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Hydrogen-Bonding and Photochemistry of Organometallics in Liquid Xenon Solution in the Presence of Proton Donors: A Low Temperature Infrared Study of the Interaction of $(CF_3)_3COH$ with $(C_5Me_5)M(CO)_2L$ (M = Mn and Re; L = CO, N_2, and H_2) and with $(C_5Me_5)V(CO)_4$

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IR spectroscopy in solutions in liquid xenon (lXe) has been used to study the interactions of perfluoro-*tert*-butyl alcohol (PFTB) with a number of organometallic half-sandwich compounds. The interaction of PFTB with $Cp^*Re(CO)_2(N_2)$, **I**, has been studied in some detail and IR spectra indicate the formation of two H-bonded species, identified as $Cp^*Re(CO)_2N_2$/PFTB, **II**, and $Cp^*Re(CO)_2N_2/(PFTB)_2$. In both cases, the spectroscopic data (in the ν(C–O), ν(N–N), and ν(O–H) regions) indicate that the hydrogen bonding occurs via an M–CO···HO interaction. The temperature dependence of the ν(N–N) bands permits the enthalpy of the M–CO···HO interaction to be estimated, −19.6 kJ mol^{-1}. The ν(N–N) region has distinct advantages over the ν(C–O) region for monitoring the equilibrium because H bonding to the CO groups does not appear to change the extinction coefficient of the ν(N–N) bands significantly. Similar interactions are observed in $Cp^*Mn(CO)_2(N_2)$ and $Cp^*Mn(CO)_2(\eta^2\text{-}H_2)$, generated *in situ* in lXe, by UV irradiation of $Cp^*Mn(CO)_3$, **IV**, in the presence of N_2 or H_2 as appropriate. Surprisingly, the presence of PFTB had little effect on the course of the photolysis of **IV**. Spectroscopic evidence has also been obtained for H bonding to a CO ligand of the *dihydride trans*-$Cp^*Re(CO)_2H_2$, **V**, and to its *cis* isomer, generated by photoisomerization of **V**. Finally, spectra indicate that even $(C_5Me_5)V(CO)_4$ is sufficiently basic to undergo M–CO···HO bonding in lXe solution and in this case the interaction permits the observation of an otherwise IR-inactive ν(C–O) vibration.

Introduction

Hydrogen bonding is known to be involved in many proton transfer reactions.[1] Therefore, it has been assumed that protonation of transition metal complexes proceeds through hydrogen bonding to the complexes. An interesting feature of transition metal complexes is that they have several centers of basicity: not only the metal center itself but also the different ligands attached to the metal. Protonation usually occurs at the metal center but, even for metallocenes, that question is still open to discussion.[2] Although protonation of carbonyl ligands has been observed in some cases,[3] the site for the proton acceptor in hydrogen bonding may be different. With that in mind, Lokshin and Kazarian initiated an extensive study[4] of the interactions of transition metal complexes with proton donors in liquid xenon (lXe), an extremely useful solvent for such investigations, because of its chemical inertness, low temperature range, and most importantly, its complete IR transparency. The other important feature of that work was the use of perfluoro-*tert*-butyl alcohol (PFTB) as the proton donor, chosen because of its high acidity and its low tendency toward self-association even at low temperatures. Their extensive results showed that carbonyl ligands in π-complexes of metal carbonyls can indeed serve as proton acceptors in hydrogen bonding of the M–CO···HO type. This result was surprising in light of the low basicity of the oxygen atom of the metal carbonyl group, which arises from the significant contribution of resonance structure A to the structure of the metal carbonyl group:

$$\underset{\mathbf{A}}{M{-}C{\equiv}O^{+}} \quad \longleftrightarrow \quad \underset{\mathbf{B}}{M=C=O}$$

It is important to note that these studies generated strong evidence for hydrogen bonding to a carbonyl ligand of neutral compounds in *solution* as distinct from similar interactions in the solid phase.[5,6] The basicity of a terminal carbonyl group is considerably smaller than that for a bridging group, the capacity of which for hydrogen bonding is well established.[4d,7–11]

Hydrogen bonding to terminal carbonyls was proposed to explain the acceleration of the methyl migration reaction

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with protic acids.[12] Such intermolecular M–CO···HO hydrogen bonding still remains relatively rare, despite the well-known recognition of the Lewis basicity of terminal carbonyl ligands.[13,14] Indeed, only one report of such a type of interaction in solution has appeared recently.[15a] At the same time, the ability of metal centers to form intermolecular hydrogen bonds with proton donors has become a topic of current interest.[16–18] Recently, we have reported evidence that the metal centers in Cp*M(CO)$_2$ (Cp* = η^5-C$_5$Me$_5$; M = Ir, Rh, and Co) can act as proton acceptors in hydrogen bonding with fluoro alcohols.[19–21] With hindsight, it is probable that, in these compounds the HOMO is a largely metal-centered orbital and may play a considerable role in this H bonding with the metal center. Although the corresponding Cp*M(CO)$_3$ complexes of Mn and Re lack such orbitals, they too are protonated at the metal center but IR spectra suggest that H bonding still occurs via the oxygen atom of the carbonyl ligand.[4c,d] However, the relative basicities of the CO groups and metal centers are finely balanced in these Cp*M(CO)$_3$ compounds; interaction of such complexes with AlCl$_3$ leads to the formation of adducts with either the oxygen atom of the CO ligand or with the metal center itself, depending on the nature of the solvent.[22] Therefore, lXe is quite attractive for studies of interactions with proton donors, since lXe minimizes solvent effects and, perhaps, provides a better comparison with gas-phase studies than other solvents can. The proton affinity of the related compound (CH$_3$C$_5$H$_4$)Mn(CO)$_3$ has been measured in the gas phase[23] and reported as 203 kcal mol^{-1}, due to protonation of the metal center.

In recent years, the photochemistry of (η^5-C$_5$R$_5$)M(CO)$_3$ (R = H and Me; M = Mn and Re) has attracted renewed attention. It has been shown, for example, that the photochemical reaction of Cp*M(CO)$_3$ with N$_2$ leads to the formation of dinitrogen complexes,[24,25] while UV photolysis with H$_2$ may lead to a dihydrogen complex in the case of Mn and to a dihydride for the Re metal center.[26a]

The success of using IR spectroscopy and lXe solutions has been already demonstrated separately for both the photochemistry[27] and the H bonding[4] of π-complexes of Mn and Re.[4,27] The objectives of this paper, therefore, are to combine photochemical reactions of Mn and Re compounds with small molecules (N$_2$ and H$_2$) and intermolecular interactions of such complexes with proton donors. We have investigated whether the presence of PFTB influences the photochemistry of Cp*Mn(CO)$_3$ and Cp*Re(CO)$_3$ and whether the photoproducts of reaction with N$_2$ and H$_2$ can themselves undergo H bonding. Our strategy has been first to study H-bonding interactions between PFTB and the stable photoproduct Cp*Re(CO)$_2$(N$_2$) and then to study interactions between PFTB and Cp*Mn(CO)$_3$, both before and after UV photolysis in the presence of N$_2$ or H$_2$.

Experimental Section

The equipment used at Nottingham for liquid xenon experiments consists of a copper cell cooled by liquid nitrogen, which has been described in detail elsewhere.[27] For this study, the cell was modified by sealing the windows with the use of indium washers, as described recently.[4] PFTB was introduced into the cell in the gas phase, in order to avoid contact with water in the air and also because this method provides an accurate way of measuring the amount of alcohol used via the intensity of the ν(O–H) bond in the gas phase. Concentrations of PFTB in lXe were between 10^{-2} and 10^{-4} M, and the concentrations of the organometallic were between 10^{-3} and 10^{-5} M. Cp*Mn(CO)$_3$ and Cp*Re(CO)$_3$ (Aldrich) were used as supplied. We are grateful to Prof. W. A. G. Graham for the gift of Cp*Re(CO)$_2$H$_2$ and to Prof. D. Sutton for the gift of Cp*Re(CO)$_2$(N$_2$).

The UV photolysis source was a Cermax 300-W Xe arc lamp with a 1-m-long Lumatec light guide, which has the safety advantage of almost totally eliminating stray UV light. A band-pass filter, $\lambda > 300$ nm, was used between the light guide and cell window. FTIR spectra were recorded on a Nicolet 730 interferometer with an MCT detector and 680D data station (0.5- and 2-cm^{-1} resolution). For each experiment, blank spectra were recorded with the relevant organometallic dissolved in lXe *in the absence* of added PFTB.

Results

Interaction of Cp*Re(CO)$_2$N$_2$ with PFTB in lXe. Cp*Re(CO)$_2$(N$_2$), **I**, was chosen for our initial study, partly because it is a stable dinitrogen complex and H bonding to dinitrogen complexes has not been reported previously but, more importantly, because it is the product of the photochemical reaction of Cp*Re(CO)$_3$ with N$_2$. Until now, interactions of PFTB with Cp*M(CO)$_2$L complexes of Mn or Re have only been studied for PR$_3$ ligands[4c,d] (R = Me, Et, etc.). Such phosphine ligands are known to increase the basicity of both the metal center and carbonyl ligands, and the effect is expected to be particularly pronounced with the Cp* complex where further electron donation can come from the π-ring.[28] By contrast, N$_2$ is not a strong electron donor and the CO groups of **I** would

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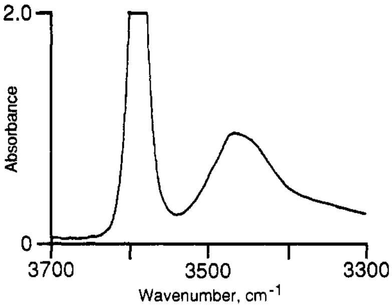

Figure 1. IR spectrum in the ν(O–H) region of PFTB in lXe solution in the presence of Cp*Re(CO)$_2$(N$_2$), **I**, at 183 K. The narrower (and more intense) band at 3590 cm^{-1} is due to ν(O–H) of free PFTB, while the band at 3465 cm^{-1} is assigned to ν(O–H) of PFTB H-bonded to **I**. Note that the band of free PFTB is so intense that it has been truncated in this spectrum.

not be expected to be much more basic than those of Cp*Re(CO)$_3$ itself.

Figure 1 shows the ν(O–H) region of the IR spectrum of a solution of **I** and PFTB in lXe at 183 K. There is a sharp band at 3590 cm^{-1}, due to the ν(O–H) stretching vibration of free (i.e. non-hydrogen bonded) PFTB.[4,29] However, in the presence of **I**, there is another broader band shifted toward a lower frequency at 3465 cm^{-1}, characteristic of a H-bonded species. This band is unlikely to be due to (PFTB)$_x$ species,[30] since PFTB does not self-associate under these conditions (ca. 5 × 10^{-3} M, at 183 K) in the *absence* of **I**. We therefore assign the band to the ν(O–H) vibration of PFTB H-bonded to **I**.

There are, however, four possible sites, which could serve as the proton acceptor in **I**: the π-ring, the metal center, the carbonyl ligands, and the dinitrogen ligand. We can distinguish between these sites from the ν(O–H) and ν(C–O) spectra and show that H bonding occurs via the CO ligand as it does with Cp*Re(CO)$_3$ itself. The wavenumber shift $\Delta\nu$(O–H) (i.e. ν(O–H)$_{\text{free}}$ minus ν(O–H)$_{\text{bonded}}$) for the interaction of PFTB with **I**, 125 cm^{-1}, is similar to that reported for the H bonding of PFTB to ferrocene and its derivatives,[4b] where interaction occurs with the π-rings. However, we can discount such an interaction in the case of **I** by inspection of the IR spectrum in the ν(C–O) and ν(N–N) regions, Figure 2. The spectrum shows that, in the presence of PFTB, there are two new ν(C–O) bands, at 1953 and 1865 cm^{-1}, both shifted down in frequency relative to the ν(C–O) bands of **I** itself. At the same time, there is a new ν(N–N) band at 2138 cm^{-1}, shifted up in frequency relative to the ν(N–N) band at 2125 cm^{-1} of the uncomplexed **I**. These shifts are not consistent with H bonding either to the metal center or to the π-ring because, in both cases, such interactions would cause shifts to *higher frequency* of all ν(C–O) bands, because of a reduction in electron density at the metal center and a concomitant reduction in back-donation to the CO groups, as was observed[19] in the case of Cp*(CO)$_2$Ir···HOR$_F$. For **I**, however, the shift of the ν(C–O) bands is to *lower wavenumber,* indicating H bonding to the oxygen atom of a CO ligand. It is important to note that the high-frequency shift for the ν(N–N) band is also consistent with H bonding of the M–CO···HO type; such bonding should lead to a decrease of back-donation from Re to the N$_2$ ligand with a corresponding increase of the ν(N–N) frequency. Thus, we can tentatively assign the ν(N–N) band at 2138 cm^{-1}, and the ν(C–O) bands at 1953 and 1865 cm^{-1} to an H-bonded complex, **II**, where one molecule of PFTB is bonded to the one molecule of **I**. Possible structures of **II** will be discussed below, but now we concentrate on the effect of changing the temperature on the ν(C–O) and ν(N–N) regions.

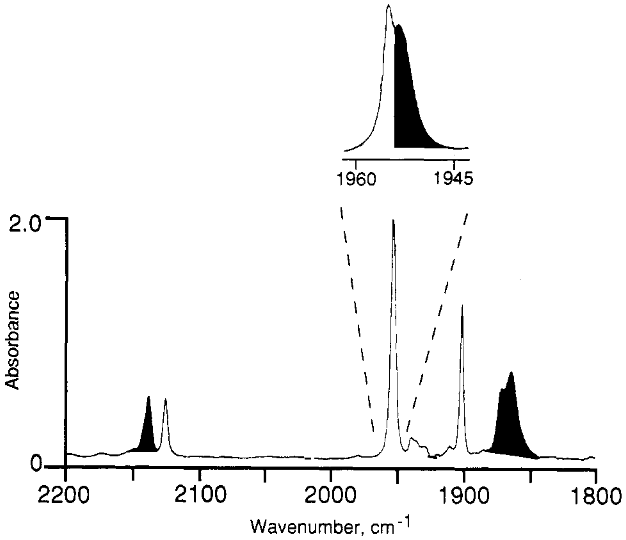

Figure 2. IR spectrum in the ν(N–N) and ν(C–O) regions of Cp*Re(CO)$_2$(N$_2$), **I**, in lXe solution in the presence of PFTB at 183 K. The uncolored bands are due to **I** and those colored black are assigned to the H-bonded complex **II** with PFTB interacting via the oxygen atom of one CO ligand. The upper spectrum shows the region between 1960 and 1945 cm^{-1} recorded at a higher resolution, 0.5 cm^{-1}.

The spectrum in Figure 2 was recorded at 185 K and only shows evidence for formation of a single H-bonded adduct, **II**. When the solution is cooled further and spectra are recorded at lower temperatures, two additional ν(C–O) bands are observed, at 1928 and 1863 cm^{-1} (not illustrated).[31] At the same a time new ν(N–N) band was observed at 2150 cm^{-1}, Figure 3, shifted even higher in wavenumber than that of **II**. These three new bands (ν(N–N) and two ν(C–O), Figure 2) always retained the same relative intensity, indicating that they belong to a single species, **III**. The absolute intensity of these bands increased reversibly as the temperature was lowered or the concentration of dissolved PFTB was increased. These observations suggest that **III** is a 1:2 H-bonded complex, where *one* molecule of **I** interacts with *two* molecules of PFTB (Scheme 1). A more detailed analysis of the ν(C–O) spectra provides some clue to the structures of **II** and **III**.

I has two equivalent CO groups. A simple energy factored force field can be used to calculated the stretching and interaction force constants,[32] k = 1502.1 N m^{-1} and i = 41.4 N m^{-1}, as defined in **a**. The most obvious structure of **III** would have two molecules of PFTB, one interacting with each of the CO groups of the Re(CO)$_2$ moiety. Thus, as in **I**, there will be two equivalent CO groups and, using the wavenumber data in Table 1, we can calculate k =

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[30] It is, however, known that traces of H$_2$O can give rise to a band at ca. 3200 cm^{-1}, through H bonding to PFTB (Mentel, T. F.; Luck, W. A. P. *J. Phys. Chem.* **1991**, *95*, 68). The wavenumber of the band due to the PFTB···H$_2$O complex is different from that observed for **I** and for other compounds used in this paper.

[31] The ν(C–O) band at 1863 cm^{-1} is partly obscured by the stronger band of **I** at 1865 cm^{-1} and can only be separated from that band by using computer subtraction.

Table 1. Wavenumbers[a] and Assignments of ν(C–O) and ν(N–N) IR Bands of Free and H-Bonded Organometallics in lXe Solution at ca. 170 K

	ν(N–N)	ν(C–O)			
$Cp^*Re(CO)_3$		2015.3 a_1	1923.8 e		
$Cp^*Re(CO)_2(CO\cdots HOR_F)$[c]		(2015)[b] a″	1936.1 a″	1887a′	
$Cp^*Re(CO)_2(N_2)$ (**I**)	2125.6	1954.5 a′	1901.5 a″		
$Cp^*Re(CO)(N_2)(CO\cdots HOR_F)$ (**II**)	2138.0	1953.0 a′	1865 a″		
$Cp^*Re(N_2)(CO\cdots HOR_F)_2$ (**III**)	2149.2	1928.0 a′	1863 a″		
trans-$Cp^*Re(CO)_2(H)_2$ (**V**)		2008.6 a_1	1938.0 b_1		
trans-$Cp^*Re(CO)(H)_2(CO\cdots HOR_F)$		(2008)[b] a′	1908.5 a″		
cis–$Cp^*Re(CO)_2(H)_2$ (**V**)		1993.8 a″	1921.3 a″		
cis-$Cp^*Re(CO)(H)_2(CO\cdots HOR_F)$		(1993)[b] a′	1889 a″		
$Cp^*Mn(CO)_3$ (**IV**)		2010.7 a_1	1927.5 e		
$Cp^*Mn(CO)_2(CO\cdots HOR_F)$[c]		(2011)[b] a′	1940.0 a″	1888.5 a′	
$Cp^*Mn(CO)_2(N_2)$	2145.8	1958.7 a′	1908.3 a″		
$Cp^*Mn(CO)(N_2)(CO\cdots HOR_F)$	2159.3	1958 a′	1874 a″		
$Cp^*Mn(CO)_2(H_2)$		1967.5 a′	1910.0 a″		
$Cp^*Mn(CO)(H_2)(CO\cdots HOR_F)$		1963 a′	1879.8 a″		
$Cp^*V(CO)_4$ (**VI**)		2016.8 a_1	1917.0 e		
$Cp^*V(CO)_3(CO\cdots HOR_F)$		(2017)[b] a′	1945.5 a′	1931.2 a″	1875.8 a′

[a] Individual spectra measured ±0.2 cm^{-1} but quoted at ±0.5 cm^{-1}. [b] A band is expected close to this wavenumber, slightly shifted from that of the free organometallic; none was observed presumably because of overlap with the band of free organometallic. [c] Wavenumbers are similar to those already reported[4c] for $(C_5Et_5)M(CO)_3$ (M = Mn and Re).

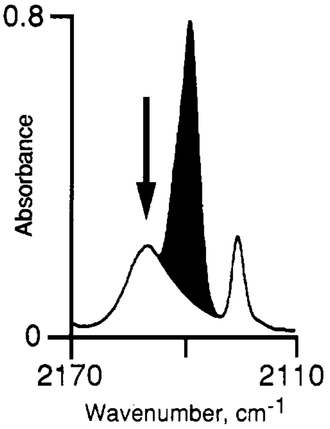
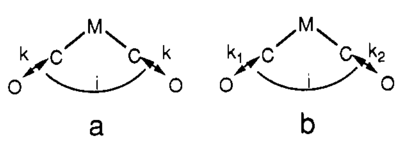
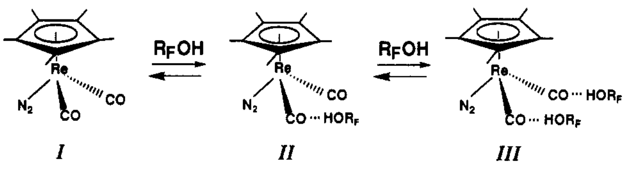


Figure 3. IR spectrum in the ν(N–N) region of **I** in lXe solution in the presence of PFTB at 168 K. The bands are assigned as follows: the uncolored band is due to **I**; the band colored black is due to **II**, the 1:1 complex of **I** with PFTB; the broader band, marked ↓, is assigned to **III**, the 1:2 complex of **I** with PFTB.



1452.1 N m^{-1} and $i = 50.2$ N m^{-1}. The calculations indicate that bonding of PFTB to the CO groups causes a decrease in the value of k while the value of i is slightly increased (cf. ref 4a). This decrease in k is to be expected since interaction with PFTB should increase the π-acceptor properties of the CO group and favor back-bonding from Re→C–O. The increase in the value of i can then be understood on the basis of Timney's relationship,[33] which states that for $M(CO)_2$ moieties with similar bond angles, k and i are related by two empirical constants A and B, eq 1. Using the data for **I** and **III**, we can then calculate $A = 223$ N m^{-1} and $B = 0.120$, consistent with values proposed by Timney for other systems.[33]

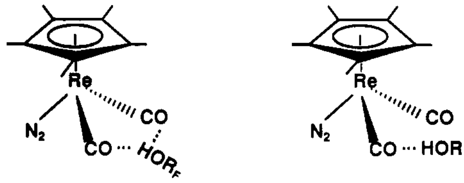
Scheme 1



I *II* *III*

$$i = A - B(k)/2 \quad \text{or more generally} \quad i = A - B(k_1 + k_2)/2 \quad (1)$$

There are two possible structures in which one molecule of PFTB interacts with one molecule of **I**; either the interaction could be symmetrical involving both CO groups, i.e. **IIa**, or it is unsymmetrical involving only a single CO group, i.e. **IIb**. The problem is similar to that encountered in assigning structures to the ion-paired $[CpM(CO)_3]^-$ anions of group 6 metals, which has been reviewed in some detail;[14a] the cation could either interact with a single CO group of the anion or interact symmetrically with two or three CO groups. In the present case, the energy factored force field for the symmetrical structure **IIa** would be identical to those of **I** and **III**, while that of **IIb** would be more complicated with *two* different C–O stretching constants, as shown in **b**. The problem in distinguishing between these two structures is that both will give rise to two ν(C–O) bands. Nevertheless, it is striking that the two ν(C–O) bands, in the spectrum observed for **II**, are more widely separated than those of either **I** or **III**. Assuming a symmetrical structure, **IIa**, we calculate force constants, $k = 1472.8$ N m^{-1} and $i = 67.9$ N m^{-1}, in which the interaction constant i has a value improbably high on the basis of the Timney relationship.



IIa *IIb*

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[32] This force constant calculation ignores any coupling between ν(N–N) and ν(C–O) vibrations. Such coupling has been shown not only to exist in the closely related $CpRe(CO)_2(N_2)$ complex but also to be significant.[25] Nevertheless, the same study showed that there was little difference in the magnitude of the coupling in $CpRe(CO)_2(N_2)$ and in $CpRe(CO)(N_2)_2$. It is therefore reasonable to assume that the effects of ν(N–N) and ν(C–O) coupling will be sufficiently similar in the series **I**–**III** to be ignored.

[33] Timney, J. A. *Inorg. Chem.* **1979**, *18*, 2502.

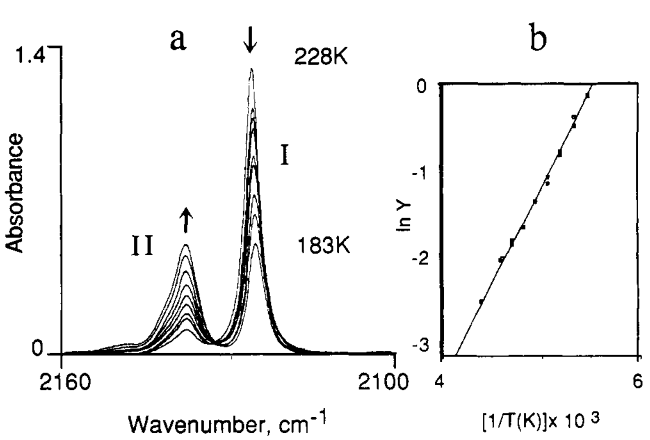

Figure 4. (a) IR spectrum in the ν(N–N) region showing the reversible change in equilibrium between **I** and its H-bonded form **II** as the temperature of the lXe solution is lowered from 228 to 183 K. The band due to **I** decreases with a corresponding increase of intensity in the band **II**. (b) A plot, equivalent to a van't Hoff plot, showing ln Y as a function of reciprocal temperature, where Y is the ratio of absorbance of the bands of **II**/**I**. Y is directly proportional to the equilibrium constant K: $Y = K\epsilon_r$[PFTB], where ϵ_r is the ratio of extinction coefficients of **II** and **I** and [PFTB] is the concentration of PFTB, effectively constant since PFTB is in a large excess compared to **I**. Thus the slope of the line gives the true value of the enthalpy difference, $\Delta H = -19.6$ kJ mol^{-1}.

Since **II** has only two observed frequencies, the unsymmetrical force field **b** cannot have a unique solution but, constraining the value of i with eq 1, we obtain $k_1 = 1525.1$ N m^{-1}, $k_2 = 1420.5$ N m^{-1}, and $i = 43.3$ N m^{-1}. These values are consistent with the view that H bonding to one CO group, as in **IIb**, should cause a decrease in the C–O stretching force constant of that group and a concomitant increase in the force constant of the other CO group, similar to the upshift in ν(N–N) described above; such changes in force constant have been discussed in more detail elsewhere.[4a,c,14a]

By contrast, the changes in the position of the ν(N–N) bands are clearer; for both **II** and **III**, new up-shifted bands were seen (Figure 3), with the wavenumber shift for **III** about twice as great as that for **II**. It should be emphasized that all spectral changes were reversible with temperature. The equilibrium between **I**, **II**, and **III** is potentially very complicated to unravel quantitatively. Fortunately, however, the conditions of our experiment mean that the equilibrium between **I** and **II** can be studied over quite a wide temperature range without detectable formation of **III**. This allows the enthalpy of the M–CO···HO interaction to be estimated from the changes in intensity of the ν(N–N) bands of **I** and its H-bonded analog, **II**. Figure 4 shows a series of IR spectra in this region at different temperatures from 228 to 183 K, and the graph shows the dependence of ln Y on reciprocal temperature, where Y is the ratio of absorbances of the ν(N–N) bands of **II** and **I**. Assuming that PFTB is in a large excess, ln Y is proportional to ln K_c, where K_c is defined in eq 2.A

$$K_c = [\mathrm{II}]/([\mathrm{I}][\mathrm{PFTB}]) \qquad (2)$$

similar approach was used to measure the enthalpy of M–CO···HO,[4a,c] π···HO,[4b,d] and Ir···HO[20] H-bonds but using the ν(O–H) and ν(C–O) bands rather than ν(N–N).[34] The enthalpy of M–CO···HO formation, $\Delta H = -19.6 \pm 1$ kJ/mol, was obtained from the slope of the graph of Figure 4 and is slightly larger than the enthalpy estimated[4c] for the same type of H bonding in $(C_5Et_5)Re(CO)_3$, −17.7 kJ/mol. Assuming that Cp* and C_5Et_5 have similar donating properties to the Re center and consequently to the carbonyl ligands, we can deduce that the exchange of one carbonyl ligand for dinitrogen increases the basicity of the remaining oxygen atoms, probably due to the poorer π-accepting ability of a dinitrogen ligand in comparison to a carbonyl. This conclusion is also supported by evidence for the formation of the 1:2 H complex between **I** and PFTB, while, for $(C_5Et_5)Re(CO)_3$, only the 1:1 H complex was observed under the same conditions.

Thus, we have shown that the dinitrogen complex **I** forms H bonds with PFTB via the oxygen atom of the carbonyl ligands. Also we concluded that the exchange of a CO ligand by N_2 makes the remaining carbonyl more basic. This work provided the background for further work, in which photoproducts were generated in lXe and the formation of H bonds with PFTB was investigated.

UV Photolysis of Cp*Mn(CO)$_3$ (IV) in the Presence of N$_2$ and PFTB in lXe. It is clearly interesting to investigate whether H bonding can occur to CO groups of more labile compounds, particularly to those of dihydrides and dihydrogen compounds, which are often synthesized in the presence of proton donors. We have, therefore, examined whether PFTB can interact with labile complexes such as $Cp^*Mn(CO)_2(H_2)$, which can be generated by UV photolysis of $Cp^*Mn(CO)_3$ and H_2 in lXe solution. Initially, we decided to attempt the photolysis of $Cp^*Mn(CO)_3$, **IV**, in lXe in presence of N_2 and PFTB. When **IV** was irradiated with UV light in lXe at 210 K, under 100 psi of N_2, new bands appeared in the ν(C–O) and ν(N–N) regions (see Table 1) corresponding to formation of the known dinitrogen complex[25] $Cp^*Mn(CO)_2(N_2)$. Clearly, the presence of PFTB in the solution does not affect significantly the formation of the dinitrogen photoproduct. When the temperature was lowered, however, two new down-shifted bands were observed in the ν(C–O) region and a single up-shifted band appeared in the ν(N–N) region (see Figure 5 and Table 1). As with $Cp^*Re(CO)_2(N_2)$, **I**, the appearance of these new bands were reversible with increased temperature and the bands can be assigned to a $Cp^*Mn(CO)_2(N_2)$/PFTB complex by analogy to H bonding of PFTB with **I**, as described above. Two further points need to be mentioned.

(1) Since $Cp^*Mn(CO)_2(N_2)$ was generated photochemically in solution from **IV**, only a limited amount of $Cp^*Mn(CO)_2(N_2)$ could be produced. This amount was insufficient for any new bands in the ν(O–H) region to observed clearly and was assigned to H-bonded PFTB.

(2) In the case of Mn complexes, we have not seen any bands assignable to formation of a 1:2 H complex. When we compared approximately similar concentrations of

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[34] In these earlier studies, it was assumed that the extinction coefficients of the ν(C–O) bands do not change when the H bond is formed, in which case, Y and K_c are related by the concentration of fluoro alcohol in the solution, [PFTB]. While this assumption is reasonable, the participation of a CO group in H bonding may well affect the extinction coefficient. The situation is much better in the cases of I and II described here, because we can measure the equilibrium constant from changes in ν(N–N) of the dinitrogen ligand which is merely a spectator to the H bonding with PFTB. We believe that the assumption of equal extinction coefficients for the bands at 2138 and 2125 cm^{-1} is much more likely to be true in this case. It should, however, be stressed that the value of the enthalpy (as opposed to K_c) is unaffected by the validity of this assumption since the ratio of the extinction coefficients affects the intercept but not the gradient of the van't Hoff plot.

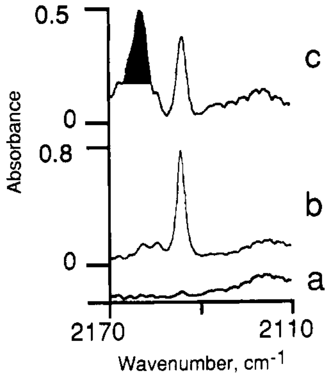


Figure 5. IR spectrum in the ν(N–N) region showing formation of $Cp^*Mn(CO)_2(N_2)$ and its H-bonded complex with PFTB: (a) spectrum recorded at 215 K, before UV photolysis of $Cp^*Mn(CO)_3$ in lXe solution in the presence of PFTB and N_2 (150 psi); (b) spectrum recorded at 215 K, after 20 min of UV photolysis of the solution, showing the ν(N–N) band of $Cp^*Mn(CO)_2(N_2)$; (c) spectrum recorded after cooling the solution to 168 K. The band colored black is assigned to the H-bonded complex of $Cp^*Mn(CO)_2(N_2)$ with PFTB. By monitoring the ν(N–N) region of the spectrum, we can focus on the interaction of $Cp^*Mn(CO)_2(N_2)$, avoiding any interference from the bands of either $Cp^*Mn(CO)_3$ or its H-bonded complex.

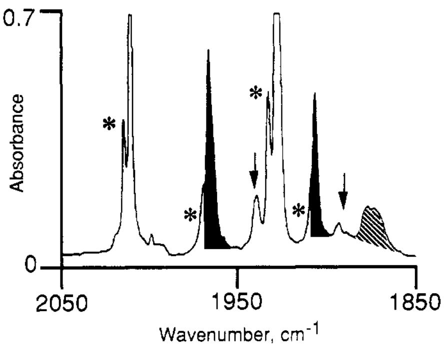


Figure 6. IR spectrum in the ν(C–O) region showing formation of $Cp^*Mn(CO)_2(\eta^2\text{-}H_2)$ and its H-bonded complex with PFTB in solution in lXe at 168 K under a pressure of H_2 (200 psi). The bands are assigned as follows: uncolored, unreacted starting material **IV**; those colored black, the dihydrogen complex $Cp^*Mn(CO)_2(\eta^2\text{-}H_2)$, generated by 30 min of UV photolysis of **IV**; shaded band, the H-bonded form of $Cp^*Mn(CO)_2(\eta^2\text{-}H_2)$; bands marked ↓, the H-bonded form of **IV**; the bands marked *, $(C_5Me_4H)Mn(CO)_3$, which was present as a minor impurity in the sample of **IV**, and its derivative, $(C_5Me_4H)Mn(CO)_2(\eta^2\text{-}H_2)$.

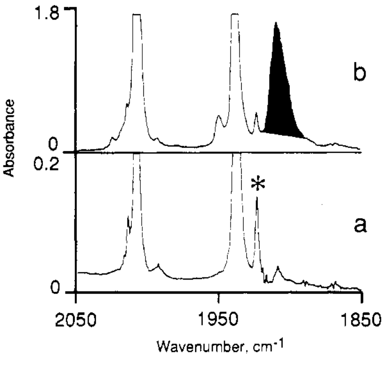
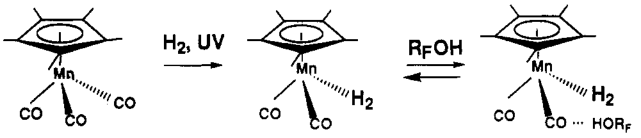


Figure 7. IR spectra in the ν(C–O) region of *trans*-$Cp^*Re(CO)_2(H)_2$, **V**, in lXe solution in the presence of PFTB recorded (a) at 220 K and (b) at 173 K. The off scale bands are due to **V**, and the asterisk indicates the natural abundance ^{13}CO satellite. The bands colored black are assigned to the H-bonded form of **V** with PFTB. Note that **V** is somewhat less soluble than **I** so that there is some precipitation of **V** as the solution is cooled. However, the precipitate does not affect the IR spectra.

Scheme 2



IV

Cp*Mn(CO)$_2$(N$_2$) and **I** at the same low temperature (165 K), we were able to show that **I** does form the 1:2 H complex, **III**, while the analogous Mn dinitrogen complex does not. This result is consistent with the higher basicity of the oxygen atom of the carbonyl ligand in Re complexes than in corresponding Mn ones, as mentioned in refs 4c,d.

UV Photolysis of $Cp^*Mn(CO)_3$ (IV) in lXe in the Presence of H_2 and PFTB. When a solution of **IV** in lXe at 210 K was pressurized with ca. 150 psi of H_2 and irradiated with UV, the bands of $Cp^*Mn(CO)_2(H_2)$ were observed in the ν(C–O) region (see Table 1). More importantly, the presence of PFTB did not affect the formation of the dihydrogen complex but, when the temperature of the solution was lowered to 165 K, new ν(C–O) bands were observed. Some of these bands can be assigned to the known H-bonded complex **IV** in solution. However, we observed additional bands which we assign to the interaction of PFTB with one CO ligand of $Cp^*Mn(CO)_2(H_2)$ (Table 1). As with the corresponding dinitrogen complex, it was difficult to observe any new band in the ν(O–H) region due to H-bonded PFTB and, as in previous studies of this compound,[26a] we were unable to see any bands attributable to $\eta^2\text{-}H_2$ in the ν(H–H) region. Nevertheless, the changes in the ν(C–O) region, reversible with temperature, clearly indicated that this dihydrogen complex of Mn is able to H bond with PFTB via the oxygen atom of the CO ligand. It is known that such a dihydrogen complex is more labile than its dinitrogen counterpart[26b] and thus it is quite surprising that H bonding does not lead to a breakdown of the compound.

Interaction of *trans*-$Cp^*Re(CO)_2H_2$ (V) with PFTB in lXe. The reaction of $Cp^*Re(CO)_3$ with H_2 led to the formation of a dihydride[26] but not to a dihydrogen complex, in accordance with the trend of most third row metal complexes. Therefore the next step of our study was to see whether the dihydride $Cp^*Re(CO)_2H_2$ would interact with PFTB, bearing in mind that the metal center will already be oxidized, lowering the basicity of the CO ligand and, hence, decreasing the ability of CO to form H bonds with PFTB.

Unlike $Cp^*Mn(CO)_2(H_2)$, **V** is stable at room temperature. Figure 7 illustrates two spectra of **V** in lXe at 180 K with and without PFTB in the solution. The positions of the carbonyl bands for **V** confirm that it is the trans-isomer.[35] In the presence of PFTB, a new ν(C–O) band is observed at 1908 cm^{-1}, indicating that the CO ligand in **V** is still able to form an H bond. A second ν(C–O) band is to be expected for a V/PFTB complex but it could not be observed, most probably because the wavenumber shift of this second band is small, and it overlaps with band of

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(35) Graham, W. A. G.; Sturgeoff, L.; Campen, A. K.; Ollino, M. A.; Rest, A. J.; Whitwell, I.; Hamley, P. A.; Kazarian, S. G. *J. Chem. Soc., Dalton Trans.*, to be submitted.

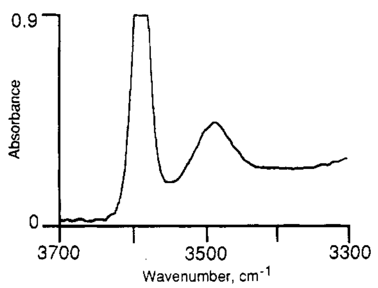
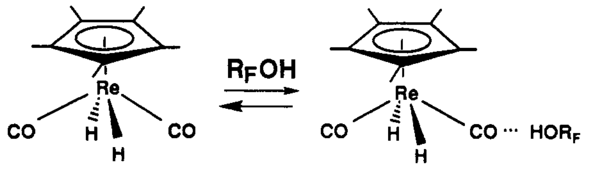


Figure 8. IR spectrum recorded at 165 K showing the ν(O–H) region of PFTB in lXe solution in the presence of *trans*-Cp*Re(CO)$_2$(H)$_2$, **V**. As in Figure 1, the broad band is assigned to the H-bonded form of **V**.

Scheme 3



V

uncomplexed **V** at 2008 cm^{-1}. However, unlike the case of Cp*Mn(CO)$_2$(H$_2$), we were able to observe a new band at 3485 cm^{-1}, Figure 8, corresponding to a ν(O–H) stretching vibration of PFTB interacting with Cp*Re(CO)$_2$H$_2$. The shift of this band from the position of the ν(O–H) band of free PFTB ($\Delta\nu$(O–H) = 110 cm^{-1}) was somewhat smaller than that for H bonding with Cp*Re(CO)$_2$(N$_2$), **I**, presumably reflecting a weaker M–CO···HO interaction due to the higher oxidation of the Re center with correspondingly less back-donation to the CO ligands.

UV photolysis of **V** in lXe has recently been shown[35] to lead to formation of the *cis*-isomer of Cp*Re(CO)$_2$H$_2$. The isomerization still occurs if the irradiation is carried out in the presence of PFTB, and after irradiation, we were able to observe an additional ν(C–O) band at a low wavenumber, presumably due to an H-bonded interaction of between PFTB and *cis*-Cp*Re(CO)$_2$H$_2$ (not illustrated; see Table 1).

Interaction of Cp*V(CO)$_4$ (VI) with PFTB in lXe. The experiments described above have shown that PFTB can interact with CO ligands both of dihydrides and of dihydrogen complexes to form H bonds. This suggested that it might be possible to influence the dihydride/dihydrogen equilibrium where both complexes coexist in solution, as in eq 3.[36] Unfortunately, none of the Cp

$$\mathrm{CpNb(CO)_3(\eta^2\text{-}H_2) \rightleftarrows CpNb(CO)_3H_2} \qquad (3)$$

derivatives of the group 5 metals appears to have sufficiently basic CO ligands to observe H bonding under the conditions of our experiments. However, analyzing the general trend in basicity of CO ligands from refs 4c,d and these results, we concluded that CO ligands with a lower ν(C–O) wavenumber are more likely to form H bonds. In the cases of Ta, Nb, and V carbonyl complexes, the complex Cp*V(CO)$_4$, **VI**, has the lowest ν(C–O) wavenumbers. Therefore, we investigated whether **VI** could form H bonds with PFTB in lXe. Figure 9 shows that new ν(C–O) bands do indeed appear in the IR spectrum of **VI** dissolved in lXe in the presence of PFTB at ca. 170 K. As with the other compounds discussed in this paper, these bands disappeared at higher temperatures. In addition, we were just able to detect a weak absorption at 3515 cm^{-1} corresponding to the ν(O–H) band of H-bonded PFTB (not illustrated). **VI** differs from the other compounds because the CO groups have localC_{4v} symmetry (see **c**), with an IR-inactive b$_1$ ν(C–O) vibration predicted to occur at ca. 1950 cm^{-1}. Interaction between one CO group and PFTB will lower the symmetry to C_s, as in **d**, rendering this b$_1$ IR-active.

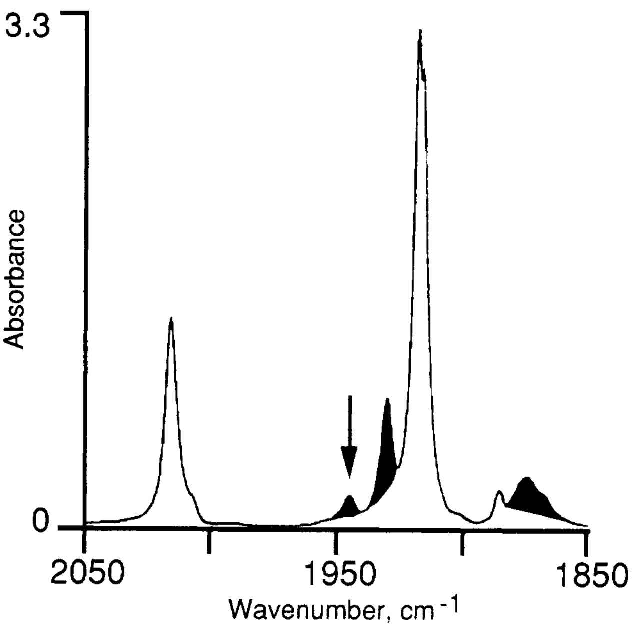
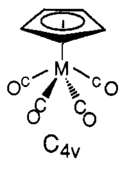


Figure 9. IR spectrum in the ν(C–O) region of Cp*V(CO)$_4$, **VI**, in lXe solution in the presence of PFTB at 170 K. The bands colored black are assigned to the H-bonded complex of **VI** with PFTB via the oxygen atom of a CO ligand. Note the appearance of the formerly IR-inactive band, arrowed at ca. 1950 cm^{-1}.

c



d

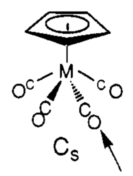


Figure 9 shows that this is indeed the case, with the former b$_1$ mode appearing (arrowed band). The observation of this band confirms directly that H bonding must be occurring to the CO groups rather than to the π-system of the Cp* ring, because interaction with the ring would not alter the local symmetry of the CO groups. It should be mentioned, perhaps, that the interaction of the Lewis acid AlCl$_3$ with CpV(CO)$_4$ has been reported previously.[37] This interaction involves either the metal center or the CO ligand, depending on the solvent; more polar solvents favor interaction with the metal. In our study, interaction with PFTB in the highly nonpolar solvent, lXe, leads to H bonding with the CO ligand.

Conclusions

Our IR study of the interaction of PFTB with dinitrogen, dihydrogen, and dihydride complexes of CpM(CO)$_2$ (M =

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(36) Haward, M. T.; George, M. W.; Hamley, P. A.; Poliakoff, M. *J. Chem. Soc., Chem. Commun.* **1991**, 1101.

(37) Lokshin, B. V.; Rusach, E. B.; Valueva, Z. P.; Ginzburg, A. G.; Kolobova, N. E.; *J. Organomet. Chem.* **1975**, *102*, 535.

Mn and Re) in lXe has shown that such complexes are all capable of H bonding. As in previous studies of this type, the evidence is spectroscopic and somewhat circumstantial but all of the data indicate that the H bonding involves M–CO···HOR$_F$ interactions. However, our observations differ from earlier work in that we have monitored these interactions through the changes in the ν(N–N) spectral region, whenever possible. Unlike the CO groups, the N_2 ligand is not directly involved in H bonding and therefore changes in this region are less likely to be subject to any artefacts. Our present study has shown that even dihydrogen complexes, and dihydrides which are known to be acidic, can still form M–CO···HO bonding with PFTB. At the same time, some dihydrides are known to be protonated,[38] forming a dihydrogen cation complex. H bonding to carbonyl ligands in some dihydrides might be the first step of such protonation, as in the case of protonation of Mn and Re carbonyls with a phosphine ligand.[4d] Moreover, we believe that M–CO···HO bonding might provide a new approach to complexes with an η^2-HD ligand, by using either an OD alcohol or a photoproduct with a D_2 ligand.

Our results confirm and complement those of Lokshin and co-workers[4] and lead to the conclusion that H bonding of the M–CO···HO type may well be quite widespread, when organometallics are in the presence of proton donors. The strengths of the interactions are less than those involving H bonding directly to the metal center.[20] Nevertheless, the interactions are strong enough to have a significant effect in determining the course of reactions, particularly those involving equilibria.

Acknowledgment. We thank the SERC, EC Human Capital and Mobility, and NATO Grant No. 920570. We thank the Royal Society for a visiting Fellowship (S.G.K.) and for a Leverhulme Trust Senior Fellowship (M.P.). We thank Ms. S. L. Morrison for her help with force constant calculations and Drs. M. W. George, S. M. Howdle, M. A. Kurikin, A. J. Rest, and A. H. Wright, Professors B. V. Lokshin, R. N. Perutz, and J. J. Turner, and Mr. A. I. Cooper, Mr. J. M. Banister, Mr. J. G. Gamble, Mr. D. R. Dye, and Mr. K. Stanley for their help and advice.

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[38] Henderson, R. A.; Oglieve, K. E. *J. Chem. Soc., Dalton Trans.* **1993**, 3431.