Identification of Intermediates in the Photosubstitution of $[(\eta\text{-}C_5H_5)Fe(CO)_2]_2$, using Time-resolved I.R. Spectroscopy: Reaction Kinetics of $[(\eta\text{-}C_5H_5)_2Fe_2(\mu\text{-}CO)_3]$ with Acetonitrile and Phosphines

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Using time-resolved i.r. spectroscopy on a 10 μs time-scale, $[(\eta\text{-}C_5H_5)_2Fe_2(\mu\text{-}CO)_3]$ (C) has been identified as the principal intermediate in photosubstitution of $[(\eta\text{-}C_5H_5)Fe(CO)_2]_2$ and the activation parameters have been measured for the reaction of (C) with PBu^n_3, PPh_3, and MeCN in cyclohexane solution; (C) does not react with P(*o*-tolyl)$_3$ or tetrahydrofuran.

The photochemistry of $[CpFe(CO)_2]_2$, Cp = $\eta\text{-}C_5H_5$, has been studied in considerable detail.[1] These studies[2—4] have shown that, on a microsecond time-scale at least, there are two primary photoproducts (B) and (C). There is, however, some confusion over the subsequent course of substitution reactions. This communication shows how time-resolved i.r. spectroscopy can help in the understanding of these processes.

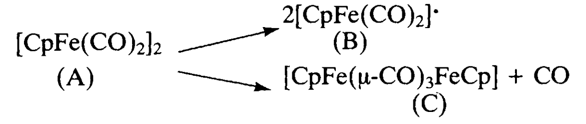

Table 1. Rate constants and activation parameters[a] for the reaction of $[Cp_2Fe_2(\mu\text{-}CO)_3]$ with MeCN, PBu^n_3, and PPh_3 in cyclohexane solution.

Ligand	$10^{-5}\,k/s^{-1}\,dm^3\,mol^{-1}$	$\Delta H^{\ddagger}/kJ\,mol^{-1}$[c]	$\Delta S^{\ddagger}/J\,mol^{-1}\,K^{-1}$[d]
MeCN	7.6 (24.0 °C)	24.4	−50.0
PBu^n_3	1.25 (24.6 °C)	28.1	−52.3
PPh_3	2.1 (24.7 °C)[b]	23.3	−64.8

[a] Calculated from data over the temperature range 16—59 °C, see Figure 3. [b] The value for 20 °C ($1.7 \times 10^5\,s^{-1}\,dm^3\,mol^{-1}$) agrees well with the value obtained by u.v.–visible flash photolysis,[2] $1.5 \times 10^5\,s^{-1}\,dm^3\,mol^{-1}$ at 20 ± 2 °C. [c] ± 1 kJ mol^{-1}. [d] ± 2 J $mol^{-1}\,K^{-1}$.

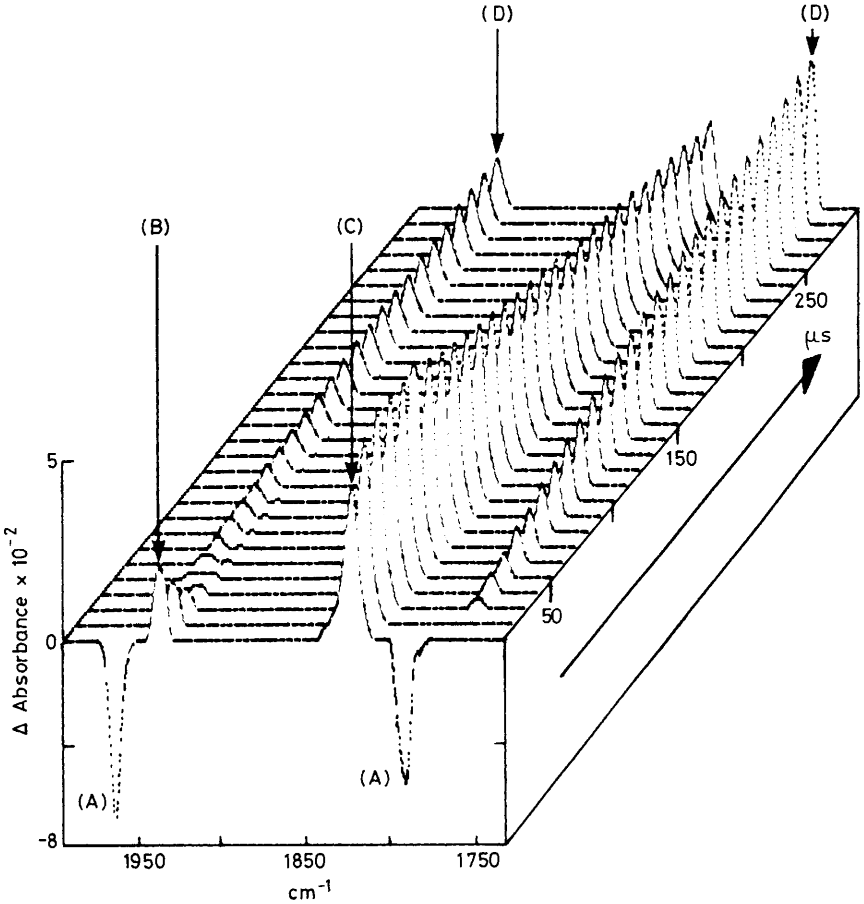

Figure 1. Time-resolved i.r. spectra obtained after u.v. flash photolysis of $[CpFe(CO)_2]_2$ (A) (6×10^{-4} M) and MeCN (6×10^{-3} M) in cyclohexane solution at 25 °C. [Only about 5% of (A) is destroyed by the u.v. flash, so that the concentration of (C) is much lower than that of (A).] The bands are labelled: (B) $[CpFe(CO)_2]^{\bullet}$; (C) $[Cp_2Fe_2(\mu\text{-}CO)_3]$; and (D) $[Cp_2Fe_2(CO)_3(MeCN)]$. The spectra have been reconstituted from ~70 kinetic traces (similar to those in Figure 2a) recorded at intervals of ~4 cm^{-1} across the wavenumber region illustrated. The spectra are drawn by interpolation between these discrete points. The first three spectra correspond to the duration of the firing of the u.v. flash lamp and subsequent spectra are shown at intervals of 10 μs. The negative peaks in the first spectrum are due to material destroyed by the flash. These negative peaks have been omitted from the subsequent traces to avoid undue confusion.

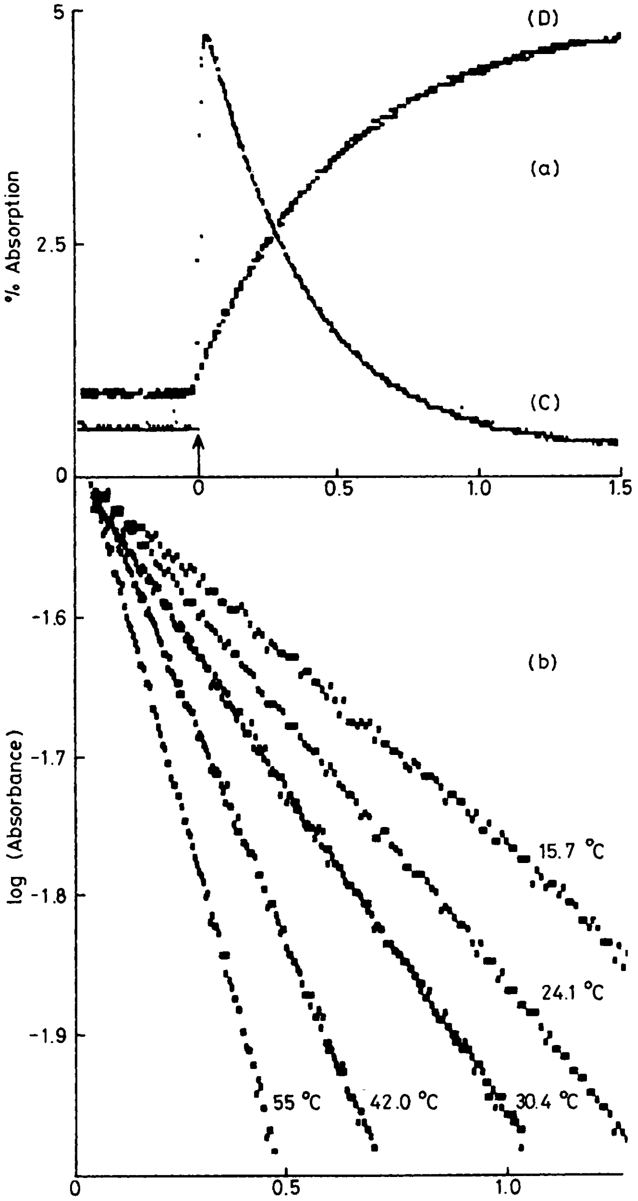

Figure 2. (a) Kinetic traces showing the formation and decay of (C), $[Cp_2Fe_2(\mu\text{-}CO)_3]$, and the associated growth of the product (D), $[Cp_2Fe_2(CO)_3(MeCN)]$. The traces were measured at 1822 cm^{-1} for (C) and 1764 cm^{-1} for (D). The arrow marks the start of the u.v. flash (which has ~15 μs full width at half-maximum). The traces are taken from the same experiment as Figure 1. (b) Traces showing the pseudo-first-order decay of (C) at different temperatures. The decays illustrated cover ~1½ half lives for all but the lowest temperature, and were recorded with a lower concentration of MeCN (1.3×10^{-3} M) than used in Figure 2a.

Time-resolved i.r. spectroscopy is a relatively new technique which combines u.v. flash photolysis and fast i.r. detection.[5] It provides a particularly sensitive means of probing these substitution reactions, because ν(C–O) i.r. bands are usually sharp, well separated and carry considerable structural information.† By contrast, the u.v.–visible absorption bands of these species are broad, frequently overlapped, and yield little structural information. In this communication we discuss substitution by MeCN, tetrahydrofuran (THF), and a number of phosphines.

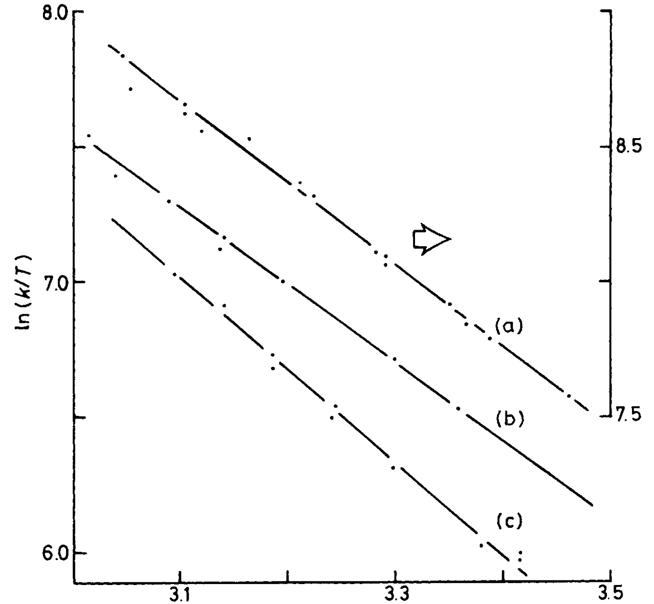

Figure 3. Eyring plot of ln(k/T) against 1/T for the reaction of $[Cp_2Fe_2(CO)_3]$ (C) with (a) MeCN; (b) PPh_3; and (c) PBu^n_3, where k is the second-order rate constant, see Table 1. Note the displaced ordinate scale for trace (a). The traces have gradient $-\Delta H^{\ddagger}/R$ and the intercept is used to calculate $\Delta S^{\ddagger}$.

Figure 1 shows a series of time-resolved i.r. spectra recorded‡ during the flash photolysis of $[CpFe(CO)_2]_2$ in the presence of MeCN. The overall photochemical reaction is substitution[2,6] of one terminal CO group by MeCN [reaction (1)]. These spectra show clearly that (i) (A) is destroyed immediately by the u.v. flash but formation of the final product (D) is relatively slow; (ii) as expected, the mononuclear radical (B) and the dinuclear fragment (C) are both generated by the flash; (iii) negligible amounts of (D) are formed during the rapid decay of the radical (B); (iv) the decay of (C) exactly mirrors the increase in the bands of (D); (v) there are no additional bands in this region of the spectrum which could be assigned to other photoproducts or intermediates.

$$\underset{\text{(A)}}{[CpFe(CO)_2]_2} + MeCN \xrightarrow[\text{cyclohexane}]{\text{u.v.}} \underset{\text{(D)}}{[Cp_2Fe_2(CO)_3(MeCN)]} + CO \quad (1)$$

The decay of (C) and the concomitant formation of (D) are shown even more clearly in the kinetic traces illustrated in Figure 2(a). The decay of (C) obeys a pseudo-first-order rate law over a broad range of temperatures, Figure 2(b).

Similarly, time-resolved i.r. spectra, not illustrated, show that (C) is the important intermediate when (A) is photolysed in the presence of PPh_3 or PBu^n_3. The reaction of (C) with both phosphines is significantly slower than with MeCN.

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† The wavenumbers of the bands of the relevant species are already known; (*i.e.* in the range 2000—1700 cm^{-1}) (A)[4] 1961, 1792; (B)[4] 1938; (C)[3,4] 1823; (D)[6] 1945, 1764; and $[Cp_2Fe_2(CO)_3PPh_3]$[7] 1961, 1936, 1738 cm^{-1}.

‡ Our apparatus based on a u.v. flash lamp and continuous wave CO (i.r.) laser has been described in detail.[4,5,8] Since photosubstitution produces a relatively stable photoproduct, $Cp_2Fe_2(CO)_3L$, the solution was changed using our i.r. flow cell[4,8] after each flash of the u.v. lamp.

Figure 3 shows Eyring plots for all three reactions and the rate constants and activation parameters are given in Table 1.

All the reactions are much slower than expected for near-diffusion-controlled processes such as the recombination of the radicals (B). The enthalpy of activation for the three reactions are very similar, which suggests that the basic mechanism in each case is the same. By analogy with its C_5Me_5 analogue,§ (C) would be expected to have a triplet ground state. The reaction (C) → (D) would thus be spin-forbidden and this may be the origin of the activation energy.¶

The entropies of activation, $\Delta S^{\ddagger}$, are consistent with associative bimolecular reactions. The value of $\Delta S^{\ddagger}$ is almost identical for MeCN and PBu^n_3, but somewhat larger for PPh_3. This may be a steric effect since PPh_3 has a larger cone angle,[10] 148°, than PBu^n_3. Furthermore, (C) does not react at all with $P(o\text{-tolyl})_3$, which has an exceptionally large cone angle, 194°.

Many of the published photosubstitution reactions of (A) have been carried out in THF solution, and $[Cp_2Fe_2(CO)_3(THF)]$ has been invoked as an intermediate.[11] It is suprising therefore that (C) was not observed to react with THF in PVC films.[3] Similarly in our experiments, the rate of decay of (C) is unaffected by addition of THF to cyclohexane (up to 50% by volume). However, the total amount of (C) formed by the u.v. flash is greatly reduced by addition of THF. This is consistent with matrix-isolation experiments[3] which suggest that (C) can be formed from the *trans*-isomer of $[CpFe(CO)_2]_2$ but not from the *cis*. THF is known to reduce the equilibrium concentration of the *trans*-isomer[12] and thus should reduce the formation of (C). Even though (C) does not react with THF, we observed the formation of the long-lived species, $[Cp_2Fe_2(CO)_3(THF)]$ within the lifetime of the u.v. flash. Since $[Cp_2Fe_2(CO)_3(THF)]$ cannot be formed *via* (C), it must be produced by a different pathway perhaps involving reactions of the radical (B). Experiments on a much shorter time-scale will be needed to confirm this.

Obviously much remains to be done before this system is completely unravelled. However, it is clear that time-resolved i.r. spectroscopy can now provide much of the detailed information which is required to understand the photochemistry of $[CpFe(CO)_2]_2$.

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§ This compound $[(\eta\text{-}C_5Me_5)Fe(\mu\text{-}CO)_3Fe(\eta\text{-}C_5Me_5)]$ has in fact been isolated and characterised by *X*-ray diffraction.[9] Like (C), it also reacts with MeCN and PPh_3.

¶ A referee has pointed out that the values of $\Delta H^{\ddagger}$ for (C) are similar to those observed in the reactions of Fe^{III} chelates where intersystem-crossing is known to occur; see *e.g.* R. A. Binstead, J. K. Beattie, T. G. Dewey, and D. H. Turner, *J. Am. Chem. Soc.*, 1980, **102**, 6442.

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