

## Intermolecular Hydrogen Bonding to Transition Metal Centres; Infrared Spectroscopic Evidence for O–H...Ir Bonding between $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{CO})_2]$ and Fluoroalcohols in Solution at Room Temperature

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IR spectra in the  $\nu(\text{C-O})$  and  $\nu(\text{O-H})$  regions provide strong evidence for intermolecular H-bonding to the iridium centre of  $[\text{cp}^*\text{Ir}(\text{CO})_2]$  ( $\text{cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ) from sterically crowded perfluoroalcohols, e.g.  $(\text{C}_3\text{F}_7)(\text{CF}_3)_2\text{COH}$  and  $(\text{CF}_3)_2\text{CHOH}$ ; the interactions are sufficiently strong,  $\Delta H^\circ = -26$  to  $-28$  kJ mol<sup>-1</sup>, to be observed at room temperature in n-heptane solution.

Intermolecular H-bonding to transition metal centres has frequently been postulated as a key step in reaction pathways in organometallic chemistry.<sup>1</sup> It is, therefore, surprising to find very little direct experimental evidence for such interactions. Intermolecular N–H...M bonds have been found in the crystal structure of Pt salts<sup>2</sup> and inferred<sup>3</sup> from the ion pairing of  $[\text{Rh}(\text{CO})_2\text{I}_2]^-$  in poorly solvating media such as  $\text{CH}_2\text{Cl}_2$ . There is good crystallographic data for intramolecular O–H...Rh bonding<sup>4</sup> but only very limited spectroscopic evidence for intermolecular O–H...M bonding.<sup>5</sup>

Cryogenic liquid xenon, IXe, has been used extensively as a 'transparent' solvent for IR studies of H-bonding.<sup>6</sup> A number of fluoroalcohols, e.g. perfluoro-tertiary butanol, PFTB  $(\text{CF}_3)_3\text{COH}$ , have been particularly successful in such experiments because they combine high acidity with an unusually low degree of self-association, even at low temperatures. A series of studies has revealed intermolecular H-bonding by these alcohols to a wide range of group 6 and 7 metal carbonyl compounds.<sup>7</sup> However, none of these experiments provided any evidence for H-bonding to the metal; instead, the interaction appeared to occur *via* the O atoms of the CO groups. In this communication, by contrast, we report

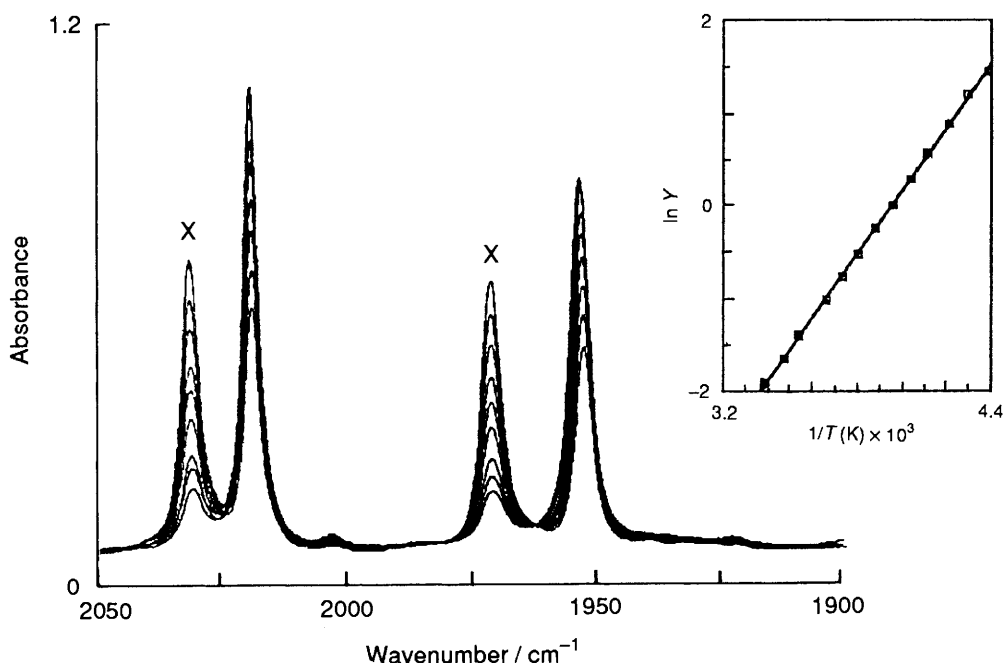
convincing IR evidence for intermolecular O–H...Ir interactions between fluoroalcohols and the neutral compound  $[\text{cp}^*\text{Ir}(\text{CO})_2]$  ( $\text{cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ), interactions which are sufficiently strong to be detected even at room temperature.

The complex  $[\text{cp}^*\text{Ir}(\text{CO})_2]$  displays two  $\nu(\text{C-O})$  bands ( $a' + a''$ ) in hydrocarbon solvents. However, when it is dissolved in n-heptane containing a small concentration of perfluoro-tertiary hexanol, PFTH  $(\text{C}_3\text{F}_7)(\text{CF}_3)_2\text{COH}$ , two extra  $\nu(\text{C-O})$  bands are observed shifted to a higher frequency, see Fig. 1. These new bands are always observed with the same relative intensity and are clearly due to a single dicarbonyl species, X, which is in thermal equilibrium with  $[\text{cp}^*\text{Ir}(\text{CO})_2]$ . As the temperature of the solution is lowered, the bands of X grow reversibly at the expense of the  $\nu(\text{C-O})$  bands of  $[\text{cp}^*\text{Ir}(\text{CO})_2]$  with a clear isosbestic point between the bands, Fig. 1.

When the experiment is repeated using n-heptane doped with hexafluoroisopropanol, HFIP  $(\text{CF}_3)_2\text{CHOH}$ , the bands of  $[\text{cp}^*\text{Ir}(\text{CO})_2]$  are observed at the same wavenumbers but the 'new' bands, X', are closer to those of  $[\text{cp}^*\text{Ir}(\text{CO})_2]$  than in the case of PFTH, see Table 1.

This effect is illustrated in Fig. 2(a) which shows the superimposed spectra from experiments with PFTH and HFIP so that the relative positions of the bands of  $[\text{cp}^*\text{Ir}(\text{CO})_2]$ , X and X' can be compared more easily. These wavenumber shifts suggest that the new bands arise from a chemical interaction between the alcohol and  $[\text{cp}^*\text{Ir}(\text{CO})_2]$  rather than from a generalised solvent effect. Although protonation does

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**Fig. 1** IR spectra in the  $\nu(\text{C-O})$  region illustrating the thermal equilibrium between  $[\text{cp}^*\text{Ir}(\text{CO})_2]$  and the H-bonded adduct X in n-heptane containing  $(\text{C}_3\text{F}_7)(\text{CF}_3)_2\text{COH}$  (ca.  $2 \times 10^{-2} \text{ mol dm}^{-3}$ ) over the temperature range  $-25$  to  $22^\circ\text{C}$ . The inset graph is equivalent to a van't Hoff plot; it shows  $\ln Y$  plotted against  $1/T$ , where  $Y$  is the ratio of absorbance of the  $\nu(\text{C-O})$  bands of X ( $1970 \text{ cm}^{-1}$ ) and  $[\text{cp}^*\text{Ir}(\text{CO})_2]$  ( $1953 \text{ cm}^{-1}$ ).

**Table 1** Wavenumbers,<sup>a</sup>  $\text{cm}^{-1}$ , of  $\nu(\text{C-O})$  bands of  $[\text{cp}^*\text{Ir}(\text{CO})_2]$  and its H-bonded adducts with fluoroalcohols in n-heptane and IXe solution<sup>b</sup>

		n-Heptane <sup>c</sup>	IXe-IKr <sup>d</sup>
$[\text{cp}^*\text{Ir}(\text{CO})_2]$		2019.2, 1953.1	2023.5, 1957.9
$(\text{C}_3\text{F}_7)(\text{CF}_3)_2\text{COH}-[\text{cp}^*\text{Ir}(\text{CO})_2]$	X	2031.0, 1970.5	
$(\text{CF}_3)_2\text{CHOH}-[\text{cp}^*\text{Ir}(\text{CO})_2]$	X'	2027.8, 1964.8	
$(\text{CF}_3)_3\text{COH}-[\text{cp}^*\text{Ir}(\text{CO})_2]$	X*		2035.7, 1975.7
$\{(\text{CF}_3)_3\text{COH}\}_2-[\text{cp}^*\text{Ir}(\text{CO})_2]$			2044.7, 1988.7

<sup>a</sup>  $\pm 0.2 \text{ cm}^{-1}$ ; IR spectra were recorded on Nicolet Model 730 or MX3600 FTIR (Fourier transform infrared) interferometers,  $2 \text{ cm}^{-1}$  resolution.

<sup>b</sup> n-Heptane (Aldrich) was dried with  $\text{CaH}_2$ ; all perfluoroalcohols were synthesised in INEOS (Moscow) and  $[\text{cp}^*\text{Ir}(\text{CO})_2]$  was prepared by literature methods. <sup>c</sup>  $22^\circ\text{C}$ . <sup>d</sup>  $-140^\circ\text{C}$ ; these data are measured at a lower temperature than the spectra illustrated in Fig. 4 so that the bands of the 2:1 complex could be measured.

not occur,<sup>‡</sup> the wavenumber shift depends apparently on the acidity of the fluoroalcohol: HFIP has lower acidity than PFTH.

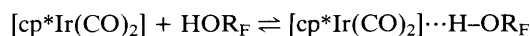
The interaction of  $[\text{cp}^*\text{Ir}(\text{CO})_2]$  and HFIP is disrupted by MeOH. Addition of increasing amounts of MeOH to the

<sup>‡</sup> The cation  $[\text{cp}^*\text{Ir}(\text{CO})_2\text{H}]^+$  has been prepared by other routes and has  $\nu(\text{C-O})$  bands at  $2111$  and  $2070 \text{ cm}^{-1}$ , much higher in wavenumber than those reported here. J. Plank, D. Riedel and W. A. Herrmann, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 937; W. A. Herrmann, J. Plank, Ch. Bauer, M. L. Ziegler, E. Guggolz and R. Alt, *Z. Anorg. Allg. Chem.*, 1982, **487**, 85 and J. R. Sowa, Jr., V. Zanotti and R. J. Angelici, *J. Am. Chem. Soc.*, 1991, **113**, 9185 where the wavenumbers of the  $\nu(\text{C-O})$  bands were somewhat higher,  $2119$  and  $2080 \text{ cm}^{-1}$ .

<sup>§</sup> The true equilibrium constant,  $K$  [defined in eqn. (1)] cannot be measured directly from our spectra. However, by measuring the absorbance of the  $\nu(\text{C-O})$  bands of the two carbonyl species, we obtain a value  $Y$ , directly proportional to  $K$ ;  $Y = rK[\text{R}_F\text{OH}]$ , where  $r$  is the ratio of the extinction coefficients and  $[\text{R}_F\text{OH}]$  is the concentration of fluoroalcohol, effectively constant since the alcohol is in large excess. If we assume that the extinction coefficients of  $[\text{cp}^*\text{Ir}(\text{CO})_2]$  and  $[\text{cp}^*\text{Ir}(\text{CO})_2] \cdots \text{H-OR}_F$  are equal (*i.e.* that  $r = 1$ ), then  $Y = K[\text{R}_F\text{OH}]$  and we can use the gradient of the plot in Fig. 3 to estimate the value of  $K$  as  $2.9 \text{ dm}^3 \text{ mol}^{-1}$  for HFIP at  $22^\circ\text{C}$ . Thus, using the value of  $\Delta H^\circ$  ( $-26.0 \text{ kJ mol}^{-1}$ ) from above, we get an estimate of  $\Delta S^\circ = -80 \text{ J K}^{-1} \text{ mol}^{-1}$ , consistent with an associative process.

n-heptane solution results in the progressive disappearance of the  $\nu(\text{C-O})$  bands of X' with a corresponding growth in the intensity of the bands of  $[\text{cp}^*\text{Ir}(\text{CO})_2]$ , see Fig. 2(b). MeOH sequesters the free HFIP and thus shifts the equilibrium in favour of  $[\text{cp}^*\text{Ir}(\text{CO})_2]$ .

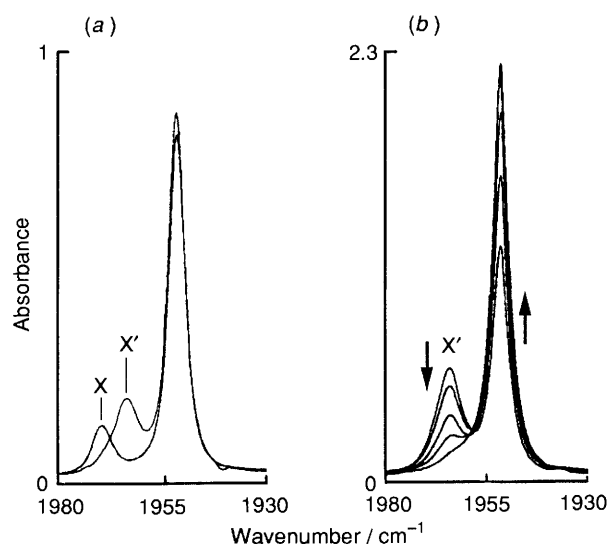
The concentration of X' depends linearly on the concentration of HFIP in solution, Fig. 3, indicating that formation of X' involves only one molecule of HFIP. Similarly, for a given concentration of HFIP, the concentration of X' depends linearly, qualitatively at least, on the amount of  $[\text{cp}^*\text{Ir}(\text{CO})_2]$  in solution. Thus, we have an equilibrium between  $[\text{cp}^*\text{Ir}(\text{CO})_2]$  and the thermodynamically more stable adduct [see eqn. (1)].



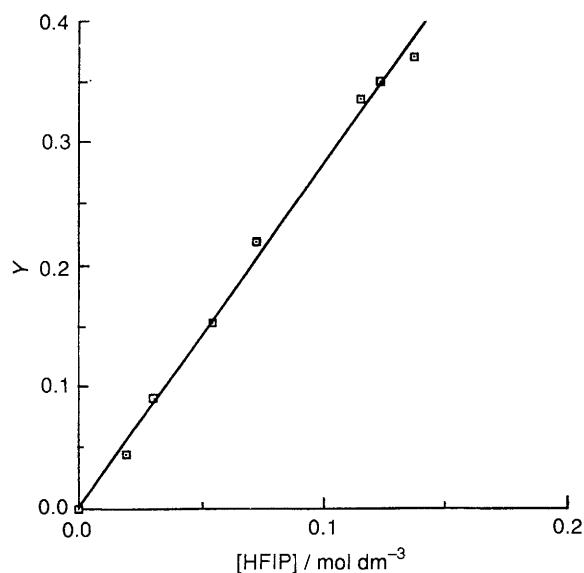
$$K = \frac{[\text{cp}^*\text{Ir}(\text{CO})_2 \cdots \text{H-OR}_F]}{[\text{cp}^*\text{Ir}(\text{CO})_2][\text{HOR}_F]} \quad (1)$$

The van't Hoff plot, inset in Fig. 1, indicates an enthalpy difference,  $\Delta H^\circ$ , of  $-28.4 \pm 0.5 \text{ kJ mol}^{-1}$  for PFTH. A slightly lower value  $-26.0 \pm 0.5 \text{ kJ mol}^{-1}$  was found for HFIP, consistent with its lower acidity. These values are very close to those found when these alcohols H-bond to organic compounds, *e.g.* ethyl acetate.<sup>8</sup>

Experiments in IXe mixed with IKr provide conclusive evidence that the interaction between fluoroalcohol and  $[\text{cp}^*\text{Ir}(\text{CO})_2]$  involves H-bonding, Fig. 4, where one can

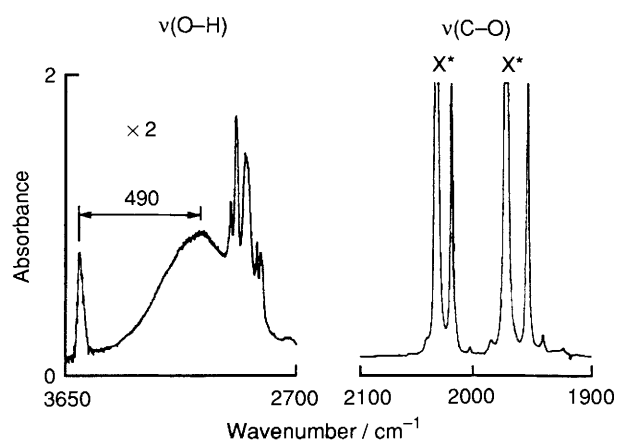


**Fig. 2** (a) Part of the  $\nu(\text{C}-\text{O})$  IR spectra showing the difference in position of bands of the H-bonded adducts, X and X', observed when  $[\text{cp}^*\text{Ir}(\text{CO})_2]$  is dissolved in n-heptane containing, respectively, the alcohols PFTH and HFIP (*ca.*  $5 \times 10^{-2} \text{ mol dm}^{-3}$ ). Note that the band of  $[\text{cp}^*\text{Ir}(\text{CO})_2]$  itself has the same wavenumber in both solutions. (b) A series of IR spectra of  $[\text{cp}^*\text{Ir}(\text{CO})_2]$  and HFIP (*ca.*  $5 \times 10^{-2} \text{ mol dm}^{-3}$ ) in n-heptane, showing the effect on X' of adding increasingly large amounts of MeOH to the solution. Final concentration of MeOH *ca.*  $10^{-1} \text{ mol dm}^{-3}$ ; the concentrations of  $[\text{cp}^*\text{Ir}(\text{CO})_2]$  and HFIP were kept constant throughout the addition of MeOH.



**Fig. 3** The effect on adduct formation of increasing the concentration of HFIP in n-heptane solution; plot of A as a function of concentration of HFIP, where Y is the ratio of absorbance of the  $\nu(\text{C}-\text{O})$  bands of X' ( $1964 \text{ cm}^{-1}$ ) and  $[\text{cp}^*\text{Ir}(\text{CO})_2]$  ( $1953 \text{ cm}^{-1}$ ). HFIP is not very soluble in n-heptane and phase separation occurs at concentrations above *ca.*  $0.2 \text{ mol dm}^{-3}$ . Similar problems of two phases are found for addition of MeOH to n-heptane as in Fig. 2(b). The concentration of HFIP was measured volumetrically and was confirmed by measuring the absorbance of  $\nu(\text{O}-\text{H})$  band of HFIP.

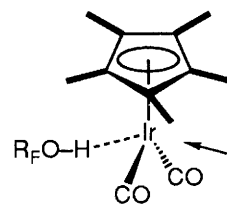
observe a broad  $\nu(\text{O}-\text{H})$  band of the H-bonded alcohol, *ca.*  $3100 \text{ cm}^{-1}$ , a region normally obscured by absorptions of hydrocarbon solvents. The strength of a hydrogen bond can be estimated from the wavenumber shift,  $\Delta\nu$ , between  $\nu(\text{O}-\text{H})$  of the free and H-bonded OH groups, by using the relationship,<sup>8</sup>  $\Delta H^\circ = -1.28 \times \Delta\nu^{1/2}$ . In the case of Fig. 4,  $\Delta\nu$  is  $490 \pm 30 \text{ cm}^{-1}$ , which gives  $-28.3 \pm 1 \text{ kJ mol}^{-1}$ , in remarkably close agreement with the van't Hoff results above.



**Fig. 4** IR spectra of  $[\text{cp}^*\text{Ir}(\text{CO})_2]$  and PFTB in a mixed IXe-IKr solution at  $-75^\circ\text{C}$ , showing the  $\nu(\text{O}-\text{H})$  region and the broad band of the H-bonded PFTB shifted down  $490 \text{ cm}^{-1}$  from the  $\nu(\text{O}-\text{H})$  band of the free alcohol and the  $\nu(\text{C}-\text{O})$  region with the bands of X\* marked. Details of the IXe cell have been given elsewhere.<sup>14</sup> Note that the relatively sharp IR bands, a little above  $2700 \text{ cm}^{-1}$ , are due to the  $\nu(\text{C}-\text{H})$  vibrations of the Me groups in the  $\text{cp}^*$  ring and to trace hydrocarbon impurities in the IXe and that the spectrum in the region  $3650-2700 \text{ cm}^{-1}$  is displayed with a twofold expansion in the Absorbance scale.

When higher concentrations of PFTB were used in the IXe solution or when the experiment was repeated at lower temperatures in IXe-IKr mixtures, a second pair of new  $\nu(\text{C}-\text{O})$  bands was observed. The wavenumber shifts of these bands, relative to  $[\text{cp}^*\text{Ir}(\text{CO})_2]$ , were approximately twice those of the bands of  $[\text{cp}^*\text{Ir}(\text{CO})_2] \cdots \text{H}-\text{OR}_F$ . These bands are assigned to a 1:2 interaction,  $\{[\text{cp}^*\text{Ir}(\text{CO})_2]-(\text{HOR}_F)_2\}$ , which will be discussed in detail elsewhere.

There are three possible sites for H-bonding to  $[\text{cp}^*\text{Ir}(\text{CO})_2]$ : (i) the  $\pi$ -system of the  $\text{cp}^*$  ring, (ii) the CO groups and (iii) the Ir centre itself. H-bonding to  $\pi$ -systems, *e.g.* to  $\text{cp}^*_2\text{Fe}^{6b}$  or benzene,<sup>9</sup> has been observed previously but typical values for these interactions, of  $\Delta\nu_{\text{O}-\text{H}}$  *ca.*  $180 \text{ cm}^{-1}$  and  $\Delta H^\circ$  *ca.*  $-18 \text{ kJ mol}^{-1}$ , are significantly lower than we have found here. H-bonding to CO groups has been invoked<sup>7</sup> in cases such as  $[\text{cp}^*\text{Re}(\text{CO})_3]$ ; again,  $\Delta H^\circ$  is lower than found here but more importantly the mean wavenumber of the  $\nu(\text{C}-\text{O})$  bands are shifted down in frequency compared to the uncomplexed compound. A shift to high wavenumbers, as observed here for  $[\text{cp}^*\text{Ir}(\text{CO})_2]$ , indicates a reduction of electron density on the Ir centre with a corresponding decrease in  $\text{M} \rightarrow \text{CO}$  backbonding.<sup>10</sup> A similar wavenumber shift has been observed in a number of compounds, *e.g.*  $[\{\text{cp}^*\text{Ir}(\text{CO})_2\}_2\text{Ag}]^+$  where  $[\text{cp}^*\text{Ir}(\text{CO})_2]$  acts as a Lewis base.<sup>11</sup> Surprisingly, interaction with  $\text{Ag}^+$  causes very little distortion of the  $\text{cp}^*\text{Ir}(\text{CO})_2$  moiety<sup>11</sup> and it is possible that there is a similar geometry around the iridium centre in the H-bonded species here. Such a structure also offers an obvious site (arrowed) for interaction with a second fluoroalcohol molecule.



Thus, all of the data suggest that we have observed H-bonding to the Ir metal centre of a neutral organometallic compound, one of the first examples of this type of interaction. Our observations are consistent with the well known

Lewis basicity<sup>11,12</sup> of  $[\text{cp}^*\text{Ir}(\text{CO})_2]$  and, presumably, such bonding would occur with other electron-rich  $\text{cp}^*\text{Ir}$  compounds. Recently, Bergman and coworkers reported<sup>13</sup> that UV photolysis of  $[\text{cp}^*\text{Ir}(\text{PMe}_3)_2\text{H}_2]$  resulted in C–H activation of MeOH at room temperature but, surprisingly, in O–H activation in cryogenic  $\text{IXe–MeOH}$ . Although MeOH has a much lower acidity than the fluoroalcohols used by us, H-bonding of MeOH to the Ir centre at low temperatures would provide a plausible rationalization of their observations.

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