Fast Time-resolved Infrared Spectroscopy of Organometallic Intermediates: Detection of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ and $[(\eta^5\text{-}C_5H_5)Fe(\mu\text{-}CO)_3Fe(\eta^5\text{-}C_5H_5)]$ in Room-temperature Solution

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A line-tunable CO laser has been used as a fast (1 μs) i.r. monitor to obtain spectra (2012—1710 cm^{-1}) and lifetimes of $[CpFe(CO)_2]$ (Cp = η^5-C_5H_5) and $[CpFe(\mu\text{-}CO)_3FeCp]$, formed during u.v.–visible flash photolysis of $[CpFe(CO)_2]_2$ in cyclohexane solution.

There is considerable argument over the identity of the primary photoproducts formed during the photolysis of $[CpFe(CO)_2]_2$ (A) (Cp = η^5-C_5H_5). Two transient u.v.–visible absorptions have been observed during the flash photolysis of (A) in cyclohexane solution at room temperature.[1] One absorption had a rapid *second*-order decay and has been generally assigned[1,2] to the radical $[CpFe(CO)_2]$ (B), formed by homolytic cleavage of the Fe–Fe bond of (A). By contrast, the second absorption had a much slower *first*-order decay, substantially accelerated by CO or phosphine. This absorption has been variously assigned to $[Cp_2Fe_2(CO)_3]$[1] or $[CpFe(CO)_2(\mu\text{-}CO)Fe(CO)Cp]$,[2] a CO-bridged compound *without* an Fe–Fe bond. Recently, u.v. photolysis of (A) in PVC films[3] at 12 K and in alkane glasses[4] at 77 K provided conclusive i.r. evidence, including enrichment[3] with ^{13}CO, for the formation of $[CpFe(\mu\text{-}CO)_3FeCp]$ (C). This reacts thermally with CO to regenerate (A), and has a visible absorption, $\lambda_{max.}$ 510 nm, almost identical to that of the long-lived transient in the flash photolysis of (A). Nevertheless, the photochemistry in room temperature solution remains controversial,[5] but the arguments can be resolved by the experiment reported in this communication.

We have constructed an i.r. flash kinetic spectrometer for the measurement of the i.r. absorbances of transient species in solution. This allows far more specific identification of such species than is possible with conventional u.v.–visible flash photolysis.

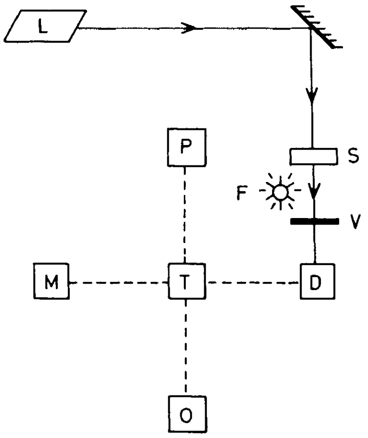

Figure 1. Schematic diagram of the u.v. flash/i.r. monitoring apparatus. Light from the CO laser, L, is passed through an evacuable i.r. cell, S, which is placed *as close as possible* (*ca.* 2 cm) to the flash lamp, F (Applied Photophysics, 100 J, FWHM 15 μs), and onto a liquid nitrogen-cooled i.r. detector, D (Nicolet MCT-A with 60 SX amplifier). The electrical signal is recorded by a 1 MHz 8 bit transient Digitizer, T (Datalab DL 902, triggered by a photodiode, P), and displayed on an oscilloscope, O. The digitized data are transferred to a microcomputer, M (BBC B), for plotting and signal averaging where necessary. Non-focusing optics are used throughout and the laser beam is heavily attenuated by a variable pathlength i.r. cell, V, filled with liquid methanol, placed immediately in front of the detector.

Time-resolved i.r. spectroscopy is beginning to play an important role in metal carbonyl photochemistry. Transient species so far detected have included $[Fe(CO)_x]$ (x = 4, 3, and

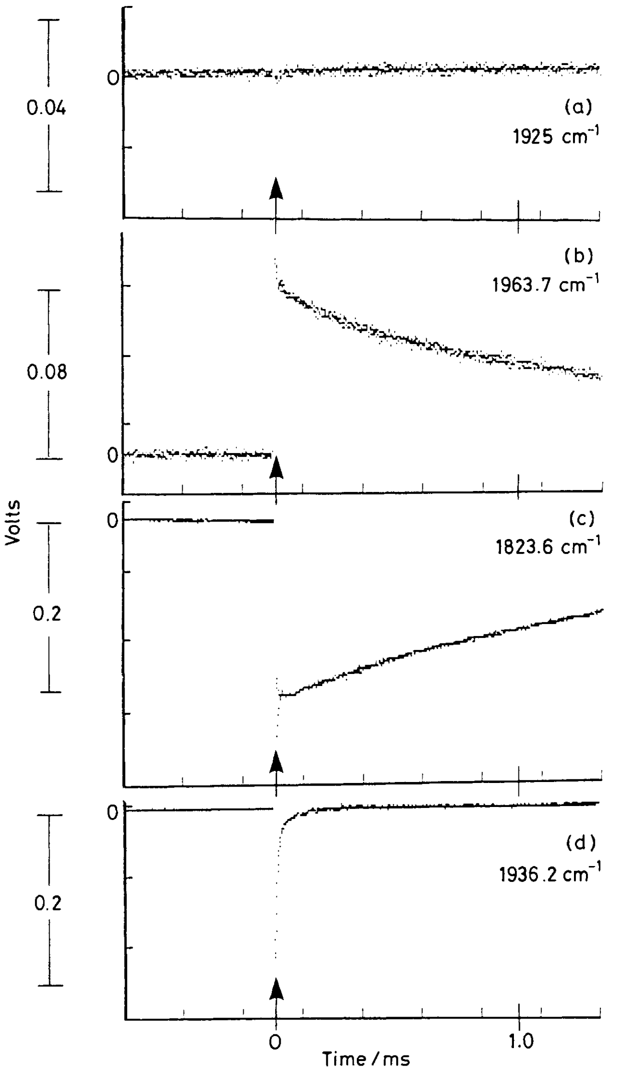

Figure 2. Transient i.r. signals recorded during the flash photolysis of $[CpFe(CO)_2]_2$ (A) in cyclohexane under 1 atm of CO: (a) 1925 cm^{-1}, where there is no change in absorption; (b) 1963.7 cm^{-1}, increase in transmission of (A); (c) 1823.6 cm^{-1}, absorption of (C); and (d) 1936.2 cm^{-1} absorption of (B). The arrow shows the time at which the u.v. flash lamp was fired. Note the difference in the voltage scales of the traces. For each wavelength, the attenuation of the laser beam was adjusted so that total absorption of the laser light gave a signal of 1.5—2 V. (*N.b.* The detector/amplifier output is linear up to ±10 V.)

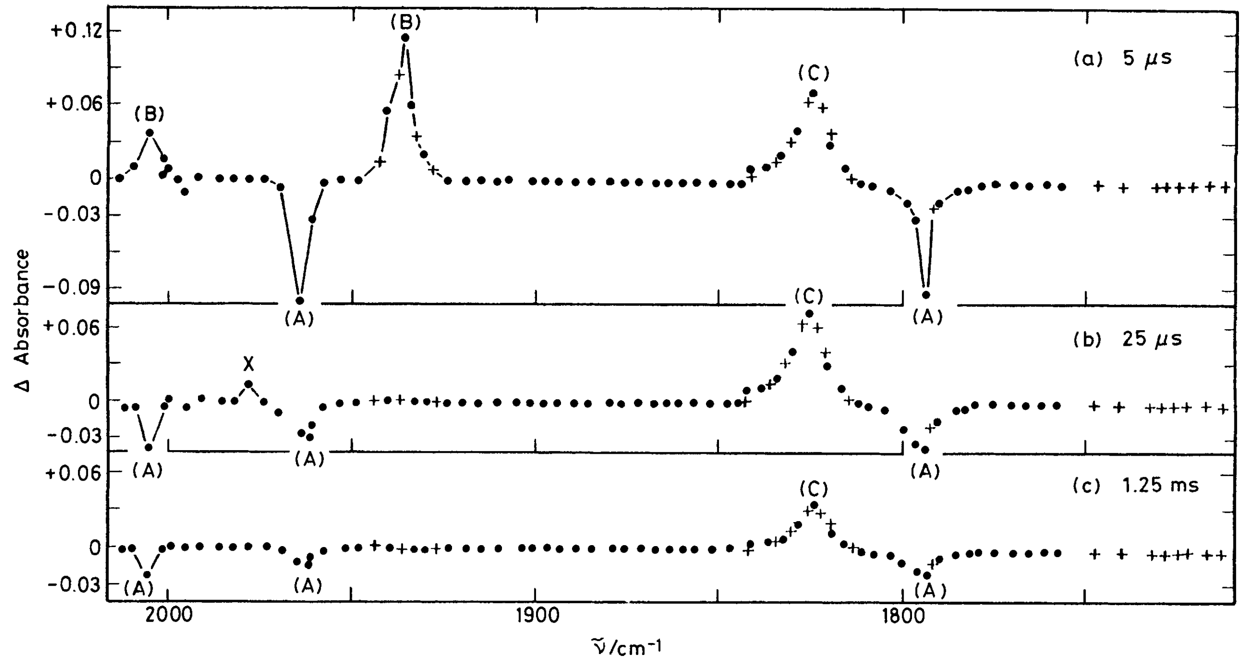

Figure 3. Transient i.r. difference spectra showing changes in absorbance: (a) 5 μs, (b) 25 μs, and (c) 1.25 ms after the u.v. flash photolysis of $[CpFe(CO)_2]_2$ (A), in cyclohexane solution under 1 atm pressure of CO. Bands pointing upwards represent an increase in absorbance (*i.e.* formation of a compound) and those pointing downwards a decrease [*i.e.* depletion of starting material, (A)]. The bands are assigned in Table 1. Points marked ● were recorded with a ^{12}CO laser and those marked + with a ^{13}CO laser.

Table 1. Wavenumber in cm^{-1} of i.r. absorptions of $[CpFe(CO)_2]_2$ and its photoproducts.

Molecule		Solvent Cyclohexane,[a] 295 K	 Hydrocarbon[b] glass, 77 K	 PVC film,[c] 12 K
$[CpFe(CO)_2]_2$	*cis*	2004	1992	1992
(A)	*trans*	1960	1957	1952
		1792	1772	1772
$[CpFe(CO)_2]$[d]		2004	—	—
(B)		1938	—	—
$[CpFe(\mu\text{-}CO)_3FeCp]$ (C)		1823	1811	1812

[a] This work, band positions ±2 cm^{-1}. Values for the absorptions of (A) agree well with a conventional i.r. spectrum of (A). [b] Ref. 4. [c] Ref. 3. [d] $[(\eta^4\text{-}C_4H_6)Fe(CO)_2]$ in an Xe matrix at 20 K: 1999 and 1936 cm^{-1}, ref. 10.

2) in the gas phase,[6] and $[Cr(CO)_5(C_6H_{12})]$,[7] $[Cr(CO)_5N_2]$,[8] $[Mn(CO)_5]$,[9] and $[Mn_2(CO)_9]$[9] in cyclohexane solution. Our apparatus, shown schematically in Figure 1, is essentially a conventional flash photolysis apparatus with an i.r. CO laser replacing the u.v.–visible monitoring beam. For each u.v. flash, the CO laser is used to monitor changes in transmission at *one* i.r. wavelength. A spectrum is built up by tuning the laser to different i.r. wavelengths† and repeating the u.v. flash. Figure 2(a) shows the laser signal at a wavelength where there is no change in i.r. absorption and it is clear that the u.v. flash introduces very little noise into the signal. The other traces in Figure 2 show the excellent signal/noise ratio achievable on a *single* shot for these transient i.r. signals. From such traces, one can construct a 'point-by-point' difference spectrum of the solution corresponding to absorbance changes at a particular time interval after the flash.

Figure 3 shows such spectra produced by flash photolysis of (A) in cyclohexane solution under 1 atm (10^5 Pa) CO pressure.‡ The spectra correspond to 5 μs, 25 μs, and 1.25 ms after the start of the flash. It is clear from the spectra that the starting material (A) is depleted and there are two principal photoproducts. The first is short-lived with two bands,§ marked (B), which have completely disappeared within 25 μs of the flash, Figure 3(b). The second product is much longer lived. It has a single absorption band, marked (C), which has decayed to half its original intensity after 1.25 ms, Figure 3(c). The decay of this band follows first-order kinetics (k_1 550 s^{-1}) under 1 atm of CO. The rate of disappearance, Figure 2(c), is the same as the rate of reappearance of (A), Figure 2(b), and is similar to the previously reported[1] decay rate (k_1 280 s^{-1}) of the longer-lived u.v.–visible transient absorption. Under 1 atm of Ar (*i.e.* in the absence of added CO) the half-life is extended to 0.6 s. Thus, it seems reasonable to conclude that

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† Our CO laser (Edinburgh Instruments PL3 with modified cooling[12]) is line-tunable over the range 2020—1700 cm^{-1} with a separation of *ca.* 4 cm^{-1} between lines. This gives at worst an effective resolution of *ca.* 8 cm^{-1}. The resolution can be improved by refilling the laser with ^{13}CO which fortuitously gives lines approximately half-way between the ^{12}CO lines over much of this wavenumber range.

‡ Solution conditions: $[CpFe(CO)_2]_2$ (PCR Inc.) 7 × 10^{-4} M in cyclohexane (B.D.H., Aristar Grade), degassed by repeated freeze–pump–thaw cycles and saturated *in situ* with CO (BOC Research Grade) or Ar (Messer-Griesheim) both at *ca.* 1 atm pressure; i.r. cell: 1 mm pathlength, CaF_2 windows.

§ The higher frequency band overlaps the absorption of the *cis*-isomer of (A). However, the signals due to the formation of (B) and the destruction of (A) can be distinguished because of their substantially different lifetimes. It is more difficult to make accurate measurements of the intensity of the 'negative' peaks of (A) immediately after the flash and so these peaks in Figure 3(a) should be regarded as somewhat less accurate than those in Figures 3(b) and (c).

this photoproduct reacts with CO to regenerate (A). The absorption band is extremely close in frequency to the absorption of the triply bridged product (C), isolated in a matrix[3] or glass[4] (see Table 1), but it is 100 cm^{-1} above the region where a singly bridged product might be expected.[2] Thus, the longer-lived photoproduct is almost certainly [CpFe(μ-CO)$_3$FeCp] (C). Under the conditions of our experiment, (C) is formed within the resolution of the apparatus, *ca.* 1 μs, and is probably a primary photoproduct.¶

The i.r. absorptions of matrix-isolated [CpFe(CO)$_2$] are unknown. However, our short-lived photoproduct has two bands almost identical in frequency to those of matrix-isolated[10] [(η^4-C_4H_6)Fe(CO)$_2$] (see Table 1). This photoproduct is most probably the radical [CpFe(CO)$_2$] (B). Unfortunately, under the conditions of our experiment, the lifetime of (B), Figure 2(d), is *shorter* than the lifetime of the u.v. flash (15 μs full width at half maximum, FWHM) and no quantitative kinetic results are possible.** The decay of the transient signal due to (B) was unchanged in the absence of added CO, which is consistent with (B) being the radical [CpFe(CO)$_2$].

There is a much weaker transient absorption, marked X in Figure 3(b), which is only observed when CO is added to the solution. Since X grows in *after* the flash [it is not present in Figure 3(a)], it cannot be due to a primary product. X decays fairly rapidly ($t_{\frac{1}{2}}$ *ca.* 150 μs) but it is too weak for the absorbing species to be identified easily.

This experiment illustrates the power of combining time-resolved i.r. spectroscopy of room-temperature solutions with results from low-temperature matrices. The spectra provide much more positive evidence for the identity of reaction intermediates than has previously been possible.

We thank the S.E.R.C. and NATO for support, and the University of Newcastle upon Tyne, Nicolet Instruments Ltd., J. K. Lasers Ltd., and Perkin-Elmer Ltd., for loan of equipment. We are grateful to Dr. J. H. Carpenter, Dr. S. P. Church, Mr. J. D. Cooper, Dr. M. Ford, Dr. M. A. Healy, Dr. J. P. Keene, Mr. R. E. Parsons, Mr. W. E. Porter, Dr. I. Powis, and Professor E. Weitz for their help and advice.

Received, 30th April 1984; Com. 601

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¶ In the matrix experiments, only the *trans*-isomer of (A) was found to be photolysed to form (C). In our experiment both the *cis*- and *trans*-isomers are destroyed by the u.v. flash. Unfortunately, extrapolation of n.m.r. data[11] suggests that the rate of *cis* $\rightleftarrows$ *trans* isomerization is comparable to the duration of the u.v. flash. This means that we cannot tell from our results whether or not (C) can be formed from the *cis*-isomer in solution. We have found a significant wavelength dependence in the relative intensities of the signals due to (B) and (C). With a filtered flash, $\lambda > 450$ nm (Wratten filter) the signal due to (B) is unaffected while that of (C) is barely detectable. It is probable that this represents a lower quantum yield for production of (C) rather than rapid secondary photolysis of (C).

** This is much shorter than in ref. 1 but presumably their solution was much more dilute than ours. Preliminary experiments using an XeCl excimer laser (pulse length 10 ns, Lumonics Model TE-861T) instead of the flash lamp show that the decay rate of (B) decreases as the solution is diluted and that the decay follows second-order kinetics.