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IR Spectroscopy of Charged Species in Supercritical Fluid Solution and in Polymer Films; the Protonation of $[(\eta^5\text{-}C_5Me_5)Ir(CO)_2]$ by HCl

Sergei G. Kazarian,[a]* Margaret Jobling[b] and Martyn Poliakoff[b]*

[a] *Institute of Spectroscopy, Russian Academy of Sciences, 142092 Troitzk, Moscow Region, Russian Federation. Fax: +7 095 334 0886*

[b] *Department of Chemistry, University of Nottingham, Nottingham NG7 2RD, UK. Fax: +44 602 513555. E-mail: PCZJJT@UK.AC.NOTT.VME*

Reaction of $[Cp^*Ir(CO)_2]$ ($Cp^*=\eta^5\text{-}C_5Me_5$) with gaseous HCl leads to formation of the protonated ion, $[Cp^*Ir(CO)_2H]^+$, both in supercritical xenon solution and in a low density polyethylene film.

Protonation of transition metal centres is one of the fundamental steps in organometallic chemistry. IR spectroscopy is particularly suited to following this process in metal carbonyl complexes because of the inherent intensity of the ν(C–O) bands and the sensitivity of their wavenumber to the oxidation state of a metal centre. It is, however, extremely difficult to obtain the IR spectra of such protonated species in solution in the absence of a coordinating solvent (*e.g.* CH_2Cl_2, THF or Et_2O). In this communication, we describe two new approaches to obtaining such spectra at room temperature, supercritical Xe (scXe) and polyethylene (PE) films. These approaches have been developed, partly from observations of protonation in liquid Xe solution at low temperatures[1] and partly from the use of polymer films for cryogenic matrix isolation experiments.[2] The new room temperature methods are illustrated by the protonation of $[Cp^*Ir(CO)_2]$ ($Cp^*=\eta^5\text{-}C_5Me_5$) with gaseous HCl.†‡

Supercritical fluids have now been applied to a range of organometallic reactions including synthesis of dihydrogen and dinitrogen complexes,[3a] C–H activation,[3b] hydroformylation[4] and hydrogen bonding.[5] Such reactions have been carried out in a number of supercritical fluids but scXe (T_c 16.8 °C) is particularly useful as it combines chemical inertness with complete transparency throughout the UV and IR regions of the spectrum.[3a,6] Recently, we have described how organometallics, including $[Cp^*Ir(CO)_2]$, can be impregnated into both low and high density PE using supercritical CO_2 ($scCO_2$), a solvent which diffuses out of the PE so easily that no residues are left in the impregnated film.[3b,7]

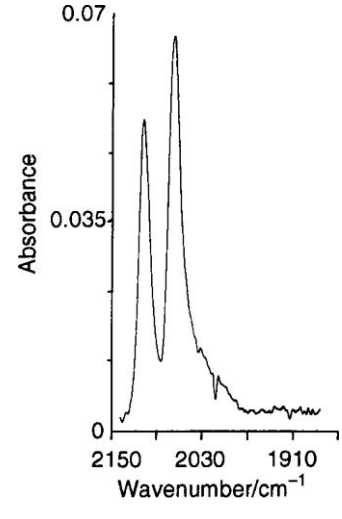

Fig. 1 IR spectrum of ν(C–O) region obtained from a solution of $[Cp^*Ir(CO)_2]$ in scXe at 82 atm. pressure doped with HCl gas, 2 atm. (1 atm. ≈ 0.1 MPa.)‡ The two bands are assigned to the protonated species $[Cp^*Ir(CO)_2H]^+$. This spectrum and those in Fig. 2 were recorded at 2 cm^{-1} resolution with a Nicolet Model 730 FTIR interferometer with 680D Data Station.

The spectrum of $[Cp^*Ir(CO)_2]$ in scXe solution§ is almost identical to that in conventional solvents with the expected *a'* and *a''* ν(C–O) bands at 2021 and 1955 cm^{-1}, respectively. By contrast, the spectrum recorded immediately after $[Cp^*Ir(CO)_2]$ is dissolved in scXe doped with HCl. Fig. 1, is quite different. The bands of $[Cp^*Ir(CO)_2]$ itself are not observed but instead there are two broader bands at 2115 and 2073 cm^{-1}, shifted *ca.* 100 cm^{-1} higher in wavenumber, close to those reported[8] for the protonated ion $[Cp^*Ir(CO)_2H]^+$ (2120 to 2110 and 2080 to 2070 cm^{-1}, depending on the

† **Safety Note:** Experiments in supercritical fluids involve high pressures and should be approached with caution. For details of the miniature spectroscopic cells used for IR spectroscopy in supercritical fluids at Nottingham, see M. Poliakoff, S. M. Howdle, M. A. Healy and J. M. Whalley, *Proc. Intl. Symp. on Supercritical Fluids*, ed. M. Perrut, Societé, Franc. de Chimie, 1988, 967; S. M. Howdle, M. Jobling, M. W. George and M. Poliakoff *Proc. 2nd Intl. Symp. on Supercritical Fluids (Boston)*, ed. M. A. McHugh, Johns Hopkins University, 1991, 189.

‡ ***Note added in proof:*** Very recent experiments have shown that $[Cp^*Ir(CO)_2]$ is also protonated by HCl in PE film at lower temperatures (*ca.* −30 °C) and $[Cp^*Ir(CO)_2H]^+$ is stable indefinitely at this temperature. The protonation can be *reversed* to regenerate $[Cp^*Ir(CO)_2]$ in at least 75% yield, by warming to *ca.* 0 °C and pumping on the film to remove the HCl. If the HCl is not removed, decomposition occurs with the formation of a violet material in the PE film (A. I. Cooper, S. G. Kazarian and M. Poliakoff, unpublished results).

§ $[Cp^*Ir(CO)_2]$ was prepared by literature methods; low density PE was hot-pressed into film 250 μm thick; HCl (Aldrich) and Xe (BOC Research Grade) were used without further purification.

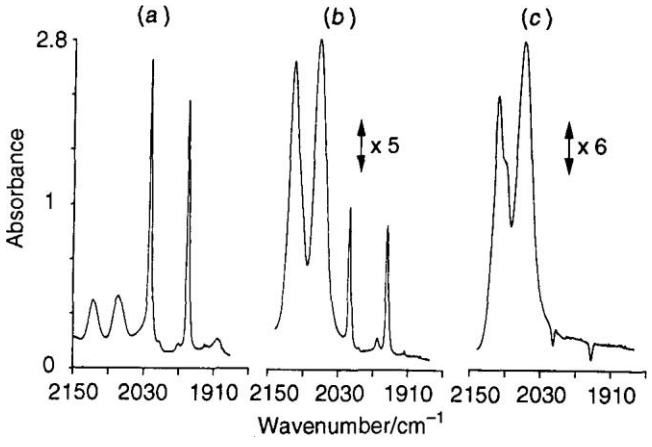

Fig. 2 A sequence of IR spectra, showing the protonation of $[Cp^*Ir(CO)_2]$ impregnated into a PE disk in the presence of HCl gas at 0.5 atm. pressure. In (*a*) and (*b*) the two sharp bands at lower wave number are due to $[Cp^*Ir(CO)_2]$ while the broad bands in all three spectra are assigned to the cation $[Cp^*Ir(CO)_2H]^+$. Before the spectra were recorded, a low density PE film (*ca.* 250 μm thick) was impregnated with $[Cp^*Ir(CO)_2]$ by using $scCO_2$ (see ref. 6, for details). The film was then placed in a high pressure IR cell (CaF_2 windows, *ca.* 2 mm pathlength), HCl was added and the spectra were recorded at 1 min intervals. Note the expanded absorbance scales in spectra (*b*) and (*c*).

conditions). In solvents as inert as scXe, ionic spcies will exist as relatively tight ion pairs. The similarity in wavenumber of the bands of $[Cp^*Ir(CO)_2H]^+$ in different solvents ranging from scXe to zeolites suggests that the nature of the anion is probably more significant than the nature of the solvent.

Although $[Cp^*Ir(CO)_2H]^+$ is relatively stable in conventional solvents, the bands in scXe disappeared in a few minutes. There are two possible reasons for this: (i) $[Cp^*Ir(CO)_2H]^+$ could be reacting with HCl further or (ii) an ionic salt, presumably $[Cp^*Ir(CO)_2H]^+Cl^-$, might be precipitating from solution. In order to distinguish between these possibilities, we repeated the protonation with $[Cp^*Ir(CO)_2]$ impregnated into PE, where the chances of precipitation of bulk salt is improbable.

Fig. 2 shows three spectra recorded sequentially while a film of PE containing $[Cp^*Ir(CO)_2]$ was exposed to HCl. They show clearly the disappearance of the two sharp ν(C–O) bands of $[Cp^*Ir(CO)_2]$ and the appearance of the bands of $[Cp^*Ir(CO)_2H]^+$. The absorbance values of the $[Cp^*Ir(CO)_2H]^+$ bands are considerably lower than those of $[Cp^*Ir(CO)_2]$, partly because they are broader but also because oxidation of a metal centre normally decreases the intensity of ν(C–O) bands. As in scXe solution, $[Cp^*Ir(CO)_2H]^+$ is unstable in the presence of HCl and the bands disappear relatively quickly, *i.e.* <5 min. Since $[Cp^*Ir(CO)_2H]^+$ cannot easily precipitate from the PE film, the disappearance probably corresponds to further reaction to form some species which no longer contain any CO groups.

These experiments have shown that it is possible to observe the spectra of such ions in relatively inert media. More importantly, our results demonstrate the possibility of generating charged species *in situ* within a polymer from neutral precursors. The method is not limited to PE and should be equally applicable to wide range of polymers.

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