Photochemistry of (η-Benzene)tricarbonylchromium, Tricarbonyl-(η-cyclopentadienyl)manganese, and (η-Cyclobutadiene)- and (Tris-methylenemethane)-tricarbonyliron in Frozen Gas Matrices at 12 K. Infrared Spectroscopic Evidence for Dicarbonylmetal and Dicarbonyl-(dinitrogen)metal Complexes

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Infrared evidence is presented for the formation of co-ordinatively unsaturated species $[ML(CO)_2]$ [ML = Cr-(η-C_6H_6), Mn(η-C_5H_5), Fe(η-C_4H_4), or Fe{$C(CH_2)_3$}] on the u.v. photolysis of $[ML(CO)_3]$ complexes in argon and methane matrices, and dinitrogen complexes $[ML(CO)_2(N_2)]$ in nitrogen matrices at 12 K. The primary photolysis step is readily reversed by visible light for $[ML(CO)_2]$ species of Cr and Fe, but not for Mn. The results are discussed in relation to the postulate of co-ordinatively unsaturated species as intermediates in the solution-phase substitution reactions.

It has been suggested[1] that the principal primary photoprocess in the photochemical reactions of the isostructural series [Cr(η-C_6H_6)$(CO)_3$], [Mn(η-C_5H_5)$(CO)_3$], and [Fe(η-C_4H_4)$(CO)_3$] is dissociation of a CO ligand. Flash-photolysis studies[2] of [Cr(η-C_6H_6)$(CO)_3$] in cyclohexane solution have demonstrated the formation of a transient species which was tentatively assigned as [Cr(η-C_6H_6)$(CO)_2$]. None of the complexes is thought to undergo substitution of the π-donor ligand with high quantum efficiency,[3] although this was implied by the early work of Strohmeier and von Hobe,[4] the recent identification of C_6H_6 and $[Cr(CO)_6]$ as the products of the photodecay of [Cr(η-C_6H_6)$(CO)_3$],[5] and competition experiments which showed that photochemical exchange of benzene in [Cr(η-C_6H_6)$(CO)_3$] may be preceded by CO loss.[2] In contrast with the photochemical reaction, the arene ligand in [M(η^6-arene)$(CO)_3$] (M = Cr or Mo) can be readily exchanged thermally.[6,7]

Many postulated intermediates in metal carbonyl photochemistry have been characterised in low-temperature gas matrices.[8,9] Despite the obvious usefulness of the matrix-isolation technique, however, much debate has centred on whether photoreactions in matrices can or should be related to the reactions in solution and vapour.[10-12]

In this paper we describe the characterisation by i.r. spectroscopy of a variety of species formed from arene- or pseudoarene-tricarbonylmetal complexes in inert (argon or CH_4) and reactive matrices (N_2) and we relate the findings to reactions in solution and vapour. While preliminary experiments on these complexes were in progress brief reports were published describing i.r. characterisation of [Mn(η-C_5H_5)$(CO)_2$] in a glass at 77 K,[13] and [Fe(η-C_4H_4)$(CO)_2$] in a krypton matrix at 10 K.[14]

EXPERIMENTAL

Cryogenic temperatures (*ca.* 12 K) were obtained using a closed-cycle helium refrigeration system (Air Products and Chemicals Inc., Displex CSA-202). Infrared spectra were recorded using Perkin-Elmer 225 and Grubb–Parsons Spectromajor (modified to have a grating change at 1 850 rather than 2 000 cm^{-1}) spectrometers. Calibration was regularly carried out using the gas-phase absorptions of DCl and CO. A coated germanium interference filter (Ocli Optical Coatings Ltd.) was used to prevent possible photolysis of matrix samples by the visible radiation from the glowbar of the i.r. spectrometer, as previously reported.[15]

Matrices containing [Cr(η-C_6H_6)$(CO)_3$] and [Mn(η-C_5H_5)-$(CO)_3$] were prepared by the slow spray-on technique because the complexes were rather involatile, subliming the complex from a glass finger, held at 35—45 °C and −5 to 0 °C respectively, and co-condensing simultaneously matrix gas from a bulb *via* a needle valve on to the cooled CsI window. Matrices containing the more volatile complexes [Fe(η-C_4H_4)$(CO)_3$] and [Fe{$C(CH_2)_3$}$(CO)_3$] were prepared by making gas mixtures of the complex and matrix gas of the required composition (1 : 2 000 to 1 : 5 000), using a vacuum line and standard manometric techniques, and depositing the gas mixture on to the cooled CsI windows by the 'pulsed' technique.[16] The pulsing volume was 10 cm^3 and the pulsing pressure was in the range 100—200 Torr,† *i.e.*

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† Throughout this paper: 1 Torr = (101 325/760) Pa; 1 atm = 101 325 Pa.

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0.06—0.12 mmol per pulse, and typically 30 pulses were deposited. Argon, CH_4, and N_2 matrix gases were of B.O.C. Grade ' X ' purity. The complexes $[Cr(\eta\text{-}C_6H_6)(CO)_3]$ and $[Mn(\eta\text{-}C_5H_5)(CO)_3]$ were purchased from Strem Chemicals Inc. and used without further purification.

The photolysis source was a Philips HPK 125-W medium-pressure mercury arc. Wavelength-selective photolysis was achieved by a combination of absorbing materials: filter A, $\lambda < 280$ and $\lambda > 550$ nm [quartz gas cell (pathlength, 25 mm) containing 3 atm of Cl_2 gas + quartz gas cell (pathlength, 25 mm) containing 200 Torr of Br_2 gas]; filter B, $\lambda > 290$ nm [Pyrex glass disc (thickness, 5 mm)]. For specific narrow-band photolysis (313 ± 2 and 366 ± 2 nm) the mercury lamp was used in conjunction with a Bausch and Lomb high-intensity monochromator.

RESULTS AND DISCUSSION

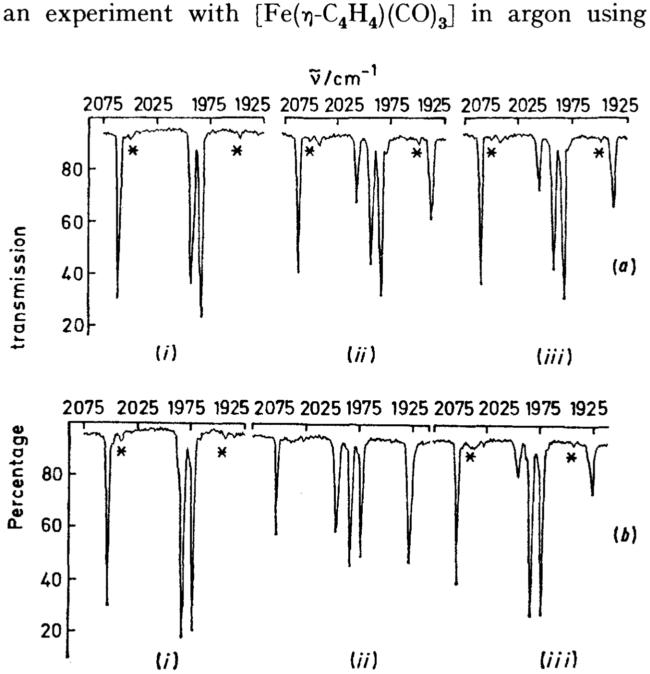

FIGURE 1 Infrared spectra from experiments with $[Fe(\eta\text{-}C_4H_4)(CO)_3]$ isolated in argon (*a*) and methane (*b*) matrices: (*i*) after deposition, (*ii*) after u.v. photolysis (filter A, 15 min), and (*iii*) after reversal with longer-wavelength radiation (filter B, 30 min). Bands marked with an asterisk are due to $[Fe(\eta\text{-}C_4H_4)(^{12}CO)_2(^{13}CO)]$ present in natural abundance

Photolysis of $[ML(CO)_3]$ *in Argon and Methane Matrices*.—(*a*) $[Fe(\eta\text{-}C_4H_4)(CO)_3]$. Infrared spectra from an experiment with $[Fe(\eta\text{-}C_4H_4)(CO)_3]$ in argon using the germanium filter are shown in Figure 1 and are representative of the other members of the series of complexes. At a dilution of 1 : 2 000 the spectrum of the parent complex [Figure 1(*a*)(*i*)] consisted of two strong bands in the terminal carbonyl-stretching region corresponding to the A_1 (2 059.9 cm^{-1}) and E (1 987.6 cm^{-1}) modes of an $M(CO)_3$ fragment having local C_{3v} symmetry.* Under somewhat higher resolution both bands showed further splitting (Table 1) due to matrix effects.[17] The two weaker bands (marked with an asterisk) in the starting spectrum [Figure 1(*a*)(*i*)] are due to $[Fe(\eta\text{-}C_4H_4)(^{12}CO)_2(^{13}CO)]$ present in natural abundance.

A period of u.v. photolysis with the filtered medium-pressure arc (filter A) produced the spectrum in Figure 1(*a*)(*ii*). New terminal CO bands were visible at 2 005.1 and 1 936.4 cm^{-1} together with a weak band (not illustrated) at 2 138.0 cm^{-1} due to photochemically generated ' free ' CO. Removal of the germanium disc filter and irradiation of the matrix at longer wavelengths (filter B) rapidly [Figure 1(*a*)(*iii*)] caused regeneration of the parent bands at the expense of the product absorptions.

The relative intensities of the new terminal-carbonyl bands remained constant under a variety of photolyses (growing and decreasing at the same rate) indicating that they arose from a single product species. The dilution used (*ca* 1 : 2 000 to 1 : 5 000) and the reversibility of the matrix reaction rule out the possibility of any polynuclear aggregate formation. The most probable explanation for the product species is $[Fe(\eta\text{-}C_4H_4)(CO)_2]$ with the new bands assigned as the A_1 (2 005.1 cm^{-1}) and B_1 (1 936.4 cm^{-1}) terminal carbonyl-stretching modes of an $[M(CO)_2]$ fragment having local C_{2v} symmetry. The i.r. band positions of $[Fe(\eta\text{-}C_4H_4)(CO)_2]$ in argon agree well with previous work[14] in a krypton matrix (2 000 and 1 931 cm^{-1}; *ca.* 5 cm^{-1} matrix shift). The spectrum of $[Fe(\eta\text{-}C_4H_4)(CO)_2]$ in Figure 1(*a*)(*ii*) is rather more convincing than that shown previously.[14]

The results for the photolysis of $[Fe(\eta\text{-}C_4H_4)(CO)_3]$ in methane matrices [dilution 1 : 2 000, Figure 1(*b*)] were very similar to those obtained for argon matrices. The matrix shift of the photolysis bands for methane relative to argon (*ca.* 10 cm^{-1}, Table 1) is very similar to that of the parent molecule (*ca.* 8 cm^{-1}) and this suggests that the photolysis product is probably $[Fe(\eta\text{-}C_4H_4)(CO)_2]$ in a methane matrix rather than $[Fe(\eta\text{-}C_4H_4)(CO)_2 \cdots (CH_4)]$ *cf.* $[Fe(CO)_4 \cdots (CH_4)]$.[18] Another possible measure of the inertness or non-interacting nature of the host argon and methane matrices is the magnitude of the interaction force constant[19] of the $[Fe(\eta\text{-}C_4H_4)(CO)_2]$ species [k_i(argon) 54.7, $k_i(CH_4)$ 54.0 N m^{-1}] in contrast to the value for $[Fe(\eta\text{-}C_4H_4)(CO)_2(N_2)]$ (k_i 42.3 N m^{-1}, Table 2). Comparison of matrix shifts and interaction force constants as a means of identifying very weak interactions of carbonyl fragments with a matrix such as methane must be treated cautiously because this

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* The local C_{3v} symmetry assumption is possibly an oversimplification as shown by the doublet nature of the E mode [Figure 1(*a*)(*i*) and 1(*b*)(*i*)]. Other $[ML(CO)_3]$ complexes show broadened E modes (half-width at half-height *ca.* 10 cm^{-1} compared with *ca.* 5 cm^{-1} for A_1 modes) which can be resolved into a number of components (Table 1) depending on the matrix gas. The doublet splitting for $[Fe(\eta\text{-}C_4H_4)(CO)_3]$ (8 cm^{-1} for argon; weighted mean positions of components at 1 991.2 and 1 982.8 cm^{-1}) is within the normal range of matrix-splitting effects. Until the causes of matrix effects are better understood it seems better not to speculate about the details of the doublet for $[Fe(\eta\text{-}C_4H_4)(CO)_3]$.

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TABLE 1

Positions (cm^{-1}) of bands and weighted mean positions (cm^{-1}) of centres of multiplets in experiments with $[ML(CO)_3]$ complexes isolated in argon, methane, and nitrogen matrices

$[Fe(\eta\text{-}C_4H_4)(CO)_3]$

	Argon		Methane		Nitrogen	
$A_1[\nu(CO)]$	2 059.9 2 058 9 *	2 059.9	2 054.8 * 2 052.7	2 052.7	2 056.5 2 052.4 *	2 056.5
$E[\nu(CO)]$	1 992.8 1 992.3 1 990.3 1 983.8 1 982.8	1 987.6	1 988.3 1 983.8 1 973.2 1 972.3	1 978.6	1 982.0 1 979.8 1 978.1 1 971.6	1 981.5

$[Fe(\eta\text{-}C_4H_4)(CO)_2]$

	Argon	Methane
$A_1[\nu(CO)]$	2 005.1	1 995.9
$B_1[\nu(CO)]$	1 936.4	1 927.8

$[Fe(\eta\text{-}C_4H_4)(CO)_2(N_2)]$

	Nitrogen
$A'[\nu(NN)]$	2 206.8
$A'[\nu(CO)]$	2 013.6
$A''[\nu(CO)]$	1 961.0

$[Fe\{C(CH_2)_3\}(CO)_3]$

	Argon		Methane		Nitrogen	
$A_1[\nu(CO)]$	2 070.0	2 070.0	2 064.4 2 063.7 2 060.0	2 063.5	2 067.3 2 063.3	2 065.2
$E[\nu(CO)]$	2 003.3 2 000.4 1 998.7	2 000.4	1 996.5 1 993.5 1 998.4 1 983.8	1 990.2	2 000.4 1 998.1 1 996.5 1 992.4 1 990.5	1 994.9

$[Fe\{C(CH_2)_3\}(CO)_2]$

	Argon	Methane
$A_1[\nu(CO)]$	2 020.7	2 012.2
$B_1[\nu(CO)]$	1 955.7	1 948.3

$[Fe\{C(CH_2)_3\}(CO)_2(N_2)]$

	Nitrogen
$A'[\nu(NN)]$	2 219.1
$A'[\nu(CO)]$	2 028.0
$A''[\nu(CO)]$	1 979.1

$[Mn(\eta\text{-}C_5H_5)(CO)_3]$

	Argon		Methane		Nitrogen	
$A_1[\nu(CO)]$	2 034.5 2 029.3	2 032.6	2 029.4 2 027.6	2 028.5	2 032.3	2 032.3
$E[\nu(CO)]$	1 953.5 1 950.5 1 949.2	1 951.0	1 945.1 1 939.4	1 943.0	1 954.0 1 952.0 1 950.5 1 948.7 1 946.7	1 948.8

$[Mn(\eta\text{-}C_5H_5)(CO)_2]$

	Argon	Methane
$A_1[\nu(CO)]$	1 972.0	1 961.4
$B_1[\nu(CO)]$	1 903.2	1 892.8

$[Mn(\eta\text{-}C_5H_5)(CO)_2(N_2)]$

	Nitrogen
$A'[\nu(NN)]$	2 175.3
$A'[\nu(CO)]$	1 978.7
$A''[\nu(CO)]$	1 927.0

$[Cr(\eta\text{-}C_6H_6)(CO)_3]$

	Argon		Methane		Nitrogen	
$A_1[\nu(CO)]$	1 991.5 * 1 990.0	1 990.0	1 982.5	1 982.5	1 984.1	1 984.1
$E[\nu(CO)]$	1 924.5 1 923.0 1 921.0	1 923.0	1 916.8 1 913.0 1 910.5	1 913.0	1 918.3 1 916.8 1 913.7 1 912.0	1 913.7

$[Cr(\eta\text{-}C_6H_6)(CO)_2]$

	Argon	Methane
$A_1[\nu(CO)]$	1 937.5	1 925.0
$B_1[\nu(CO)]$	1 885.0	1 870.0

$[Cr(\eta\text{-}C_6H_6)(CO)_2(N_2)]$

	Nitrogen
$A'[\nu(NN)]$	2 148.4
$A'[\nu(CO)]$	1 939.8
$A''[\nu(CO)]$	1 895.8

* Shoulder which was not included in weighting.

TABLE 2

Energy-factored CO stretching (k) and interaction (k_i) force constants (N m^{-1}) for $[ML(CO)_3]$, $[ML(CO)_2]$, and $[ML(CO)_2(N_2)]$ complexes in various matrices

	$[Fe(\eta\text{-}C_4H_4)(CO)_3]$			$[Fe(\eta\text{-}C_4H_4)(CO)_2]$		$[Fe(\eta\text{-}C_4H_4)(CO)_2(N_2)]$
	Argon	Methane	Nitrogen	Argon	Methane	Nitrogen
k	1 635.0	1 621.6	1 627.6	1 570.4	1 556.2	1 596.6
k_i	39.7	40.5	40.9	54.7	54.0	42.3

	$[Fe\{C(CH_2)_3\}(CO)_3]$			$[Fe\{C(CH_2)_3\}(CO)_2]$		$[Fe\{C(CH_2)_3\}(CO)_2(N_2)]$
	Argon	Methane	Nitrogen	Argon	Methane	Nitrogen
k	1 655.3	1 648.5	1 646.9	1 598.2	1 585.5	1 622.8
k_i	38.5	38.1	38.7	52.2	51.2	39.6

	$[Mn(\eta\text{-}C_5H_5)(CO)_3]$			$[Mn(\eta\text{-}C_5H_5)(CO)_2]$		$[Mn(\eta\text{-}C_5H_5)(CO)_2(N_2)]$
	Argon	Methane	Nitrogen	Argon	Methane	Nitrogen
k	1 580.5	1 569.9	1 575.1	1 518.0	1 501.6	1 535.2
k_i	43.8	45.8	44.1	53.9	53.4	40.3

	$[Cr(\eta\text{-}C_6H_6)(CO)_3]$			$[Cr(\eta\text{-}C_6H_6)(CO)_2]$		$[Cr(\eta\text{-}C_6H_6)(CO)_2(N_2)]$
	Argon	Methane	Nitrogen	Argon	Methane	Nitrogen
k	1 528.5	1 514.1	1 517.1	1 476.8	1 455.7	1 487.9
k_i	35.3	36.4	36.7	40.6	42.2	34.9

method while identifying $[Fe(CO)_4 \cdots (CH_4)]$[18] would not identify $[Cr(CO)_5 \cdots (CH_4)]$ which was only detected[20] using electronic spectroscopy and mixed matrices. In the latter case, the approach of the CH_4 molecule along the C_4 axis caused little distortion of the C_{4v} structure although it produced a large change in electronic energy levels. The structure of the $[Fe(CO)_4]$ fragment was very sensitive to interaction with the CH_4 molecule because it was entering the equatorial plane of a trigonal bipyramid. It seems reasonable to expect the $[ML(CO)_2]$ fragment also to be structurally sensitive to interaction with CH_4 because of changes in the bond angle between CO ligands from *ca.* 90° for $[ML(CO)_2]$ to *ca.* 97° for $[ML(CO)_3]$ and $[ML(L')(CO)_2]$ species.

(*b*) $[Cr(\eta\text{-}C_6H_6)(CO)_3]$, $[Mn(\eta\text{-}C_5H_5)(CO)_3]$, *and* $[Fe\{C(CH_2)_3\}(CO)_3]$. The spectra of the other $[ML(CO)_3]$ complexes and their photolysis products in argon and methane matrices were very similar to those already described for $[Fe(\eta\text{-}C_4H_4)(CO)_3]$ and the results [forward photolysis with u.v. light (filter A) and reversal with longer-wavelength radiation] are shown in Table 1. It is obviously more difficult to quantify dilutions for slow spray-on experiments with $[Cr(\eta\text{-}C_6H_6)(CO)_3]$ and $[Mn(\eta\text{-}C_5H_5)(CO)_3]$, but spraying on host matrix at the rate of *ca.* 2 mmol h^{-1} (as determined by the initial and final pressures in the host matrix bulb) and obtaining similar optical densities of $[ML(CO)_3]$ bands as observed for 30 pulses of a 1 : 2 000 $[Fe(\eta\text{-}C_4H_4)(CO)_3]$-argon gas matrix suggests that the dilution for the complexes of Cr and Mn was at least 1 : 2 000 so that aggregation effects on photolysis were minimal.

The i.r. band positions for $[Mn(\eta\text{-}C_5H_5)(CO)_2]$ in argon and methane matrices at 12 K (Table 1) agree well with those for $[Mn(\eta\text{-}C_5H_5)(CO)_2]$ in a methylcyclohexane–Nujol glass at 77 K [ν(CO) at 1 955 and 1 886 cm^{-1}].[13] The probably non-interacting nature of the methylcyclohexane–Nujol glass is confirmed (see above) through the value of the interaction force constant for the $[Mn(\eta\text{-}C_5H_5)(CO)_2]$ species (k_i 53.5 N m^{-1})[13] in contrast to the values for $[Mn(\eta\text{-}C_5H_5)(CO)_2(N_2)]$ [see below; k_i(matrix) 40.3, k_i(n-hexane) 45 N m^{-1}].[21]

Although the photoproduction of $[Cr(\eta\text{-}C_6H_6)(CO)_2]$ occurs most rapidly with shortwavelength radiation ($\lambda < 280$ nm), some forward photolysis does occur with 313 and 366 nm radiation which explains why the reversal step with longer-wavelength radiation ($\lambda > 290$ nm) does not go to completion. Irradiation times of the order of hours were required with $\lambda = 366$ nm to produce detectable conversion of $[Cr(\eta\text{-}C_6H_6)(CO)_3]$ into $[Cr(\eta\text{-}C_6H_6)(CO)_2]$ in contrast to minutes with $\lambda < 280$ nm.

Photolysis of $[ML(CO)_3]$ *in Nitrogen Matrices.*—(*a*) $[Fe(\eta\text{-}C_4H_4)(CO)_3]$. Infrared spectra from an experiment with $[Fe(\eta\text{-}C_4H_4)(CO)_3]$ in nitrogen using the germanium filter are shown in Figure 2 and are representative of other members of the series of complexes. At a dilution of 1 : 2 000 the spectrum of the parent complex [Figure 2(*i*)] is very similar to that in an argon matrix with a wealth of matrix splittings under high-resolution conditions (Table 1). Again weak bands (marked with an asterisk) are observed in the starting spectrum [Figure 2(*i*)] due to natural abundance $[Fe(\eta\text{-}C_4H_4)(^{12}CO)_2(^{13}CO)]$.

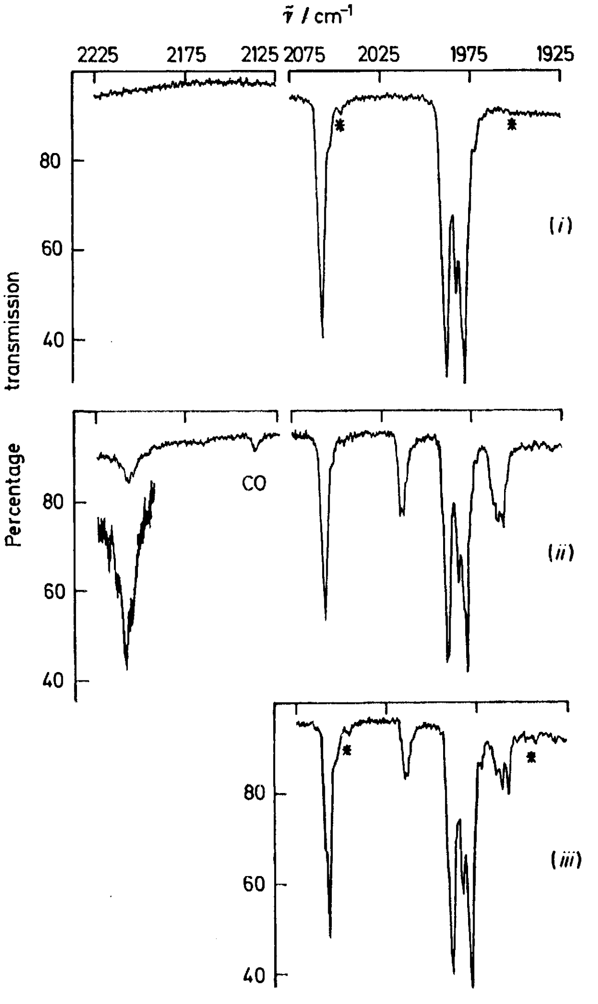

FIGURE 2 Infrared spectra from an experiment with $[Fe(\eta\text{-}C_4H_4)(CO)_3]$ isolated in a nitrogen matrix. For details see Figure 1. Inset spectrum taken using signal expansion (5×)

A period of u.v. photolysis with the medium-pressure mercury lamp and filter A produced a spectrum [Figure 2(*ii*)] containing four new bands at 2 206.8, 2 138.0, 2 013.6, and 1 961.0 cm^{-1}. One of the new bands (2 138.0 cm^{-1}) corresponds to the position of ' free ' CO, while the highest-wavenumber band is between the positions of ν(NN) in $[Ni(CO)_3(N_2)]$ (2 256 cm^{-1})[22] and $[Mn(\eta\text{-}C_5H_5)(CO)_2(N_2)]$ (2 169 cm^{-1}).[21] The assignment of the bands at 2 013.6 and 1 961.0 cm^{-1} as terminal carbonyl-stretching modes leads to the identification of the primary photoproduct as $[Fe(\eta\text{-}C_4H_4)(CO)_2(N_2)]$. Irradiation at longer wavelengths (filter B) rapidly reversed the primary photolysis [Figure 2(*ii*)]. With prolonged u.v. photolysis further new weak bands appeared at *ca.* 2 170 and *ca.* 1 967 cm^{-1} which may

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tentatively be assigned to a bis(dinitrogen) complex [Fe(η-C_4H_4)(CO)(N_2)$_2$].

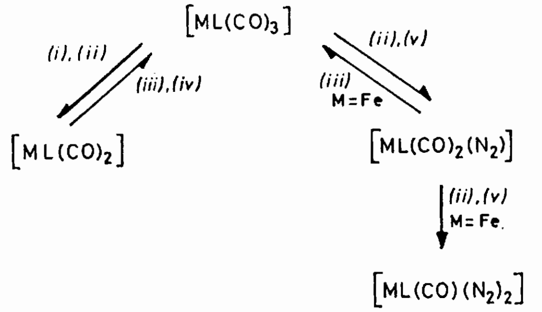
(*b*) [Cr(η-C_6H_6)(CO)$_3$], [Mn(η-C_5H_5)(CO)$_3$], *and* [Fe{C(CH_2)$_3$}(CO)$_3$]. The i.r. spectra of the other [ML(CO)$_3$] complexes and their photolysis products (filter A) in nitrogen matrices were very similar to those described above for [Fe(η-C_4H_4)(CO)$_3$] and the band positions are given in Table 1. The band positions of [Cr(η-C_6H_6)(CO)$_2$(N_2)] and [Mn(η-C_5H_5)(CO)$_2$(N_2)] in nitrogen matrices (Table 1) agree well with the positions in n-hexane solutions {[Cr(η-C_6H_6)(CO)$_2$(N_2)], ν(NN) at 2 145, ν(CO) at 1 940 and 1 898 cm^{-1};[23] [Mn(η-C_5H_5)(CO)$_2$(N_2)], ν(NN) at 2169, ν(CO) at 1 980 and 1 923 cm^{-1} (ref. 21)}. Unlike [Fe(η-C_4H_4)(CO)$_2$(N_2)] which underwent rapid photoconversion into [Fe(η-C_4H_4)(CO)$_3$] on irradiation at long wavelengths (filter B), the dinitrogen complexes of neither Cr nor Mn underwent reversal. The [Fe{C(CH_2)$_3$}(CO)$_2$(N_2)] complex, however, behaved analogously to [Fe(η-C_4H_4)(CO)$_2$(N_2)] even to the extent of undergoing secondary photolysis with u.v. radiation to give possibly [Fe{C(CH_2)$_3$}(CO)(N_2)$_2$] [ν(NN) at 2 180 and ν(CO) at 1 985 cm^{-1}].

Mechanism.—Two separate studies [2,24] are in close agreement for the quantum efficiencies of the photoreactions of [Cr(η-C_6H_6)(CO)$_3$] as measured by quantum yields ($\phi_{CO} = 0.72 \pm 0.07$ for irradiation at 313, 366, and 436 nm; $\phi_{C_6H_6} = ca.\ \frac{1}{6}\phi_{CO}$). A measurement of the estimated quantum yield for [Fe(η-C_4H_4)(CO)$_3$] gave a similar result ($\phi_{C_4H_4} = ca.\ 10^{-1}\phi_{CO}$).[3] It seems reasonable to represent the *principal* photosubstitution process for the [ML(CO)$_3$] complexes as in Scheme 1. This scheme is contrary to observations [25] of 'free' C_4H_4 by mass spectrometry following gas-phase flash-photolysis of [Fe(η-C_4H_4)(CO)$_3$] and an e.s.r. signal assigned to [Fe(CO)$_3$] on photolysis of [Fe(η-C_4H_4)(CO)$_3$] in C_3F_8 and neopentane glass matrices at 77 K. The intermediacy of [M(η^n-C_nH_n)(CO)$_2$] species has been suggested because the quantum yield of formation of [ML(L')(CO)$_2$] is independent of the concentration of ligand L',[2,3,24,26,27] whereas if some partial detachment of the arene ligand took place, *e.g.* [Cr(η^4-C_6H_6)(CO)$_3$], the photoreaction should show a dependence on the incoming nucleophile.

$$[ML(CO)_3] \xrightarrow{h\nu} [ML(CO)_3]^* \longrightarrow [ML(CO)_2] \xrightarrow{+L'} [ML(L')(CO)_2]$$

SCHEME 1

The reactions of [ML(CO)$_3$] complexes in argon and methane matrices show that CO ejection can take place to give co-ordinatively unsaturated species [ML(CO)$_2$] as the primary photolysis products in agreement with previous work on complexes of Fe[14] and Mn.[13] The reactivity of the [ML(CO)$_2$] species is demonstrated both by the recombination with CO, when the matrix was irradiated with light of a different wavelength and in some cases {[Fe(η-C_4H_4)(CO)$_2$][14]} by annealing the matrix, and also by the reaction with N_2 to give [ML(CO)$_2$(N_2)] complexes. No evidence was obtained in this study for the ejection of the arene ligand to give [M(CO)$_3$] species {[Fe(CO)$_3$][28] and [Cr(CO)$_3$][29] have been well characterised in matrices}, and even when the complexes were photolysed in CO matrices no evidence was found for replacement of the arene ligand {*cf.* formation of [Ni(CO)$_4$] on photolysis of [Ni(η-C_5H_5)(NO)] in CO matrices[30]} except for [Fe(η-C_4H_4)(CO)$_3$].[31] The reactions of [ML(CO)$_3$] complexes in matrices are summarised in Scheme 2.



SCHEME 2 (*i*) Argon or CH_4; (*ii*) $h\nu$ (filter A); (*iii*) $h\nu$ (filter B); (*iv*) anneal; (*v*) N_2

The transient species observed in the solution flash-photolysis experiments[2] on [Cr(η-C_6H_6)(CO)$_3$] could either be [Cr(η-C_6H_6)(CO)$_2$] (Scheme 1) or [Cr(η-C_6H_6)(CO)$_2$S], where S denotes a co-ordinated solvent molecule (cyclohexane). Comparison of the interaction force constants for [Cr(η-C_6H_6)(CO)$_2$] in argon and methane matrices [k_i (argon) 40.6, k_i(CH_4) 42.2 N m^{-1}], *cf.* those of [Mn(η-C_5H_5)(CO)$_2$] [k_i(argon) 53.9, k_i(CH_4) 53.4, k_i(methylcyclohexane–Nujol) 53.5 N m^{-1}], suggests (see above) that the transient is probably [Cr(η-C_6H_6)(CO)$_2$]. This is in obvious contrast to the photochemistry of [ML(CO)$_3$] complexes in tetrahydrofuran (thf) solutions where intermediate [ML(CO)$_2$(thf)] complexes have a long lifetime, *e.g.* [Fe(η-C_4H_4)(CO)$_2$(thf)].[3]

The formation of [Mn(η-C_5H_5)(CO)$_2$(N_2)] and [Cr-η-C_6H_6)(CO)$_2$(N_2)] in nitrogen matrices is not surprising since both complexes have been synthesised and characterised by elemental analysis.[21,23] Attempted synthesis of [Fe(η-C_4H_4)(CO)$_2$(N_2)] by a low-temperature synthetic route {*cf.* [Cr(η-C_6Me_6)(CO)$_2$(N_2)],[32] equation (1)} and following communication of preliminary results

$$[Cr(\eta\text{-}C_6Me_6)(CO)_3 \xrightarrow[thf]{h\nu} [Cr(\eta\text{-}C_6Me_6)(CO)_2(thf)] + CO$$

$$[Cr(\eta\text{-}C_6Me_6)(CO)_2(thf)] + N_2 \xrightarrow{thf} [Cr(\eta\text{-}C_6Me_6)(CO)_2(N_2)] \quad (1)$$

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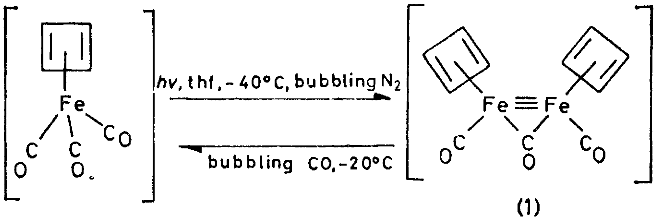
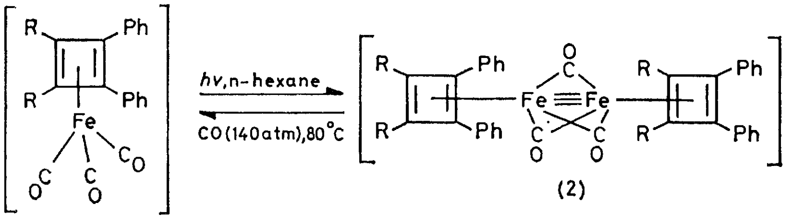
of this study led to the isolation of a binuclear complex (1) [equation (2)].[3] A related binuclear complex (2)[33] was obtained when photolysis was carried out without N_2 bubbling in n-hexane instead of thf solution (equation (3)]. The formation of these binuclear species is not so surprising when the ease of stripping CO ligands off $[\mathrm{Fe}(\eta\text{-}C_4H_4)(CO)_3]$ is compared to the complexes of Cr and Mn both in forming $[\mathrm{Fe}(\eta\text{-}C_4H_4)(CO)_2]$ and $[\mathrm{Fe}(\eta\text{-}C_4H_4)(CO)_2(N_2)]$ and also the secondary photolysis to give $[\mathrm{Fe}(\eta\text{-}C_4H_4)(CO)(N_2)_2]$. The value of ν(NN) can be used to assess the relative stabilities of the $[\mathrm{ML}(CO)_2(N_2)]$ complexes on the basis that the stronger the N–N bond is then the weaker M–N will be. Both the complexes of Cr and Mn have values of ν(NN) (Table 1) at *ca.* 2 150 cm^{-1} which is near the upper limit found for stable dinitrogen complexes. The two iron complexes have values of ν(NN) (Table 1) at *ca.* 2 210 cm^{-1} which is much closer to ν(NN) for uncomplexed N_2 (2 331 cm^{-1}) and hence they will be much less stable. The reactivity of the iron complexes is reflected in the ready reversal to the parent molecules, *cf.* the easy reversal reaction of (1) [equation (2)].[3] In these circumstances, irradiation of $[\mathrm{Fe}(\eta\text{-}C_4H_4)(CO)_3]$ in solution will produce $[\mathrm{Fe}(\eta\text{-}C_4H_4)(CO)_2]$ {or $[\mathrm{Fe}(\eta\text{-}C_4H_4)(CO)_2(N_2)]$} which, in the absence of a good nucleophile, will attack another molecule of $[\mathrm{Fe}(\eta\text{-}C_4H_4)(CO)_3]$ and produce a dimeric complex.



(2)



(3)

The observation of extensive solution photochemistry of $[\mathrm{Fe}(\eta\text{-}C_4H_4)(CO)_3]$ proceeding with retention of the $\mathrm{Fe}(\eta\text{-}C_4H_4)$ group[3] and the gas-matrix results described above suggest that ejection of cyclobutadiene is not a major photoprocess in contrast to the work of Tyerman *et al.*[25] Several explanations are possible to account for the e.s.r. results following the photolysis of $[\mathrm{Fe}(\eta\text{-}C_4H_4)(CO)_3]$ in glasses at 77 K.[25]

(*i*) The material forming the glass was not extensively purified and rigorously degassed before forming the glass and photolysing $[\mathrm{Fe}(\eta\text{-}C_4H_4)(CO)_3]$. Failure to purify solvents led to conflicting results in the solution flash photolysis of $[\mathrm{Cr}(CO)_6]$ and the source of the discrepancies was identified as trace solvent impurities which the highly reactive transient co-ordinated with readily.[34,35] Failure to degass solvents carefully also provides ligands O_2 and N_2 with which the reactive fragment can react, *cf.* the ready conversion of $[\mathrm{Cr}(\eta\text{-}C_6H_6)_2]$ into $[\mathrm{Cr}(\eta\text{-}C_6H_6)_2]^+$ by oxygen in solution.[2]

(*ii*) The e.s.r. technique is very much more sensitive as a detection technique than i.r. spectroscopy, in terms of the number of molecules needed to give a detectable signal. It may well be that e.s.r. is able to detect a transient corresponding to $\phi_{C_4H_4} = 10^{-1}$—$10^{-3}\phi_{CO}$ whereas i.r. spectroscopy is a better test of the principal macroscopic photoprocess.

Until there is corroboration by a repeat of the e.s.r. preferably with simultaneous investigation of the photoproducts by i.r. spectroscopy, the case for ejection of C_4H_4 in solution must remain open. Similarly the detection[25] of C_4H_4 in the gas-phase flash photolysis–mass spectroscopy does not seem to have been unequivocably established.

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