Formation of (η-Cyclopentadienone)tricarbonyliron on the Photolysis of (η-Cyclobutadiene)tricarbonyliron in a Carbon Monoxide Matrix at 12 K

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Summary I.r. spectroscopic evidence, including ^{13}CO labelling and energy-factored force-field fitting, is presented to show that photolysis of $(\eta^4\text{-}C_4H_4)Fe(CO)_3$ in a CO matrix at 12 K leads to the formation of $(\eta^4\text{-}C_5H_4O)\text{-}Fe(CO)_3$.

The reactions of $Fe(CO)_5$ with acetylenes have led to the isolation of a wide variety of products including (η-cyclopentadienone)tricarbonyliron and (η-quinone)tricarbonyliron complexes, (1) and (2) respectively.[1-5] Some of these

(1)   **(2)**
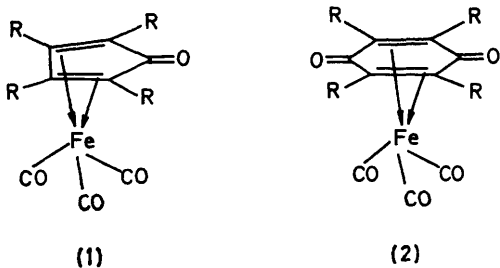
R = H, Me, Ph

reactions were photochemical reactions. Corresponding reactions starting from $(\eta\text{-}C_5H_5)Co(CO)_2$ afforded (η-cyclobutadiene)(η-cyclopentadienyl)cobalt complexes (3) and hexasubstituted benzenes in addition to (η-cyclopentadienone)(η-cyclopentadienyl)cobalt complexes (4).[3]

(3)   **(4)**

R = Me, Ph

Recent careful work has shown that, in the latter reaction, monoacetylene complexes (5) and metallocycle complexes (6) could be considered as reaction intermediates.[6] We now

(5)   **(6)**
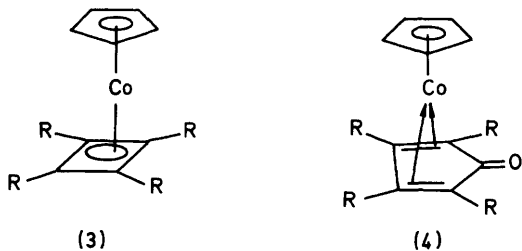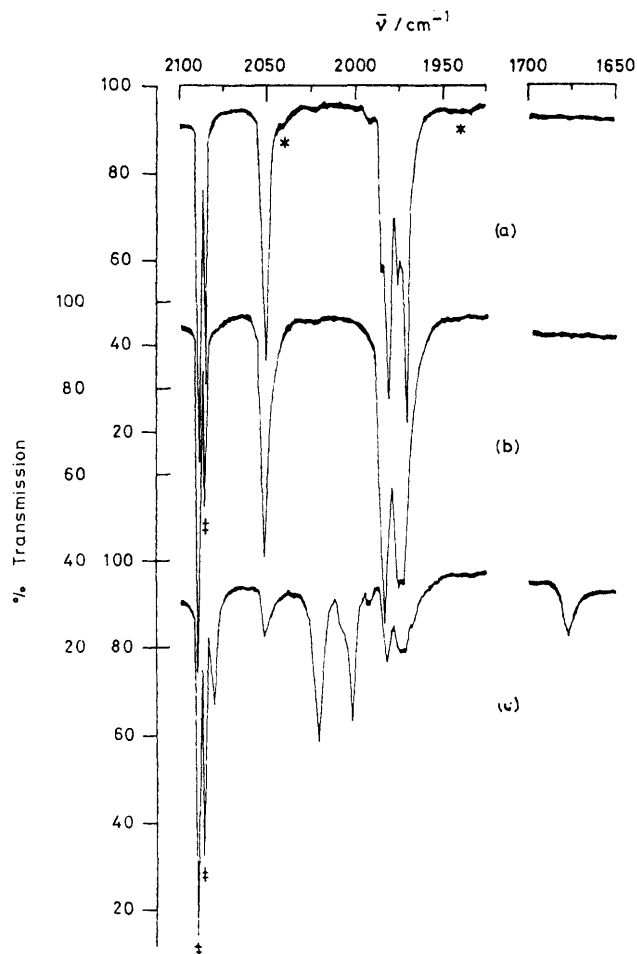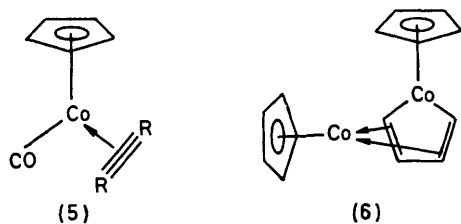
report evidence to show the formation of (1) on the photolysis of $(\eta^4\text{-}C_4H_4)Fe(CO)_3$ isolated in a CO matrix at 12 K.

Figure. I.r. spectra in the 2150—1600 cm^{-1} region (Grubb Parsons Spectromajor) from an experiment with $(\eta^4\text{-}C_4H_4)Fe(CO)_3$ isolated in a CO matrix (1:2000) at 12 K: (a) after deposition, (b) after brief photolysis with a filtered medium pressure Hg arc ($\lambda < 270$, $\lambda > 550$ nm), and (c) after prolonged photolysis with an unfiltered medium-pressure Hg arc. See text for an explanation of bands marked * and ‡.
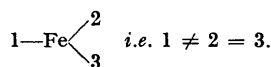
The i.r. spectra obtained from an experiment with $(\eta^4\text{-}C_4H_4)Fe(CO)_3$ isolated in a CO matrix are shown in the Figure. After pulsed deposition of a 1:2000 gas mixture the spectrum in the 2150—1600 cm^{-1} region, Figure (a), shows the two terminal carbonyl stretching modes corresponding to the symmetric (A_1, 2053·7 cm^{-1}) and antisymmetric (E, 1980·8 cm^{-1}) modes of the C_{3v} $Fe(CO)_3$ fragment, the natural abundance bands of isotopes of CO (bands marked ‡) and the natural abundance bands of $(\eta^4\text{-}C_4H_4)Fe(^{12}CO)_2$-

(^{13}CO) (bands marked *). Brief u.v. photolysis ($\lambda < 270$, $\lambda > 550$ nm; filtered medium-pressure mercury arc, Philips HPK 125 W) produced no new bands, Figure (b), but caused a change in the splitting pattern† of the E mode, which was reversed by annealing the matrix. Further photolysis with the unfiltered arc caused the growth, Figure (c), of three new bands in the terminal carbonyl stretching region (2081·5, 2024·8, and 2005·6 cm^{-1}), together with a band at 1673·5 cm^{-1}. In a number of experiments these bands grew with the same relative intensities and thus they can be assigned to a single product which must, on account of the dilution, be a mononuclear complex. The overall shift of the band pattern to high wavenumbers for the product is characteristic of an increase in the number of CO ligands, i.e. (η^2-C$_4$H$_4$)Fe(CO)$_4$ by analogy with (η^3-C$_5$H$_5$)Co(CO)$_3$, formed on photolysis of (η^5-C$_5$H$_5$)Co(CO)$_2$ in a CO matrix.[7] However, a number of observations suggest that this possibility is unlikely. (i) Having obtained the bands for a ^{13}CO enriched product it proved impossible to fit them, using an energy-factored force-field, to an Fe(CO)$_4$ fragment no matter what local symmetry was assumed. However, fitting of the observed and calculated bands for a C_s Fe(CO)$_3$ fragment gave excellent agreement (Table). (ii) The low wavenumber band (1673·5 cm^{-1}) shifted to 1632·6 cm^{-1} in the ^{13}CO-enriched product. This shift is con-

sistent with the expected[8] (^{12}C/^{13}C) isotope shift (1635·5 cm^{-1}) and the band position enables this band to be assigned as a ketonic carbonyl stretching band rather than an M–CO–M bridging band (1850—1700 cm^{-1}).

The identification of the new species as (η^4-C$_5$H$_4$O)-Fe(CO)$_3$ (1) was confirmed by separate experiments with an authentic sample isolated at high dilution in CO [ν_{CO} (terminal): 2081·2, 2024·5, and 2005·6 cm^{-1}, ν_{CO} (ketonic): 1673·5 cm^{-1}] and Ar [ν_{CO} (terminal): 2085·0, 2027·5, and 2066·8 cm^{-1}, ν_{CO} (ketonic): 1690·0 cm^{-1}] matrices.[9] It is surprising that there is a large shift of the ketonic carbonyl stretching vibration on going from CO to Ar matrices whereas the terminal metal carbonyl stretching vibrations are much less sensitive with respect to the medium. The ketonic carbonyl stretching vibration shows a similar large shift for a variety of solvents, e.g. Et$_2$O (1673 cm^{-1}), CCl$_4$ (1667 cm^{-1}), KBr (1630 cm^{-1}), and Nujol (1634 cm^{-1}).[10,11]

Table. Observed and calculated[a] wavenumbers (cm^{-1}) of terminal CO stretching bands of ^{13}CO-enriched (η-C$_5$H$_4$O)Fe(CO)$_3$ in a CO matrix at 12 K.

Complex	Point group	Observed	Calculated
(η-C$_5$H$_4$O)Fe(^{12}CO)$_3$	C_s	2081·5	2080·8
		2024·8	2024·9
		2005·6	2004·9
(η-C$_5$H$_4$O)Fe(^{12}CO)$_2$(^{13}CO)	C_s	—[b]	2064·9
		2005·6	2004·9
		1995·0	1995·1
(η-C$_5$H$_4$O)Fe(^{12}CO)$_2$(^{13}CO)	C_1	2074·4	2073·8
		1971·7	1971·9
		2019·6	2019·8
(η-C$_5$H$_4$O)Fe(^{12}CO)(^{13}CO)$_2$	C_1	2053·6	2052·9
		1996·9	1997·1
		—[b]	1969·8
(η-C$_5$H$_4$O)Fe(^{12}CO)(^{13}CO)$_2$	C_s	2067·3	2066·8
		1993·8	1993·3
		1959·6	1960·3
(η-C$_5$H$_4$O)Fe(^{13}CO)$_3$	C_s	2033·9	2034·6
		1980·9	1979·6
		1959·6	1960·3

[a] Refined energy-factored force constants: $K_1 = 1705\cdot3$, $K_2 = 1662\cdot2$, $k_{12} = 32\cdot7$ and $k_{23} = 38\cdot3$ N m^{-1} as defined by the numbering

$$1-Fe\begin{matrix}2\\\\3\end{matrix} \quad i.e. \; 1 \neq 2 = 3.$$

[b] Band obscured by other bands.

(7)

Scheme

The insertion of CO into the cyclobutadiene ring may possibly be considered to occur via the equilibrium shown in the Scheme, where (7) is a metallocycle complex similar to (6).[6] Future work will seek further to probe the mechanisms of the reactions of Fe(CO)$_5$ and (η^5-C$_5$H$_5$)Co(CO)$_2$ by photolysing these complexes in acetylene or acetylene-doped matrices and will also investigate the photoreactions of (η^4-C$_5$H$_4$O)Fe(CO)$_3$ in matrices at 12 K.

† The local C_{3v} symmetry assumption is an oversimplification but the main ca. 8 cm^{-1} splitting of the E mode, Figure (a), is within the normal range of matrix-splitting effects ('Vibrational Spectroscopy of Trapped Species,' ed. H. E. Hallam, Wiley, London, 1973) and until the causes of such effects are better understood it seems better not to speculate here about the splitting patterns.

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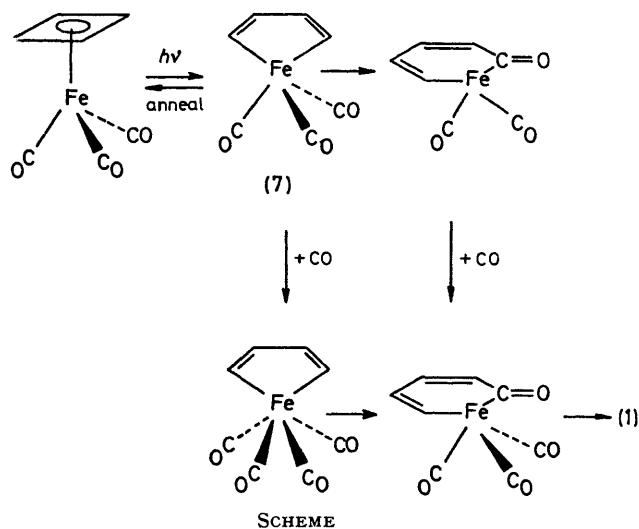[8] P. S. Braterman, 'Metal Carbonyl Spectra,' Academic Press, London, 1975.
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