Spectroscopic Evidence for the Formation of Tri-μ-carbonyl-bis-[(η^5-cyclopentadienyl)iron] on Photolysis of Bis[(dicarbonyl)(η^5-cyclopentadienyl)iron] in Low Temperature Matrices

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Photolysis of $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ in CH_4 (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 ^{13}CO enrichment and u.v.–visible spectra, to be the CO-bridged dimer $[(\mu\text{-}CO)_3\{(\eta^5\text{-}C_5H_5)Fe\}_2]$.

A recent flash photolysis study[1] of the photochemistry of $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$ (**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 lifetimes 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.

$$\underset{(\mathbf{1})}{[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]} \xrightarrow{h\nu} \underset{(\mathbf{2})}{[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3]} + CO \qquad (1)$$

$$[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2] \xrightarrow{h\nu} 2\underset{(\mathbf{3})}{[(\eta^5\text{-}C_5H_5)Fe(CO)_2{}^{\bullet}]} \qquad (2)$$

The photoreactions of (**1**) with phosphine and phosphite ligands[2] to give substitution products, *e.g.* $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(PPh_3)]$ have been proposed to proceed *via* the CO-bridged intermediate $[(\eta^5\text{-}C_5H_5)(CO)_2Fe\text{-}(\mu\text{-}CO)\text{-}Fe(CO)(\eta^5\text{-}C_5H_5)]$[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† matrix at 12 K is shown in Figure 1(a). Two terminal CO

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

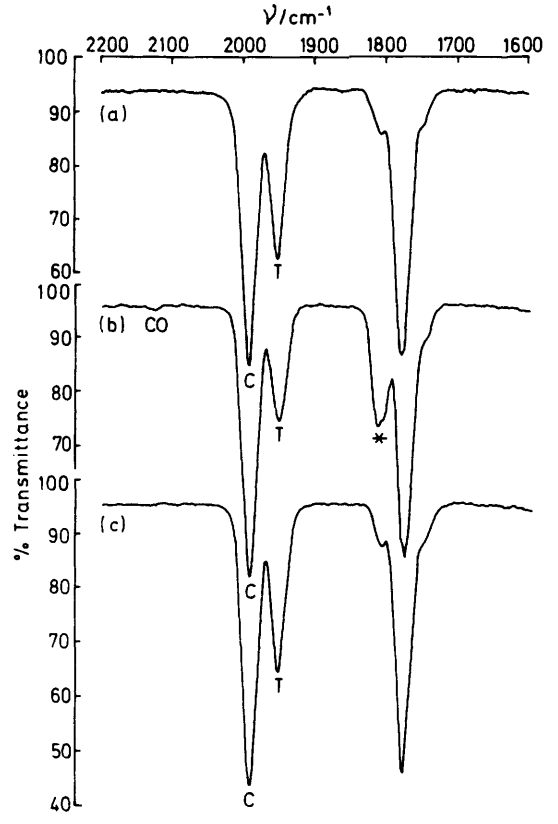
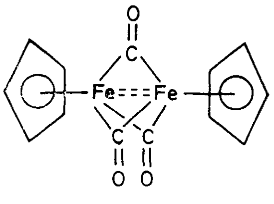


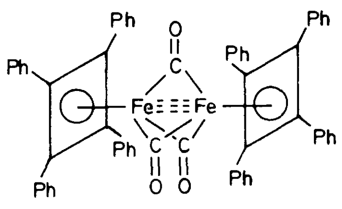
Figure 1. I.r. spectra from an experiment with [{(η^5-C_5H_5)Fe-$(CO)_2$}$_2$] (**1**) in a pvc film matrix at 12 K: (a) before irradiation, (b) after 150 min irradiation (λ>400 nm), and (c) after warming the matrix to 200 K. (Nicolet 7199 FTIR spectrometer; resolution 1 cm^{-1}, 100 scans.) The bands 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 CH_4 matrices at 12 K, has an electronic absorption band exhibiting vibronic fine structure (λ_{max} = 510 nm, $\bar{\nu}$ = 194 cm^{-1}; CH_4 matrix) which is indicative of a highly symmetric species, *cf.* (η^5-C_5H_5)$_2$W.[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)].

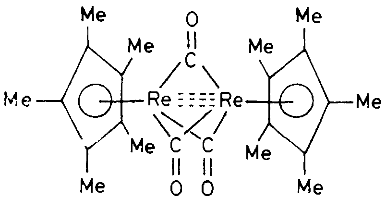
The photoproduct‡ is evidently formed by dissociative loss of CO from (**1**) and in particular from the *trans*-isomer exclusively. The fact that it has only one bridging CO stretching band which is i.r. active and this band is at a higher wavenumber than those of (**1**) suggests that the new species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



(**4**)



(**5**)



(**6**)

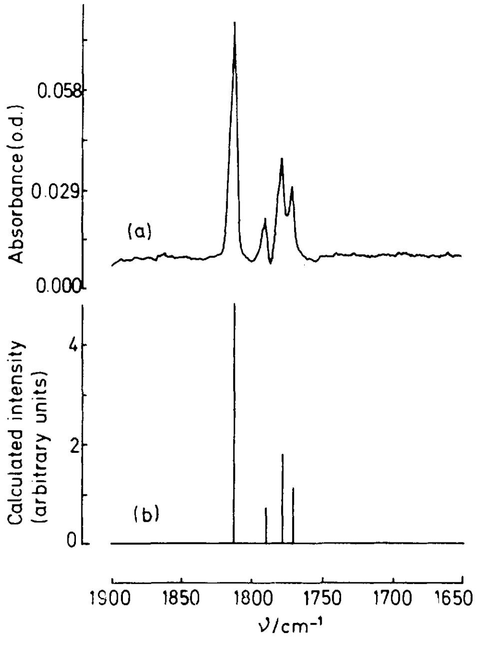


Figure 2. (a) I.r. spectrum (Nicolet 7199 FTIR spectrometer; resolution 1 cm^{-1}, 100 scans) obtained following irradiation (λ>400 nm) of a ^{13}CO-enriched (30%) sample of (**1**) in a CH_4 matrix at 12 K and from which the absorptions for the remaining starting material have been subtracted out; (b) calculated spectrum for the CO-bridged species [M(^{12}CO)$_{3-m}$(^{13}CO)$_m$M] (m = 0—3) where the intensities were obtained for a ^{12}CO:^{13}CO ratio of 1:0.33 and used the energy-factored CO force constants (K = 1369.1 and k_i = 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 band[9] at 1828 cm^{-1}. The product (**4**) is also similar to the photogenerated dimers [(μ-CO)$_3$ {(η^4-C_4Ph_4)Fe}$_2$] (**5**) and [(μ-CO)$_3${(η^5-C_5Me_5)Re}$_2$] (**6**) which are proposed to have iron–iron[10] and rhenium–rhenium[11] triple bonds.

Irradiation (λ>400 nm) of [{(η^5-C_5H_5)Fe(^{12}CO)$_{2-n}$(^{13}CO)$_n$}$_2$] (n = 0—2)§ in a CH_4 matrix gave new i.r. absorption bands at 1813, 1791, 1779, and 1772 cm^{-1}. The intensity pattern and

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‡ Irradiation of (**1**) in pvc films at 12—77 K with u.v. light (300 < λ < 390 nm) gave rise to another photoproduct which, on warming, reacts with the matrix to form [(η^5-C_5H_5)Fe$(CO)_2$Cl].[8]

§ Prepared by photolysis (λ >300 nm) of (**1**) in hexane–tetrahydrofuran in an atmosphere of ^{13}CO (300 Torr) for 2 h.

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

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