Associative Substitution Reactions in 17 Electron Organometallic Radicals: Direct Observation of the Reaction of [(C₅H₅)Fe(CO)₂]· with P(OMe)₃ using Very Fast Time-resolved I.R. Spectroscopy
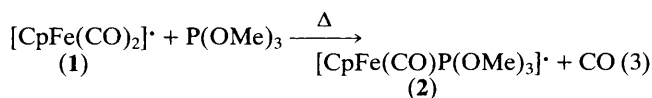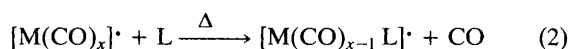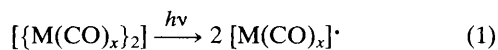
Andrew J. Dixon,ᵃ Steven J. Gravelle,ᵇ Lambertus J. van de Burgt,ᵇ Martyn Poliakoff,ᵃ James J. Turner,ᵃ and Eric Weitzᵇ

ᵃ *Department of Chemistry, University of Nottingham, Nottingham NG7 2RD, U.K.*
ᵇ *Department of Chemistry, Northwestern University, Evanston, Ilinois, 60201, U.S.A.*

Time-resolved i.r. spectroscopy is used to monitor directly the formation of [(C₅H₅)Fe(CO)P(OMe)₃]· in the reaction of P(OMe)₃ with [(C₅H₅)Fe(CO)₂]·, generated by 351 nm photolysis of [{(C₅H₅)Fe(CO)₂}₂] in n-heptane solution at room temperature; the reaction is an associative process with a bimolecular rate constant of $8.9 \pm 2.0 \times 10^8$ dm³ mol⁻¹ s⁻¹.

Recently, there has been renewed interest in the mechanism of substitution reactions in dinuclear metal carbonyl compounds.[1—3] A key step in many of the postulated mechanisms is ligand substitution in '17 electron' radicals formed by homolysis of the metal–metal bond, equations (1) and (2).

$$[\{M(CO)_x\}_2] \xrightarrow{h\nu} 2\,[M(CO)_x]^\bullet \qquad (1)$$

$$[M(CO)_x]^\bullet + L \xrightarrow{\Delta} [M(CO)_{x-1}\,L]^\bullet + CO \qquad (2)$$

$$\underset{(\mathbf{1})}{[CpFe(CO)_2]^\bullet} + P(OMe)_3 \xrightarrow{\Delta} \underset{(\mathbf{2})}{[CpFe(CO)P(OMe)_3]^\bullet} + CO \quad (3)$$

Surprisingly, the substitution of such radicals, equation (2), has never been observed directly. However, Poë and coworkers devised ingenious competition experiments which allowed the substitution rates of [Re(CO)₅]· by various ligands to be

calculated.[4] This work has since been extended by Herrinton and Brown, who have found that [Mn(CO)₅]· reacts with some phosphines (*e.g.* PBuⁿ₃) at rates approaching the diffusion controlled limit.[5] Although conventional flash photolysis has sufficient time resolution to follow such processes,[1,6] the u.v.–visible absorption bands of [M(CO)ₓ]· and [M(CO)ₓ₋₁L]· radicals are usually very similar making substitution reactions difficult to monitor by u.v.–visible spectroscopy. I.r. spectroscopy is much more useful in these cases because ν(CO) i.r. bands are more sensitive to changes in structure than are u.v.–visible absorptions.

In this communication, we show that the rate of a substitution reaction can be measured directly using time-resolved i.r. spectroscopy (TRIR), which is a combination of u.v. flash photolysis and fast i.r. spectroscopy.[7,8] We have used TRIR to monitor the thermal reaction between [CpFe(CO)₂]· (Cp = η⁵-C₅H₅) and P(OMe)₃, in n-heptane at room temperature, equation (3), a reaction previously postulated in the mechanism of photosubstitution of [{CpFe(CO)₂}₂] by P(OMe)₃.[9]
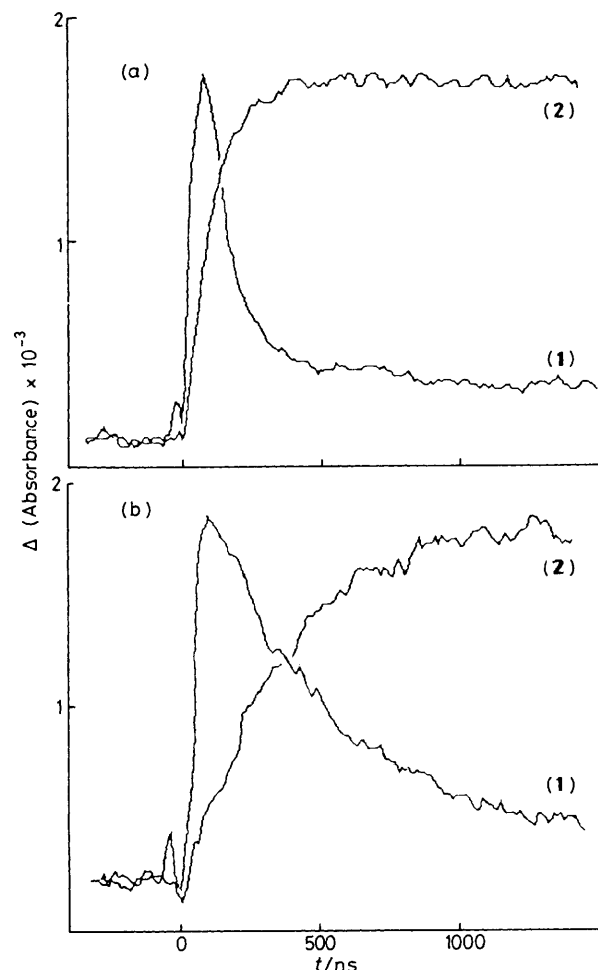
TRIR experiments with [{CpFe(CO)₂}₂] have already

Figure 1. Very fast i.r. kinetic traces, which provide the evidence for associative substitution reaction of $[CpFe(CO)_2]$· (1) with $P(OMe)_3$ to form $[CpFe(CO)P(OMe)_3]$· (2). The two sets of traces were obtained by photolysis of two solutions in n-heptane both containing $[\{CpFe(CO)_2\}_2]$ 8.5×10^{-5} M but with different concentrations of $P(OMe)_3$, (a) 1.4×10^{-2} M and (b) 2.3×10^{-3} M. I.r. monitoring wavenumbers (a) (1) 2007 cm^{-1}, (2) 1907 cm^{-1}; (b) (1) 1938 cm^{-1}, (2) 1907 cm^{-1}.

shown that (1) has two $\nu(CO)$ bands at 2007 and 1938 cm^{-1}[10] and similar experiments† show that (2) has a single $\nu(CO)$ absorption at 1907 cm^{-1}. Thus the $\nu(CO)$ bands of (1) and (2) are well separated and can be used to monitor the course of the reaction.

Traces for the reaction of (1) with $P(OMe)_3$ at two different concentrations of phosphite are shown in Figure 1 and the relevant rate constants are given in Table 1.‡ For a given concentration of $P(OMe)_3$ the disappearance of (1) and the

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† The characterisation of $[CpFe(CO)P(OMe)_3]$· has involved a whole series of TRIR studies on $[\{CpFe(CO)_2\}_2]$ and on an authentic sample of $[Cp_2Fe_2(CO)_3P(OMe)_3]$, which on photolysis yields both $[CpFe(CO)_2]$· and $[CpFe(CO)P(OMe)_3]$·.[14]

‡ The experiments described here were carried out at Northwestern University using the TRIR apparatus as described in ref. 15, together with the i.r. flow cell[8] from Nottingham. The photolysis source was a XeF excimer laser (351 nm) and the i.r. detector was a 77K InSb photovoltaic detector (Santa Barbara). All traces were averaged over 16 shots and background subtraction was used to minimize the effects of shock waves.


Table 1. Concentrations and rate constants for the reaction of $[CpFe(CO)_2]$· with $P(OMe)_3$ in n-heptane solution at 25 °C.[a]

Concentration of $P(OMe)_3$/mol dm^{-3}	Rate of decay of $[CpFe(CO)_2]$· /s$^{-1} \times 10^6$	Rate of formation of $[CpFe(CO)P(OMe)_3]$· /s$^{-1} \times 10^6$
2.3×10^{-3}	1.81[b]	2.39[d]
	2.25[c]	
1.4×10^{-2}	11.9[b]	10.8[d]

[a] Overall second order rate constant $8.9 \pm 2.0 \times 10^8$ dm^3 mol^{-1} s^{-1}. Rates monitored at: [b] 1938 cm^{-1}. [c] 2007 cm^{-1}. [d] 1907 cm^{-1}.

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formation of (2) both follow pseudo first-order kinetics and, within experimental error, both processes occur at the same rate. The pseudo first-order rate constant increases linearly with increasing concentration of $P(OMe)_3$. With the concentration at 1.4×10^{-2} M, the whole substitution process is complete within 500 ns, Figure 1(a), making it by far the fastest reaction yet detected by i.r. in solution.

These observations imply that the reaction proceeds via an associative pathway,§ as might have been expected by analogy with other 17 electron species, e.g. $[Mn(CO)_5]$·[5] or $[V(CO)_6]$·.[11] An associative pathway might be expected to involve slippage of the C_5H_5 ring with $[(\eta^4-C_5H_5)Fe(CO)_2-P(OMe)_3]$·, (3), as an intermediate, similar to that proposed for the photoreactions of $[CpFe(CO)_2Bz]$[12], (Bz = benzyl). However, we have no evidence for the formation of any intermediate such as (3). If (3) is formed in our experiment its lifetime must be very short compared to the rate of the reaction.

$$[(\eta^4-C_5H_5)Fe(CO)_2P(OMe)_3]·$$
(3)
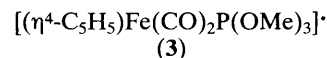
The rate of reaction of (1) with $P(OMe)_3$ is about one order of magnitude slower than the diffusion controlled limit and it is only slightly slower than the rate of dimerisation of (1) to form $[\{CpFe(CO)_2\}_2]$. By contrast (1) appears to react more slowly with MeCN, PBu^n_3, and PPh_3. Thus, at ligand concentrations below 10^{-2} M at least, substitution of (1) by these ligands is not a significant process in the photochemistry of $[\{CpFe(CO)_2\}_2]$.

The difference in reactivity of (1) with $P(OMe)_3$ as opposed to other ligands was not reflected in the addition reactions of $[Cp_2Fe_2(CO)_3]$. In that case, $P(OMe)_3$ reacted at the same rate as PBu^n_3 and rather slower than MeCN, a difference attributed to steric effects.[13] Thus, in the present case, steric effects do not provide a complete explanation for the much greater reactivity of (1) towards $P(OMe)_3$ than towards the other ligands.

We have shown that time-resolved i.r. spectroscopy can be used to observe fast processes in solution. Quantitative measurements can now be carried out on a sub-microsecond timescale. This opens up the fascinating possibility of detecting electronic excited states of organometallic compounds, states which are still largely uncharacterized.

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§ Under certain circumstances it is possible for the rate of a dissociative substitution reaction to depend upon the concentration of the incoming ligand.[16] This only occurs when the concentration of the leaving group, in our case CO, is comparable to the concentration of the incoming ligand $P(OMe)_3$. This condition was not fulfilled in our experiments where $[CO]/[P(OMe)_3] < 10^{-2}$.

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