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Steric Effects in the Kinetics of Organometallic Reactions: A Time-Resolved Infrared Study of $[(\eta^5\text{-}C_5R_5)Mn(CO)_2]$ (R = H, Me or Et) in n-heptane Solution

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Fast time-resolved IR spectroscopy (microsecond timescale) is used to record the spectra and kinetics of photochemical reactions of $[(\eta^5\text{-}C_5R_5)Mn(CO)_3]$ (R = H, Me or Et) in n-heptane solution; second-order rate constants for reaction with H_2, N_2 and CO are *ca.* six times faster for $[(C_5Et_5)Mn(CO)_2$(n-hept)] than for $[(C_5H_5)Mn(CO)_2$(n-hept)] while the rate constants for the reaction of all three $[(C_5R_5)Mn(CO)_2$(n-hept)] intermediates with PPh_3 are almost identical.

Organometallic reactions in solution are often very much slower than the corresponding reactions in the gas phase, even allowing for differences in diffusion rates.[1] One reason is that in solution many, if not most, 16 electron intermediates are solvated on a picosecond timescale even by apparently inert hydrocarbon solvents.[2] The breaking of the M $\cdots$ solvent bond then becomes a significant factor in determining the overall rate of the reaction.[3] There is experimental evidence for the presence of this token solvent ligand in a wide range of organometallic intermediates. In the case of $[(C_5H_5)Mn(CO)_2$(n-hept)], the principal intermediate in the photolysis of $[(C_5H_5)Mn(CO)_3]$ in n-heptane solution, there is both kinetic[4] and thermochemical evidence[5] for a significant interaction (*ca.* 40 kJ mol^{-1}) between the Mn centre and n-heptane. It is important to establish which factors determine the strength of such interactions. Are they an inherent property of the metal centre itself or can they be influenced by steric factors such as substituents on the cyclopentadienyl ring?

Time-resolved infrared spectroscopy (TRIR) has become a well established technique for identifying and studying intermediates in the photochemical reactions of transition metal carbonyl compounds.[1,6,7] The IR spectra provide a considerable amount of structural information while the relatively narrow linewidths of the ν(C—O) bands allow several different species to be monitored independently without significant spectral overlap. In this communication, we report TRIR measurements on the reactions of $[(\eta^5\text{-}C_5R_5)Mn(CO)_3]$ (R = H, Me and Et). These molecules are particularly suitable for TRIR experiments not only because the spectra of reactant and intermediates are comparatively simple but also because most of the reaction products are well characterized.[8,9]

Fig. 1 illustrates a representative set of TRIR spectra† for the flash photolysis of $[(C_5Et_5)Mn(CO)_3]$ in n-heptane under a pressure of H_2. These spectra show clearly the destruction of the parent $[(C_5Et_5)Mn(CO)_3]$ (band marked *P*), the transient formation of the $[(C_5Et_5)Mn(CO)_2$(n-hept)] intermediate, *I*, and the growth of the product $[(C_5Et_5)Mn(CO)_2(\eta^2\text{-}H_2)]$, *H*. Although these spectra are the first observation of both $[(C_5Et_5)Mn(CO)_2$(n-hept)] and $[(C_5Et_5)Mn(CO)_2(\eta^2\text{-}H_2)]$ in hydrocarbon solution, there is little doubt about the assignment of the bands; $[(C_5Et_5)Mn(CO)_2(\eta^2\text{-}H_2)]$ has previously been observed in high pressure supercritical CO_2 solution[10] and, apart from a shift to lower wavenumber, the bands of $[(C_5Et_5)Mn(CO)_2$(n-hept)] are similar to those of $[(C_5H_5)Mn(CO)_2$(n-hept)].[4] It is interesting, however, that the ν(C—O) bands of $[(C_5Et_5)Mn(CO)_2$(n-hept)] appear to have considerably lower extinction coefficients than the corresponding bands of $[(C_5Et_5)Mn(CO)_2(\eta^2\text{-}H_2)]$. This compound is one of an ever-increasing number of so-called 'non-classical' dihydrogen complexes.[11] Under these low pressure conditions, $[(C_5Et_5)Mn(CO)_2(\eta^2\text{-}H_2)]$ has a lifetime which is longer than

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† For further details of the TRIR equipment in Nottingham (pulsed 308 nm XeCl excimer laser, cw CO IR laser, HgCdTe detector) see ref. 7. n-Heptane (Aldrich HPLC grade) was dried over CaH_2. $[(C_5Et_5)Mn(CO)_3]$ (a gift from Dr A.G. Ginzburg of INEOS, Moscow), $[(C_5Me_5)Mn(CO)_3]$ (Strem) and $[(C_5H_5)Mn(CO)_3]$ were used without further purification and at a concentration of 1.0×10^{-3} mol dm^{-3}. Ar, CO, N_2 and H_2 (BOC Research grade) were used at a pressure of 2 atm (*ca.* 0.2 MPa) and the concentrations of these gases dissolved in n-heptane were taken from ref. 12.

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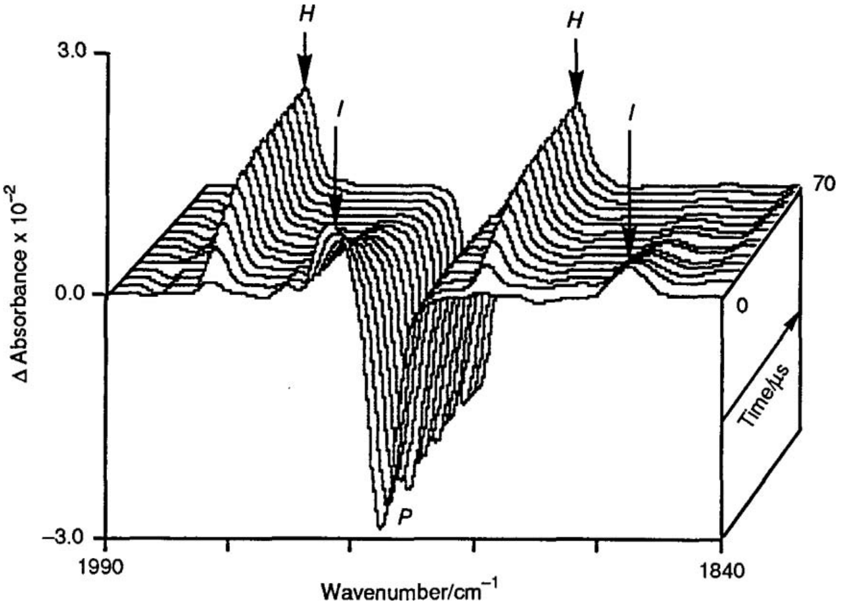

Fig. 1 Time-resolved IR difference spectra obtained in the ν(C—O) region illustrating the UV flash photolysis of $[(C_5Et_5)Mn(CO)_3]$ in n-heptane solution under 2 atm pressure of H_2. Bands are marked as follows: *P*, $[(C_5Et_5)Mn(CO)_3]$; *I*, $[(C_5Et_5)Mn(CO)_2(\text{n-hept})]$ intermediate; *H*, $[(C_5Et_5)Mn(CO)_2(\eta^2\text{-}H_2)]$. Spectra were recorded 'point-by-point' (with 37 points, *ca.* 4 cm^{-1} apart, over the spectral region illustrated) and were then interpolated by computer. The first spectrum illustrated corresponds to a time immediately after the UV flash which was instantaneous (*ca.* 20 ns) on this timescale; subsequent spectra are shown at 5 μs intervals.

can be measured with our TRIR apparatus (*i.e.* > 200 ms). Thus, the overall reaction is as shown in eqns. (1) and (2).

$$[(C_5Et_5)Mn(CO)_3] \xrightarrow{UV} [(C_5Et_5)Mn(CO)_2(\text{n-hept})] \quad (1)$$

$$[(C_5Et_5)Mn(CO)_2(\text{n-hept})] \xrightarrow[+H_2]{k_2} [(C_5Et_5)Mn(CO)_2(\eta^2\text{-}H_2)] \quad (2)$$

Fig. 2 illustrates TRIR kinetic traces for the reactions of all three complexes $[(C_5R_5)Mn(CO)_3]$ (R = H, Me and Et) with H_2. Similar traces were recorded for a series of other reactants. In each case, a large excess of reactant was used to ensure that the $[(C_5R_5)Mn(CO)_2(\text{n-hept})]$ intermediates displayed pseudo-first order kinetics. The values of the first-order rate constants increased with increasing concentration of ligand added to the solution. Table 1 summarizes the observed values together with the second-order rate constants calculated from them.‡

The following points are clear from Fig. 2 and the data in Table 1: (*a*) The rate constants for reaction of H_2, N_2 and CO with $[(C_5R_5)Mn(CO)_2(\text{n-hept})]$ increase significantly as R is changed from H to Me to Et. (*b*) For a particular substituent, R, the rate constants for reaction of H_2 and CO with $[(C_5R_5)Mn(CO)_2(\text{n-hept})]$ are similar while that for N_2 is slightly smaller. By contrast, the rate constant for reaction with the bulkier ligand, PPh_3, is substantially larger. (*c*) All three $[(C_5R_5)Mn(CO)_2(\text{n-hept})]$ intermediates have almost identical rate constants for reaction with PPh_3.

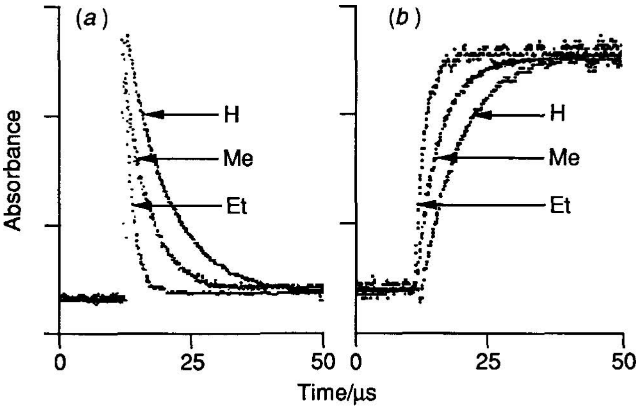

Fig. 2 Time-resolved IR kinetic traces illustrating (*a*) the disappearance of $[(C_5R_5)Mn(CO)_2(\text{n-hept})]$ (R = H, Me and Et) in n-heptane solution under 2 atm pressure of H_2 and (*b*) the appearance of the corresponding $[(C_5R_5)Mn(CO)_2(\eta^2\text{-}H_2)]$ complexes. Note that, although all three complexes are illustrated in a single Figure, the traces for each substituent (H, Me and Et) were recorded in separate experiments. The wavenumbers of the traces are listed in Table 1. Note that the traces have been normalized to the same absorbance (for absolute values see Fig. 1).

These results show that substitution on the cyclopentadienyl ring does indeed change the rates of reaction of the $[(C_5R_5)Mn(CO)_2(\text{n-hept})]$ intermediates with small molecules. The numerical values of the rate constants show significant differences not only between C_5H_5 and C_5Me_5 complexes but

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‡ Photolysis destroys less than 10% of the $[(C_5R_5)Mn(CO)_3]$ complex. Thus, even in the absence of added ligand (*e.g.* under an atmosphere of Ar), the $[(C_5R_5)Mn(CO)_2(\text{n-hept})]$ intermediates decay with pseudo-first order kinetics, because of reaction with starting material to form a dinuclear $[(C_5R_5)_2Mn_2(CO)_5]$ complex.[4] The value of k_{obs} for reaction with added ligand depends on the concentration of the ligand. Thus, for $[(C_5H_5)Mn(CO)_2(\text{n-hept})]$ and PPh_3, the reaction is first order in concentration of PPh_3 following a rate law: $k_{obs} = k_2[PPh_3] + c$, where *c* is the value of k_{obs} found for formation of the dinuclear species under Ar. This type of rate law has been used in calculating the second-order rate constants shown in Table 1. However, the corrections are relatively small and our overall conclusions are not therefore dependent on this particular calculation.

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Table 1 Rate constants[a] for the reactions of $[(C_5R_5)Mn(CO)_2$ (n-heptane)] (R = H, Me and Et) and the IR wavenumbers[b] used for monitoring the kinetics at 298 K

	ν(CO)/cm^{-1}		
Compound	R = H	Me	Et
$[(\eta^5\text{-}C_5R_5)Mn(CO)_3]$[c]	2028	2008	2008
	1947	1925	1927
$[(\eta^5\text{-}C_5R_5)Mn(CO)_2$(n-hept)]	1962	1942	1942
	1894	1873	1873
$[(\eta^5\text{-}C_5R_5)Mn(CO)_2(N_2)]$	[d]	1958	1958
	1932	1911	1912
$[(\eta^5\text{-}C_5R_5)Mn(CO)_2(\eta^2\text{-}H_2)]$	[d]	1967	1967
	1932	1907	1907

		Observed pseudo-first order rate constants[e] $k_{obs}/10^4$ s^{-1}		
Reactant	Conc./10^{-3} mol dm^{-3}	R = H	Me	Et
Ar	35	0.5	0.4	1.3
CO	24	2.4	4.3	14
N_2	19	1.4	2.5	6.0
H_2	9.1	1.3	2.0	6.1
PPh_3	2.0	3.0[f]	2.2	3.2

	Calculated second-order rate constants $k_2/10^6$dm^{3}mol^{-1}s^{-1}		
Reactant	R = H	Me	Et
CO	0.81	1.6	5.4
N_2	0.47	1.1	2.6
H_2	0.88	1.7	5.3
PPh_3	9.0	8.8	9.5

[a] Error of ± 10%. [b] Error of ± 2 cm^{-1}. [c] Wavenumbers of the parent compounds were obtained using FTIR (resolution 2 cm^{-1}). [d] Outside the tuning range of the CO laser. [e] Rates averaged over all wavenumbers monitored. [f] Concentration of PPh_3 2.8 × 10^{-3} mol dm^{-3}; values of $k_{obs}/10^4$ s^{-1} for other concentrations of PPh_3 2.0 [1.6 × 10^{-3} mol dm^{-3}] and 4.2 [4.1 × 10^{-3} mol dm^{-3}].

also between C_5Me_5 and C_5Et_5. This suggests that the origin of the effect is steric rather than electronic, because electronic factors§ should be similar for C_5Me_5 and C_5Et_5.

Recent studies on the reactions of solvated organometallic intermediates[13] have shown that displacement of the solvent is often a delicate balance between associative and dissociative processes. Our data do not allow us to distinguish between these processes in the case of $[(C_5R_5)Mn(CO)_2$(n-hept)]. However, given the differences in reaction rates with small molecules, it might seem surprising that all three $[(C_5R_5)Mn(CO)_2$(n-hept)] intermediates should react with PPh_3 at the same rate. There are, however, two processes which can be influenced by steric factors; the approach of the incoming ligand and the displacements of the n-heptane ligand. Steric interactions with molecules such as CO or H_2 are likely to be small and a weakening of the Mn ··· n-heptane interaction is probably the major effect. On the other hand, steric interactions with the incoming PPh_3 ligand are likely to be appreciable.

Whatever the precise nature of the steric interactions, these experiments show that substituents some distance from a metal centre can influence the rate of reaction at that centre. The size of the effect depends on the particular ligand involved in the reaction. This has significant implications for processes which involve competition between different ligands at a single metal centre; apparently minor modifications to peripheral ligands may well affect the competitive reaction substantially.

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§ In a series of similar compounds, the wavenumbers of the ν(C—O) bands gives an indication of electron density on a metal centre: the higher the wavenumber the lower the density. Thus, from the data in Table 1, the C_5H_5 compound has a lower electron density on the Mn centre than do the C_5Me_5 and C_5Et_5 complexes which have similar electron densities.