

Transient Spectroscopy and Kinetics of Monomeric Molybdenocene $\text{Mo}(\eta\text{-C}_5\text{H}_5)_2$ in Solution

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Flash photolysis of $\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2$ in tetrahydrofuran solution results in formation of $\text{Mo}(\eta\text{-C}_5\text{H}_5)_2$, identified by comparison of flash and matrix spectra; it decays in *ca.* 10 μs by reaction with $\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2$ or with CO.

Until the application of matrix isolation methods to the photochemistry of $\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{H}_2$ (**1**) and related complexes,¹ the monomeric metallocenes of molybdenum and tungsten were unknown. However, molybdenocene (**2**) had been postulated as the precursor to several complexes of the type $\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{L}$ and to dimeric complexes formed by insertion of Mo into a C–H bond of a co-ordinated C_5H_5 ligand.

The dimers are synthesised by photolysis of (**1**),² by photolysis of $\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{CO}$ (**3**),³ or by reduction of $\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2$.³ The matrix experiments demonstrated that both (**2**) and $\text{W}(\eta\text{-C}_5\text{H}_5)_2$ have paramagnetic ground states and parallel sandwich structures, but that Jahn–Teller effects are important in (**2**).^{1,4} We report flash photolysis experiments on (**1**) which show production of molybdenocene and the kinetics of its reactions with (**1**) and with CO.

Laser flash photolysis‡ of N_2 -saturated, dry tetrahydrofuran (thf) solutions of (**1**) yielded a transient with a risetime of *ca.* 25 ns, which decayed with a lifetime of *ca.* 10^{-5} s. The decay was first order in the transient but the lifetime was significantly dependent on the concentration of (**1**) ($k_1 = 1.1\text{--}1.8 \times 10^5 \text{ s}^{-1}$). Assuming a first order dependence on (**1**), the second order rate constant is $0.34 \pm 0.05 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. A difference spectrum of the transient between 295 and 770 nm showed a prominent peak at 394 nm (onset 419 nm)§ and significant bleaching at 325 and 295 nm (Figure 1a). Comparison of the transient spectrum with that of (**2**) in Ar (Figure 1b, maximum 395.8, onset 420 nm) shows remarkable agreement between the spectra, strongly supporting the identification of the transient with (**2**). The bleaching at short wavelength is consistent with loss of (**1**),⁶ complicated by an absorption of (**2**) at 315 nm (305 nm in Ar).¹

If our identification of the transient is correct it should react with suitable donor ligands faster than it forms dimers. Matrix isolation experiments show reaction of (**2**) with CO at 60 K, suggesting a very low activation energy.¹ Flash photolysis of (**1**) in CO-saturated solutions showed a reduction in lifetime of the transient by a factor of two relative to the same solution under N_2 (Figure 2, $k_2 = 7 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$).§ The reaction product is assumed to be (**3**) as in the matrix. The transient was not quenched by cyclohexene (up to 0.03 mol dm^{-3}) or acrylonitrile (up to 1.1 mol dm^{-3}).

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‡ The apparatus is identical to that described in ref. 5 except that a Lumonics XeCl laser (wavelength 308 nm, flash duration *ca.* 4 ns, energy 80 mJ/pulse) was used as the excitation source. The solutions were $3\text{--}5 \times 10^{-4} \text{ M}$ in (**1**) and were flowed through a 7 mm pathlength cuvette. The onset of absorption is defined as the wavelength at which the absorbance is 10% of maximum.

§ Assuming a first order dependence on [CO] and a CO concentration of $1.8 \times 10^{-2} \text{ mol dm}^{-3}$.⁷

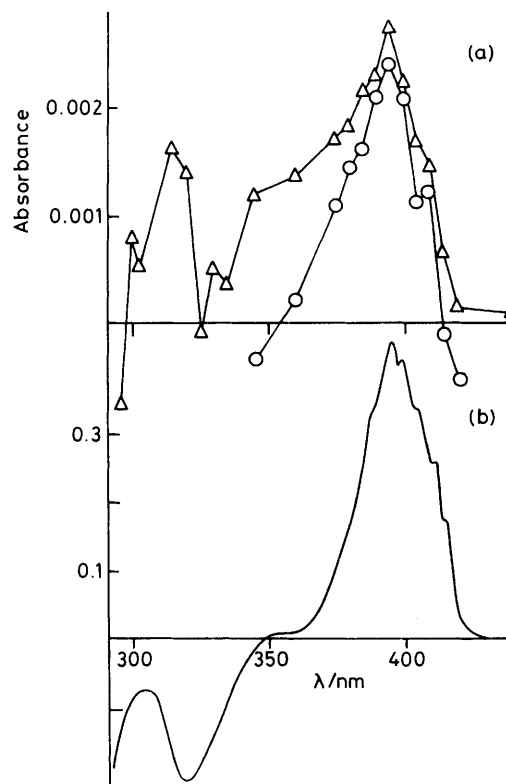


Figure 1. (a) Difference spectrum generated by flash photolysis of (**1**) in thf at 300 K ($4 \times 10^{-4} \text{ mol dm}^{-3}$). Each point is the average of 8 shots. Δ , Average of data recorded in the first 4 μs after the flash. \circ , Same but with the residual absorption remaining after 20 μs subtracted. (b) Difference spectrum resulting from photolysis of (**1**) in Ar at 20 K (see ref. 1). In both (a) and (b) positive absorptions are due to (**2**) and negative absorptions to (**1**).

A plausible reaction scheme which takes account of the flash photolysis experiments, the static photolysis experiments on (**1**) and on the dimer (**4**)² is shown in Scheme 1.¶

The flash photolysis results establish by direct detection: (i), that the product of photolysis of (**1**) in solution is the metallocene (**2**); (ii), that molybdenocene is highly reactive towards (**1**) and towards CO; (iii), that the primary reaction pathway in matrices and in solution is the same. Moreover, the similarity of the solution and matrix spectra of (**2**) shows that intersystem crossing to the 3E_2 ground state of (**2**) must occur within 25 ns. The interpretation of these results highlights the

¶ An alternative assignment of the transient to the solvent adduct $(\eta\text{-C}_5\text{H}_5)_2\text{Mo}(\text{thf})$ has been suggested by a referee. However, it is inconsistent with the position of the intense absorption maximum at 394 nm. The first intense ($\epsilon \geq 1000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) u.v. band of known $(\eta\text{-C}_5\text{H}_5)_2\text{ML}$ (M = Mo, W) complexes lies in the range 264–275 nm; a similar spectrum is expected for $(\eta\text{-C}_5\text{H}_5)_2\text{Mo}(\text{thf})$.

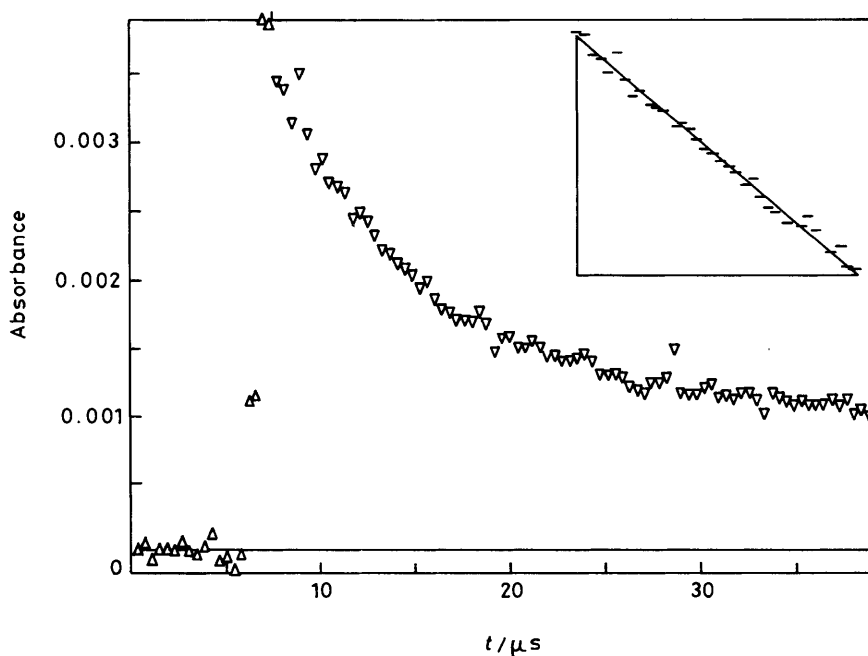
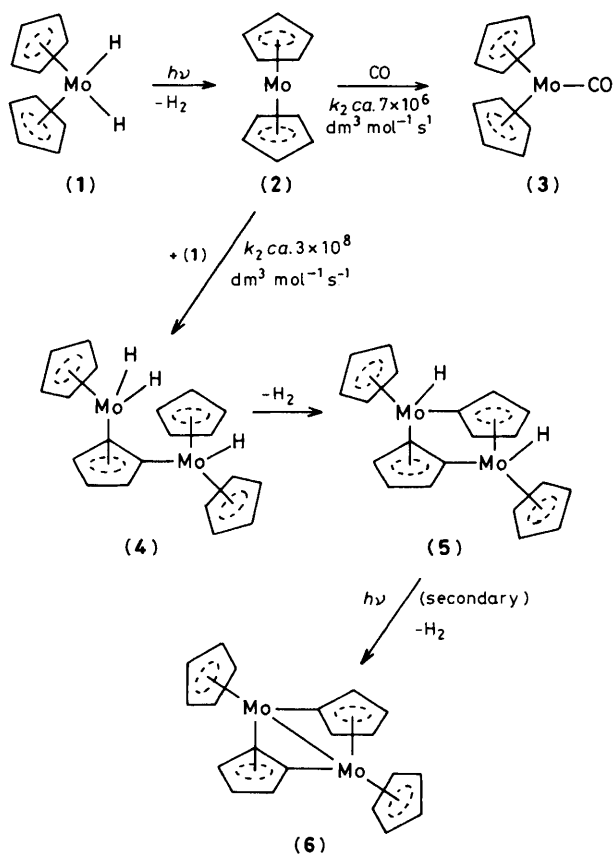


Figure 2. Kinetic plot of (2) following flash photolysis of (1) in thf (5×10^{-4} mol dm $^{-3}$) saturated with CO (average of 15 shots, monitoring wavelength 395 nm, temp. 298 K). The inset shows a semi-logarithmic plot giving a lifetime of 7.8 μ s. The same solution gave a lifetime for (2) of 15.3 μ s when saturated with N $_2$.



Scheme 1

complementary use of matrix isolation and flash photolysis, a combination which has also proved most effective in interpreting the photochemistry of $M(\text{CO})_6$ ($M = \text{Cr}, \text{Mo}, \text{W}$).⁸⁻¹¹

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