to calculate formation constants and to estimate reasonable hydrogen-bonding lengths.

Energetic studies: ΔH and ΔS values for the adduct formation reaction $\mathbf{1} + HOR' \rightarrow \mathbf{2}$ were obtained from van't Hoff plots, using the K values determined by NMR spectroscopy. The data showed surprisingly good linear regressions and were therefore used with confidence. These values are collected in Table 2. For the reactions **1a** + PFTB → **2a** and **1c** + PFTB → **3c**, we have previously determined ΔH by IR spectroscopy.[22] These measurements were carried out in the nonpolar solvent hexane and yielded values of 6.1 kcal mol^{-1} and 4.5 kcal mol^{-1}, respectively. The ΔHs determined by NMR spectroscopy in this work in toluene are lower by 3.0 kcal mol^{-1} and 3.1 kcal mol^{-1}. This again can be explained in terms of a solvent effect, in which toluene establishes weak 'aromatic' hydrogen bonds to acidic substrates in the $-\Delta H$ range of 1.5–2 kcal mol^{-1}.[34, 35] The fluorinated Pirkle alcohol, which is assumed to be a good chemical model for HFIP and PFTB, is capable of establishing even stronger hydrogen bonds of approximately 2.5–3.0 kcal mol^{-1} in a self-association process.[36] In analogy to these observations, we anticipate that HFIP or PFTB can give rise to interactions with toluene, which are of similar strength. The differences in the interaction enthalpies obtained from IR and NMR experiments are apparently in the same range as the expected hydrogen-bonding enthalpies of toluene with fluorinated alcohols. Consequently, this indicates that the lower enthalpies for hydrogen bonding of the hydrides in toluene result from the need to break the hydrogen bonds to toluene. Mapping of the hydrogen bonding of fluorinated alcohols in toluene onto an "absolute scale" (that is a solvent with no hydrogen-bonding capabilities) requires the addition of 2.5–3.0 kcal mol^{-1} to the toluene values. In order to confirm this, we have additionally determined the thermodynamic data for the equilibrium of **1a** with PFTB in [D_{14}]methylcyclohexane. We obtained a ΔH value of -6.2 kcal mol^{-1} (Table 4), which is very close to that determined by IR spectroscopy for the **1a**/PFTB mixture in hexane.[22] The $\Delta\Delta H$ between methylcyclohexane and toluene thus was determined to be 3.1 kcal mol^{-1}, which is very close to the value expected from the foregoing consideration based on aromatic hydrogen bonding.

Otherwise, the ΔH values of Table 2 parallel our conclusions drawn so far. We see, for instance, a weaker affinity of PFTB for **1c** as compared to **1a**. Also, the HFIP adduct series reproduce the overall binding trend, that is stronger interaction with the hydrides than with the O_{NO} atom. The bond between PFTB and H_a is 1 kcal mol^{-1} stronger than that for HFIP. As a consequence, HFIP looses binding selectivity, which leads to two parallel equilibria with contacts to H_a and H_b of **1a**. This is substantiated by the finding of two distinct ΔH values with a $\Delta\Delta H$ value of 0.4 kcal mol^{-1}.

Finally it is worth analyzing the entropy effects. Irrespective of the solvent type, ΔS adopts the most negative values in the case of the binding of PFTB to H_a of **1a**. Supposedly this is due to a relatively tight binding in the adduct state, which causes a strong loss of degrees of freedom upon attachment. For HFIP associated with H_a in **2a**, the magnitude of the loss of entropy is only about half, which is presumably due to the fact that this alcohol possesses a more flexible hydrogen-bonded arrangement. Because of the smaller $-\Delta S$ value for HFIP, the total factor $-T\Delta S$ does not contribute so much to the decrease of the $-\Delta G$ value. As a consequence of this, the K values are, in this case, largest of all studied hydrogen-bonded adducts despite a lower $-\Delta H$ value (Table 2).

Conclusion

Protonation is one of the most fundamental reactions in the chemistry of transition metal complexes. In the last ten years, it has also become a traditional route to dihydrogen complexes: when a metal hydride is protonated, coordinated H_2 is formed as a kinetic product.[2, 7] The synthetic evidence has always been regarded as a strong indication that the hydride ligand is the proton accepting site. This paper confirms once again that there is attractive interaction that results in the formation of hydrogen-bonded species of the type $ReH\cdots HOR'$, which, depending on the acid strength, could eventually transform into a dihydrogen complex.[9]

Furthermore, our investigations demonstrated that the studied nitrosyl complexes possess not only chemically different hydride positions, but also the O_{NO} atom as competing sites for hydrogen bonding. The activity order of these sites could mainly be related to the steric bulk of the phosphane ligands. Without dominating steric influence, the electronic order of the hydrogen bonding was disclosed, which was revealed to be $H_a > H_b > O_{NO}$. Site selectivity was thus established as an important factor in these adduct formation processes. Our studies then showed that hydrogen bonding as an initial stage to full protonation is not only a function of the nature of the offered basic sites, but it is also influenced by the chemical nature of the acid and the solvent. It is important to recognize that these parameters may be used to tune hydride reactivity under the influence of proton donors. A special case of reactivity with great potential and perspectives is ionic hydrogenation.[37] It takes place under heterolytic splitting of H_2[30a] and thus provides at some stage the necessary conditions for a hydride/protic substrate interaction. Further investigations will have to demonstrate, whether this secondary binding phenomenon is crucial to such biological or organometallic catalyses.

Experimental Section

Measurements: NMR data were obtained on a Varian Gemini 300 spectrometer (300 MHz, ^{1}H). The inversion-recovery method (180-t-90) was used to determine T_1 relaxation times. The calculation of the relaxation times was made using the nonlinear three-parameter fitting routine of the spectrometer. In each experiment, the waiting period was 10 times the expected relaxation time and 12 variable delays were employed. The duration of the pulses was controlled at every studied temperature. For the T_1 NMR samples, in a typical case: The solvent ([D$_8$]toluene) was transferred into a 5 mm tube containing a weighed amount of [Re(CO)H$_2$(NO)(PR$_3$)$_2$] and then HFIP or PFTB was added. The solution was then degassed and the tube flame sealed under vacuum. The T_1 experiments were run starting at room temperature (295 K).

Standard Varian software was used for the NOE (DIFNOE) measurements. Preparation of the NOE samples: The NMR solvent was added into a 5 mm NMR tube containing a weighed amount of [Re(CO)H$_2$(NO)(PR$_3$)$_2$]. The tube was transferred into a cold bath (190 K) for the addition of HFIP or PFTB and then was degassed and sealed. IR spectra were recorded on a Biorad FTS 15 instrument. FAB-MS(+) spectra were recorded on a Finnigan MAT 8400 mass spectrometer. Solutions of the samples in dichloromethane were dissolved in a 3-nitrobenzyl alcohol matrix; m/z was based on ^{187}Re.

Equilibrium analysis: The K and δ(add) values were obtained by a nonlinear fit using a Levenberg–Marquardt algorithm.[38] For this purpose, Equation (5) (modified Eq. (2)) was used in the following form.[19]

$$\delta(\mathrm{eq}) = (\delta(\mathrm{ReH}) + Q \times \delta(\mathrm{add}))/(1 + \mathrm{Q}) \quad (5)$$

In this equation, $Q = 0.5 \times (S - a)$, $S = (a^2 + 4 \times K \times c_t(\mathrm{ReH}))^{1/2}$ and $a = K \times (c_t(\mathrm{ReH}) - c_t(\mathrm{alc})) + 1$. For the interaction of **2a** with HFIP, the two equilibria resulting in **2a^a** and **2a^b** were treated in a coupled fashion. Alternately one of the two sets of δ and K parameters was kept fixed and the other was fitted until a self consistent solution for both equilibria was obtained.

Chemicals: HFIP and PFTB were available from Fluka. The NMR solvents [D$_8$]toluene and [D$_{14}$]methylcyclohexane were purchased from Deutero GmbH, D-56288 Kastellaun. Sodium borodeuteride was available from CIL (Cambridge Isotope Laboratories).

Preparative procedures: All manipulations were performed under a dry nitrogen atmosphere by standard Schlenk-tube techniques. Solvents were dried and deoxygenated by conventional procedures and were freshly distilled before use. Compounds **1a–c** and [ReCl(CO)H(NO)(PR$_3$)$_2$] were prepared as described in the literature.[39]

Synthesis of [Re(CO)DH(NO)(PMe$_3$)$_2$]: The monodeuterated complex was prepared by the reaction of [ReCl(CO)H(NO)(PMe$_3$)$_2$] (150 mg, 0.35 mmol) and sodium borodeuteride (100 mg, 2.39 mmol) in ethanol (ca. 20 mL). The suspension was heated to reflux for 5 min. The solvent was removed under reduced pressure and then the residue was extracted with hexane (five times with 10 mL). The yellow solution was filtered through Celite and the solvent evaporated, which gave a lemon yellow powder (a 1:1 mixture of the isomers D *trans* NO and D *trans* CO). Yield: 130 mg (93 %); IR (hexane, cm^{-1}): $\tilde{\nu} = \nu$(CO) 1965, 1961 (vs), ν(Re–H) 1799 (w, br), ν(NO) 1679, 1659 (s), ν(Re–D, KBr) 1266 (w); ^{1}H NMR (300 MHz, [D$_8$]toluene, 295 K): $\delta = 1.33$ (t, J(P,H) = 8.2 Hz, P(CH$_3$)$_3$), -0.99 (t, J(P,H) = 27.0 Hz, ReH$_a$), -4.39 (t, J(P,H) = 27.9 Hz, ReH$_b$); ^{13}C{^{1}H} NMR (75.46 MHz, [D$_8$]toluene, 295 K): $\delta = 209.7$ (t, J(PC) = 5.7 Hz, ReCO), 23.0 (t, J(PC) = 35.9 Hz, P(CH$_3$)$_3$); ^{31}P{^{1}H} NMR (121.47 MHz, [D$_8$]toluene, 295 K) $\delta = -32.8$ (s); FAB-MS (positive ion): m/z (%): 396 (15) [M – H, – D]$^+$, 366 (6), [M – H, – D, – NO]$^+$.

Synthesis of [Re(CO)DH(NO)(PEt$_3$)$_2$]: [Re(CO)DH(NO)(PEt$_3$)$_2$] was prepared as described for [Re(CO)DH(NO)(PMe$_3$)$_2$] using [ReCl(CO)H(NO)(PEt$_3$)$_2$] (80 mg, 0.15 mmol) and sodium borodeuteride (100 mg, 2.39 mmol) in ethanol (ca. 15 mL). Evaporation to dryness in vacuo yielded the product (70 mg, 93 %) as a yellow oil (isomeric mixture) with a melting point below 0 °C. IR (hexane, cm^{-1}): $\tilde{\nu} = \nu$(CO) 1960, 1954 (vs), ν(Re–H) 1814 (w, br), ν(NO) 1672, 1654 (s); ^{1}H NMR (300 MHz, [D$_8$]toluene, 295 K): $\delta = 1.54$ (m, P(C*H*$_2$CH$_3$)$_3$), 0.91 (tt, J(H,H) = 7.6 Hz, J(P,H) = 15.9 Hz, P(CH$_2$C*H*$_3$)$_3$), -1.64 (t, J(P,H) = 26.5 Hz, ReH$_a$), -5.29 (t, J(P,H) = 26.3 Hz, ReH$_b$); ^{13}C{^{1}H} NMR (75.46 MHz, [D$_8$]toluene, 295 K): $\delta = 23.8$ (t, J(P,C) = 32.2 Hz, P(*C*H$_2$CH$_3$)$_3$), 8.5 (s, P(CH$_2$*C*H$_3$)$_3$); ^{31}P{^{1}H} NMR (121.47 MHz, [D$_8$]toluene, 295 K) $\delta = 8.0$ (s); FAB-MS (positive ion): m/z (%): 481 (100) [M – H, – D]$^+$, 450 (66) [M – H, – D, – NO]$^+$, 422 (38) [M – H, – D, – NO, – CO]$^+$; elemental analysis calcd for C$_{13}$H$_{31}$DNO$_2$P$_2$Re: C 32.23, H 6.24, N 2.9; found: C 32.35, H 6.10, N 2.8.

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