Supercritical fluid impregnation of polyethylene films, a new approach to studying equilibria in matrices; the hydrogen bonding of fluoroalcohols to $(\eta^5\text{-}C_5Me_5)Ir(CO)_2$ and the effect on C–H activation

Andrew I. Cooper [a], Sergei G. Kazarian [b] and Martyn Poliakoff [a,1]

[a] *Department of Chemistry, University of Nottingham, Nottingham NG7 2RD, UK*

[b] *Institute of Spectroscopy, Russian Academy of Sciences, 142092 Troitzk, Moscow Region, Russian Federation*

Received 27 January 1993; in final form 15 February 1993

Polyethylene (PE) film is used as a matrix for studying temperature-dependent equilibria by IR spectroscopy; the film is impregnated with $Cp^*Ir(CO)_2$ ($Cp^*=\eta^5\text{-}C_5Me_5$) using supercritical CO_2 and subsequently saturated with HOR_F ($R_F=(CF_3)_2CH$ or $(CF_3)_3C$). At 200 K, the equilibrium between $Cp^*Ir(CO)_2$ and the hydrogen-bonded complex, $Cp^*Ir(CO)_2...HOR_F$, is frozen out and can be disturbed photochemically, because $Cp^*Ir(CO)_2$ is more efficient than $Cp^*Ir(CO)_2...HOR_F$ for C–H activation of polyethylene.

1. Introduction

For many years, matrix isolation and IR spectroscopy have played a central role in the characterization of intermediates in organometallic chemistry [1]. A huge variety of matrix materials have been investigated, including solid noble gases (for a recent example see ref. [2]), hydrocarbon glasses [3] and doped polymer films (for a recent example see ref. [4]). Each of these techniques has its strengths and its limitations but none has been very successful for studying intermolecular interactions between organometallic centres and organic compounds, interactions which are crucial in many reactions. Ideally, such studies require matrices with the following properties:

(i) the IR spectra of the organometallic species should not be unnecessarily degraded by the presence of the organic compound;

(ii) the organometallic and organic components should be sufficiently mobile for thermodynamic equilibrium to be established between the free compounds and the interacting complex;

(iii) the matrix should allow the interaction to be studied over as wide a temperature range as possible to give the option of "freezing out" the equilibrium;

(iv) it should be possible to cycle the temperature repeatedly and reproducibly without change to the matrix.

In general, existing matrix techniques fail to meet these criteria. Thus, the simultaneous doping of noble gas matrices with organics and organometallics is difficult, leads to substantial degradation of IR spectra of the organometallics and such matrices can only be used over a very limited temperature range. Similarly, attempts to vary the temperature of frozen hydrocarbon glasses frequently lead to precipitation of the organometallic. In this Letter, we outline a method for studying such interactions in polyethylene (PE) films, which overcomes some of the limitations of previous matrix experiments.

PE film has been used previously for matrix isolation, particularly for experiments where molecules were oriented by stretching the film [5] or where spectra were to be measured over a wide temperature range [6]. Recently, we reported how organometallic compounds can be efficiently impregnated into PE films using supercritical CO_2 ($scCO_2$) [7].

---

[1] To whom correspondence should be addressed.

The role of the $scCO_2$ appears to be twofold: (i) to increase the concentration of the organometallic in the "vapour" phase and (ii) to swell the polymer so facilitating impregnation, which is unexpectedly rapid and relatively uniform [8,9]. This technique has the great advantage that $scCO_2$ does not leave any solvent residue in the polymer.

The experiments described in this Letter largely involve $Cp^*Ir(CO)_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$), a compound well known for its photochemical activation of aliphatic C–H bonds [10]. We have already reported [7] how, using $scCO_2$, $Cp^*Ir(CO)_2$ can be impregnated into PE and can activate the C–H bonds of the polymer photochemically,

$$Cp^*Ir(CO)_2 + C\text{–}H_{\text{polymer}} \xrightarrow{UV} Cp^*Ir(CO)(H)(C_{\text{polymer}}) + CO\,. \qquad (1)$$

$CP^*Ir(CO)_2$ can also act as a Lewis base and, very recently, we described [11] how $Cp^*Ir(CO)_2$ can form relatively strong hydrogen bonds with fluoroalcohols via an Ir...H–O interaction. Although *intermolecular* H-bonding to a metal centre is believed to be important in organometallic reactions, this is one of the first well-established cases of such bonding. The equilibrium between the H-bonded and free organometallic is temperature dependent (see eq. (2) below), and, for $(CF_3)_2CHOH$, the equilibrium constant, $[Cp^*(CO)_2Ir...H\text{–}OR_F]/([CP^*Ir(CO)_2]\times[R_FOH])$, is estimated to be $\approx 3\ M^{-1}$ in *n*-heptane solution at room temperature [10],

$$Cp^*Ir(CO)_2 + R_FOH \rightleftharpoons Cp^*(CO)_2Ir...H\text{–}OR_F\,,$$

$$R_F = (CF_3)_2CH\,,\ (CF_3)_3C\,,\ \text{etc}\,. \qquad (2)$$

These fluoroalcohols are liquid at room temperature and can easily penetrate PE film. The $Cp^*Ir(CO)_2$/fluoroalcohol system is, therefore, particularly suitable for evaluating the potential of PE as a matrix in the study of thermal equilibria.

2. Experimental

The details of polymer impregnation using $scCO_2$ have been described elsewhere [8]. Briefly, the PE film, 500 μm thick, is formed from powdered low density PE (Aldrich), using a constant thickness melt press Specac (model 15620). The film is then cut into discs (≈1 cm in diameter), placed in a high-pressure cell together with a few milligram of $Cp^*Ir(CO)_2$, and pressurised with $scCO_2$ to ≈2500 psi. After a few hours, the cell is vented and the surface of the disc is wiped with a tissue to remove any deposits of solid carbonyl compound. (Slight warming of the $scCO_2$, i.e. to 50°C, accelerates the impregnation significantly [9].) The disc, impregnated with $Cp^*Ir(CO)_2$, is then immersed in fluoroalcohol for ≈1 h. The disc, by now saturated with alcohol, is mounted in a holder attached to the cold stage of an Air Products Displex CS-202 cooler [12]. The vacuum jacket of the Displex is briefly evacuated and then the cooling is started before much of the alcohol is lost through evaporation.

The use of $scCO_2$ is essential to the process because $Cp^*Ir(CO)_2$ has insufficient vapour pressure for effective impregnation in vacuo and use of other solvents, e.g. xylene, would leave solvent residues which could interfere with the experiment. Equally, one cannot impregnate the PE using a solution of $Cp^*Ir(CO)_2$ in neat fluoroalcohol because, in these alcohols, the compound is largely protonated [13] and $[Cp^*Ir(CO)_2H]^+$ is insoluble in the hydrophobic PE environment. PE containing $[Cp^*Ir(CO)_2H]^+$, (ν(C–O) 2115 and 2071 cm^{-1}) can be obtained by in situ protonation of $Cp^*Ir(CO)_2$ using gaseous HCl and this will be discussed more fully elsewhere [12,13].

IR spectra were recorded on a Nicolet MX3600 interferometer with a Model 1200 data station (16000 data points, 2 cm^{-1} resolution). Although PE does not have any strong absorptions in the ν(C–O) region of the spectrum, there are some weak absorptions, the intensity of which is somewhat temperature dependent. Thus, for best results, "background" spectra were run at a variety of temperatures across the range with a pure PE disc of the appropriate thickness.

$Cp^*Ir(CO)_2$ was synthesized by literature methods. $(CF_3)_3COH$, synthesized at INEOS (Moscow) and $(CF_3)_2CHOH$, Aldrich, were used without further purification.

3. Results

Fig. 1a shows a series of spectra recorded while a film containing $Cp^*Ir(CO)_2/(CF_3)_2CHOH$ was cooled from 290 to 170 K. It can be seen that, as the film cools, the two bands of $Cp^*Ir(CO)_2$ decrease in intensity with a corresponding growth of two new bands, almost identical in wavenumber and intensity to those already assigned to $Cp^*Ir(CO)_2...HOCH(CF_3)_2$ in fluid hydrocarbon solution [11]. The changes are both reversible and reproducible as the temperature of the film is cycled up and down, as shown by the trace in fig. 1b, the difference of two spectra recorded at different times at the same temperature, 190 K. Similar spectra were obtained with the more acidic alcohol, $(CF_3)_3COH$, but the shifts from the ν(C–O) bands of $Cp^*Ir(CO)_2$ were larger, 13 and 20 cm^{-1}, than those observed with $(CF_3)_2CHOH$, 9 and 14 cm^{-1}. These larger shifts are consistent with our earlier observations in fluid solvents and result from a stronger interaction with the more acidic alcohol [10].

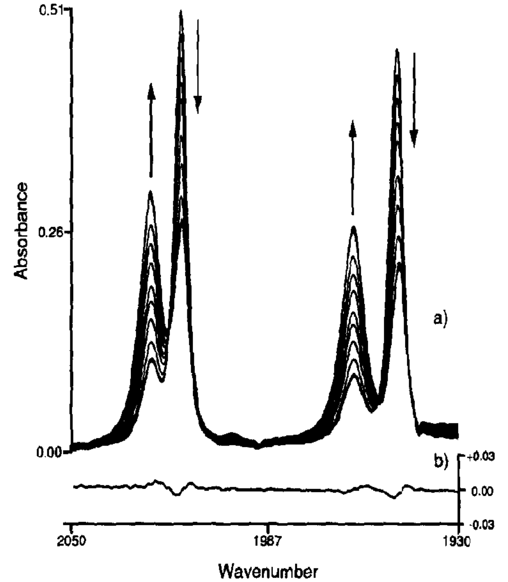

Fig. 1. (a) The ν(C–O) region of IR spectra of $Cp^*Ir(CO)_2/(CF_3)_2CHOH$ in PE, recorded over the range 290 to 170 K. The arrows show the direction in which the absorbance of each band changes on cooling. The two stronger bands, 2016 and 1948 cm^{-1}, are due to $Cp^*Ir(CO)_2$ and the weaker bands, at 2025 and 1962 cm^{-1}, which grow in intensity with decreasing temperature, are due to the hydrogen-bonded complex, $Cp^*(CO)_2Ir...H–OR_F$. (b) IR difference spectrum showing the complete thermal reversibility of the $Cp^*Ir(CO)_2/(CF_3)_2CHOH$ system. The spectrum was obtained by direct subtraction (i.e. *without* any scaling factor) of two spectra both recorded at 190 K, one as the PE was cooling down to an ultimate temperature of 150 K and the other as it was warming up again.

Thus, the behaviour of $Cp^*Ir(CO)_2$ and fluoroalcohols within the impregnated polymer film is similar to that in fluid solution but there is an important difference. As the temperature is lowered, the amount of hydrogen-bonded compound in fluid solution continues to increase, given an excess of alcohol, until almost none of the free organometallic remains and the corresponding van 't Hoff plot is linear [11]. In the PE film, the formation of hydrogen-bonded complex is initially comparable to that in solution. Indeed, the gradient of the plot in fig. 2 gives a value of ΔH^0 for $(CF_3)_2CHOH$, 25± 3 kJ mol^{-1}, close to

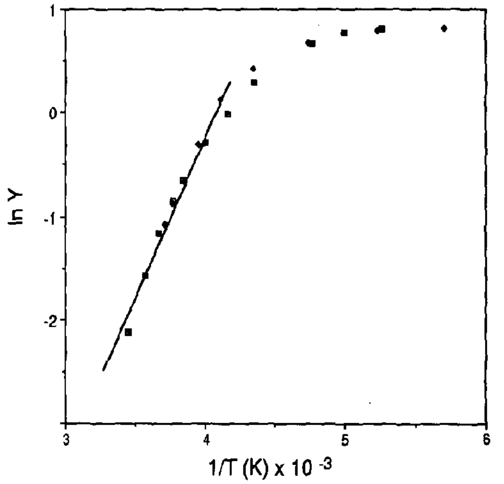

Fig. 2. Plot, equivalent to a van 't Hoff plot, derived from the spectra in fig. 1, showing ln Y plotted against $1/T$, where Y is the ratio of absorbance of the 1962 cm^{-1} band of $Cp^*(CO)_2Ir...HOCH(CF_3)_2$ and the 1948 cm^{-1} band of $Cp^*Ir(CO)_2$. The true equilibrium constant, K, for the reaction shown in eq. (2), is defined as $[Cp^*(CO)_2Ir...H–OR_F]/[Cp^*Ir(CO)_2][R_FOH]$. Y and K are related by $Y=rK[R_FOH]$, where r is the ratio of IR extinction coefficients of $Cp^*IR(CO)_2$ and $Cp^*(CO)_2Ir...H–OR_F$. Thus, if it is assumed that the fluoroalcohol is in large excess, Y is directly proportional to K. Points marked ♦ were derived from spectra recorded as the sample cooled and those marked ⊡ as it was warming up again. The line has been drawn to indicate the region of *approximate* linearity at higher temperatures.

that measured in solution, 26 kJ mol^{-1} [11]. (Similar experiments with $(CF_3)_3COH$ gave a somewhat higher value of ΔH^0, 28 ± 2 kJ mol^{-1}, again consistent with observations in solution.) As the temperature of the PE falls, however, the rate of growth of H-bonded complex becomes slower and eventually stops at ≈ −70°C (200 K). No further changes are observed on cooling even as low as 20 K. This effect is quite clear from fig. 2, where the ratio of H-bonded to free $Cp^*Ir(CO)_2$ reaches a limiting value at −70°C. Although $(CF_3)_2CHOH$ is known to dimerize in some circumstances at low temperature [14], one can eliminate the possibility that the fluoroalcohol is dimerizing at low temperature in PE, thus reducing the concentration of free alcohol in the PE, because the IR spectrum clearly shows the ν(O–H) band of the free alcohol at low temperature. Similarly, it is unlikely that the concentration of fluoroalcohol in the PE is so low that, by −70°C, all of the available alcohol is already hydrogen bonded, because similar effects have been observed with different loadings of alcohol in the PE. Thus, the most likely explanation is that cooling increases the rigidity of the PE matrix, eventually preventing diffusion of the fluoroalcohol and "freezing out" the interaction. The photochemical reaction of $Cp^*Ir(CO)_2$ with PE doped with $(CF_3)_3COH$ provides a simple way to establish whether the equilibrium is indeed frozen as well as an unusual opportunity to probe dynamics within the polymer.

Fig. 3 shows the results of UV photolysis of $Cp^*Ir(CO)_2/(CF_3)_3COH$ in PE at 200 K. The overall reaction is C–H activation of the polymer as shown by the growth of a single new ν(C–O) band, ≈1978 cm^{-1}, previously assigned in room temperature studies to $Cp^*Ir(CO)(H)(C_{polymer})$ [7]. The interesting feature of the photolysis, however, is the difference in effect on the ν(C–O) bands of $Cp^*Ir(CO)_2$ and $Cp^*(CO)_2Ir...H–OR_F$, fig. 3b. It is clear that the bands of $Cp^*Ir(CO)_2$ are reduced substantially in intensity, while those of $Cp^*(CO)_2Ir...H–OR_F$ are, proportionately, reduced much less. Indeed, after photolysis, the bands of $Cp^*(CO_2Ir...H–OR_F$ are nearly twice as intense relative to those of $Cp^*Ir(CO)_2$ than they were before photolysis. These spectra show that, at 200 K, free $Cp^*Ir(CO)_2$ is significantly more effective in photochemical C–H activation than is the H-bonded form, $Cp^*Ir(CO)_2...H–OR_F$ (possible reasons for this are discussed below), and that the rate of equilibration between free and H-bonded $Cp^*Ir(CO)_2$ must be slow compared to the photolysis time. Thus, fortuitously, photolysis provides an excellent means of disturbing the thermodynamic equilibrium.

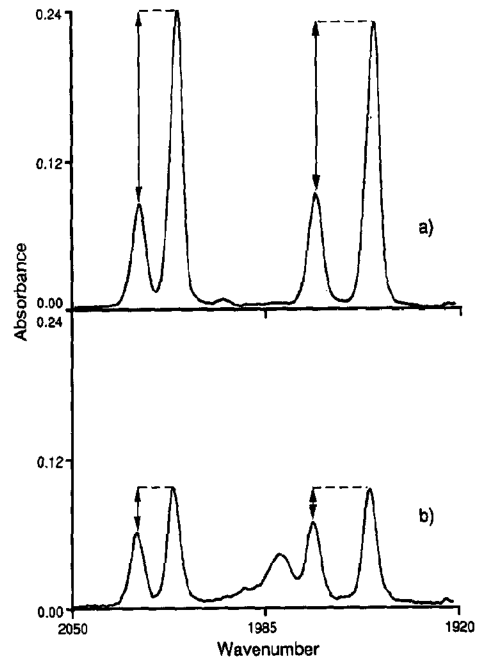

Fig. 3. IR spectra showing the effects of UV photolysis of $Cp^*Ir(CO)_2/(CF_3)_3COH$ in PE at 200 K. (a) Before photolysis; the arrows indicate the relative intensities of the bands due to $Cp^*Ir(CO)_2$ and $Cp^*(CO)_2Ir...H–OR_F$ (cf. fig. 1a). (b) After 18.5 min. UV photolysis (300 W Cermax Xe lamp). The new band at 1978 cm^{-1} is due to $Cp^*Ir(CO)(H)(C_{polymer})$. Note in particular the change in relative intensities of the bands of $Cp^*Ir(CO)_2$ and $Cp^*(CO)_2Ir...H–OR_F$ compared to spectrum (a).

Fig. 4 shows how this effect can be exploited. First, the impregnated polymer film was irradiated at 200 K to disrupt the equilibrium between $Cp^*Ir(CO)_2$ and $Cp^*(CO)_2Ir...H–OR_F$. Then, on warming to 270 K, the bands of $Cp^*Ir(CO)_2$ increased in intensity and those of $Cp^*(CO)_2Ir...H–OR_F$ decreased, as expected. On recooling, the ν(C–O) bands of $Cp^*Ir(CO)_2$ and $Cp^*(CO)_2Ir...H–OR_F$ had *exactly* the same relative intensities as they did before photolysis. Thus, the process of warming and recooling restored the equilibrium between free and H-bonded

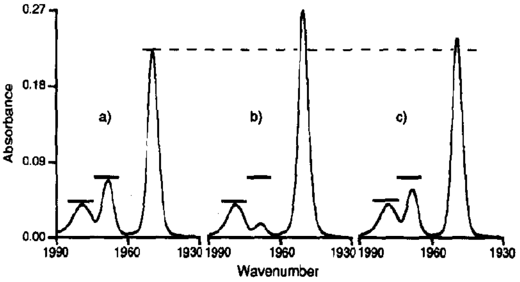

Fig. 4. IR spectra illustrating the "unfreezing" of the equilibrium between $Cp^{*}Ir(CO)_2$ and $Cp^{*}(CO)_2Ir...H\text{-}OR_F$. (a) Spectrum recorded after 10 min photolysis of $Cp^{*}Ir(CO)_2/(CF_3)_3COH$ in PE at 200 K. The three bands are assigned, in order of descending wavenumber, to $Cp^{*}Ir(CO)(H)(C_{polymer})$, $Cp^{*}(CO)_2Ir...H\text{-}OR_F$ and $Cp^{*}Ir(CO)_2$ respectively. (b) Spectrum recorded on warming to 270 K; relative to spectrum (a) the band of $Cp^{*}Ir(CO)(H)(C_{polymer})$ is unchanged, that of $Cp^{*}(CO)_2Ir...H\text{-}OR_F$ is weaker and that of $Cp^{*}Ir(CO)_2$ has grown. (c) Spectrum obtained after recooling to 200 K; note that the relative intensities of the bands of $Cp^{*}(CO)_2Ir...H\text{-}OR_F$ and $Cp^{*}IR(CO)_2$ are different from spectrum (a) and correspond exactly to those observed in the sample before photolysis.

molecules to its original position. The molecules must have sufficient mobility within the PE at 270 K to remove all "memory" of the non-equilibrium distribution created by UV photolysis at 200 K.

Fig. 5 illustrates the result of an experiment comparing the results of UV photolysis at 200 K and 260 K under as similar conditions as possible. As before irradiation at 200 K produced preferential photolysis of $Cp^{*}Ir(CO)_2$, fig. 5a. By contrast, irradiation at 260 K causes the ν(C–O) bands of *both* $Cp^{*}Ir(CO)_2$ and the H-bonded form, $Cp^{*}(CO)_2Ir...H\text{-}OR_F$ to decrease and their *relative intensities remain constant*, indicating that both species are photolysed at the same rate, fig. 5b. Thus, at this relatively high temperature, equilibration between $Cp^{*}Ir(CO)_2$ and $Cp^{*}(CO)_2Ir...H\text{-}OR_F$ occurs on a time scale which is fast compared to the time needed for photolysis.

4. Discussion

H-bonding has long been studied in noble gas matrices, where the equilibria are completely frozen out [15]. By contrast, the experiments described in this paper show how PE matrices allow equilibria to be not only frozen and but also *unfrozen* with unusual ease. Thus, near room temperature, PE should perhaps be regarded as a viscous liquid rather than as a solid matrix while, at lower temperatures, diffusion is effectively frozen out for molecules as large as $Cp^{*}Ir(CO)_2$ or $(CF_3)_3COH$.

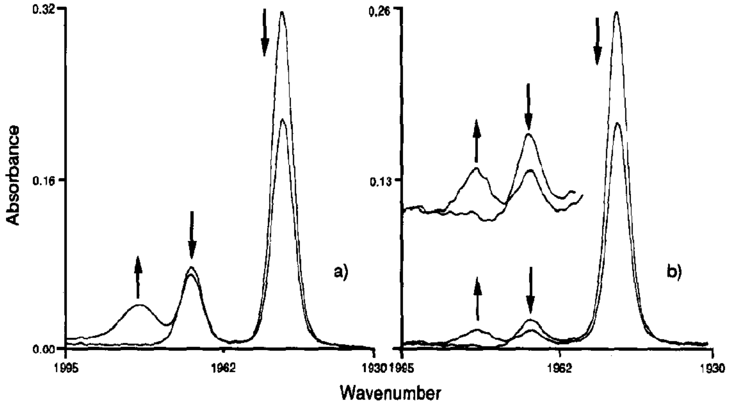

Fig. 5. IR spectra illustrating the difference between UV irradiation of $Cp^{*}IR(CO)_2/(CF_3)_3COH$ in PE at (a) 200 K and at (b) 260 K. In both cases, "before" and "after" spectra have been superimposed and, in (b), part of the wavenumber region is repeated with an expanded ordinate scale. The three bands are assigned as in fig. 4. Notice that irradiation at 260 K causes substantial depletion of $Cp^{*}(CO)_2Ir...H\text{-}OR_F$ while, at 200 K, it does not. The spectra in (a) and (b) were obtained sequentially, spectra (b) after spectra (a), from the *same* sample of PE which contained a lower concentration of $(CF_3)_3COH$ than did the sample used in figs. 1 to 3. Since $Cp^{*}Ir(CO)(H)\text{-}(C_{polymer})$ is thermally quite stable, the contribution to the IR absorption due to $Cp^{*}IR(CO)(H)(C_{polymer})$ generated in the first part of the experiment has been removed, by computer subtraction, from the spectra in (b).

These experiments have also revealed that free $Cp^*Ir(CO)_2$ was more effective in C–H activation than was the hydrogen-bonded form. This observation is quite surprising and, because of the unusual nature of this experiment, there are few precedents for comparison. The most interesting interpretation is that this effect is chemical, reflecting the lower electron density at the metal centre in $Cp^*(CO)_2Ir...H\text{–}OR_F$. There are, however, a number of more prosaic rationalisations. Formation of the H-bond could cause a significant shift in wavelength or reduction in extinction coefficient of the photoactive UV absorption of the $Cp^*Ir(CO)_2$. Unfortunately, the rather scattering nature of the PE discs and the presence of free $Cp^*Ir(CO)_2$ would make such spectroscopic effects difficult to detect. Alternatively, quantum yields for metal carbonyl compounds frequently show a solvent effect and the close proximity of a rather acidic fluoroalcohol may merely reduce the quantum yield without playing a particular role in the C–H activation reaction. The change in quantum yield may well be the consequence of the lower ground state energy of $Cp^*(CO)_2Ir...H\text{–}OR_F$. Finally, there is the possibility that the effect is merely due to steric bulk of the additional HOR_F ligand attached to the metal centre.

The use of impregnated PE clearly provides new opportunities for investigating equilibrium processes by matrix isolation, particularly in cases such as $Cp^*Ir(CO)_2$ where the equilibrium can be perturbed photochemically. The curvature of the van 't Hoff plot in fig. 2 means that thermodynamic parameters obtained by such experiments will, at best, be only approximate but this disadvantage is probably more than offset by the absence of detectable precipitation or aggregation of the impregnated organometallic compound and the ease with which the system can be cycled thermally. Although the method is particularly effective for metal carbonyl compounds with their very intense ν(C–O) absorptions, IR bands of less strongly absorbing ligands can also be detected and we are currently exploring the use of these films in probing the reactions of transition metal carbene complexes.

Acknowledgement

We are grateful for support from SERC Grant No. GR/G0823, the VW Stiftung and Nicolet Instruments Ltd. We thank Mr. J.A. Banister, Dr. S.M. Howdle, Dr. M. Jobling, Mr. P.A. Hamley, Mr. J.G. Gamble, Mr. K. Stanley, Dr. M.A. Kurikin and Professor J.J. Turner for their help and advice.

References

[1] M. Almond and A.J. Downs, Spectroscopy of Matrix Isolated Species, Advan. Spectry. 17 (1989).

[2] S. Firth, A. Horton-Mastin, M. Poliakoff, J.J. Turner, D.C. McKean, G.P. McQuillan and J. Robertson, Organometallics 8 (1989) 2876.

[3] R.H. Hill and M.S. Wrighton, Organometallics 4 (1985) 413; 6 (1987) 632.

[4] A.K. Campen, A.J. Rest and K. Yoshihara, J. Photochem. Photobiol. A 55 (1991) 301.

[5] E.W. Thulstrup and J.M. Michl, J. Am. Chem. Soc. 104 (1982) 5594.

[6] J.K. Burdett, J.M. Gryzbowski, R.N. Perutz, M. Poliakoff, J.J. Turner and R.F. Turner, Inorg. Chem. 17 (1978) 147; C.M. Gordon, Ph.D. Thesis, University of Nottingham (1991).

[7] M. Jobling, S.M. Howdle and M. Poliakoff, J. Chem. Soc. Chem. Commun. (1990) 1762.

[8] A.I. Cooper, S.M. Howdle and J.M. Ramsay, to be published.

[9] A.I. Cooper, C. Hughes, S.M. Howdle, K.P. Johnston, S.G. Kazarian, M. Poliakoff and L.A. Shepherd, to be submitted to Analyst.

[10] J.K. Hoyano and W.A.G. Graham, J. Am. Chem. Soc. 104 (1982) 3723;
J.K. Hoyano, A.D. McMaster and W.A.G. Graham, J. Am. Chem. Soc. 105 (1983) 7190;
A.J. Rest, I. Whitwell, W.A.G. Graham, J.K. Hoyano and A.D. McMaster, J. Chem. Soc. Chem. Commun. (1984) 624;
M. Jobling, S.M. Howdle, M.A. Healy and M. Poliakoff, J. Chem. Soc. Chem. Commun. (1990) 1287.

[11] S.G. Kazarian, P.A. Hamley and M. Poliakoff, J. Chem. Soc. Chem. Commun. (1992) 994.

[12] M. Jobling, Ph.D. Thesis, University of Nottingham (1992).

[13] S.G. Kazarian, M. Jobling and M. Poliakoff, to be published.

[14] A.J. Barnes and J. Murto, J. Chem. Soc. Faraday Trans. II 68 (1972) 1642.

[15] H.E. Hallam, in: The hydrogen bond – recent developments in theory and experiment, Vol. 2, eds. P. Schuster, G. Zundel and C. Sandorfy (North-Holland, Amsterdam, 1970) p. 1065;
O. Schrems, H.M. Oberhoffer and W.A.P. Luck, J. Phys. Chem. 88 (1984) 4335;
L. Schriver and A. Burneau, J. Chem. Soc. Faraday Trans. II 81 (1985) 503.