J. CHEM. SOC., CHEM. COMMUN., 1983

Spectroscopic Evidence for the Formation of Tri-μ-carbonyl-bis-[(η⁵-cyclopentadienyl)iron] on Photolysis of Bis[(dicarbonyl)(η⁵-cyclopentadienyl)iron] in Low Temperature Matrices

Richard H. Hooker, Khalil A. Mahmoud, and Antony J. Rest*

Department of Chemistry, The University, Southampton SO9 5NH, U.K.

Photolysis of $[{(\eta^5-C_5H_5)Fe(CO)_2}_2]$ in CH₄ (12 K) and polyvinyl chloride film (12—77 K) matrices leads to the formation of a novel species proposed, on the basis of i.r. evidence including ¹³CO enrichment and u.v.-visible spectra, to be the CO-bridged dimer $[(\mu$ -CO)₃{(η^5 -C₅H₅)Fe}_2].

A recent flash photolysis study¹ of the photochemistry of $[\{(\eta^5-C_5H_5)Fe(CO)_2\}_2]$ (1) provided evidence for two distinct primary photoprocesses [equations (1) and (2)]. The identities of species (2) and (3) were proposed on the basis of their life-times and u.v.-visible spectra together with the observation of a back reaction of (2) with CO; (2) was long lived and (3) was short lived. No definitive structural evidence was provided.

$$[\{(\eta^{5}\text{-}C_{5}H_{5})\text{Fe}(\text{CO})_{2}\}_{2}] \xrightarrow{h\nu} [(\eta^{5}\text{-}C_{5}H_{5})_{2}\text{Fe}_{2}(\text{CO})_{3}] + \text{CO} \quad (1)$$
(1)
(2)

$$[\{ (\eta^{\delta} - C_5 H_5) Fe(CO)_2 \}_2] \xrightarrow{h\nu} 2[(\eta^{\delta} - C_5 H_5) Fe(CO)_2^{\bullet}]$$
(2)
(3)

The photoreactions of (1) with phosphine and phosphite ligands² to give substitution products, *e.g.* $[(\eta^5-C_5H_5)_2Fe_2-(CO)_3(PPh_3)]$ have been proposed to proceed *via* the CO-bridged intermediate $[(\eta^5-C_5H_5)(CO)_2Fe-(\mu-CO)-Fe(CO)(\eta^5-C_5H_5)]^3$ and also *via* a radical pathway.⁴

We have studied the photoreactions of (1) isolated in polyvinyl chloride films at 12-298 K and in frozen gas matrices at 12 K and we report here the generation of a novel dimeric species which we relate to the intermediates proposed in flash photolysis and solution photoreactions.

The i.r. spectrum of (1) in a polyvinyl chloride (pvc) film^{\dagger} matrix at 12 K is shown in Figure 1(a). Two terminal CO

[†] The preparation of pvc film matrices and their use over a wide temperature range have been described previously.⁵



Figure 1. I.r. spectra from an experiment with $[\{(\eta^5-C_5H_5)Fe-(CO)_2\}_2]$ (1) in a pvc film matrix at 12 K: (a) before irradiation, (b) after 150 min irradiation ($\lambda > 400$ nm), and (c) after warming the matrix to 200 K. (Nicolet 7199 FTIR spectrometer; resolution 1 cm⁻¹, 100 scans.) The bands marked C and T are for the *cis*- and *trans*-isomers of (1), respectively, and that marked * is for (4).

stretching bands at 1992 and 1952 cm⁻¹, which have been assigned to the cis- and trans-isomers respectively,6 are seen together with bridging CO stretching bands at 1804 and 1772 cm⁻¹. On irradiation (λ >400 nm) a new absorption appeared at 1812 cm⁻¹ together with a band due to free CO at 2133 cm⁻¹ whilst the parent bands at 1952 and 1772 cm⁻¹ decreased in intensity [Figure 1(b)]. A spectral subtraction showed that there were no new product bands in the terminal CO stretching region and that only a slight reduction in the band of the cis-isomer of (1) had occurred. The photoproduct, which is also observed to be formed at 77 K and in CH₄ matrices at 12 K, has an electronic absorption band exhibiting vibronic fine structure ($\lambda_{max} = 510$ nm, $\bar{\nu} = 194$ cm⁻¹; CH₄ matrix) which is indicative of a highly symmetric species, cf. (η^{5} - $C_5H_5)_2W$.⁷ The reaction is reversible so that irradiation with visible light (λ >500 nm) or warming a pvc matrix to *ca*. 200 K completely regenerates the parent complex (1) [Figure 1(c)].

The photoproduct[‡] is evidently formed by dissociative loss of CO from (1) and in particular from the *trans*-isomer exclusively. The fact that it has only one bridging CO stretching band which is i.r. active and this band is at a higher wavenumber than those of (1) suggests that the new species is $[(\mu-CO)_3 \{(\eta^5-C_5H_5)Fe\}_2]$ with three equivalent bridging CO ligands $[(4); D_{3h}$ local symmetry]. The similarly symmetric



Figure 2. (a) I.r. spectrum (Nicolet 7199 FTIR spectrometer; resolution 1 cm⁻¹, 100 scans) obtained following irradiation (λ >400 nm) of a ¹³CO-enriched (30%) sample of (1) in a CH₄ matrix at 12 K and from which the absorptions for the remaining starting material have been subtracted out; (b) calculated spectrum for the CO-bridged species [M(¹²CO)₈-m(¹³CO)_mM] (m = 0-3) where the intensities were obtained for a ¹²CO:¹³CO ratio of 1:0.33 and used the energy-factored CO force constants (K = 1369.1 and $k_1 = 41.1$ N m⁻¹) which gave the best fit between observed and calculated band positions.

dimer $[Fe_2(CO)_9]$ has one bridging CO stretching band⁹ at 1828 cm⁻¹. The product (4) is also similar to the photogenerated dimers $[(\mu$ -CO)₃ {(η^4 -C₄Ph₄)Fe }₂] (5) and $[(\mu$ -CO)₃{ η^5 -C₅Me₅)Re}₂] (6) which are proposed to have iron-iron¹⁰ and rhenium-rhenium¹¹ triple bonds.

Irradiation $(\lambda > 400 \text{ nm})$ of $[\{(\eta^5-C_5H_5)\text{Fe}(^{12}\text{CO})_{2-n}(^{13}\text{CO})_n\}_2]$ (n = 0-2) in a CH₄ matrix gave new i.r. absorption bands at 1813, 1791, 1779, and 1772 cm⁻¹. The intensity pattern and

[‡] Irradiation of (1) in pvc films at 12–77 K with u.v. light (300 $<\lambda <$ 390 nm) gave rise to another photoproduct which, on warming, reacts with the matrix to form $[(\eta^5-C_8H_5)Fe(CO)_2CI].^8$

[§] Prepared by photolysis ($\lambda > 300$ nm) of (1) in hexane-tetrahydrofuran in an atmosphere of ¹³CO (300 Torr) for 2 h.

positions of these bands could be fitted exactly by using an energy-factored force field for D_{3h} symmetry¹²⁻¹⁴ (Figure 2) and are consistent with the formation of the species $[(\mu^{-12}CO)_{3-m}(\mu^{-13}CO)_m \{(\eta^5-C_5H_5)Fe\}_2]$ (m = 0-3).

The electronic absorption band of (4) is at the same wavelength (λ_{max} 510 nm) as that of the CO-loss species (2) detected in the flash photolysis experiment.¹ It seems probable, therefore, that (2), which has been proposed to have the stoicheiometry shown in equation (1), is identical with (4). Thus the work in low temperature matrices provides the *first* direct evidence for the structure of an intermediate proposed in the photochemical reactions of a metal-metal bonded dimer.

We thank Professor A. Oskam and Dr. J. S. Ogden for helpful discussions, the S.E.R.C. for a Research Studentship (to R.H.H.) and for support (to A.J.R.), and the University of Lebanon Faculty of Science for a Studentship (to K.A.M.).

Received, 1st June 1983; Com. 687

References

1 J. V. Caspar and T. J. Meyer, J. Am. Chem. Soc., 1980, 102, 7794.

- R. J. Haines and A. L. duPreez, *Inorg. Chem.*, 1969, 8, 1459.
 H. B. Gray, M. A. Schmidt, and D. R. Tyler, *J. Am. Chem. Soc.*, 1979, 101, 2753.
- 4 H. B. Abrahamson, M. C. Palazotto, C. L. Reichel, and M. S. Wrighton, J. Am. Chem. Soc., 1979, **101**, 4123.
- 5 T. Cassen, N. Geacintov, and G. Oster, J. Opt. Soc. Am., 1968, 58, 1217; R. H. Hooker and A. J. Rest, J. Organomet. Chem., 1983, 249, 127.
- 6 A. R. Manning, J. Chem. Soc. A, 1968, 1319.
- 7 J. Chetwynd-Talbot, P. Grebenik, R. N. Perutz, and M. H. A. Powell, *Inorg. Chem.*, 1983, **22**, 1675.
- 8 R. H. Hooker and A. J. Rest, unpublished work.
- 9 K. S. Pitzer and R. K. Sheline, J. Am. Chem. Soc., 1950, 72, 1107.
 10 S. I. Murahashi, T. Mizozushi, T. Hooskaus, J. Maritari, Y.
- 10 S. I. Murahashi, T. Mizoguchi, T. Hosokawa, I. Moritani, Y. Kai, M. Kohara, N. Yasuoka, and N. Kasai, J. Chem. Soc., Chem. Commun., 1974, 563.
- 11 J. K. Hoyano and W. A. G. Graham, J. Chem. Soc., Chem. Commun., 1982, 27.
- 12 E. B. Wilson, J. C. Decius, and P. C. Cross, 'Molecular Vibrations,' McGraw-Hill, New York, 1955.
- 13 J. H. Darling and J. S. Ogden, J. Chem. Soc., Dalton. Trans., 1972, 2496.
- 14 H. Huber, E. P. Kündig, M. Moskovits, and G. A. Ozin, J. Am. Chem. Soc., 1973, 95, 332.