Is Intermolecular Hydrogen-Bonding to Uncharged Metal Centers of Organometallic Compounds Widespread in Solution? A Spectroscopic Investigation in Hydrocarbon, Noble Gas, and Supercritical Fluid Solutions of the Interaction between Fluoro Alcohols and $(\eta^5\text{-}C_5R_5)ML_2$ (R = H, Me; M = Co, Rh, Ir; L = CO, C_2H_4, N_2, PMe_3) and Its Relevance to Protonation

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Abstract: IR spectroscopy has been used to investigate the interaction of fluoro alcohols with neutral group 9 transition metal half-sandwich complexes $(\eta^5\text{-}C_5R_5)ML_2$ (R = H, Me; M = Co, Rh, Ir; L = CO, C_2H_4, N_2, PMe_3) in fluid solution. The interaction involves hydrogen-bonding by the acidic alcohol to the basic metal center, $(\eta^5\text{-}C_5R_5)L_2M\cdots H\text{–}OR_F$, i.e., with the metal center acting as a proton acceptor. The H-bonding has been studied via ν(C–O) and ν(O–H) vibrations in both room temperature solvents—*n*-heptane, supercritical xenon (scXe), and supercritical ethane (scC_2H_6)—and cryogenic solutions—liquid xenon (lXe) and krypton (lKr). A detailed study of $Cp^*Ir(CO)_2$ (**1**) has been used to establish that (a) a lower pK_a of the fluoro alcohol gives a stronger interaction, (b) the shift in the ν(O–H) vibration on deuteration, using $(CF_3)_3COH$ (PTFB) and $(CF_3)_3COD$, is similar to the shift of other nonmetallic H-bonded systems, (c) lower temperatures favor H-bonding, including the formation of a second complex $\{[Cp^*Ir(CO)_2]\cdots(HOR_F)_2\}$ and its Rh analog, (d) *neat* fluoro alcohol solution leads to the protonation of the Ir center in the case of PTFB and $(CF_3)_2CHOH$ (HFIP), (e) the interaction of HFIP with **1** in scXe demonstrates the relationship between protonation and H-bonding to the metal center in scXe solution, (f) H-bonding is disfavored by increasing solvent *density* at constant concentration in scC_2H_6, (g) similar H-bonding occurs with both Co and Rh compounds, but the strength of interaction increases down the group, (h) H-bonding is weaker for C_5H_5 complexes than for C_5Me_5, (i) H-bonding occurs with a range of compounds where one or both of the CO groups are replaced (i.e. by C_2H_4, N_2, or PMe_3, and (j) in lXe solution, the wavenumber shift in the ν(O–H) vibration of the H-bonded complex relative to that of free PFTB mirrors the strength of the H-bonded interaction. Finally, the chemical implications of this type of H-bonding are briefly discussed and it is suggested that this shift in the ν(O–H) band could be used as a semiquantitative measure of the basicity of the metal centers.

Introduction

The protonation of a metal center is recognized as one of the key steps in organometallic chemistry.[1] The mechanism of this process, however, is far from understood. In many cases, it is believed that reaction intermediates involve hydrogen-bonding with the metal center acting as the proton acceptor.

Although hydrogen-bonding is frequently reported for organometallic compounds, there are very few examples of metal centers acting as proton *acceptors*, rather than proton donors, in intermolecular H-bonding. There have been a number of reports of *intramolecular* H-bonding to metal centers,[2] as distinct from the well-known agostic interaction of a C–H bond with a metal center.[3] X-ray crystallography has revealed a few examples of *intermolecular* H-bonding to metal centers in the solid state, but most merely represent cation/anion interactions.[4] Similarly, those intermolecular examples reported in solution have usually involved ion pairing.[5] Indeed, prior to our own work, there has only been one report of *intermolecular* H-bonding to a metal center by a neutral proton donor in solution, involving the H-bonding of CF_3CH_2OH (TFE) to the *16-electron* Ir center in Vaska's compound.[6a]

Recently, we reported[7] the first IR evidence for intermolecular M···H–O hydrogen-bonding between the *18-electron* iridium center in $Cp^*Ir(CO)_2$ (**1**) and a number of fluoro alcohols (e.g. PFTH, PFTB, and HFIP; see Table I for abbreviations) both in *n*-heptane and in liquid xenon (lXe) solutions. Perfluoro alcohols

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Table I. Fluoro Alcohols and Their pK_a Values,[a] with the Abbreviations Used in This Paper

alcohol	abbrev	pK_a
$(C_3F_7)(CF_3)_2COH$	PFTH	5.4
$(CF_3)_3COH$	PFTB	5.4
$(CF_3)_2CHOH$	HFIP	9.2
CF_3CH_2OH	TFE	12.3
$CF_3CF_2CF_2CH_2OH$	HFB	12.2
CH_3OH	MeOH	15.5

[a] pK_a values taken from: Dyatkin, B. L.; Mochalina, E. P.; Knunyants, I. L. *Tetrahedron* **1965**, *21*, 2991.

have previously been widely used to study H-bonding to proton acceptors,[8] including a range of metal carbonyl compounds, particularly in lXe solution by Lokshin et al.,[9] who found a previously unknown type of H-bonding to the *oxygen atom* of the carbonyl ligand, O–H···OC–ML_n, for group 6 and 7 metals.[10] Even though protonation of the metal occurred in some of their experiments,[9c,d] no evidence was found for intermolecular bonding to the actual metal center. By contrast, our experiments[7] with the group 9 compound $Cp^*Ir(CO)_2$ (**1**) have provided convincing IR spectroscopic evidence for the iridium center acting as a proton acceptor:

$$\underset{\mathbf{1}}{Cp^*Ir(CO)_2} + HOR_F \rightleftharpoons \underset{\mathbf{2}}{Cp^*(CO)_2Ir\cdots H\text{–}OR_F} \qquad (1)$$

This evidence included the following observations:

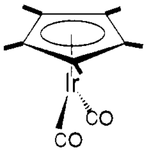
(i) With *n*-heptane/fluoro alcohol solutions of **1**, new bands appear in the ν(C–O) region, shifted up by 12–18 cm^{-1} from the corresponding ν(C–O) bands of **1**, indicating a reduction in electron density on the metal center. The wavenumber shift is smaller than that which might be expected for protonation at the metal (100–150 cm^{-1}),[11,12] but the direction of the shift is the same. Similar shifts of ν(C–O) to higher wavenumber have also been observed for the interaction of **1** with Lewis acids at the meal atom.[12c,d] This spectroscopic behavior is in sharp contrast to that observed with H-bonding to the O atom of the M–CO group,[9,10] which causes a significant shift to *lower* wavenumber of at least one ν(C–O) band.

(ii) In lXe/fluoro alcohol solutions of **1**, a new and rather broad band, characteristic of an H-bonded species, can be observed in the ν(O–H) region, together with the new ν(C–O) bands, as seen in *n*-heptane. This ν(O–H) band is shifted to lower wavenumber relative to the ν(O–H) band of the free fluoro alcohol with a corresponding increase in the integrated intensity of the band. The size of the shift is much larger than that previously observed for H-bonding of PFTB to the π-ring of organometallic compounds in, for example, Cp^*_2Fe,[9a,d] to the π-system of benzene itself,[8d] or to the C=C bond of C_3H_6 in lXe solution.[8c]

(iii) All these new bands, ν(O-H) and ν(C-O), are found to grow reversibly in intensity as the temperature of the solution is lowered. Under these conditions, the H-bonded complex is thermodynamically more stable than the free alcohol/organometallic and the enthalpy of the interaction can be measured, ca. 28.3 kJ mol^{-1} for PFTB/**1** in *n*-heptane. This enthalpy difference is significantly higher than that found for Cp^*_2Fe/PFTB or PFTB/benzene.

(iv) At low temperatures, there is evidence, discussed in more detail below, for the formation of a 1:2 adduct, e.g. $Cp^*Ir(CO)_2(PFTB)_2$.

Although these experiments constitute strong spectroscopic evidence for the Ir···H–O interaction, they do not provide any information regarding the structure of the H-bonded adducts. However, electron-rich half-sandwich complexes, $Cp^*M(CO)_2$, of Co, Rh, and particularly Ir are well-known to act as bases for interaction with protons, Lewis acids, and zeolites,[11,12] e.g. to form $[Cp^*Ir(CO)_2H]^+$, $Cp^*Ir(CO)_2HgCl_2$, or $[(Cp^*Ir(CO)_2)_2Ag]^+$. Recent studies show that the interaction of Ag^+ with **1** causes very little distortion of the $Cp^*Ir(CO)_2$ moiety,[11d] and the X-ray structure of $Cp^*Ir(CO)_2HgCl^+$ also indicates relatively little rearrangement of the metal carbonyl groups.[12c] Thus, by analogy with these Lewis acid/base species, we proposed[7] structure **2** for the H-bonded adducts.



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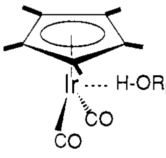

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The observation of an Ir···H–O interaction in these experiments was the result of two particular properties of the fluoro alcohols, namely their high acidity (see Table I) and their small degree of self-association, even at low temperatures. Very recently, we showed that the interaction between **1** and PTFB also has a chemical effect, reducing significantly the efficiency of photochemical C–H activation by the Ir center.[13] Examples of three-center four-electron interactions involving a metal center are rare, and so the Ir···H–O interaction certainly deserves more detailed study. This paper, therefore, has several objectives: (i) to investigate how H-bonding between fluoro alcohols and $(C_5R_5)M(CO)_2$ compounds is affected by changing the fluoro alcohol, the substituents on the cyclopentadienyl ring, the CO ligands, and even the metal itself, (ii) to present evidence to connect H-bonding to Ir with the protonation of the metal center, and (iii) to demonstrate that the shifts in the ν(O–H) infrared bands associated with this form of H-bonding could form the basis for a semiquantitative scale of metal basicity.

Experimental Section

The equipment used at Nottingham for liquid xenon experiments consists of a miniature copper cell (path length 2.5 cm) cooled by liquid nitrogen, which has been described in detail elsewhere.[14] For this study,

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the cell was modified with a more efficient and reliable sealing system for the CaF$_2$ windows (8-mm diameter, 5-mm thickness), in which the window is sandwiched between indium washers inside a holder[14b]. Details of high-pressure cells for IR spectroscopy in supercritical fluids (1–7-mm path lengths) have been published previously.[15]

In a typical lXe experiment, the cell was loaded with ca. 5–30 mg of an organometallic compound and evacuated using a turbo molecular pump, and the Teflon tube leading to the vial containing the degassed sample of PFTB was heated to remove moisture. Fluoro alcohol *vapor* was then introduced into the cell at a temperature between +5 and +25 °C. The cell was then cooled to ca. –80 °C and filled with xenon (BOC research grade). An IR peak absorbance of 1 for the ν(O–H) band of PFTB corresponds to a concentration of ca. 5×10^{-3} M in our cell. The UV photolysis source (when used) was a Cermax 300-W Xe arc lamp with a 1-m-long Lumatec light guide, which almost eliminates stray UV light. Normally a band-pass filter, >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 680 data station or on an MX3600 interferometer with a TGS detector and 1280 data station (16K data points, 32K transform points, and Happ–Genzel apodization with 2-cm^{-1} resolution).

Experiments in heptane and in pure alcohols were conducted in either KCl or CaF$_2$ windowed cells with path lengths between 0.1 and 1.0 mm, the temperature being varied in some experiments from +25 to –25 °C. The concentrations in dried *n*-heptane were 10^{-1}–10^{-2} M for the fluoro alcohols and ca. 10^{-3} M for the organometallic. In pure alcohols, the concentration of the organometallic was approximately 10^{-2} M. *n*-Heptane (Aldrich) was distilled over CaH$_2$ before use. Fluoro alcohols, HFIP, HFB, and TFE (Aldrich) and PFTH, PFTB, and deuterated PFTB (from INEOS, Moscow), and Cp*Rh(CO)$_2$ (Strem) were used as supplied. Cp*Ir(CO)$_2$ was prepared by literature methods.[16a] We are grateful for gifts of the other organometallics used in this work.[16b]

Results and Discussion

Our approach in this study has been to investigate, by IR spectroscopy, the interaction of **1** and related compounds with fluoro alcohols. For experiments involving the ν(C–O) region, both *n*-heptane and lXe have been used, depending on the purpose of the experiment. For the ν(O–H) region, however, experiments had to be carried out in lXe because the IR spectrum is partly obscured by the ν(C–H) bands of *n*-heptane itself. Equally, lXe is more effective than *n*-heptane for temperatures below –45 °C, where the low solubility of compounds such as **1** makes long optical paths desirable. Additional experiments have been carried out in supercritical Xe and supercritical ethane and in polyethylene matrices.[13] We now examine, systematically, the different factors affecting H-bonding to metal centers. We begin with the effects of different fluoro alcohols.

Interaction of Cp*Ir(CO)$_2$ (1) with Different Fluoro Alcohols. In pure *n*-heptane, **1** has *two* IR bands in the ν(C–O) regions; see Table II. H-bonding gives rise to two additional ν(C–O) bands, one shifted to the high-wavenumber side of each band of **1**. Figure 1 shows the superimposed spectra of three solutions of **1** in *n*-heptane, each containing a different fluoro alcohol. It can be seen that all three alcohols give rise to the additional bands of H-bonded species but that the wavenumber shifts are different: the highly acidic alcohol, PFTB, causes the largest shifts while the least acidic, TFE, gives the smallest; see Table II. On the other hand, almost identical shifts are observed with pairs of alcohols with similar pK_a values, i.e. PFTH and PFTB or TFE and HFB; see Table II.

Table II. Wavenumbers (cm^{-1}) of ν(C–O) Bands of Cp*Ir(CO)$_2$ (**1**) (and CpIr(CO)$_2$) and the H-Bonded Complexes **2** and **3**, Formed by Interaction with Different Fluoro Alcohols

		wavenumber[a]			
alcohol	solvent	**1**	**2** (**3**)[b]	$\Delta\nu$ (**2** minus **1**)	assgnt
		Cp*Ir(CO)$_2$			
TFE	*n*-heptane	2019.1	2024.0	4.9	a′
		1953.0	1961.0	8.0	a″
HFB	*n*-heptane	2019.1	2024.0	4.9	a′
		1953.0	1961.0	8.0	a″
HFIP	*n*-heptane	2019.1	2028.0	8.9	a′
		1953.0	1964.7	11.7	a″
HFIP	scC$_2$H$_6$[c]	2025	2031.0	6	a′
		1960.0	1970.	10	a″
HFIP	scXe[c]	2025	2030.0	5	a′
		1960	1970	10	a″
PFTH	*n*-heptane	2019.1	2031.0	11.9	a′
		1953.0	1970.5	17.4	a″
PTFB	*n*-heptane	2019.1	2031.5	12.4	a′
		1953.0	1970.5	17.4	a″
PTFB	lXe/lKr[d]	2023.6	2036.0	12.4	a′
		1957.9	1975.5	17.6	a″
		2023.6	(2044.8)	(21.2)	a′
		1957.9	(1988.4)	(30.5)	a″
		CpIr(CO)$_2$			
HFIP	*n*-heptane	2040.7	2048.0	7.3	a′
		1979.5	1990.0	11.5	a″

[a] Error ±0.2 cm^{-1}. [b] Values for **3** in parentheses. [c] Bands in supercritical solution are rather broader than those in *n*-heptane, with a corresponding increase in uncertainty in the precise wavenumber (probable error in $\Delta\nu$ > ±0.5 cm^{-1}). [d] The precise wavenumber is somewhat temperature dependent.

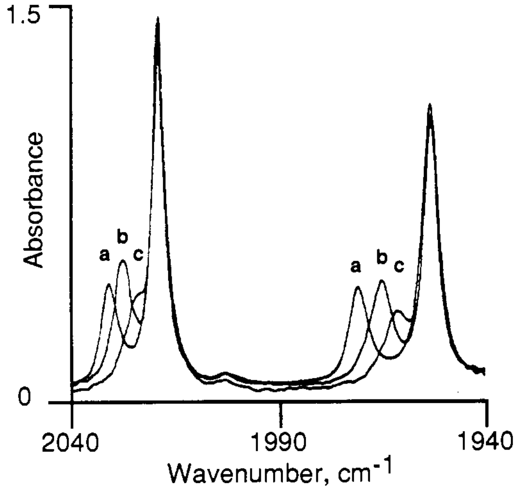

Figure 1. Superimposed IR spectra, in the ν(C–O) region, comparing the effect of adding different fluoro alcohols to a solution of Cp*Ir(CO)$_2$ (**1**) in *n*-heptane at room temperature. The strong unlabeled bands are due to **1** itself, and the weaker bands correspond to the addition of (a) PFTB, (b) HFIP, and (c) TFE to the solution. In each case the bands are assigned to Cp*(CO)$_2$Ir···H–OR$_F$ complexes (**2**). The absorbance scales of the three superimposed spectra have been normalized to the absorbance of the bands of **1**, and in each case, the concentration of the fluoro alcohol was chosen to give similar intensity bands for the H-bonded complex, **2**. See Table II for the wavenumbers of all bands.

Acidity appears to be the most important factor in determining the magnitude of the shift in the ν(C–O) bands. It is, therefore, clear that our success in observing the H-bonding of **1** with fluoro alcohols, via shifts in the ν(C–O) region, was due to the high acidity of these alcohols. If the experiments were to be extended to nonfluorinated alcohols, such as methanol or ethanol, acidity arguments would suggest that the ν(C–O) shift for **1** would be small, even if hydrogen bonds did form. Adding MeOH to a solution of **1** in *n*-heptane mixtures does cause a slight broadening to the high-wavenumber side of both ν(C–O) bands.[17] Thus, IR

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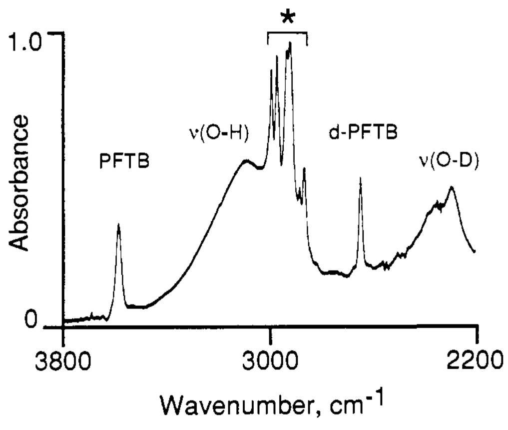

Figure 2. IR spectrum of a solution of $Cp^*Ir(CO)_2$ (**1**) in lXe containing a mixture of $(CF_3)_3COH$ (PFTB) and $(CF_3)_3COD$ (d-PFTB) at −100 °C. The bands are labeled as follows: PFTB, ν(O–H) band of free PFTB; d-PFTB, ν(O–D) band of free d-PFTB; ν(O–H) and ν(O–D), bands of the $Cp^*(CO)_2Ir\cdots H–OR_F$ and $Cp^*(CO)_2Ir\cdots D–OR_F$ complexes (**2**), respectively. The sharp bands labeled with an asterisk are the ν(C–H) bands of the C_5Me_5 groups of **1** and **2**.

spectroscopy cannot be easily be used to prove that H-bonding of ethanol or methanol to **1** does occur, because the band shifts are too small to resolve. Such H-bonding of **1** with ethanol might explain the difficulties of using this solvent to obtain complexes with MCl_2 (M = Zn, Cd, or Hg),[12c] as the solvent may compete for the interaction site.

Our previous report[7] showed that the shift in ν(C–O) also reflects the strength of the $Ir\cdots H–OR_F$ interaction. We show below, however, that this is not always true; the ν(C–O) shifts, produced by one alcohol interacting with a series of *different metals*, do not indicate the strength of the interaction. In these cases, it is the ν(O–H) region which is more informative. First, we examine the effect of deuteration to prove that the bands can indeed be assigned to ν(O–H) vibrations.

Effect of Deuterated Fluoro Alchols. Free PFTB has a ν(O–H) band at 3590 cm^{-1} in lXe solution. A major part of our spectroscopic evidence for Ir···H–O bonding was the observation of a broad new band at 3100 cm^{-1} in solutions where **1** and PFTB were both present. This shift and increase in band intensity are characteristic of H-bonded hydroxyl groups. In order to strengthen this assignment, we have repeated the experiment with a mixture of $(CF_3)_3COH/(CF_3)_3COD$ (Figure 2). As well as the bands of the O–H species, the spectrum shows the ν(O–D) band of free PTFB at 2680 cm^{-1} and a broad band at 2330 cm^{-1}, the deuterated analog of the H-bonded ν(O–H) band. The isotopic frequency ratio ν(O–H)/ν(O–D) for these broad bands of the H-bonded complex is 1.35, slightly less than that predicted for an isolated O–H harmonic oscillator (1.414) but very close to that observed for ν(O–H)/ν(O–D) of free PFTB. The observed isotopic ratio is exactly the same as values reported for other H-bonded complexes of PFTB involving nonmetallic bases such as acetonitrile or dimethyl ether in lXe.[8c] Similar bands are seen for $Cp^*Rh(CO)_2$/PFTB, (see below), but unfortunately, the ν(O–D) band of the D-bonded complex is very close to that of CO_2 (both atmospheric and dissolved in lXe) and it is, therefore, more difficult to observe than that for $Cp^*Ir(CO)_2$ without computer subtraction of the spectra.

Effect of Temperature: Formation of the 1:2 Complex. Formation of the H-bonded complex $Cp^*(CO)_2Ir\cdots H–OR_F$ (**2**) is favored by lower temperatures. Xenon freezes at −111 °C, and studies at lower temperatures require the use of lXe/lKr mixtures. Figure 3 shows the ν(C–O) spectral region of a solution of **1** and PFTB in lXe/lXr at two different temperatures. Spectrum a, recorded at −73 °C, is similar to that in *n*-heptane at higher temperatures, with bands of **1** and the H-bonded complex **2** shaded. As the temperature was lowered, the bands of **1** were reduced in intensity and two further bands appeared, shifted up in wavenumber from those of **2**. By −125 °C, these new bands, marked "Y", were the most intense in the spectrum and the bands of **1** had completely disappeared; see Figure 3b. These spectral changes are completely reversible with temperature, and it is clear that **1**, **2**, and Y are in thermodynamic equilibrium.

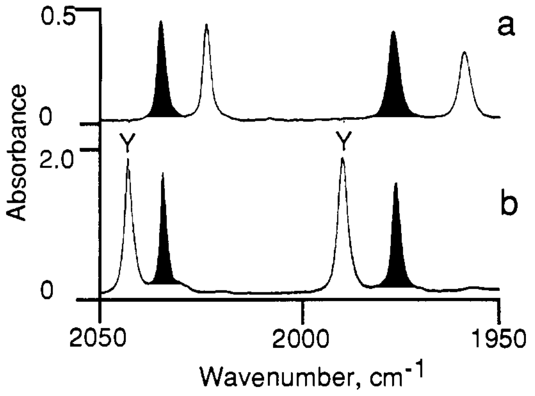

Figure 3. IR spectra, in the ν(C–O)region, of a solution of $Cp^*Ir(CO)_2$ (**1**) and PFTB in mixed lXe/lKr solution (ca. 50% lKr) at (a) −73 °C and (b) −125 °C. The bands are assigned as follows: unlabeled, **1**; shaded, $Cp^*(CO)_2Ir\cdots H–OR_F$, **2**; "Y", the complex $\{[Cp^*Ir(CO)_2]\cdots(HOR_F)_2\}$ (**3**).

Furthermore, the formation of Y is favored by higher concentrations of PFTB in solution, although all of our solutions were relatively dilute. Unfortunately, the kinetics of the interconversion $\mathbf{1} \rightleftharpoons \mathbf{2} \rightleftharpoons Y$ cannot be deduced from these experiments because the equilibrium is established far more rapidly than the temperature for the lXe cell can be changed. Similar spectral changes have been observed with $Cp^*Rh(CO)_2$/PFTB; see below.

The high wavenumbers of these new bands, Y, relative to those of **2**, indicate a further increase in positive charge on the metal center but still not enough to assign them to the protonted form; see Table II. We, therefore, assign the bands to an H-bonded complex, $\{[Cp^*Ir(CO)_2]\cdots(HOR_F)_2\}$, where a second molecule of PFTB also forms a hydrogen bond to the metal center.[18] By an extension of our analogy with Lewis acid/base species (see above), we suggest **3** as a possible structure for this *1:2* adduct. In **1**, there are two orbitals very close in energy and it is to some extent arguable which is the true HOMO.[12b,19] One orbital is largely localized in an Ir–Cp* interaction and does not provide a suitable site for H-bonding or formation of Lewis adducts. However, the other orbital, **4**, has precisely the correct symmetry, $2a_1$, to interact with the two molecules of PFTB.

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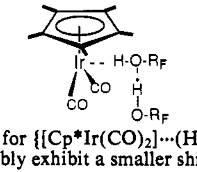
(17) We have also tried to investigate possible $MeOH/Cp^*Ir(CO)_2$ interactions using variable-temperature experiments with **1** impregnated into polyethylene which was then saturated with MeOH. As in MeOH/*n*-heptane solutions, we observed an asymmetrical broadening of both ν(C–O) bands of **1**, which occurred reversibly as the temperature was lowered, but again the wavenumber shift was too small to be conclusive.

(18) It is unlikely that Y could be an $\{[Cp^*Ir(CO)_2]\cdots(HOR_F)_n\}$ species ($n > 2$), since PFTB is known not to self-associate in solution at these temperatures in the absence of $Cp^*Ir(CO)_2$. On the other hand, there is extensive spectroscopic evidence[9] for formation of 1:2 adducts of PFTB with metal carbonyl complexes (via H-bonding to the CO groups) under similar conditions. Furthermore, the formation of $\{[Cp^*Ir(CO)_2]\cdots(HOR_F)_n\}$ ($n > 2$) would be expected to show an extreme sensitivity to the concentration of PFTB in solution. We did not investigate whether $\{[Cp^*Ir(CO)_2]\cdots(HOR_F)_2\}$ could be observed with less acidic alcohols, e.g., HFIP, because these are known to dimerize relatively easily at low temperatures. The structure **6**

6 

cannot be totally eliminated for $\{[Cp^*Ir(CO)_2]\cdots(HOR_F)_2\}$, but we believe such a structure would probably exhibit a smaller shift of the ν(C–O) bands than was observed in Figure 3.

(19) Lichtenberg, D. L.; Blevins, C. H., II; Ortega, R. B. *Organometallics* **1984**, *3*, 1614. Lichtenberger, D. L.; Calabro, D. C.; Kellogg, G. E. *Organometallics* **1984**, *3*, 1623.

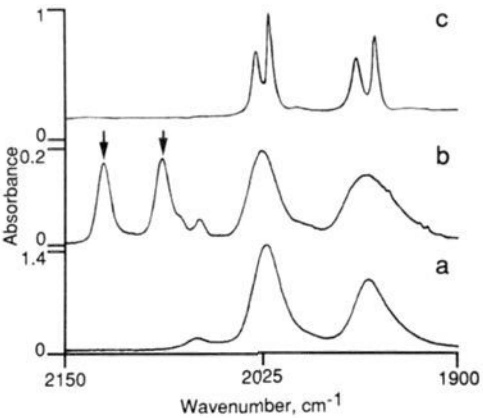
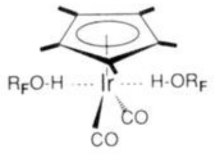


Figure 4. IR spectra, in the ν(C–O)region, of a solution of $Cp^*Ir(CO)_2$ (**1**) dissolved in (a) neat TFE, (b) neat HFIP, and (c) a saturated solution of HFIP in *n*-heptane. The broad bands in (a) are either those of the H-bonded complex **2** or the overlapped and unresolved bands of **1** and **2**. The corresponding bands in (b) are assigned similarly, and the two high-wavenumber bands are due to the protonated cation, $[Cp^*Ir(CO)_2H]^+$; see Table III. The bands in (c) are due to **1** and **2**; cf. Figure 1.



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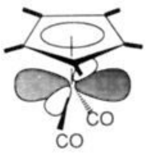

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The fact that formation of the $\{[Cp^*Ir(CO)_2]\cdots(HOR_F)_2\}$ adduct is favored by increased concentrations of PTFB in lXe at low temperature prompted us to investigate what would happen if **1** were dissolved in *pure* fluoro alcohols at room temperature where the concentration of alcohol is very much higher than that in lXe solution.

Interaction with *Pure* Fluoro Alcohols. With **1** dissolved in neat TFE, the least acidic of the fluoro alcohols which we have used, the spectra were similar to those in TFE/*n*-heptane mixtures but the polar nature of the solvent broadened the bands so that the absorptions of **1** and the H-bonded adduct, **2**, could not be resolved (Figure 4a). The spectra in pure HFIP were quite different (Figure 4b). There were two new bands at relatively high wavenumber (arrowed), as well as two broad bands at lower wavenumber, assignable either to **2** or to **1** and **2** (overlapped bands), by comparison with spectra in HFIP/*n*-heptane (Figure 4c). A similar pair of bands at high wavenumber were observed with pure PFTB, but in this case, the bands of **1**/**2** disappeared completely (not illustrated). The high-wavenumber bands in HFIP and PFTB can be assigned to the protonated cation $[Cp^*Ir(CO)_2H]^+$, since the band positions are close to the values reported for this cation (Table III). Similar results were obtained with $CpIr(CO)_2$/HFIP with the formation of $[CpIr(CO)_2H]^+$; see Table III. It is interesting to note that there is no spectroscopic evidence, in any of these experiments, for H-bonding to the protonated metal center. We now present evidence to connect the protonation of the metal center and the H-bonding to that center.

H-Bonding and Protonation. In pure HFIP, two or three distinct species appear to coexist: the H-bonded complex **2**, the cation $[Cp^*Ir(CO)_2H]^+$, and, perhaps, free **1**. On the other hand, when **1** is dissolved in *n*-heptane saturated with HFIP, only **1** and **2** are observed and no protonation occurs, most probably because of the lower dielectric constant of *n*-heptane, although other explanations are also possible.[20] Unfortunately, *n*-heptane and HFIP are only partially miscible, so one cannot prove the existence of an equilibrium between $[Cp^*Ir(CO)_2H]^+$ and $Cp^*(CO)_2Ir\cdots H–OR_F$ by diluting HFIP with *n*-heptane. However, one can demonstrate the conversion of $[Cp^*Ir(CO)_2H]^+$ into $Cp^*(CO)_2Ir\cdots H–OR_F$ in supercritical xenon, scXe.

Table III. Wavenumbers (cm⁻¹) of ν(C–O) Bands of $Cp^*Ir(CO)_2$ (**1**), the H-Bonded Complex **2**, and the Protonated Cation $[Cp^*Ir(CO)_2H]^+$ and Their Cp Analogs in Neat Fluoro Alcohol and Other Solvents

		wavenumber		
complex	solvent	**1**/**2**[a]	protonated species	assgnt
$Cp^*Ir(CO)_2$	neat TFE	2021.2		a′
		1955.4		a″
$Cp^*Ir(CO)_2$	neat HFIP	2024	2125.3	a′
		1958	2088.3	a″
$Cp^*Ir(CO)_2$	neat PTFB		2124.4	a′
			2087.5	a″
$Cp^*Ir(CO)_2$	HFIP/scXe[b]		2120.5	a′
			2080.8	a″
$Cp^*Ir(CO)_2$	HCl/scXe		2115	a′
			2073	a″
$[Cp^*Ir(CO)_2H]^+$	various		2119,[c] 2117[d], 2111[e]	a′
			2080,[c] 2078,[d] 2070[e]	a″
$CpIr(CO)_2$	neat HFIP	2051.8	2140.0	a′
		1989	2104.9	a″
$[CpIr(CO)_2H]^+$	solid zeolite[d]		2138	a′
			2098	a″

[a] Unresolved bands of **1** and **2**. [b] Immediately after mixing scXe and HFIP; see Figure 5. [c] Reference 11d. [d] Solid zeolite; ref 11e,f. [e] Reference 11a,b.

scXe is now firmly established as an extremely useful, if somewhat exotic, solvent for both analytical and reaction chemistry. scXe has unique transparency for IR spectroscopy at room temperature, and for this reason, we intended to use scXe to study the spectrum of **1**/HFIP in the ν(O–H) region. It is less widely known that scXe is quite dense; at the critical point, 16.7 °C and 847 psi, the density of scXe is 1.096 g/mL, and even small increases in temperature and/or pressure cause a significant rise in density. Indeed, at only 23 °C and 1180 psi, the density of scXe increases by nearly 50% compared to its critical value, and under the pressure/temperature conditions used in this paper, scXe is slightly *denser* than HFIP, which has a density of 1.596 g/mL. In our experiment, HFIP and Xe were not premixed, but instead, we used HFIP with **1** dissolved in it. A 10-μL portion of this solution was injected into an empty high-pressure cell, ca. 2 mL in volume, which was immediately pressurized with Xe. Thus, we had the extremely unusual phenomenon of a *liquid* mixing with a *gas* of similar or even greater density.

Figure 5 shows the surprising IR spectra which we obtained. Initially, spectrum a was dominated by the ν(C–O) bands of $[Cp^*Ir(CO)_2H]^+$, but these bands quickly decreased in intensity while those of **1** and **2** grew until spectrum b resembled that in *n*-heptane/HFIP mixtures. Our explanation is that, when mixed with scXe of very similar density, the liquid HFIP rapidly broke up into small droplets (containing dissolved $[Cp^*Ir(CO)_2H]^+$) and then, more slowly, these droplets dissolved to give a homogeneous solution. Changes in the ν(O–H) region of the spectrum are consistent with this explanation; initially, the bands were broad, similar to those of neat HFIP, and subsequently, spectra resembled those of HFIP in inert solvents (e.g. in *n*-heptane). We have also confirmed our assignment of the ν(C–O) bands of $[Cp^*Ir(CO)_2H]^+$ by generating it by a different route, the reaction of **1** with HCl in scXe; see Table III. (Under

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(20) An alternative explanation, which has been put forward in another context,[9d] is that a second molecule of HFIP might bond to the O atom of a molecule of HFIP, which is already H-bonded to the Ir center, as shown schematically in **6**.[18] The effect of this second HFIP molecule might be to increase the overall acidity and facilitate proton transfer to the metal center. The formation of **6** would, perhaps, be more probable in *pure* HFIP than in lXe solution, given the very much higher concentration of alcohol in the neat liquid.

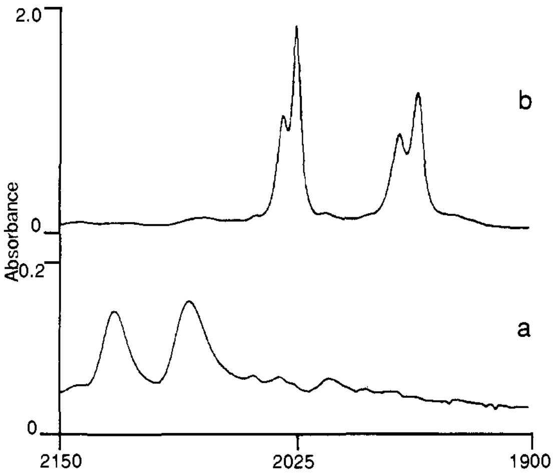

Figure 5. IR spectra recorded in supercritical Xe solution, scXe: (a) spectrum recorded shorter after mixing pure scXe with a solution of **1** in neat HFIP at 23 °C; (b) spectrum of the *same* sample recorded ca. 30 min later at 40 °C. The two strong bands in (a) are assigned to $[Cp^*Ir(CO)_2H]^+$ (see Table III) while those in (b) are due to **1** and **2** (see Table II).

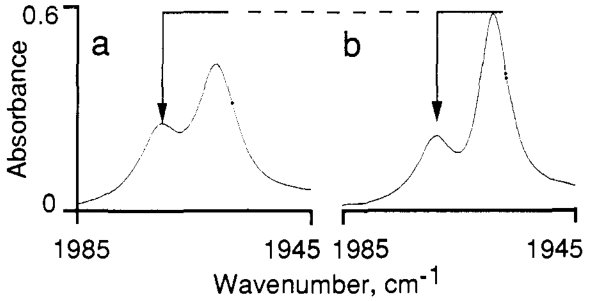

Figure 6. IR spectra of **1** and HFIP in supercritical C_2H_6, at 35 °C. Spectrum a was recorded with the pressure of scC_2H_6 at 680 psi (ρ 0.12 g/mL) and spectrum b with the pressure at 3050 psi (ρ 0.41 g/mL) and the concentrations of HFIP and iridium unchanged. In both spectra, the arrowed band is assigned to **2** and the unlabeled band to **1**. There is some change in the bandwidths between the two spectra, but nevertheless, it is quite clear that the ratio of **1**:**2** changes as the pressure and density are increased even though the concentration of HFIP remains unchanged.

these conditions, no H-bonding was observed between **1** and HCl.) Thus, quite fortuitously, one can observe the disappearance of $[Cp^*Ir(CO)_2H]^+$ and concomitant formation of $Cp^*(CO)_2Ir\cdots H-OR_F$ in scXe. As far as we are aware, this is the first case where definite evidence has been found to connect the protonation of a metal center and the formation of an M···H–O bond.

Supercritical solvents have an additional advantage which permits H-bonding to be studied in a unique way; namely, one can observe the effect of solvent density *at constant solute molarity* on the H-bonded equilibrium because, unlike that of other solvents, the density of a supercritical fluid can be "tuned" with pressure.[21] We now describe how the H-bonding of **1** and HFIP can be studied in this way in supercritical ethane (scC_2H_6) solution.

Effect of Varying Solvent Density: H-Bonding in Supercritical Ethane. As with scXe, the scC_2H_6 experiment started with HFIP/**1** mixtures in the cell, but $[Cp^*Ir(CO)_2H]^+$ was not observed even transiently in scC_2H_6 solution, probably because scC_2H_6(ρ_c = 0.204 g/mL) is much less dense than HFIP. We have recorded spectra over a wide range of pressures at temperatures close to the critical point (T_c = 32.3 °C) to see how H-bonding is affected by density. Figure 6 shows two spectra representing extreme values of pressure. It is clear that an increase in pressure shifts the equilibrium in favor of the free alcohol and organometallic; low solvent density favors H-bonding.

The effect of solvent density has been studied previously by a number of groups[22] who have noted similar changes in equilibria. However, this experiment has a number of significant differences from earlier studies. The exceptionally high IR extinction coefficient of the ν(C–O) bands and the relatively strong H bond means that the experiment has been carried out in a much more dilute solution than has previously been possible. In addition, this is the first occasion on which the shift in equilibrium has been verified by observation of the proton *acceptor* rather than the donor and on which a supercritical H-bonded equilibrium has been monitored from both sides simultaneously (i.e. the decrease in concentration of the H-bonded complex *and* the concomitant increase in the free molecule). Although the shift in equilibrium is initially surprising, it can be rationalized, nonrigorously, as follows. An increase in solvent density also increases the enthalpy of solvent/solute interaction. If the sum of the "solvation" enthalpies of **1** and PFTB is greater than the solvation enthalpy of the H-bonded complex, **2**, an increase in density will reduce the enthalpy of formation of the H-bond, thus shifting the equilibrium in favor of **1** and PFTB. In reality, the energetics will be more complicated because solute "clustering" may occur close to the critical point and because the explanation, as presented, ignores possible changes in entropy.

Although the equilibrium between **1** and **2** is probably too complex for modeling of the system, it is important to stress that the spectroscopic properties of such organometallics render them significantly more sensitive as probes for supercritical behavior than are most of the compounds currently used for such studies. Thus, it should be possible to investigate extremely dilute solutions in which the bulk properties should deviate very little from those of the pure fluid itself. We now look at the effect on H-bonding of changing the metal center.

H-Bonding to Other Metal Centers. All of the experiments described up to this point have involved H-bonding to Ir as the metal center. Clearly, it is important to establish whether this phenomenon occurs with other metals. Generally, third-row elements exhibit higher basicity than their first- and second-row counterparts. However, it has already been reported[9c,d] that PFTB does *not* form a hydrogen bond to the third-row group 7 metal center of $Cp^*Re(CO)_3$, which lacks a suitable acceptor orbital; instead, H-bonding occurs via the *O atom* of a carbonyl group, with a substantial shift of one ν(C–O) band to lower wavenumber. Recently, we observed a similar effect with PFTB/$Cp^*Re(CO)_2(N_2)$ in lXe solution.[23] (Arene)OsL_2 complexes appear to have a relatively low solubility in lXe, and Pt does not form mononuclear $(C_nR_n)M(CO)_n$ complexes. Thus, we have focused our investigations on the same periodic group as that of Ir, studying the interaction of PFTB with Rh and Co centers.

Figure 7 shows the ν(C–O) region for three lXe solutions containing PFTB and respectively $Cp^*Co(CO)_2$, $Cp^*Rh(CO)_2$, and $Cp^*Ir(CO)_2$. Immediately, it can be seen that *both* Co and Rh behave in a manner similar to that of Ir. All three metals show two new ν(C–O) bands, shaded in the figure, shifted to higher wavenumber relative to those of $Cp^*M(CO)_2$, characteristic of H-bonding to the metal center. The relative intensities of the bands of H-bonded and free $Cp^*M(CO)_2$ are different for the three metals. For Ir, the bands of the H-bonded complex are slightly more intense than those of free $Cp^*M(CO)_2$, and for Rh, they are somewhat less intense while, for Co, the H-bonded bands are very much less intense. Assuming that, for each metal, the relative extinction coefficients of the H-bonded and free forms of $Cp^*M(CO)_2$ are similar, the changes in intensity indicate a difference in the equilibrium between H-bonded and free $Cp^*M(CO)_2$ for the three metals; the equilibrium increasingly favors the free $CpM^*(CO)_2$ as the metal changes from Ir to Co. Differences in equilibrium suggest that there should be a corresponding difference in $\Delta H°$ for the three metals. This

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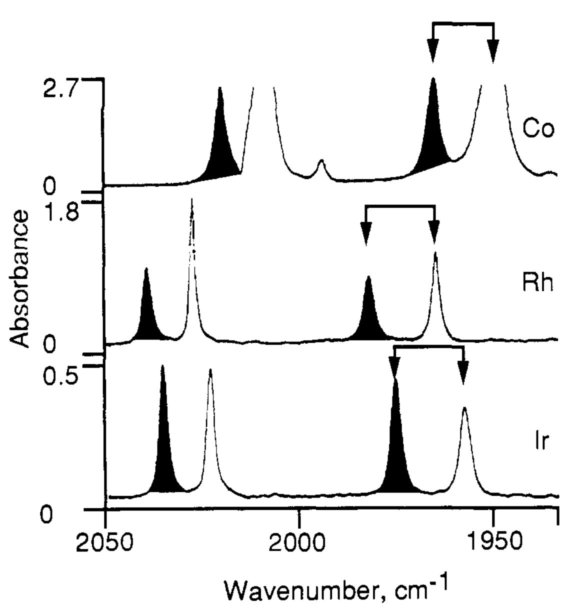

Figure 7. IR spectra, in the ν(C–O) region, of Cp*M(CO)$_2$ (M = Co, Rh, and Ir) in lXe doped with PFTB. In each case, the spectra show two pairs of bands, the shaded components of which are due to the H-bonded complex Cp*(CO)$_2$M···H–OR$_F$. Note that, for all three metals, there are similar wavenumber shifts as indicated by the arrows between the ν(C–O) bands of Cp*(CO)$_2$M···H–OR$_F$ and Cp*M(CO)$_2$; see Table I. By contrast, the *intensities* of the bands of Cp*(CO)$_2$M···H–OR$_F$ increase relative to those of Cp*M(CO)$_2$ from Co through Ir. Spectra were recorded at temperatures of –87 °C (Co), –65 °C (Rh), and –73 °C (Ir).

difference in the strength of interaction is confirmed by our observation that, at very low temperatures in lXe/lKr, Cp*Rh(CO)$_2$/PFTB gives rise to weak ν(C–O) bands similar to those assigned to the 1:2 complex, {[Cp*Ir(CO)$_2$]···(HOR$_F$)$_2$} (**3**), while Cp*Co(CO)$_2$ does not form an analogous 1:2 complex under these conditions.

These differences in the strength of the M···H–O interaction are reflected by significant differences between the three metals in the ν(O–H) region of the spectrum (Figure 8). For each PFTB/Cp*M(CO)$_2$ interaction, one can observe a rather broad band, shifted down in wavenumber from the ν(O–H) band of free PFTB and having increased integrated intensity, characteristic of H-bonding. Despite the broadness of these bands, it is clear from the figure that the wavenumber shift, between free and bonded PFTB, increases steadily from Co to Ir. Even for Co, the shift is much greater than the largest shift, 175 cm^{-1}, observed for H-bonding to CO groups bonded to group 6 or 7 metals,[9] underlining the qualitative difference of the H-bonding to these group 9 centers. As discussed below, Iogansen and co-workers[8b] have shown that, for H-bonding to a range of non-metal compounds, such shifts correlate well with the enthalpy of the A···H–O interaction. We have already reported that this correlation also applies to Cp*(CO)$_2$Ir···H–OR$_F$. It is reasonable, therefore, to assume that the shifts in ν(O–H) do indeed reflect the differences in $\Delta H°$ for Co, Rh, and Ir, deduced from the relative intensities of the ν(C–O) bands in Figure 7.

Our attempts to study interactions of the Rh and Co compounds with PFTB or HFIP in *n*-heptane were unsuccessful, as irreversible reaction occurred with precipitation of unidentified products. Results with Cp*Rh(CO)$_2$/TFE in *n*-heptane were more successful. When TFE was added to a solution of Cp*Rh(CO)$_2$, partially resolved shoulders were observed on both ν(C–O) bands, shifted ca. 2–4 cm^{-1} to higher frequency, indicating that H-bonding to the Rh center indeed occurs. This shift is significantly smaller than the shifts observed with PFTB in lXe[24] (Figure 7). Thus, as for Cp*Ir(CO)$_2$ interacting with a series of different fluoro alcohols, the magnitude of the shift in the ν(C–O) bands of Cp*Rh(CO)$_2$ appears to be at least a qualitative indication of the strength of the Rh···H–OR$_F$ interaction. By contrast, the shift in the ν(C–O) bands for Cp*M(CO)$_2$/PFTB is similar for all three metals (Figure 7 and Table IV) and therfore cannot be considered a good indicator of the strength of the M···H–O interaction. The change from one metal center to another involves a series of quite subtle changes in the nature of the M–C–O σ and π interactions, which are reflected in the positions of the ν(C–O) bands; for example, the ν(C–O) bands of Cp*Rh(CO)$_2$ are at *higher*

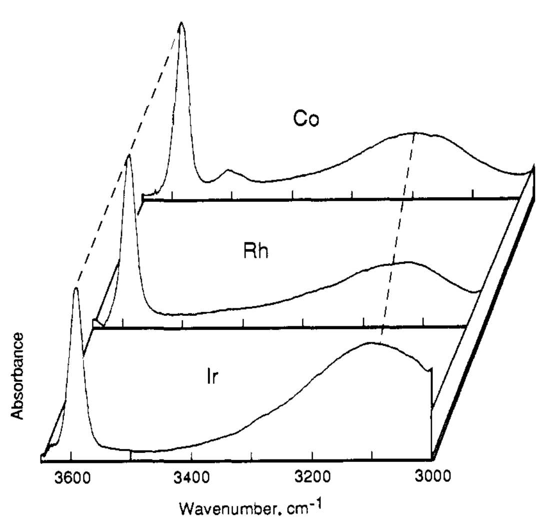

Figure 8. IR spectra, in the ν(O–H) region, of Cp*M(CO)$_2$ (M = Co, Rh, Ir) in lXe doped with PFTB. These spectra were recorded with the same solutions as those used in Figure 7 but at slightly different temperatures: –105 °C (Co), –90 °C (Rh), and –80 °C (Ir). In each spectrum, the sharp band near 3600 cm^{-1} is due to free PFTB, and the broad band at lower wavenumber is the ν(O–H) band of Cp*(CO)$_2$M···H–OR$_F$. Note that the separation of the bands of PFTB and Cp*(CO)$_2$M···H–OR$_F$ increases from Co to Ir; see Table V. The three spectra have been normalized to the same absorbance, and the dotted lines are merely drawn to aid visualization of the peak positions. Note that the weak feature close to 3500 cm^{-1} in the Co spectrum may be due to an H-bonded interaction of PFTB with traces of free carbon monoxide in solution. (The position of the band of CO···H–OR$_F$ was verified in a separate experiment with PFTB in lXe doped with CO.)

Table IV. Wavenumbers (cm^{-1}) of ν(C–O) Bands of (C$_5$R$_5$)ML$_2$ Compounds and Their H-Bonded Complexes in lXe Solution Doped with PTFB at ca. –90 °C

	wavenumber[a]			
compound	free	H-bonded[b]	$\Delta\nu$ (H-bonded minus free)	assgnt
CpCo(CO)$_2$	2030	2043.0	13.0	a′
	1973	1987.2	14.2	a″
	4052.7	4074.9	22.2	2 × a′
	3977.6	4005.0	27.4	a′ + a″
	3929.9	3962.0	32.1	2 × a″
CpIr(CO)$_2$	2041.9	2055.3	13.4	a′
	1980.8	1999.0	18.2	a″
Cp*Co(CO)$_2$	2009.2	2020.6	11.4	a′
	1949.2	1965.5	16.3	a″
Cp*Rh(CO)$_2$	2028.9	2039.5 (2048)[c]	10.6 (19.1)[c]	a′
	1966.1	1982.6 (1995)[c]	16.5 (30.9)[c]	a″
Cp*Ir(CO)$_2$[d]	2020.7	2033.7 (2043.0)[c]	13.0 (22.3)[c]	a′
	1954.4	1973.1 (1986.7)[c]	18.7 (32.3)[c]	a″
CpRh(CO)PMe$_3$	1969.5	1983.0	13.5	ν(C–O)
CpRh(CO)(C$_2$H$_4$)	1990.7	2001.8	11.1	ν(C–O)
CpRh(N$_2$)(C$_2$H$_4$)	2173.1	2190.0	16.9	ν(N–N)
CpRh(C$_2$H$_4$)$_2$		1354		uncertain[e]
CpIr(CO)(C$_2$H$_4$)	1980.8	1996.0	15.2	ν(C–O)

[a] Error ±0.2 cm^{-1}. [b] Wavenumbers for the 1:1 complex. [c] Values in parentheses for the 1:2 complex, Cp*(CO)$_2$M···(HOR$_F$)$_2$. [d] The values in Table II differ from those here because the data in Table II refer to a mixed lXe/lKr solvent. [e] For a discussion of this band, see main text and Figure 10.

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[24] TFE cannot easily be used for study *weak* interactions in lXe because TFE is well-known to self-associate at low temperatures, readily forming H-bonded dimers rather than interacting with other acceptors.

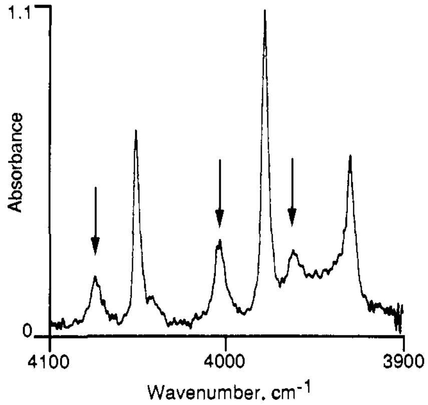


Figure 9. IR spectrum, recorded in the ν(C–O) overtone/combination region, for $CpCo(CO)_2$ in lXe doped with PFTB at −100 °C. The three unlabeled bands are due to uncomplexed $CpCo(CO)_2$, and the arrowed bands are assigned to the corresponding vibrations of $Cp(CO)_2Co \cdots H–OR_F$; see Table IV.

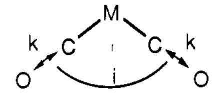
wavenumber than those of Co and Ir. Thus, it is perhaps not surprising that few conclusions can be drawn from a comparison of the shifts of the ν(C–O) bands of the H-bonded species of different metals. We now examine how H-bonding changes when Cp* is replaced by Cp.

Effect of Replacing η^5-C_5Me_5 with η^5-C_5H_5. In order to understand the electronic factors responsible, it was logical to study complexes not only with different metal centers but also with different π-ligands. We have therefore repeated these experiments with the cyclopentadienyl, Cp, complexes of Co and Ir for comparison with their Cp* analogs. We found clear IR evidence, both ν(C–O) and ν(O–H), for H-bonding to the metal center of both $CpIr(CO)_2$ and $CpCo(CO)_2$; see Table IV. For both metals, the shift in the ν(O–H) band of the H-bonded complex from that of free PFTB is smaller than that for the corresponding $Cp^*M(CO)_2$/PFTB interaction, indicating a weaker H bond. There was no evidence for the formation of a 1:2 complex, $\{[CpM(CO)_2] \cdots (HOR_F)_2\}$, even for Ir, again consistent with weaker M···H–O interactions. Thus, it is clear that PFTB can form H bonds to the metal center of Cp compounds almost as easily as to those of Cp* complexes but that the interaction is weaker. Preliminary experiments have already shown that the interactions of fluoro alcohols with indenyl compounds may well be more complicated; experiments with (η^5-indenyl)$Ir(CO)_2$ in HFIP/*n*-heptane suggest that even under these conditions protonation occurs but there are additional processes, possibly the formation of η^3 or η^6 species[11c] via protonation at the metal center.

$CpCo(CO)_2$ has particularly high solubility in lXe, and for $CpCo(CO)_2$/PFTB, it was possible to observe combination and overtone bands of the ν(C–O) vibrations (Figure 9). An $M(CO)_2$ moiety has two ν(C–O) vibrations, a′ and a″, which give rise to *three* overtone and combination bands, 2 × a′, a′ + a″, and 2 × a″. It can be seen from Figure 9 that $Cp(CO)_2Co \cdots H–OR_F$ shows exactly the same pattern of three bands as $CpCo(CO)_2$ but the bands are shifted *up* in wavenumber relative to those of $CpCo(CO)_2$. The shifts are approximately twice as large as the corresponding shifts of the fundamental bands. This is not the first time that overtones have been observed for H-bonded metal carbonyl compounds, but the previous examples have involved H-bonding to the O atom, and the overtone bands have been shifted *down* in wavenumber.[9c]

It will be noticed from Table IV that, for all $Cp^*M(CO)_2$ and $CpM(CO)_2$ compounds which we have studied, H-bonding causes a larger shift of the low-wavenumber ν(C–O) band, a″, than of the higher wavenumber a′ band. This is a consequence of the empirical fact, first quantified by Timney,[25] that an *increase* in C–O stretching force constants is accompanied by a *decrease* in the CO/CO interaction force constant.

In an energy factored force field, the ν(C–O) vibrations of $M(CO)_2$ can be defined by two force constants, *k* and *i*, as shown in



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The symmetrized force constants for the two vibrations are then given by

$$K_{a'} = k + i \qquad K_{a''} = k - i \tag{2}$$

If it is supposed that H-bonding increases *k* by δ_k with a concomitant decrease in *i* of δ_i, then the force constants for the H-bonded $M(CO)_2$ unit will be

$$K'_{a'} = (k + \delta_k) + (i - \delta_i) \qquad K'_{a''} = (k + \delta_k) - (i - \delta_i) \tag{3}$$

The difference in symmetrized force constants, H-bonded *minus* nonbonded, will then be given by

$$K'_{a'} - K_{a'} = \delta_k - \delta_i \qquad K'_{a''} - K_{a''} = \delta_k + \delta_i \tag{4}$$

From this, one can see that a larger difference in force constant is predicted for the lower wavenumber band, a″. Since the wavenumber of a band is proportional to the square root of the force constant, the wavenumber shift of the a″ band is also predicted to be greater than that of the a′ band, just as is observed in our experiments. We now investigate the effect of replacing one or more of the CO groups in $CpM(CO)_2$ by other two-electron-donor ligands.

Effect of Replacing CO Ligands by C_2H_4 and N_2. Results with $CpIr(CO)(C_2H_4)$/PFTB in lXe are similar to those with $CpIr(CO)_2$ itself. $CpIr(CO)(C_2H_4)$ has only one ν(C–O) IR band, and, when the temperature is lowered, the intensity of this band decreases with a corresponding growth of a single new ν(C–O) band, shifted to higher wavenumber; see Table IV. These changes are accompanied by the growth of a broad band in the ν(O–H) region, confirming the formation of an H bond. As with all of the compounds described earlier in this paper, blank experiments with PFTB/lXe show that such ν(O–H) bands are not observed in the absence of the organometallic. It is, however, known[8d] that traces of H_2O can give rise to a band in this region (3200 cm^{-1}) through H-bonding to PFTB. The wavenumber of the band due to the $PFTB \cdots H_2O$ complex is different from that observed for **1** and most of the other organometallics used in this study, and clearly an artifact due to H_2O should not vary with the nature of the organometallic under study. Nevertheless, in all cases, we have performed blank experiments to eliminate any possibility that our results could be artifacts, due to the presence of H_2O.

Similar growth of a ν(O–H) band at low temperatures is found for $CpRh(C_2H_4)_2$/PFTB in lXe, indicating H-bonding (Figure 10a). In this case, however, there are no ν(C–O) bands to indicate the site of the H-bonding (i.e. metal center, π-ring, or olefin ligands). There is a weak band (1353 cm^{-1}) which grows reversibly at low temperature (Figure 10b). The band appears to be associated with the H-bonded form of $CpRh(C_2H_4)_2$, but the precise assignment of this band is not clear; comparison with spectra obtained using $Cp^*Rh(CO)_2$ show that the band is not a deformation mode of H-bonded PFTB itself. The vibrational spectrum of coordinated C_2H_4 is considerably more complicated to assign than that of CO, and in this case, some bands due to the C_2H_4 ligands in free $CpRh(C_2H_4)_2$ are obscured by the ν(C–F) bands of PFTB. Thus, in this case, we are forced to draw conclusions about the site of H-bonding merely from the magnitude of the shift, $\Delta\nu$(O–H), between the ν(O–H) band of the H-bonded complex and that of free PFTB. The observed

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

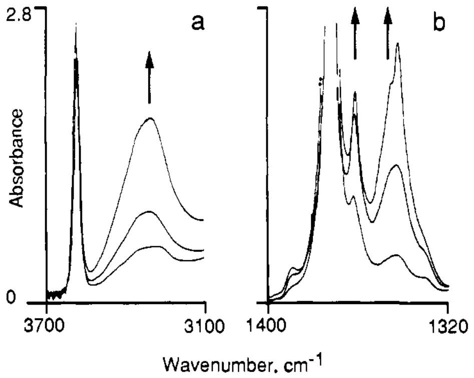

Figure 10. Superimposed IR spectra, recorded at three temperatures from −74 to −106 °C, of $CpRh(C_2H_4)_2$ in lXe doped with excess PFTB. (a) shows the growth at low temperatures of a broad band, arrowed, assigned to the ν(O–H) vibration of $Cp(C_2H_4)_2Rh\cdots H{-}OR_F$ and the concomitant small reduction in intensity of the ν(O–H) band of free PFTB, and (b) shows the corresponding growth of two bands at lower wavenumbers, arrowed; the higher wavenumber of these two bands is assigned to a δ(O–H) vibration of H-bonded PFTB, and the other band is due to $Cp(C_2H_4)_2Rh\cdots H{-}OR_F$ but its assignment is uncertain.

Table V. Wavenumbers (cm^{-1}) of ν(O–H) Bands of PFTB H-Bonded to $(C_5R_5)ML_2$ Compounds in lXe Solution at ca. −100 °C and the Enthalpy of Interaction Derived from the Shift, $\Delta\nu$(O–H), Using the Method of Iogansen

	wavenumber[a]		
compound	H-bonded[b]	$\Delta\nu$(O–H) (free PFTB minus H-bonded)	$-\Delta H°$/kJ mol^{-1}
$CpRh(CO)PMe_3$	3080	510	28.9
$Cp^*Ir(CO)_2$	3090	500	28.6[c]
$Cp^*Rh(CO)_2$	3130	460	27.5
$CpIr(CO)_2$	3190	400	25.6
$Cp^*Co(CO)_2$	3195	395	25.5
$CpIr(CO)(C_2H_4)$[d]	3210	380	25.0
$CpCo(CO)_2$	3330	260	20.6
$CpRh(C_2H_4)_2$[d]	3335	255	20.4
$CpCo(C_2H_4)_2$[d]	3420	170	16.7
free PTFB[e]	*3590*		

[a] Error ±2 cm^{-1}. [b] Data refer to the 1:1 complex $(C_5R_5)L_2M\cdots H{-}OR_F$. [c] A van't Hoff plot[7] for $Cp^*Ir(CO)_2$/PTFB in *n*-heptane gave a value of $\Delta H°$ −28.4 kJ mol^{-1}. [d] See text for discussion of possible steric influences on the interaction of PFTB with ethene complexes. [e] Although PTFB does not undergo self-association easily, it is possible to observe small amounts of $(PFTB)_2$ in lXe solutions (3410 cm^{-1}) when the concentration of PFTB is high and the temperature is very low.

value of $\Delta\nu$(O–H), −255 cm^{-1} (Table V), is comparable to the values for other M···H–O bonds (e.g. −260 cm^{-1} for $CpCo(CO)_2$; Table IV) but is substantially larger than those observed for interaction of PFTB with the π-ring of Cp_2Fe[9d] or olefins.[8c] Thus, we favor the metal center as the site of H-bonding to $CpRh(C_2H_4)_2$.[26] Our attempts to observed H-bonding between $CpCo(C_2H_4)_2$ and PFTB in lXe solution were slightly less conclusive. If interaction occurs, it is considerably weaker than that with $CpCo(CO)_2$/PFTB, and it only occurs at very low temperature.

There is less uncertainty over the site of H-bonding in $CpRh(CO)(C_2H_4)$ and $CpRh(N_2)(C_2H_4)$, since both of these contain strong IR chromophores (i.e. CO and N_2). Although $CpRh(N_2)(C_2H_4)$ is thermally labile[27] and we did not have access to a pure sample of $CpRh(CO)(C_2H_4)$, we managed to generate both compounds in situ in lXe by photolysis of $CpRh(C_2H_4)_2$ in the presence of N_2 or CO. These reactions were reported by us some years ago[27] and, surprisingly, are quite unaffected by the presence of PFTB in the lXe solution. The behavior of $CpRh(CO)(C_2H_4)$ was almost identical to that of $CpIr(CO)(C_2H_4)$, discussed above, with a single new ν(C–O) band shifted to higher wavenumber relative to that of $CpRh(CO)(C_2H_4)$ (Table IV). Very similar changes were observed in the ν(N–N) region of the spectrum of $CpRh(N_2)(C_2H_4)$. When the temperature of the lXe/PFTB solution was lowered, a new ν(N–N) band grew at higher wavenumber at the expense of the ν(N–N) band of $CpRh(N_2)(C_2H_4)$ itself (Figure 11). Once again, this process was reversible with a change in temperature. The direction and magnitude of the shift of the new ν(N–N) band suggest that it is due to a $Cp(C_2H_4)(N_2)Rh\cdots H{-}OR_F$ complex, where the *Rh center* serves as the proton acceptor. If the H-bond were to involve interaction with a coordinated C_2H_4 ligand, there would still be a shift in the ν(N–N) band to higher wavenumber but the shift would be smaller, as shown by our experiments with $Cp^*Re(CO)_2(N_2)$/PFTB, mentioned above, where H-bonding involves interaction with the CO group.[23] Thus, in this case, the $\Delta\nu$(N–N) shift for $CpRh(N_2)(C_2H_4)$ is 16.9 cm^{-1}, somewhat greater than that observed for $Cp^*Re(CO)_2(N_2)$, (13 cm^{-1} under similar conditions). Now, as a final example, we examine the interaction of PFTB with a very basic metal center.

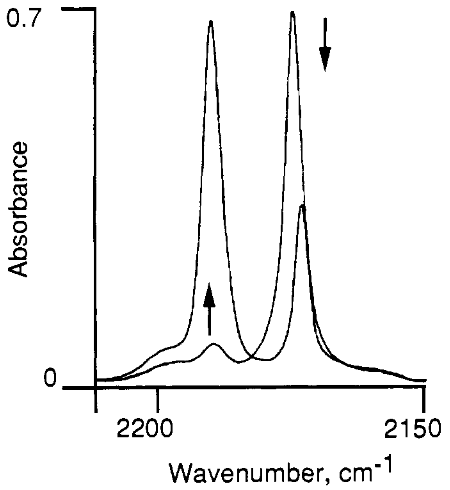

Figure 11. Superimposed IR spectra of $CpRh(C_2H_4)(N_2)$/PFTB in lXe doped with N_2, showing the changes in the ν(N–N) region between −52 and −103 °C. The higher wavenumber band which increases in intensity as the temperature is lowered is assigned to $Cp(C_2H_4)(N_2)Rh\cdots H{-}OR_F$; the other band which decreases correspondingly in intensity is the ν(N–N) band of $CpRh(C_2H_4)(N_2)$. At the start of the experiment, $CpRh(C_2H_4)(N_2)$ was generated photochemically from $CpRh(C_2H_4)_2$ by 35-min UV photolysis. Although unreacted $CpRh(C_2H_4)_2$ remains in the solution, it does not have any IR bands in this region of the spectrum.

H-Bonding to $CpRh(CO)PMe_3$. Interesting results were obtained when the interaction of $CpRh(CO)PMe_3$ with PFTB was studied in lXe. In this complex, the Rh atom possesses a particularly high basicity. It has only one CO ligand and, consequently, only one ν(C–O) band in the IR spectrum (at 1970 cm^{-1} in lXe). When PFTB was added to the solution, *two* new ν(C–O) bands appeared, at 1983 and 2085 cm^{-1}; see Figure 12. The band at 1983 cm^{-1} increased in intensity as the temperature was lowered, consistent with its being the ν(C–O) band of $Cp(CO)(PMe_3)Rh\cdots H{-}OR_F$, in equilibrium with $CpRh(CO)PMe_3$ and free PFTB. Regrettably, $CpRh(CO)PMe_3$ has quite a low solubility in lXe, and although this does not prevent the observation of the very intense ν(C–O) bands, the observation of the ν(O–H) bands under such conditions is very difficult. Nevertheless, on cooling the solution, we were just able to observe a new broad band centered at ca. 3080 cm^{-1}, which we believe to be due to the ν(O–H) vibration of $Cp(CO)(PMe_3)Rh\cdots H{-}OR_F$.

The ν(C–O) band at 2085 cm^{-1} also increased somewhat in intensity at lower temperature, but its intensity changed relative to that of the band at 1983 cm^{-1}, clearly indicating that the two bands do not belong to the same species. The high wavenumber

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(26) (a) The *protonation* of the corresponding Cp* compound, $Cp^*Rh(C_2H_4)_2$, has been shown to involve a delicate thermodynamic equilibrium between different isomers of $[Cp^*Rh(C_2H_4)_2H]^+$: Brookhart, M.; Lincoln, D. M.; Bennet, M. A.; Pelling, S. *J. Am. Chem. Soc.* **1990**, *112*, 2691. (b) The interaction of CpRh(olefin)$_2$ complexes with *HCl* has been examined in some detail: Seiwell, L. P. *Inorg. Chem.* **1976**, *15*, 2560.

(27) Haddleton, D. M.; Jackson, S. A.; Upmacis, R. K.; Poliakoff, M.; Perutz, R. N. *J. Organomet. Chem.* **1986**, *311*, C15.

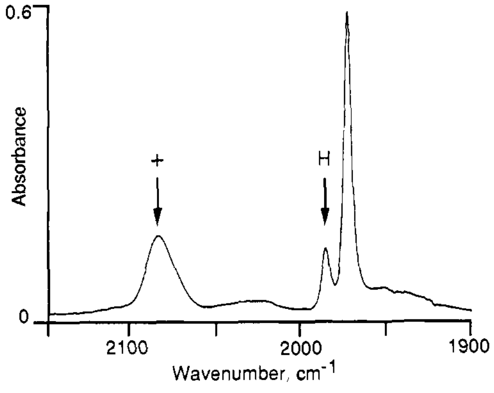

Figure 12. IR spectrum, in the ν(C–O) region, of CpRh(CO)(PMe$_3$) and PTFB in lXe at −102 °C. The unlabeled band is due to CpRh(CO)(PMe$_3$) while that marked "+" is assigned to the protonated cation [CpRh(CO)(PMe$_3$)H]$^+$, and the band marked "H", which grows reversibly in intensity at low temperature, is assigned to Cp(CO)(PMe$_3$)-Rh···H–OR$_F$.

of this band suggests that it is due to the protonated cation, [CpRh(CO)(PMe$_3$)H]$^+$. If this assignment is correct, CpRh(CO)PMe$_3$ is one of the few examples where the starting π-complex coexists in solution with both its protonated ion[28] *and* its complex, hydrogen-bonded at the metal center. This observation lends further support to our suggestion, based on our results with Cp*Ir(CO)$_2$ in scXe, that H-bonding to a metal center can be an important step in the protonation of that center.

CpRh(CO)PMe$_3$ probably represents the limit of basicity for which H-bonding to the metal center can be observed using PFTB. Any compound with greater basicity will almost certainly be completely protonated under these conditions. However, such a compound might well be able to form H bonds with an alcohol rather less acidic than PFTB, even perhaps with MeOH. Indeed, there is some asymmetric broadening on the high-wavenumber side of the ν(C–O) band of CpRh(CO)PMe$_3$ in *n*-heptane/MeOH solution.

Correlation of the Shifts of ν(O–H) Bands with the Basicity of the Metal Center. We have already described how, in our experiments, spectral changes in the ν(C–O) region were accompanied by changes in the ν(O–H) region. In all of the cases discussed above where new bands could be observed in this region, the bands were shifted *down* in wavenumber relative to the ν(O–H) band of free (i.e. not H-bonded) PFTB. It is well-known[8a,b] that the shift in the wavenumber of the stretching vibration ν(O–H) for proton donors, $\Delta\nu$(O–H), and the absolute intensity of this ν(O–H) band parallel the strength of the H bond and that both this shift and the intensity can serve as measures of the strength of the H-bonding interaction. Different equations have been proposed to quantify this dependence,[29] including the well-known Badger–Bauer correlation between the enthalpy change and $\Delta\nu$(O–H)[29a] or the increase in integrated IR absorbance,[8b] ΔA; $\Delta H° = 12.1(\Delta A)^{1/2}$. In our lXe experiments, it is difficult to quantify accurately the absolute increase in integrated absorbance so we have restricted our analysis to $\Delta\nu$(O–H). We have shown[7] that, for Cp*Ir(CO)$_2$/PFTB in lXe, Iogansen's equation[8b] for the enthalpy of hydrogen-bonding ($\Delta H° = -1.28(\Delta\nu)^{1/2}$) gives quite good agreement with the value which we derived from temperature dependence studies.[7] Table V presents the appropriate values of $\Delta\nu$(O–H) for the interaction of PFTB with the compounds discussed above. These $\Delta\nu$(O–H) values can be converted, using Iogansen's relationship, into enthalpies for the M···H–O interaction (eq 5). The values of

$$(C_5R_5)ML_2 + HOR_F \rightarrow (C_5R_5)L_2M\cdots H\text{–}OR_F \quad (5)$$

$\Delta H°$ derived in this way range from −16.7 kJ mol^{-1} for CpCo(C$_2$H$_4$)$_2$ to −28.9 kJ mol^{-1} for CpRh(CO)PMe$_3$ (Table V).

We now suggest that this shift, $\Delta\nu$(O–H), could be used more generally as a qualitative tool to compare the electron-donating abilities of different metal compounds by studying their interaction with a common proton donor, in our case PFTB. The data in Table V indicate that $\Delta\nu$(O–H), and hence the electron-donating ability of the metal center, increases on changing the metal from Co to Ir, on introduction of donor substituents (e.g. Me groups) into the π-ring, or, provided that the $\Delta\nu$(O–H) value is reliable, on substitution of CO with a donor ligand, PMe$_3$. Equally, $\Delta\nu$(O–H), and hence the apparent electron-donating ability, decreases only slightly, if at all, on substitution of one CO ligand by C$_2$H$_4$. On the other hand, there appears to be a significant decrease when both CO groups are replaced by C$_2$H$_4$. However, this interaction with the M(C$_2$H$_4$) and M(C$_2$H$_4$)$_2$ moieties may be influenced by steric factors since PFTB is quite a bulky molecule. Steric constraints for the interaction with M(C$_2$H$_4$)$_2$ may well be considerably greater than those for the interaction with an M(CO)$_2$ center, and therefore the shift in ν(O–H) may underestimate the inherent basicity of the M(C$_2$H$_4$)$_2$ center

Conclusions and Implications

Fluoro alcohols interact with Cp*Ir(CO)$_2$ and related compounds via H bonds. The experiments described in this paper show that such H-bonding is really quite widespread, at least within the compounds of group 9 metals, Co, Rh, and Ir. The strength of the H-bonding interaction increases with the acidity of the fluoro alcohol and with the basicity of the metal center. In addition, there is evidence, particularly from our experiments in supercritical Xe, to connect this H-bonding with the protonation of the metal center. As far as we are aware, this is the first time that the connection between the protonation of a metal center and H-bonding to that center has been demonstrated so directly. These experiments suggest that H-bonding can be viewed as "arrested" protonation, similar in principle to the arrested oxidative addition found in "nonclassical" dihydrogen compounds[30] or η^2-H–SiR$_3$ complexes.[31] The difference between H-bonding and these other systems is that H-bonding is a three-center *four-electron* interaction with coordinatively *saturated* metal centers while arrested oxidative addition involves a three-center *two-electron* interaction with coordinatively *unsaturated* metal centers.

Our experiments also show that it is not only the basicity of the metal center which influences the balance between H-bonding and protonation but also the nature of the solvent itself; the influence of the solvent arises because protonation involves electrostatic forces between ions. Thus, it seems that the solvent determines whether further reaction of the H-bonded complex Cp*(CO)$_2$Ir···H–OR$_F$ leads to the protonated cation [Cp*Ir(CO)$_2$H]$^+$ or to the 1:2 complex {Cp*(CO)$_2$Ir···(H–OR$_F$)$_2$}; see Scheme I. A more subtle influence of the solvent can be seen from the difference in wavenumber shift of the ν(C–O) bands which occurs when HFIP bonds to Cp*Ir(CO)$_2$; see Table II. The shifts are significantly greater in *n*-heptane than in scXe or scC$_2$H$_6$, presumably because the dielectric constants of these supercritical solvents are lower than that of *n*-heptane.

It is important to distinguish between the interactions discussed in this paper and those investigated by Norton and co-workers.[1b,32] Their work was also aimed at H-bonding between metals and

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[28] There have been previous reports (e.g. ref 9d) of the coexistence, in lXe solution, of metal cations protonated at the metal center and complexes H-bonded to the O atom of a CO ligand.

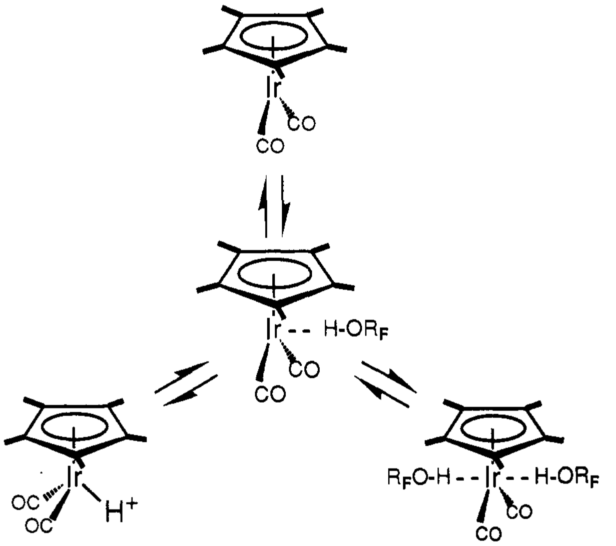
[29] (a) Badger, R. M.; Bauer, S. H. *J. Chem. Phys.* **1937**, *5*, 839. (b) For a more recent and more general discussion, see: Zeegers-Huyskens, T. In *Intermolecular Forces; an Introduction to Modern Methods and Results*; Huyskens, P. L., Luck, W. A. P., Zeegers-Huyskens, T., Eds.; Springer-Verlag: Berlin, 1991; p 123.

[30] See e.g.: Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120. Crabtree, R. H.; Hamilton, D. G. *Adv. Organomet. Chem.* **1989**, *28*, 299. Ginsburg, A. G.; Bagaturyants, A. A. *Organomet. Chem. USSR* **1989**, *2*, 111.

[31] For a recent review on silane complexes, see: Schubert, U. *Adv. Organomet. Chem.* **1990**, *30*, 151.

[32] Kristjansdottir, S. S.; Norton, J. R.; Moroz, A.; Sweany, R. L.; Whittenburg, S. L. *Organometallics* **1991**, *10*, 2357.

Scheme I



oxygen, but the metals were the *acidic center* and the O atom was the base, i.e. the M–H···O rather than the M···H–O interaction in our experiments.

Our studies have largely been restricted to IR spectroscopy and the thermodynamic values derived from them. The spectroscopic evidence that these compounds are involved in H-bonding is extremely strong. The evidence for bonding to the *metal center* is necessarily more circumstantial, since many of the compounds have more than one potential site for H-bonding. Nevertheless, the wide range of compounds for which the phenomenon has been observed leaves little room for alternative explanations. Further techniques, particularly NMR, will clearly be needed to explore the full extent of these interactions, but already it is quite clear that the H-bonding is qualitatively different from the H-bonding previously found for $(\eta\text{-}C_xR_x)M(CO)_n$ complexes of group 6 and 7 metals.[9] The $Cp^*(CO)_2Ir\cdots H\text{–}OR_F$ interaction is relatively weak even with alcohols as acidic as PFTB and, naturally, will be weaker still with the alcohols, such as MeOH, which are conventionally used as solvents for organometallic reactions. However, these alcohols are usually used in high concentrations or even as neat liquids and frequently at low temperatures, a combination which would lead to a significant concentration of H-bonded complexes even for weakly interacting species.

Some authors have drawn attention to the relationship between the basicity of metal centers and C–H activation.[12b] We have already suggested that H-bonding by MeOH to the metal center of $Cp^*IrH_2PMe_3$ could explain why the photochemical reaction of $Cp^*IrH_2PMe_3$ and MeOH is temperature dependent;[33] at low temperatures O–H activation is observed, while at ambient temperature C–H activation predominates. $Cp^*Ir(CO)_2$ also activates the C–H bonds of MeOH at room temperature.[16a] Very recently, we demonstrated[13] that H-bonding of PFTB to $Cp^*Ir(CO)_2$ substantially reduces its effectiveness in photochemical activation of C–H bonds, at least in polyethylene matrices under conditions in which uncomplexed $Cp^*Ir(CO)_2$ promotes C–H activation quite easily. In this case, our experiments could not distinguish between a genuine chemical effect and a physical effect, such as H-bonding causing a shift of UV/vis absorption bands with a concomitant reduction in the rate of C–H activation. Nevertheless, it is apparent that H-bonding may well have a significant chemical effect, and it is probable that many processes (e.g. the formation of alkoxides, protonation, etc.) may involve intermediates with H-bonding to a metal center.

Although many chemists feel that they have a qualitative understanding of the relative basicity of the metal centers in different compounds, it is far from clear which criteria should be used to quantify the basicity of a particular metal center. A variety of approaches have been suggested. One of the more relevant to this paper, perhaps, is an elegant study[11d] by Angelici and co-workers, who measured calorimetrically the enthalpy of protonation of the Ir center in various $CpIr(CO)PR_3$ complexes and then used the value of the enthalpy to determine the effect of the phosphine substituents on the basicity of the metal center. Such experiments necessarily involve disruption of the metal center since addition of a proton to the inner coordination sphere will affect the coordination geometry.

In this paper, we have shown that a measure of the basicity of the metal center in $CpML_2$ complexes can, in principle, be obtained from the shift in the position of the ν(O–H) band of the $M\cdots H\text{–}OR_F$ complex relative to that of the free HOR_F. The advantage of this approach is that the H bond is weak and apparently causes minimal disruption of the metal center. In addition, lXe is a particularly inert solvent so that solvent/solute interactions should be extremely small compared to those of conventional solvents (e.g. THF). One is, therefore, probably coming close to probing the basicity of the unperturbed metal centers. Of course, even in lXe, the ν(O–H) bands are relatively broad with some uncertainty over the exact position of the band maximum, but nevertheless, the method should certainly be sufficiently precise for semiquantitative comparisons of metal centers. Thus, the study of H-bonding promises to be a valuable, and complementary, addition to the currently available methods for probing the basicity of metal centers.

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(33) Sponsler, M. B.; Weiller, B. H.; Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 6841.