Photochemistry of Methyl- and Acetyl-dicarbonyl(η-cyclopentadienyl)-iron in Frozen Gas Matrices at 12 K. Infrared Spectroscopic Evidence for the Formation of Tricarbonyl(η-cyclopentadienyl)methyliron and Acetyl-monocarbonyl(η-cyclopentadienyl)iron

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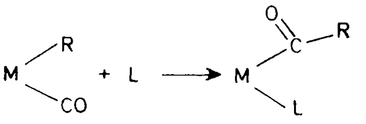
Infrared spectroscopic evidence is presented to show that, on photolysis of [Fe(η^5-C_5H_5)(CO)$_2$(CH$_3$)] at high dilution in CO matrices at 12 K, a new species [Fe(η^3-C_5H_5)(CO)$_3$(CH$_3$)] is produced. No evidence has been found for the formation of [Fe(η^5-C_5H_5)(CO)(CH$_3$)] in Ar, CH$_4$, and N$_2$ matrices nor [Fe(η^5-C_5H_5)(CO)$_2$-(COCH$_3$)] in CO matrices, although in ^{13}CO-doped matrices rapid exchange was observed. Wavelength-selective photolysis of [Fe(η^5-C_5H_5)(CO)$_2$(COCH$_3$)] in Ar, CH$_4$, and CO matrices produces [Fe(η^5-C_5H_5)(CO)$_2$(CH$_3$)] *via* the co-ordinatively unsaturated intermediate [Fe(η^5-C_5H_5)(CO)(COCH$_3$)]. The rapid exchange of ^{12}CO ligands in [Fe(η^5-C_5H_5)(CO)$_2$(CH$_3$)] with ^{13}CO in the matrix, the expanded-co-ordination-number species [Fe(η^3-C_5H_5)-(CO)$_3$(CH$_3$)], and the co-ordinatively unsaturated species [Fe(η^5-C_5H_5)(CO)(COCH$_3$)] are discussed in relation to the mechanisms of the insertion reactions of [Fe(η^5-C_5H_5)(CO)$_2$(CH$_3$)] and the thermal and photochemical decarbonylation reactions of [Fe(η^5-C_5H_5)(CO)$_2$(COCH$_3$)].

MANY organometallic reactions are covered by the general equation (1), where M is a metal complete with ancillary ligands and X and Y are monoatomic or polyatomic species.

$$M-X + Y \longrightarrow M-Y-X \qquad (1)$$

These processes are termed ' insertion ' reactions.[1] The description carries no mechanistic connotations but merely reflects the overall structural change that has taken place. Some examples of M–X in equation (1) are M–H, M–C, M–halogen, M–O, and M–M, and examples of Y are CO, SO$_2$, SO$_3$, carbenes, olefins, and organic isocyanides.[1] Insertion reactions can be regarded as intra- or inter-molecular depending on whether Y was preco-ordinated to M or not. The most common reaction is of the type shown in equation (2),



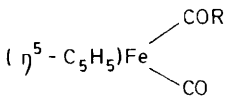
(2)

where an acyl addition (1,1) occurs rather than a carbene addition (1,2), *e.g.* the thermal reaction [equation (3)] of [Fe(η^5-C_5H_5)(CO)$_2$(CH$_3$)] with phosphines. When CO is the incoming nucleophile [equation (2)] forcing conditions

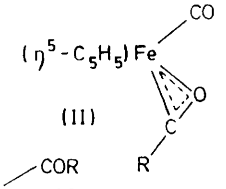
$$[Fe(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)] + PR_3 \longrightarrow [Fe(\eta^5\text{-}C_5H_5)(CO)(COCH_3)(PR_3)] \qquad (3)$$

(125 °C, 2 000 p.s.i.† CO) are required in order to obtain [Fe(η^5-C_5H_5)(CO)$_2$(COCH$_3$)].[1]

Kinetic studies of the thermal insertion reactions of [Fe(η^5-C_5H_5)(CO)$_2$R] complexes indicate that the alkyl-migration reactions are solvent and/or nucleophile assisted and are suggested to proceed *via* an intermediate [(I), (II), or (III)] which is attacked by the incoming ligand (L).[2,3] The photochemical reactions of [Fe-(η^5-C_5H_5)(CO)$_2$R] with phosphine donors yield [Fe(η^5-C_5H_5)(CO)(L)R] and CO[4-6] but in some circumstances acyl complexes [Fe(η^5-C_5H_5)(CO)L(COR)] are observed.[4,7,8] In the absence of incoming nucleophiles, a pathway involving radicals has been proposed[6] to account for the photochemical formation of the dimer [{Fe(η^5-C_5H_5)(CO)$_2$}$_2$]. Recently, in an e.s.r. study,[9] weak signals due to CH$_3^{\bullet}$ and [Fe(η-C_5H_5)(CO)$_2$]$^{\bullet}$ radicals have been detected on photolysis of [Fe(η^5-C_5H_5)(CO)$_2$-(CH$_3$)] at −30 °C. However, similar studies on the acetyl complex have showed the absence of any CH$_3$CO$^{\bullet}$ radical, indicating that photolysis does not cause M–C homolysis in this complex.



(I)



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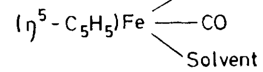

(III)

Decarbonylation reactions of [Fe(η^5-C_5H_5)(CO)L(COR)] complexes [equation (4)] have been shown to involve the

$$[Fe(\eta^5\text{-}C_5H_5)(CO)L(COR)] \xrightarrow[\text{heat}]{h\nu} [Fe(\eta^5\text{-}C_5H_5)(CO)(L)R] + CO \qquad (4)$$

terminal CO ligand rather than the ketonic CO group because the ^{13}C in the acetyl group of [Fe(η^5-C_5H_5)-(CO)$_2$(^{13}COCH$_3$)] was retained in the alkyl product.[10] When the photochemical decarbonylation of [Fe(η^5-C_5H_5)(CO)$_2$(^{13}COCH$_3$)] was carried out in the presence of PPh$_3$ the reactive intermediate, which was proposed to be the co-ordinatively unsaturated species (I), was found to persist for long enough for attack by the nucleophile to give [Fe(η^5-C_5H_5)(CO)(^{13}COCH$_3$)(PPh$_3$)] in competition with methyl migration, which afforded [Fe(η^5-C_5H_5)(^{12}CO)(^{13}CO)(CH$_3$)].[10]

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† Throughout this paper: 1 p.s.i. ≈ 7.09 × 10^3 Pa; 1 atm = 101 325 Pa; 1 Torr = (101 325/760) Pa.

Matrix-isolation studies have been shown to be very useful for investigating photochemical reactions and for characterising reactive species, particularly metal carbonyl species.[11] In this paper we report on the species formed following photolysis of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)]$ and $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(COCH_3)]$ in a variety of matrices at 12 K and we relate the results to the mechanisms of carbonylation and decarbonylation reactions.

EXPERIMENTAL

Cryogenic temperatures (*ca.* 12 K) were obtained using a Displex CSA-202 closed-cycle helium refrigeration system (Air Products and Chemicals Inc.). Matrices of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)]$ (1 : 2 000—1 : 5 000) were prepared by ' pulsed ' deposition [12] of gas mixtures which were made up by standard manometric techniques. The complex $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(COCH_3)]$ was not volatile enough to prepare gas mixtures so that to prepare matrices of this compound a slow deposition technique was used employing the apparatus described elsewhere.[13] Vapour from the solid, held at *ca.* 18 °C, was co-condensed with matrix gas on to a cooled CaF_2 window. Monomer isolation (*ca.* 1 : 2 000) was ensured by having a substantially higher gas flow for the host matrix gas than for the complex to be isolated. Deposition (*ca.* 2.5 h) was monitored throughout by running i.r. spectra of the matrix and checking that the half-width at half-height of the terminal CO stretching bands did not exceed *ca.* 2 cm^{-1}.

Infrared spectra were recorded on a Grubb–Parsons Spectromajor grating spectrometer modified to have a grating change at 1 850 cm^{-1} rather than at 2 000 cm^{-1}. Calibration in the 1 550—2 200 cm^{-1} region was carried out regularly using the gas-phase absorption of CO, DCl, and H_2O. Resolution was better than 1 cm^{-1} and the reproducibility of measurements was ± 0.5 cm^{-1}. Ultraviolet–visible spectra were recorded on a Pye–Unicam SP1800B spectrometer.

The photolysis source was a water-cooled medium-pressure mercury lamp (Philips HPK, 125 W). Wavelength-selective photolysis was achieved by combinations of absorbing materials: filter A, $330 < \lambda < 370$ nm and $\lambda > 550$ nm, quartz cell (pathlength 25 nm) containing Br_2 gas (300 Torr) + a soda glass disc (thickness 5 mm); filter B, $280 < \lambda < 370$ nm and $\lambda > 550$ nm, quartz gas cell containing Br_2 gas + Pyrex glass disc (thickness 2 mm); filter C, $\lambda < 280$ and > 550 nm, quartz gas cell (pathlength 25 mm) containing Cl_2 gas (2 atm) and quartz gas cell containing Br_2 gas; filter D, $\lambda < 370$ and > 550 nm, quartz gas cell containing Br_2 gas; filter E, $\lambda > 350$ nm, Corning filter 3850.

Matrix gases (Ar, CH_4, CO, and N_2) were of ' Grade X ' purity (BOC Ltd.) and ^{13}C-enriched CO (95%) was obtained from BOC Prochem Ltd. Samples of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)]$ and $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(COCH_3)]$ were prepared by standard reactions [14] of CH_3I and CH_3COCl with $Na[Fe(\eta^5\text{-}C_5H_5)(CO)_2]$, obtained by sodium amalgam reduction of $[\{Fe(\eta^5\text{-}C_5H_5)(CO)_2\}_2]$.

RESULTS

Photolysis of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)]$ *in* CH_4, Ar, *and* N_2 *Matrices.*—The i.r. spectra of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)]$ isolated at high dilution in matrices showed two terminal CO stretching bands at *ca.* 2 010 and *ca.* 1 955 cm^{-1} [Figure 1(*a*), Table 1] corresponding to the symmetric (A') and antisymmetric (A'') modes expected for a molecule with C_s symmetry together with two weak bands (marked with an asterisk) corresponding to $[Fe(\eta^5\text{-}C_5H_5)(^{12}CO)(^{13}CO)(CH_3)]$. The observed relative intensity of the two terminal CO bands, *e.g.* 0.654 for $A' : A''$ in a CH_4 matrix and obtained by tracing and weighing bands, was used to calculate a OC–M–CO angle of $102 \pm 1°$, using the standard expression [15] $I_{sym}/I_{antisym} = \cot^2(\theta/2)$. This value is in reasonable agreement with the value (96°) found for $[Fe(\eta^5\text{-}C_5H_5)(\sigma\text{-}C_5H_5)(CO)_2]$ by *X*-ray crystallography.[16]

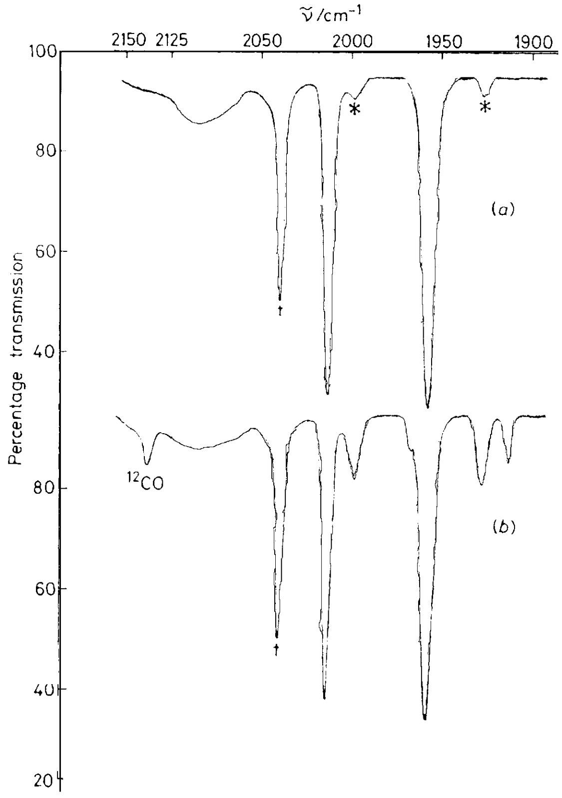


FIGURE 1 Infrared spectra from an experiment with $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)]$ isolated at high dilution in a ^{13}CO-doped (5%) Ar matrix at 12 K: (*a*) after deposition and (*b*) after photolysis for 60 min using filter A. Bands marked with an asterisk are due to $[Fe(\eta^5\text{-}C_5H_5)(^{12}CO)(^{13}CO)(CH_3)]$ in natural abundance and those marked with a dagger to $^{13}C^{18}O$

Irradiation of the matrices using the filtered medium-pressure mercury arc (filter A) to give radiation corresponding to the long-wavelength absorption band of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)]$ [Figure 2(*a*)] led to the production of *no* new photoproduct bands. Irradiation using progressively high energy and broader band-pass radiation (filters B—D) also failed to cause photolyis in contrast to the behaviour observed for other metal alkyl complexes, *e.g.* $[Mn(CO)_5(CH_3)]$ [17] and $[Mo(\eta^5\text{-}C_5H_5)(CO)_3(CH_3)]$.[18] Lack of formation of a photoproduct, *e.g.* $[Fe(\eta^5\text{-}C_5H_5)(CO)(CH_3)]$ + CO, was intially attributed to reverse photolysis occurring in the beam of the i.r. spectrometer and caused by visible radiation from the Nernst glowbar.[19] Use of a germanium disc filter (Ocli Optical Coatings Ltd.) to protect the sample while in the i.r. spectrometer beam also failed to lead to the observation of new bands. This finding is analogous to the failure to observe evidence for the formation of $[Co(\eta^5\text{-}C_5H_5)(CO)]$ on photolysis of $[Co(\eta^5\text{-}C_5H_5)(CO)_2]$ in Ar and

TABLE 1

Band positions (cm^{-1}) * for [Fe(η^5-C_5H_5)(CO)$_2$(CH_3)] and [Fe(η^5-C_5H_5)(CO)$_2$($COCH_3$)] complexes in the terminal and ketonic CO stretching regions and their photoproducts in argon, methane, nitrogen, and carbon monoxide matrices at 12 K

Complexes		ν(CO)	Ar	CH_4	N_2	CO
[Fe(η^5-C_5H_5)(CO)$_2$(CH_3)]	C_s	A′	2 018.6s 2 016.7s	2 014.2s 2 010.3s	2 017.0s 2 015.4s	2 015.4s 2 013.1s
		A″	1 965.0s 1 962.1s	1 958.6s 1 954.3s	1 963.4s 1 961.0s (sh)	1 961.0s
[Fe(η^3-C_5H_5)(CO)$_3$(CH_3)]	C_s	A′				2 050.3
		A′				1 982.7
		A″				1 975.1
[Fe(η^5-C_5H_5)(CO)$_2$($COCH_3$)]	C_s	A′	2 029.4s 2 025.5s 2 021.9s	2 027.3m 2 020.3m 2 015.4s	2 026.3m 2 020.5m	2 025.1s 2 020.6s
		A″	1 972.1s 1 968.1s 1 965.8s 1 964.9s	1 967.2m 1 960.4s 1 957.9s	1 965.0s	1 964.5s
		A′	1 680.3m 1 670.6m 1 631.9w 1 624.1w	1 663.8m 1 630.7w	1 677.1m 1 672.3m 1 630.4w	1 665.8m 1 629.7w
[Fe(η^5-C_5H_5)(CO)($COCH_3$)]	C_s	A′	1 955.4	1 947.5	1 955.5	1 952.4 1 948.1

* Relative intensities: w = weak, m = medium, s = strong, sh = shoulder. Bands bracketed together arise from a single fundamental with matrix splitting unless otherwise stated.

CH_4 matrices.[20] However, [Co(η^5-C_5H_5)(CO)$_2$] on photolysis in a N_2 matrix gave the substitution product [Co(η^5-C_5H_5)(N_2)(CO)].[20] Alternatively, the lack of observation of photoproducts is possibly due to reversible $CH_3^{\bullet}$ loss being the dominant pathway. The $CH_3^{\bullet}$ and [Fe(η^5-C_5H_5)(CO)$_2$]$^{\bullet}$ radicals may readily recombine within the matrix cage. Bond homolysis (Fe–Me) has been observed in solution at low temperatures although the process is comparatively inefficient,[9] while in gas matrices no evidence for alkyl radical formation has been reported. In poly(vinyl chloride) matrices at low temperatures, however, evidence for the radical pathway has been observed for [Fe(η^5-C_5H_5)(CO)$_2$(CH_3)].[21]

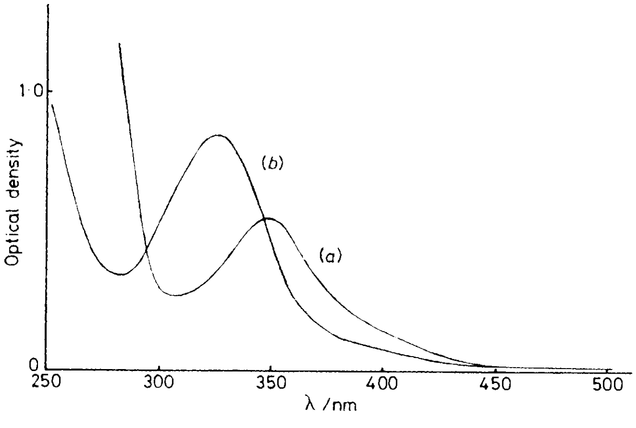


FIGURE 2 Electronic absorption spectra from experiments with compounds isolated at high dilution in Ar matrices at 12 K: (*a*) [Fe(η^5-C_5H_5)(CO)$_2$(CH_3)] and (*b*) [Fe(η^5-C_5H_5)(CO)$_2$($COCH_3$)]

Photolysis of [Fe(η^5-C_5H_5)(CO)$_2$(CH_3)] *in a* ^{13}CO-*doped* (5%) Ar *Matrix*.—The i.r. spectrum of [Fe(η^5-C_5H_5)(CO)$_2$(CH_3)] isolated at high dilution in a ^{13}C-doped (5%) Ar matrix [Figure 1(*a*)] shows the two strong bands of the di-^{12}CO species together with two weak bands (marked with an asterisk) corresponding to the natural-abundance amount of [Fe(η^5-C_5H_5)(^{12}CO)(^{13}CO)(CH_3)]. Irradiation of the matrix with light corresponding to the long-wavelength absorption band (filter A) caused rapid growth of bands corresponding to [Fe(η^5-C_5H_5)(^{12}CO)(^{13}CO)(CH_3)] and [Fe(η^5-C_5H_5)(^{13}CO)$_2$(CH_3)] [Figure 1(*b*)], as confirmed by the excellent correspondence between observed and calculated [15,17,20] band positions (Table 2).

TABLE 2

Observed[a] and calculated[b] wavenumbers (cm^{-1}) of the terminal CO stretching bands of ^{13}CO-enriched [Fe(η^5-C_5H_5)(CO)$_2$(CH_3)] isolated in a mixed ^{13}CO (95% enriched) : Ar (1 : 20) matrix at 12 K

Complex		ν(CO)	Obs.	Calc.
[Fe(η^5-C_5H_5)(^{12}CO)$_2$(CH_3)]	C_s	A′	2 014.4	2 013.6
		A″	1 959.2	1 958.4
[Fe(η^5-C_5H_5)(^{12}CO)(^{13}CO)(CH_3)]	C_1	A	1 999.3	1 999.0
		A	1 928.5	1 928.8
[Fe(η^5-C_5H_5)(^{13}CO)$_2$(CH_3)]	C_s	A′	1 968.0	1 968.8
		A″	1 914.0	1 914.8

[a] In the event of matrix splitting, *cf*. Table 1, the strongest contributions to matrix-split bands were used to give band positions for computer fitting. [b] Refined energy-factored CO stretching and interaction force constants (N m^{-1}) are K = 1 593.7 and k_i = 44.3.

Photolysis of [Fe(η^5-C_5H_5)(CO)$_2$(CH_3)] *in* CO *Matrices*.—The i.r. spectrum of [Fe(η^5-C_5H_5)(CO)$_2$(CH_3)] isolated at high dilution in a CO matrix [Figure 3(*a*)] showed bands whose positions are very similar to those for CH_4, Ar, and N_2 matrices (Table 1). Irradiation of the matrix with broad band-pass radiation (filter D) produced three new bands in the terminal CO stretching region [Figure 3(*b*); 2 050.3, 1 982.7, and 1 975.1 cm^{-1}]. The relative intensities of the new bands remained constant under a variety of photolysis conditions (time and radiation) indicating that these bands arose from a single product species, although the yield of this species was rather modest. The dilution used (*ca*. 1 : 2 000—1 : 5 000) rules out the possibility of formation of a polynuclear species. The shift of bands to higher wavenumber is typical of a situation where an increase in the number of CO ligands has taken place, *e.g.* [Co(η^5-C_5H_5)(CO)$_2$] (2 032.1 and 1 971.9 cm^{-1}) compared to [Co(η^3-C_5H_5)(CO)$_3$] (2 075.0 and 2 018.0 cm^{-1}).[20] The identity of the photoproduct is therefore probably [Fe(η^3-C_5H_5)(CO)$_3$(CH_3)], *cf*. [Co(η^3-

$C_5H_5)(CO)_3]$,[20] or $[Fe(\eta\text{-}C_5H_5Me)(CO)_3]$ formed by the migration of the Me group from the metal to the cyclopentadienyl ring. In both these complexes the change in hapticity of the cyclopentadienyl ring avoids the need to propose a 20-electron configuration for the central Fe atom. Metal-to-ring alkyl migration has only been observed under forcing conditions (50 atm, 50 °C) for $[Mo(\eta\text{-}C_5H_5)_2EtCl]$ in the presence of CO,[22] whereas a hydrogen transfer has been demonstrated in the reactions of $[Re(\eta\text{-}C_5H_5)_2H]$ in a low-temperature CO matrix.[23] In view of the observations that the Me–Fe bond homolysis is inefficient [9] and that the alkyl migration from metal to ring would require vigorous conditions, it seems likely that the photoproduct observed is $[Fe(\eta^3\text{-}C_5H_5)(CO)_3(CH_3)]$ and *not* $[Fe(\eta\text{-}C_5H_5Me)(CO)_3]$. The existence of a η^3-cyclopentadienyl group has been demonstrated by an *X*-ray crystallographic study of $[W(\eta^3\text{-}C_5H_5)(\eta^5\text{-}C_5H_5)(CO)_2]$, where there is an angle of 20° between the co-ordinated allylic system and the non-co-ordinating olefinic double-bond system of the $\eta^3\text{-}C_5H_5$ group.[24] Unfortunately, because of the modest yield of the photoproduct, it was not possible to conclusively prove the existence of the $Fe(CO)_3$ fragment by ^{13}CO labelling followed by energy-factored force-field fitting of the terminal CO stretching bands, *cf.* $[Co(\eta^3\text{-}C_5H_5)(CO)_3]$.[20] The i.r. bands of the photoproduct may either be assigned as the symmetric (A_1, 2 050.3 cm^{-1}) and matrix-split antisymmetric *E*, 1 982.7 and 1 975.1 cm^{-1}) bands of a $Fe(CO)_3$ fragment with C_{3v} local symmetry, or, more probably, as the *A'* (2 050.3 cm^{-1}), *A'* (1 982.7 cm^{-1}), and *A''* (1 975.1 cm^{-1}) bands of a fragment with C_s symmetry. Some $M(CO)_3$ fragments with C_{3v} local symmetry show a similar split lower-wavenumber band, *e.g.* $[Fe(\eta^4\text{-}C_4H_4)(CO)_3]$,[25] but the lowering of the symmetry to C_s does not always lead to band splitting, *e.g.* $[Mo(\eta^5\text{-}C_5H_5)(CO)_3(CH_3)]$ shows a single low-wavenumber band because of a band coincidence between the *A''* and the lower *A'* bands.[18]

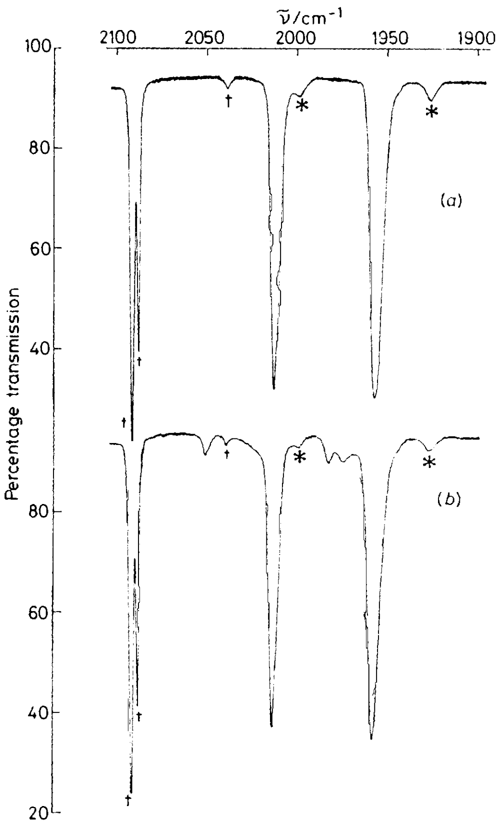
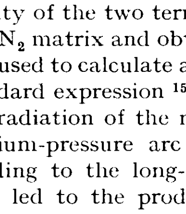


FIGURE 3 Infrared spectra from an experiment with $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)]$ isolated at high dilution in a CO matrix at 12 K: (*a*) after deposition, and (*b*) after photolysis for 12 min using filter D. Bands marked with an asterisk are due to $[Fe(\eta^5\text{-}C_5H_5)(^{12}CO)(^{13}CO)(CH_3)]$ and those marked with a dagger are due to natural-abundance isotopes of CO

Photolysis of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(COCH_3)]$ *in* CH_4, Ar, N_2, *and* CO *Matrices*.—The spectrum of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(COCH_3)]$ isolated at high dilution in CH_4, Ar, N_2, and CO matrices showed multiply split *A'* and *A''* terminal CO bands and a much larger splitting (*ca.* 36 cm^{-1}) in the acetyl CO band [Figure 4(*a*), Table 1]. Such a large splitting is beyond the range (0—10 cm^{-1}) attributable to matrix effects [26] and must arise from conformational isomerism about the metal–acetyl bond [(IV), (V)]. A smaller splitting of the acetyl band (*ca.* 20 cm^{-1}) is observed in the solution i.r. spectrum [27–29] but no conformer splitting is observed in the ^1H n.m.r. spectrum.[28,29] The observed relative intensity of the two terminal CO bands, *e.g.* 0.735 for *A'* : *A''* in a N_2 matrix and obtained by tracing and weighing bands, was used to calculate a OC–M–CO angle of 99 ± 1°, using the standard expression [15] $I_{sym}/I_{antisym} = \cot^2(\theta/2)$.



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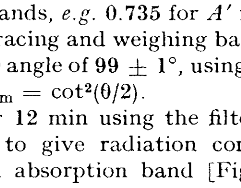


(V)

Irradiation of the matrices for 12 min using the filtered medium-pressure arc (filter B) to give radiation corresponding to the long-wavelength absorption band [Figure 2(*b*)] led to the production of the terminal CO bands of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)]$ together with 'free' CO (2 138 cm^{-1}) and almost total destruction of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(COCH_3)]$ [Figure 4(*c*)]. A much shorter photolysis time (2 min) afforded a weak doublet [Figure 4(*b*)] in addition to the appearance of bands due to $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)]$. Further short periods of photolysis using filter B and the other filters resulted in an increase in the overall conversion of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(COCH_3)]$ into $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)]$ without an increase in the weak doublet band. Ultimately this doublet band disappeared as conversion into $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)]$ went to completion. The high dilution used in the experiment and the intermediacy of the species responsible for the doublet between $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(COCH_3)]$ and $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)]$ suggests that the intermediate product is the mononuclear $[Fe(\eta^5\text{-}C_5H_5)(CO)(COCH_3)]$. No band attributable to the acetyl CO stretching vibration was observed but this is perhaps not surprising considering that the intensity of the terminal CO bands is weak and the acetyl CO stretching band in $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(COCH_3)]$ is much weaker than the terminal CO stretching bands (Table 1). Support for the assignment of the intermediate species as $[Fe(\eta^5\text{-}C_5H_5)(CO)(COCH_3)]$ is afforded by the observation of $[Mn(CO)_4(COCH_3)]$ in the photochemical decarbonylation of $[Mn(CO)_5(COCH_3)]$ in

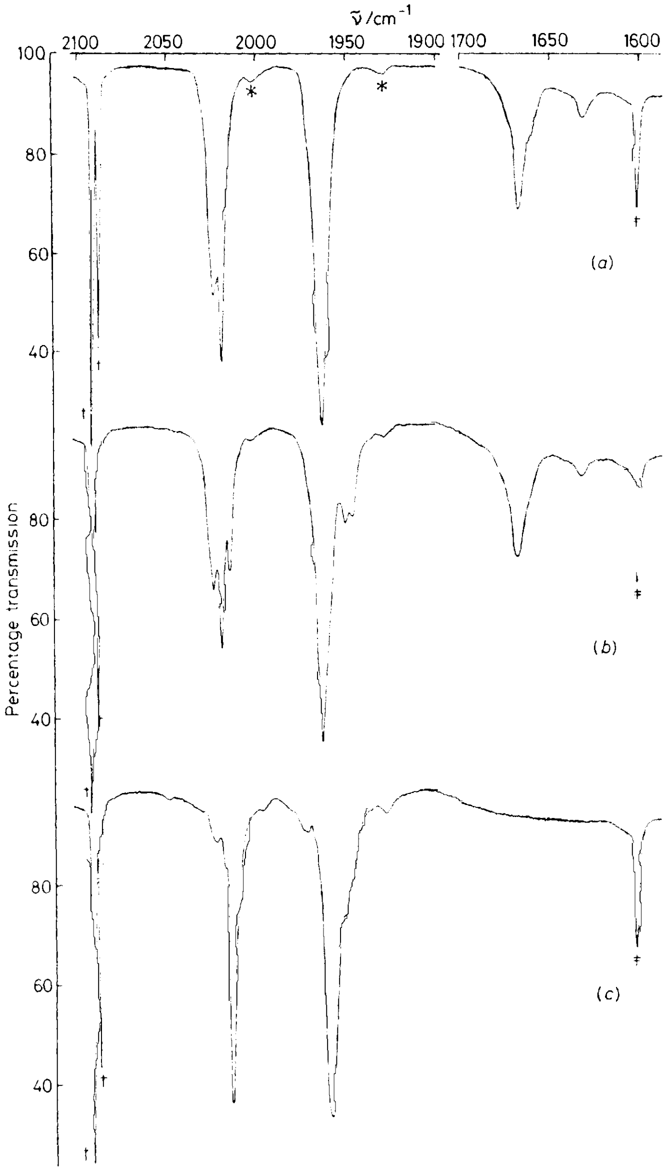


FIGURE 4 Infrared spectra from an experiment with $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(COCH_3)]$ isolated at high dilution in a CO matrix: (*a*) after deposition, (*b*) after photolysis for 2 min using filter B, and (*c*) after photolysis for 12 min using filter B. Bands marked with an asterisk are due to $[Fe(\eta^5\text{-}C_5H_5)(^{12}CO)(^{13}CO)(COCH_3)]$ in natural abundance, those marked with a dagger are due to natural-abundance isotopes of CO, and those marked with a double dagger to a trace of matrix-isolated H_2O

matrices at 12 K.[17] Photolysis of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(COCH_3)]$ in a ^{13}CO-doped (5%) Ar matrix led to the growth of terminal CO stretching bands at 2 014.4 and 1 959.2 cm^{-1}, *i.e.* the formation of $[Fe(\eta^5\text{-}C_5H_5)(^{12}CO)_2(CH_3)]$ rather than $[Fe(\eta^5\text{-}C_5H_5)(^{12}CO)(^{13}CO)(COCH_3)]$ (2 002.5 and 1 930.9 cm^{-1}) or $[Fe(\eta^5\text{-}C_5H_5)(^{12}CO)(^{13}CO)(CH_3)]$.

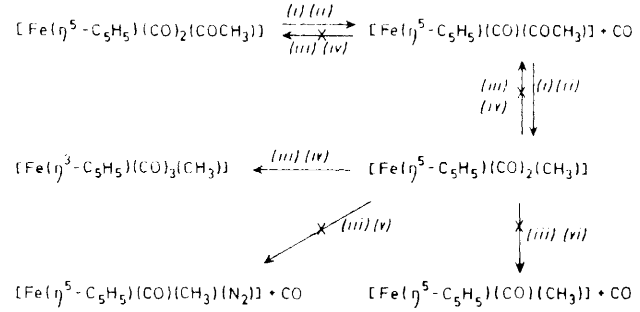
DISCUSSION

The photoreactions of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)]$ and $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(COCH_3)]$ at high dilution in various matrices are shown in the Scheme.

The observation of the expanded-co-ordination-number species, $[Fe(\eta^3\text{-}C_5H_5)(CO)_3(CH_3)]$, and the ready exchange of ^{13}CO from the matrix with ^{12}CO ligands in $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)]$, suggest, by analogy with $[Co(\eta^5\text{-}C_5H_5)(CO)_2] + CO \rightleftharpoons [Co(\eta^3\text{-}C_5H_5)(CO)_3]$, an equilibrium [equation (5)] [L = nucleophile (CO or PR_3)

$$[Fe(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)] + L \rightleftharpoons [Fe(\eta^3\text{-}C_5H_5)(CO)_2L(CH_3)] \quad (5)$$

or solvent (CH_3CN or tetrahydrofuran)]. The species $[Fe(\eta^3\text{-}C_5H_5)(CO)_2L(CH_3)]$ may eject L to give back the parent compound, eject CO to give $[Fe(\eta^5\text{-}C_5H_5)(CO)L(CH_3)]$, or rearrange by alkyl migration to give $[Fe(\eta^5\text{-}C_5H_5)(CO)L(COCH_3)]$ depending on the nature of L. Such a species as $[Fe(\eta^3\text{-}C_5H_5)(CO)_2L(CH_3)]$ is consistent with the associative mechanism for the rate-determining



SCHEME (*i*) *hν* (filter B); (*ii*) CH_4, Ar, N_2, CO; (*iii*) *hν* (filters A—E); (*iv*) CO; (*v*) N_2; (*vi*) CH_4, Ar

step of the thermal insertion reactions of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)]$ as deduced by kinetic studies.[2,3] However, the matrix studies suggest that the intermediate is none of the species [(I)—(III)] proposed earlier.

Similarly an expanded-co-ordination-number species $[Fe(\eta^3\text{-}C_5H_5)(CO)_2L(CH_3)]$ accounts for the variety of products observed in the photochemical reactions of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)]$ [4,5,7,8] with the exception of the formation of $[\{Fe(\eta^5\text{-}C_5H_5)(CO)_2\}_2]$.[6] The u.v. irradiation possibly excites a metal-to-ligand charge-transfer (m.l.c.t.) transition $[Fe \longrightarrow (\eta^5\text{-}C_5H_5)]$, thus assisting the attack of L on Fe, with a concerted η^5—η^3 change in the mode of the ring co-ordination. A m.l.c.t. $[Fe \longrightarrow CO(\pi^*)]$ transition may be excited in the intermediate, $[Fe(\eta^3\text{-}C_5H_5)(CO)_3]$, assisting with ejection of CO and followed by a $\eta^3 \rightarrow \eta^5$ ring co-ordination change. Evidence for radical formation on photolysis of the $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)]$ complex has been noted in the e.s.r. studies, while the corresponding acetyl complex does not form a $CH_3CO^{\bullet}$ radical.[9] Alkyl radicals have not been detected, so far, on photolysis of organometallic compounds in gas matrices at low temperatures, whereas the $H^{\bullet}$ radical species has been observed.[10,30] More work is urgently needed on the assignment of the electronic spectra and structure of organometallic compounds [31] and to provide proof of a radical path [6] in the formation of $[\{Fe(\eta^5\text{-}C_5H_5)(CO)_2\}_2]$.

The observation of the co-ordinatively unsaturated species $[Fe(\eta^5\text{-}C_5H_5)(CO)(COCH_3)]$, on photolysis of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(COCH_3)]$ even in CO matrices, is in accord with the mechanistic pathway for decarbonylation proposed from ^{13}CO labelling studies.[10] In this case perhaps u.v. irradiation excites a m.l.c.t. $[Fe \longrightarrow CO(\pi^*)]$ transition facilitating ejection of one of the two terminal ligands. Upon the arrival of a signal-averaging multiple-scanning and averaging i.r. spectrometer, future work will seek to find the 'missing' ketonic CO vibration of $[Fe(\eta^5\text{-}C_5H_5)(CO)(COCH_3)]$ in order to determine whether the acetyl is acting as a σ- or η^2-ligand, *i.e.* (I) or (II). Structural evidence for η^2-acyls is steadily accumulating[32,33] but molecular-orbital calculations showed[34] that η^2-acyls are more favoured for the early transition metals, *e.g.* Ti and Zr, than for later transition metals, *e.g.* Mn.

We thank the S.R.C. for support (to A. J. R.), Drs. H. Alt and P. Hoffmann for helpful discussions, and Professor M. F. Lappert for allowing us to see a preprint of his paper describing e.s.r. studies of alkyl-metal complexes.

[1/395 *Received*, 10*th March*, 1981]

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