1522 *Inorg. Chem.* **1997,** *36,* 1522−1525

Intermolecular Hydrogen Bonding of $ReH_2(CO)(NO)L_2$ Hydrides with Perfluoro-*tert*-butyl Alcohol. Competition between M−H···H−OR and M−NO···H−OR Interactions

Natalia V. Belkova,[†] **Elena S. Shubina,**[†]
Aleksei V. Ionidis,[†] **Lina M. Epstein,***[,†]
Heiko Jacobsen,[‡] **Andreas Messmer,**[‡] **and**
Heinz Berke*[,‡]

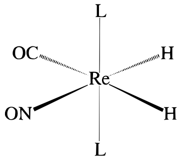
Institute of Organo-Element Compounds, Russian Academy
of Sciences, Vavilov Str. 28, Moscow B-334, Russia, and
Anorganisch-Chemisches Institut der Universität Zürich,
Winterthurerstrasse 190, CH-8057 Zürich, Switzerland

Received July 17, 1996

Introduction

Currently, intense scrutiny is given to a novel hydrogen−hydrogen bonding mode[1−5] ("dihydrogen bonding") involving transition metal hydrides of the M−H···HX type. We recently provided IR and NMR spectroscopic evidence for the intermolecular M−H···HOR interaction between $WH(CO)_2(NO)L_2$ hydrides and acidic alcohols.[1] In nonpolar and low-polarity solvents, we found a presumable linear H···H bond of medium strength, $-\Delta H$ ranging from 4.1 to 6.9 kcal/mol. For L = PMe_3, the H···H distance could be determined as $d_{H\cdots H} = 1.77$ Å. In contrast, recent X-ray and neutron diffraction studies[5] on $ReH_5(PPh_3)_3$·indole·C_6H_6 show the presence of a 3-center intermolecular $N{-}H\cdots H_2Re$ bond. Nonlinear H···H contacts are observed, with two distinct H···H bond distances of 1.73 and 2.21 Å.

In this work, we present the results of IR studies on the interaction of the rhenium hydrides[6] **1**−**3** with perfluoro-*tert*-butyl alcohol (PFTB) in the nonpolar solvent hexane.



1 L = PMe_3
2 L = PEt_3
3 L = $PiPr_3$

Table 1. ν(OH) Bands[a] of PFTB in the Presence of Complexes **1**−**3** and the Corresponding Hydrogen Bond Strengths[b]

	L	$\nu(OH)_{bonded}$	$\Delta\nu(OH)^c$	$-\Delta H$
1	PMe_3	3218	370	6.1
2	PEt_3	3294	294	5.2
3	$PiPr_3$	3347	243	4.5

[a] In cm^{-1}. [b] In kcal/mol. [c] $\nu(OH)_{free} = 3588$ cm^{-1}.

Our work was prompted by the fact that protonation of the rhenium hydrides **1**−**3** leads to the formation of dihydrogen complexes.[7] The possible adducts which precede the formation of the nonclassical dihydrogen complexes are in the focus of the present study. We further support our experimental findings with theoretical investigations of the model system $ReH_2(CO)(NO)(PH_3)_2 \cdot H_2O$. The calculations are based on density functional theory (DFT), which during the past 15 years has emerged into a valuable tool in studies of organometallic structures and energetics.[8]

Experimental Section

The dihydrides $ReH_2(CO)(NO)L_2$ studied in this work were prepared as described elsewhere.[6] PFTB was prepared as described in the literature.[9]

Temperature-dependent IR measurements were made in the range from 200 to 290 K. A detailed description of a typical IR experiment is given in ref 1.

The calculations utilized the Amsterdam density functional package ADF,[10] release 2.0.1. The ADF basis set III was chosen for the main group elements, whereas Re was described with a modified basis set IV, including 5s and 5p as valence shells, and $\alpha_{6p} = 1.05$, 1.65, and 2.60. Nonlocal gradient corrections were included self-consistently. Relativistic effects are treated within a quasi-relativistic approach.

Results and Discussion

The stretching vibration of the OH group of PFTB in the presence of an excess of complexes **1**−**3** reveals the typical picture of hydrogen bonding.[11] The intensity of $\nu(OH)_{free}$ decreases, and a new broad $\nu(OH)_{bonded}$ band appears, which is shifted to lower wavenumbers and is increased in intensity. The shift $\Delta\nu$(OH) of the OH stretching frequency correlates with the strength of the hydrogen bond, $-\Delta H$. We have shown[1] that the following empirical correlation, originally proposed by Ioganson[12] for linear hydrogen bonding between organic molecules, is also applicable to transition metal hydrides:

$$-\Delta H = 18(\Delta\nu(\mathrm{OH}))/(\Delta\nu(\mathrm{OH}) + 720) \qquad (1)$$

The hydrogen bond strengths found for the PFTB adducts of complexes **1**−**3**, together with values for the OH stretching frequencies, are collected in Table 1. One sees that the rhenium hydrides under investigation form hydrogen bonds of medium strengths ($-\Delta H = 4.5{-}6.1$ kcal/mol), which are about 1 kcal/mol weaker than those found in $WH(CO)_2(NO)L_2$·PFTB adducts with the same phosphine ligands.[1]

Although the IR data in the ν(OH) range supply spectroscopic evidence for hydrogen bonding, they do not provide any structural information. In particular, there is no indication which

---

[†] Russian Academy of Sciences.

[‡] Universität Zürich.

(1) Shubina, E. S.; Belkova, N. V.; Krylov, A. N.; Vorontsov, E. V.; Epstein, L. M.; Gusev, D. G.; Niedermann, M.; Berke, H. *J. Am. Chem. Soc.* **1996**, *118*, 1105.

(2) (a) Park, S.; Ramachandran, R.; Lough, A. J.; Morris, R. H. *J. Chem. Soc., Chem. Commun.* **1994**, 2201. (b) Lough, A. J.; Park, S.; Ramachandran, R.; Morris, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 8356. (c)Xu, W.; Lough, A. J.; Morris, R. H. *Inorg. Chem.* **1996**, *35*, 1549. (d) Park, S.; Lough, A. J.; Morris, R. H. *Inorg. Chem.* **1996**, *35*, 3001.

(3) (a) Peris, E.; Lee, C. J., Jr.; Crabtree, R. H. *J. Chem. Soc., Chem. Commun.* **1994**, 2573. (b) Lee, C. J., Jr.; Rheingold, A. L.; Müller, B.; Pregosin, P. S.; Crabtree, R. H. *J. Chem. Soc., Chem. Commun.* **1994**, 1021. (c) Lee, C. J., Jr.; Peris, E.; Rheingold, A. L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 11014. (d) Yao, W.; Crabtree, R. H. *Inorg. Chem.* **1996**, *35*, 3007.

(4) Liu, Q.; Hoffmann, R. *J. Am. Chem. Soc.* **1995**, *117*, 10108.

(5) Wessel J.; Lee J. C.; Peris E.; Yap G. P. A. Fortin J. B.; Ricci J. S; Sini G.; Albinati A.; Koetzle T. F.; Eisenstein O.; Rheingold A. L.; Crabtree R. H. *Angew. Chem.* **1995**, *107*, 2711; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2507.

(6) Hund, H.-U.; Ruppli, U.; Berke, H. *Helv. Chim. Acta* **1993**, *76*, 963.

(7) Feracin, S.; Bürgi, T.; Bakhmutov, V. I.; Eremenko, I.; Vorontsov, E. V.; Vymenits, A. B.; Berke, H. *Organometallics* **1994**, *13*, 4194.

(8) (a) Ziegler, T. *Chem. Rev.* **1991**, *91*, 651. (b) Ziegler, T. *Can. J. Chem.* **1995**, *73*, 743.

(9) Filler, R.; Schure, R. M. *J. Org. Chem.* **1967**, *32*, 1217.

(10) (a) Baerends, E. J.; Ellis, D. E.; Ros, P. E. *Chem. Phys.* **1973**, *2*, 41. (b) teVelde, G.; Baerends, E. J. *J. Comput. Phys.* **1992**, *99*, 84.

(11) The concentrations of PFTB were varied in the range 0.005−0.01 mol/L to exclude self-association.

(12) Ioganson, A. V. *Hydrogen Bond;* Nauka: Moscow, 1981; p 112.

S0020-1669(96)00829-4 CCC: $14.00 © 1997 American Chemical Society

Scheme 1

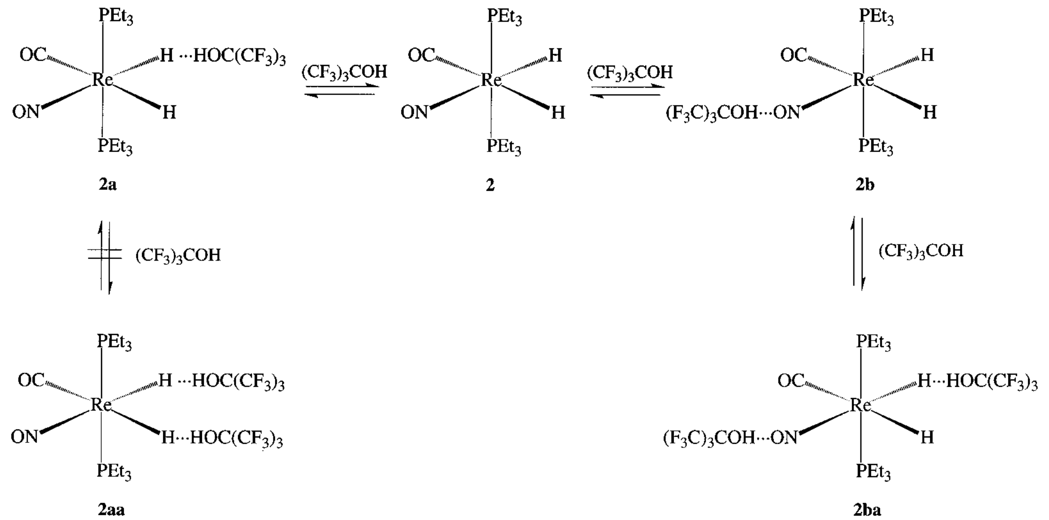


Table 2. ν(CO) and ν(NO) Bands[a] for the Free Complexes **1**−**3** and for the Corresponding PFTB Adducts (1:1 Alcohol/Hydride)

	L	$\nu(\mathrm{CO})_{\mathrm{free}}$	$\nu(\mathrm{CO})_{\mathrm{bonded}}$	$\Delta\nu$(CO)	$\nu(\mathrm{NO})_{\mathrm{free}}$	$\nu_{+}(\mathrm{NO})_{\mathrm{bonded}}$	$\Delta\nu_{+}$(NO)	$\nu_{-}(\mathrm{NO})_{\mathrm{bonded}}$	$\Delta\nu_{-}$(NO)
1	PMe_3	1962	1973	+11	1652	1671	+19	1597	−55
2	PEt_3	1957	1968	+11	1650	1666	+16	1592	−58
3	$PiPr_3$	1952	1963	+11	1645			1592	−53

[a] In cm^{-1}.

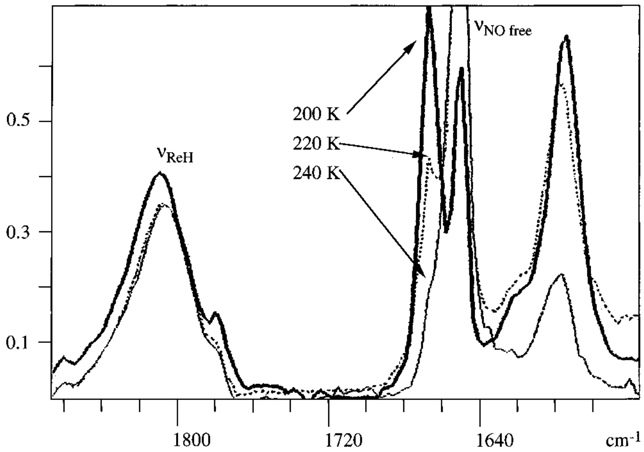


Figure 1. Variable-temperature IR spectra of $ReH_2(CO)(NO)(PEt_3)_2$/PFTB (0.008/0.016 M) in the range of ν(NO) and ν(ReH).

of the possible coordination sites of the transition metal complex is involved in the bonding interaction. We therefore thoroughly investigated the absorption regions of the ν(CO), ν(NO), and ν(ReH) vibrations. Important spectral data are presented in Table 2.

The IR spectra of solutions of $ReH_2(CO)(NO)L_2$ in the presence of an equimolar amount or slight excess (1:2) of PFTB reveal the appearance of one new CO band, shifted by 11 cm^{-1} to higher frequencies. The intensity of this new band is temperature dependent and increases by decrease of the intensity of $\nu(\mathrm{CO})_{\mathrm{free}}$ on lowering the temperature. These changes are reversible, indicating that the formation of the new species is an equilibrium process. The shift to higher wavenumbers clearly points to the fact that the CO ligand is not involved in hydrogen bonding;[1] for an interaction in RO−H···OC−M fashion, one would expect shifts of ν(CO) to lower wavenumbers.[13ab]

The observed changes in the ranges of the ν(NO) and ν(ReH) stretching frequencies provide further insight into the nature of the hydrogen bond. Most interesting is the spectral picture of complex **2** in the presence of an equimolar amount of PFTB, as shown in Figure 1. Two new ν(NO) bands of adducts are observed, which are shifted to higher, $\nu_{+}(\mathrm{NO})_{\mathrm{bonded}}$, as well as to lower, $\nu_{-}(\mathrm{NO})_{\mathrm{bonded}}$, frequencies. The temperature dependency of the ν(NO) stretching frequencies is similar to that observed for ν(CO), again indicating an equilibrium process. The band $\nu_{+}(\mathrm{NO})_{\mathrm{bonded}}$ is assigned to a complex in which the NO ligand does not take part in hydrogen bonding. The corresponding low-frequency shoulder of the ν(ReH) band, which intensity increases upon cooling, can be attributed to a complex with a hydride ligand as the site of protonation. The significant shift to lower frequencies, as well as the broadening of $\nu_{-}(\mathrm{NO})_{\mathrm{bonded}}$, is consistent with the changes known for hydrogen bonding with the oxygen atom of a nitrosyl in O−H···ON fashion.[13c] Thus, we conclude that **2** forms with PFTB two types of hydrogen-bonded complexes, which are in equilibrium with the starting materials (Scheme 1).

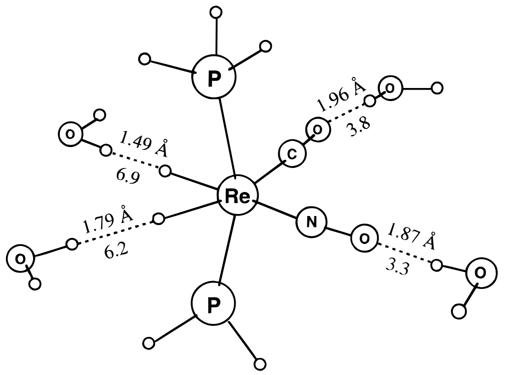


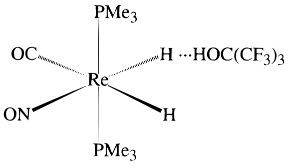
Figure 2. Calculated H···H distances and bond strengths (in kcal/mol) for various isomers of $ReH_2(CO)(NO)(PH_3)_2 \cdot H_2O$.

For **1**, the amount of the RO−H···ON−Re adduct **1b** analogous to **2b** is very low (<6%). The dominant feature in

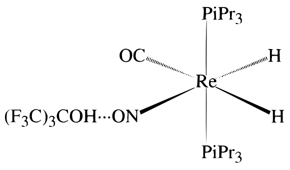
---

(13) (a) Lokshin, B. V.; Kazarian, S. G.; Ginzburg, A. J. *J. Mol. Struct.* **1988**, *174*, 29. (b) Lokshin, B. V.; Kazarian, S. G.; Ginzburg, A. J. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1986**, 2605. (c) Lokshin, B. V.; Kazarian, S G.; Ginzburg, A. J. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1987**, 948.

the IR spectrum is the appearance of $\nu_{+}(NO)_{bonded}$ at 1671 cm^{-1}. Although the ν(ReH) band does not show a low-frequency shoulder, upon addition of PFTB it broadens and its integral intensity increases by a factor of 1.2. We therefore suggest that adduct **1a** is the major species in solution. Finally, for complex **3**, one only observes the $\nu_{-}(NO)_{bonded}$ band. Furthermore, the very broad and low-intensity ν(ReH) band does not change under addition of PFTB and is not temperature dependent. This is consistent with the formation of only complex **3b**.



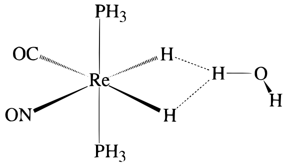
1a



3b

To better understand the observed diversity in the modes of hydrogen bonding, we performed DFT calculations on the model system $ReH_2(CO)(NO)(PH_3)_2{\cdot}H_2O$. The main results of the calculations are summarized in Figure 2. The optimized geometries for the HO−H···H−M bonding modes show H···H contacts of 1.49 and 1.79 Å, respectively. These distances compare reasonably well with the experimental values (vide supra), given the fact that the adducts possess a very shallow energy surface around the H···H bond. The most important result is that HO−H···H−M bonding is energetically favored over HO−H···ON−M bonding by about 3.0−3.5 kcal/mol. The strengths of the HO−H···ON−M and HO−H···OC−M bonding interactions are comparable but are slightly in favor for the carbonyl bonding. One has, however, to keep in mind the model character of the calculations. Effects, as for example solvation of the species, as well as the true nature of the phosphorus donor ligands, are certainly of importance in the description of such delicate bonding interactions.

We further optimized the structure of an adduct with a 3-center intermolecular $O{-}H{\cdots}H_2Re$ bond, as displayed in **4**.



4

The calculated H···H distances are 1.63 and 1.87Å, respectively. The strength of this hydrogen bond amounts only to 2.6 kcal/mol, and it is considerable weaker than the 2-center bonds considered. Thus, the calculation supports the notion of a linear H···H bond, as observed for the $ReH_2(CO)(NO)L_2$ complexes and for the tungsten hydrides[1] $WH(CO)_2(NO)L_2$.

The experimental and theoretical findings suggest that the competition between electronic and steric effects is important for the type of hydrogen bonding observed. The compound with the sterically most demanding phosphorus ligands shows a coordination mode which is least favorable on electronic grounds. On reducing the steric bulk, one notices that now the RO−H···H−M bonding mode is realized, which becomes the major interaction for the sterically least demanding phosphorus donor.

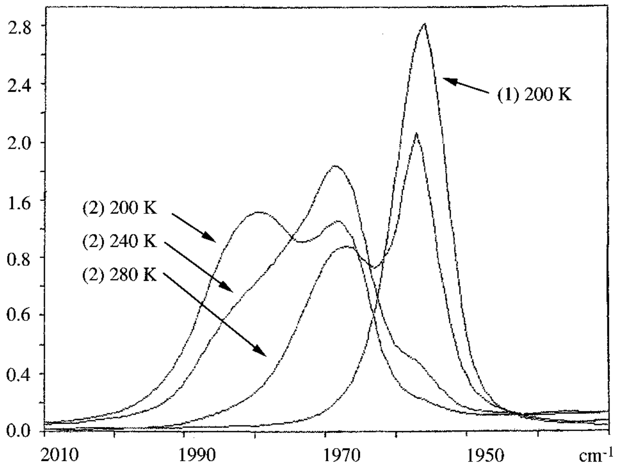


Figure 3. (1) IR spectra of $ReH_2(CO)(NO)(PEt_3)_2$ (0.008 M) at 200 K, and (2) variable-temperature IR spectra of $ReH_2(CO)(NO)(PEt_3)_2$/PFTB (0.008/0.032 M) in the range of ν(CO).

Table 3. ν(CO) and ν(NO) Bands[a] for the 1:1 and 2:1 PFTB/$ReH_2(CO)(NO)L_2$ Adducts

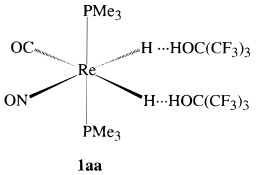
	L	$\nu(CO)_{1:1}$	$\nu(CO)_{2:1}$	$\Delta\nu$	$\nu(NO)_{1:1}$	$\nu(NO)_{2:1}$	$\Delta\nu$
1	PMe_3	1973	1986	+13	1671 (**a**)	1686 (**aa**)	+15
					1597 (**b**)	1622 (**ba**)	+25
2	PEt_3	1968	1980	+12	1666 (**a**)	1666	0
					1592 (**b**)	1613 (**ba**)	+21
3	$PiPr_3$	1963	1975	+12	1592 (**ba**)	1625 (**ba**)	+33

[a] In cm^{-1}.

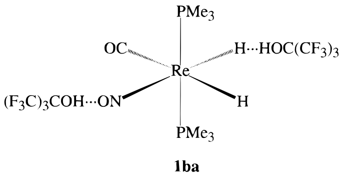
The question remains, how such a variety of complex formation in all cases leads only to one product of protonation, namely the dihydrogen complex.[7] To this end, we recorded IR spectra of complexes **1**−**3** in greater excess of the alcohol ($PFTB/ReH_2(CO)(NO)L_2 \geq 4:1$). At low temperatures (200−240 K), new species were detected, which are interpreted in terms of 2:1 $PFTB/ReH_2(CO)(NO)L_2$ adducts. The most important spectral data for these compounds are collected in Table 3.

For all of the complexes **1**−**3**, we observe a second $\nu(CO)_{bonded}$ stretching band, which is shifted by 12−13 wavenumbers to higher frequencies, compared to that of the 1:1 adduct. This points to the fact that the carbonyl ligand is not involved in the coordination of a second molecule PFTB. The behavior of all the ν(CO) bands under variation of temperature once again establishes an equilibrium process. A representative spectrum is shown in Figure 3.

For the system **1a**,**b**, both bands, $\nu_{+}(NO)_{bonded}$, as well as $\nu_{-}(NO)_{bonded}$, are shifted to higher wavenumbers, when the 2:1 adducts are formed. This is indicative for the fact that a hydride ligand is responsible for the second coordination. The resulting complexes are shown in **1aa** and **1ba**, although the latter again is only the minor component (<6%).

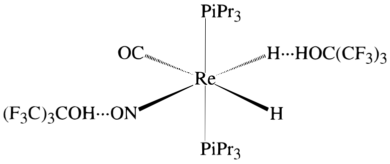


1aa



1ba

Interestingly, for complex **2** there exists only one 2:1 adduct, namely **2ba**. A complex of the type **2aa** could not be detected in solution, even in the low temperature regime down to 200 K (Scheme 1). **2a** does not undergo a second coordination, since the $\nu_{+}(NO)_{bonded}$ band at 1666 cm^{-1} remains unchanged (compare Table 3). Last, the spectral changes observed for complex **3** are consistent with the formation of the double-bonded adduct **3ba**.



3ba

Since all the compounds **1**−**3** show at least one RO−H···H−M bonding mode, it is very likely that hydrogen bonding to the hydride precedes the formation of dihydrogen complexes.[7]

Concluding Remarks

In summary, we can state that rhenium hydride complexes of the type $ReH_2(CO)(NO)L_2$ (L = PMe_3, PEt_3, $PiPr_3$) do form a variety of hydrogen-bonded complexes with acidic alcohols, such as PFTB. The strengths of these bonds range from 4.5 to 6.1 kcal/mol and are slightly less than those for the related tungsten systems $WH(CO)_2(NO)L_2$.[1] The steric requirements of the phosphine ligands exert a strong influence on the hydrogen bonding site at the metal center (H−Re and/or ON−Re). However, RO−H···H−M bonding is always observed for the hydrogen-bonded 2:1 adducts.

Acknowledgment. This work was supported by the Russian Found for Fundamental Research (Grant N96-03-34114) and the Swiss National Science Foundation (SNFS). We acknowledge access to the IBM/RS6000 work stations of the Rechenzentrum at the Universität Zürich.

IC9608298