Photochemistry of Tricarbonyl(η-cyclopentadienyl)methylmolybdenum in Frozen Gas Matrices at 12 K. Infrared Spectroscopic Evidence for the Formation of Dicarbonyl(η-cyclopentadienyl)methylmolybdenum and Dicarbonyl(η-cyclopentadienyl)(dinitrogen)methylmolybdenum

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Infrared spectroscopic evidence, including ^{13}CO labelling and energy-factored CO force-field fitting, is presented to show that on photolysis of $[Mo(\eta^5\text{-}C_5H_5)(CO)_3(CH_3)]$ at high dilution in CH_4, Ar, CO, and N_2 matrices at 12 K new species $[Mo(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)]$ and $[Mo(\eta^5\text{-}C_5H_5)(CO)_2(N_2)(CH_3)]$ are produced. The reversibility of the reaction $[Mo(\eta^5\text{-}C_5H_5)(CO)_3(CH_3)] \rightleftharpoons [Mo(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)] + CO$ is interpreted as confirming the existence of a reduced co-ordination number species as the intermediate in the substitution reactions of $[Mo(\eta^5\text{-}C_5H_5)(CO)_3(CH_3)]$. The results are discussed in relation to the mechanisms of thermal and photochemical solution reactions.

THE primary process dominating the photochemistry of $[M(\eta^5\text{-}C_5H_5)(CO)_3X]$ (M = Cr, Mo, or W; X = Cl, I, or CH_3) complexes is the dissociative loss of CO.[1-6] In the presence of ligands, mono- and di-substituted products are normally formed. The loss of CO induced by photolysis can apparently be achieved regardless of X or the metal atom. For example, the ligand triphenylphosphine can substitute for CO in the complexes $[M(\eta^5\text{-}C_5H_5)(CO)_3(CH_3)]$ (M = Cr, Mo, or W) thermally or photochemically to yield $[M(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)(PPh_3)]$ and $[M(\eta^5\text{-}C_5H_5)(CO)_2(COCH_3)(PPh_3)]$.[1,6,7] The photolysis reaction proceeds at much faster rate than the thermal reaction, but the yield of the products is often lower due to photodecomposition. The above two products are believed to arise through initial photosubstitution of CO by PPh_3 with the acetyl derivative forming from a secondary thermal insertion reaction with CO. In the case of the tungsten complex, no acetyl derivative was obtained. Similar reactions have been observed[8] for the corresponding iron complex $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)]$.

Photolysis of $[M(\eta^5\text{-}C_5H_5)(CO)_3(CH_3)]$ complexes in hydrocarbon solvents in the absence of any external ligands leads[6,7,9] to the formation of CH_4 and the dimeric complexes $[\{M(\eta^5\text{-}C_5H_5)(CO)_3\}_2]$ and $[\{M(\eta^5\text{-}C_5H_5)(CO)_2\}_2]$ suggesting that homolysis of the M–CH_3 bond could be the primary photochemical step. In $CHCl_3$ (or CCl_4) solution, the molybdenum and tungsten derivatives also form the complexes $[M(\eta^5\text{-}C_5H_5)(CO)_3Cl]$. Severson and Wojcicki[10] examined the photoreactivity of $[W(\eta^5\text{-}C_5H_5)(CO)_3(CH_3)]$ and presented a more definitive mechanism. While confirming earlier observations, it was noted that the quantum yield of $[\{W(\eta^5\text{-}C_5H_5)(CO)_3\}_2]$ was greatly suppressed when the irradiation was performed under a CO atmosphere compared to photolysis under argon. This observation strongly suggests that the dissociation of CO is the primary step in the photochemical reaction rather than M–CH_3 homolytic cleavage. Photoinduced M–CH_3 bond cleavage in $[M(\eta^5\text{-}C_5H_5)(CO)_3(CH_3)]$ (M = Cr, Mo, or W) has been studied by e.s.r. techniques[11] and the signal observed was assigned to a paramagnetic species, $[M(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)]^{\cdot-}$, formed by a mechanism involving both electron and methyl transfer.

The matrix-isolation technique has been shown to be very useful for investigating photochemical reactions and for characterising reactive species, in particular metal carbonyl species.[12] In this paper, we present i.r. spectroscopic evidence for the formation of the co-ordinatively unsaturated species $[Mo(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)]$ on the photolysis of $[Mo(\eta^5\text{-}C_5H_5)(CO)_3(CH_3)]$ in a variety of frozen gas matrices at 12 K. We relate the results to the mechanisms of thermal and photochemical solution reactions[1-7,9,10] and also to studies of $[Mo(\eta^5\text{-}C_5H_5)(CO)_3(CH_3)]$ in polyvinyl chloride polymer (pvc) film matrices at 12—293 K.[13]

EXPERIMENTAL

Cryogenic temperatures (*ca.* 12 K) were obtained using a Displex CSA-202 closed-cycle helium refrigeration system (Air Products and Chemicals Inc.). The complex $[Mo(\eta^5\text{-}C_5H_5)(CO)_3(CH_3)]$ is intermediate between those which are volatile enough to give gas mixtures for 'pulsed' deposition and those which need high temperatures to sublime them onto the cold window. The vapour from the cooled solid (5—12 °C) was co-condensed with host matrix gas onto the cold CaF_2 window. Monomer isolation (dilution *ca.* 1 : 2 000) was ensured by having a substantially higher gas flow for the host matrix than for the complex to be isolated. Deposition (*ca.* 2 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} and that there was no tailing of bands to lower wavenumbers.

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

The photolysis source was a water-cooled medium-pressure mercury arc lamp (Philips HPK 125-W). Wavelength-selective photolysis was achieved using the following combinations of absorbing materials: filter A, $310 < \lambda <$

370 nm, quartz gas cell (pathlength 25 mm) containing Br_2 gas (300 Torr) * + Pyrex glass disc (thickness 18 mm); filter B, $\lambda > 400$ nm, quartz gas cell (pathlength 25 mm) containing Cl_2 (2 atm) * + Pyrex glass disc (thickness 18 mm). Matrix gases (Ar, CH_4, CO, N_2) were BOC 'Grade X' purity and ^{13}CO (95% enriched) was obtained from BOC Prochem Limited. The sample of $[Mo(\eta^5\text{-}C_5H_5)(CO)_3(CH_3)]$ was prepared according to the literature procedure and purified by sublimation.[14] The ^{13}CO-enriched complex $[Mo(\eta^5\text{-}C_5H_5)(CO)_3(CH_3)]$ was prepared by photolysing (filter A) the complex in hexane (25 mg in 100 cm^3) in an atmosphere of ^{13}CO (300 Torr) for 2 h.† The solvent was removed by pumping under vacuum and the solid was purified by sublimation.

RESULTS

Photolysis of $[Mo(\eta^5\text{-}C_5H_5)(CO)_3(CH_3)]$ *in* Ar, CH_4, *and* CO *Matrices*.—The i.r. spectrum of $[Mo(\eta^5\text{-}C_5H_5)(CO)_3(CH_3)]$ isolated at high dilution in a CH_4 matrix (*ca.* 1 : 2 000—1 : 5 000) is shown in Figure 1(*a*). The spectrum shows that although the $Mo(CO)_3(CH_3)$ fragment has a local C_s symmetry, *i.e.* three i.r. active CO stretching bands are expected, only a single low-wavenumber band (*ca.* 1 940 cm^{-1}) is observed in addition to the symmetric (A') band (*ca.* 2 025 cm^{-1}, Table 1). The single low-wavenumber band must, therefore, arise from an accidental coincidence between the A'' and the lower A' bands. This is not the same thing as effective C_{3v} symmetry, as ^{13}CO data (Table 2) show.

Irradiation of the matrices using the filtered medium-pressure mercury arc (filter A) giving light corresponding to the long-wavelength absorption [Figure 2 (*a*)] produced free CO (*ca.* 2 138 cm^{-1}) and two new bands at 1 966.0 and 1 880.1 cm^{-1} [Figure 1 (*b*) and (*c*)]. The production of these two bands is accompanied by the decrease of bands of the parent and increase of the band due to free CO. After irradiation with long-wavelength light from the mercury arc lamp (filter B), *cf.* the long-wavelength tail [Figure 2(*b*)], or annealing the matrix for 3 min and then re-cooling to 12 K, the new product bands were observed to decrease with the regeneration of bands due to $[Mo(\eta^5\text{-}C_5H_5)(CO)_3(CH_3)]$ [Figure 1(*d*)]. The relative intensity of the new terminal CO-stretching bands remained constant under a variety of photolysis conditions (time and wavelength of radiation), indicating that the bands arose from a single product species. The dilution used (*ca.* 1 : 2 000) and the reversibility of the matrix reaction rule out the possibility of formation of polynuclear aggregate species, *e.g.* $[\{Mo(\eta^5\text{-}C_5H_5)(CO)_3\}_2]$, as confirmed [15] by separate matrix-isolation studies of $[\{Mo(\eta^5\text{-}C_5H_5)(CO)_3\}_2]$. We therefore assign these new bands to the dicarbonyl complex $[Mo(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)]$ (see below), corresponding to the A' (1 966.0 cm^{-1}) and A'' (1 880.1 cm^{-1}) terminal CO-stretching modes with a local C_s symmetry (Table 1).

Analogous results were obtained for Ar and CO matrices (Table 1) although the rates of photoreactions were slower as has been observed elsewhere.[16,17]

Photolysis of ^{13}CO*-enriched* $[Mo(\eta^5\text{-}C_5H_5)(CO)_3(CH_3)]$ *in* CH_4 *Matrices*.—The i.r. spectrum of ^{13}CO-enriched $[Mo(\eta^5\text{-}C_5H_5)(CO)_3(CH_3)]$ (see Experimental section) isolated in a

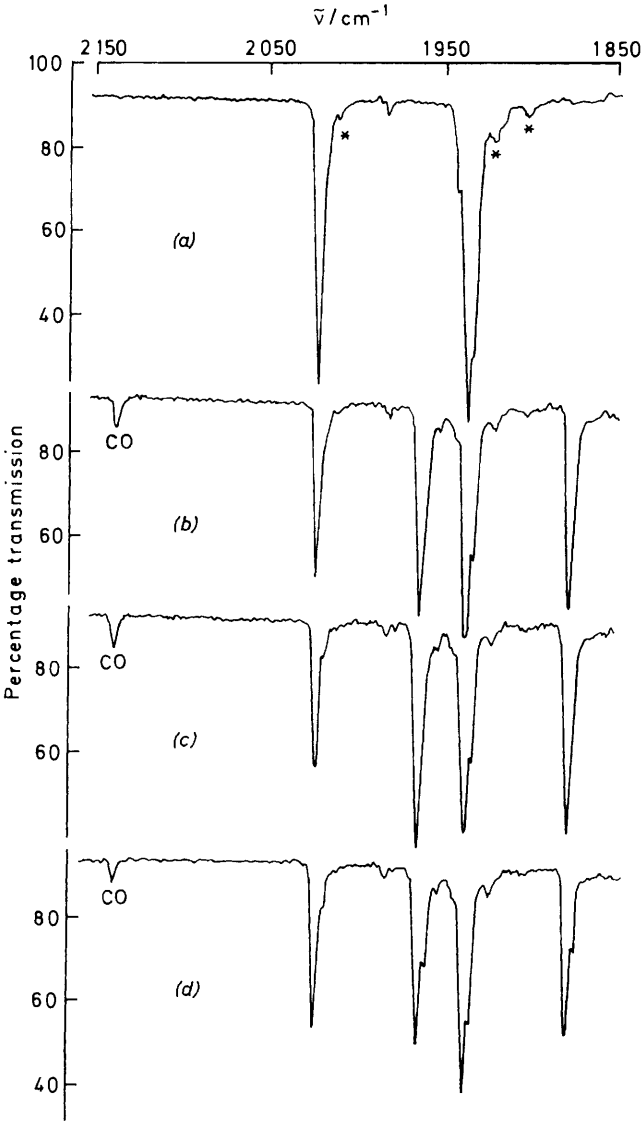

FIGURE 1 Infrared spectra from an experiment with $[Mo(\eta^5\text{-}C_5H_5)(CO)_3(CH_3)]$ isolated at high dilution in a CH_4 matrix at 12 K: (*a*) after deposition, (*b*) after 15 min photolysis using filter A, (*c*) after further 15 min photolysis using filter A, and (*d*) after annealing the matrix to *ca.* 30 K. Bands marked (*) are due to $[Mo(\eta^5\text{-}C_5H_5)(^{12}CO)_2(^{13}CO)(CH_3)]$ in natural abundance

TABLE 1

Infrared band positions (cm^{-1}) observed in the CO-stretching region for $[Mo(\eta^5\text{-}C_5H_5)(CO)_3(CH_3)]$ and its photoproducts in various matrices at 12 K

Complex	CH_4	Ar	N_2	CO
$[Mo(\eta^5\text{-}C_5H_5)(CO)_3(CH_3)]$	2 023.9	2 030.7	2 028.6	2 025.8
	1 937.9	1 945.8	1 941.4	1 945.2 1 938.8 $\}^{a}$
$[Mo(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)]$	1 966.0	1 972.0	1 972.8	1 962.4 [b]
	1 880.1	1 886.8	1 884.4	1 876.8
$[Mo(\eta^5\text{-}C_5H_5)(CO)_2(N_2)\text{-}(CH_3)]$			1 969.7 [c]	
			1 913.7	

[a] Matrix splitting. [b] Long photolysis time required. [c] $\nu(NN)$ at 2 190.8 cm^{-1}.

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* Throughout this paper: 1 Torr = (101 325/760) N m^{-2}; 1 atm = 101 325 N m^{-2}.

† Such a period of irradiation was insufficient to produce total scrambling of ^{12}CO and ^{13}CO ligands which, on the basis of the amount of ^{13}CO used, should have resulted in the formation of $[Mo(\eta^5\text{-}C_5H_5)(^{13}CO)_3(CH_3)]$ as the major product.

pure CH_4 matrix [Figure 3 (*a*)] shows bands due to the complexes $[Mo(\eta^5\text{-}C_5H_5)(^{12}CO)_{3-n}(^{13}CO)_n(CH_3)]$ (n = 0—3) as confirmed by the excellent correspondence between observed and calculated [16,18,19] band positions (Table 2), obtained using an energy-factored force field. Photolysis of the complexes using a medium-pressure mercury arc (filter A) gave new ^{13}CO-enriched product bands at 1 947.8, 1 852.7, and 1 836.8 cm^{-1} in addition to the bands for the ^{12}CO species at 1 965.9 and 1 879.6 cm^{-1} [Figure 3(*b*)]. In this case, a good fit was obtained for the observed and calculated bands of a C_s $Mo(CO)_2$ fragment (Table 2). The photoproduct in Ar, CH_4, and CO matrices (see above) can, therefore, be conclusively assigned as $[Mo(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)]$. The observed relative intensity of the two terminal bands (1.32 : 1 for $A' : A''$ and obtained by tracing and weighing the bands) was used to calculate a OC–Mo–CO angle of 82 ± 1° from the standard expression [19] $I_{sym}/I_{antisym} = \cot^2(\theta/2)$.[*]

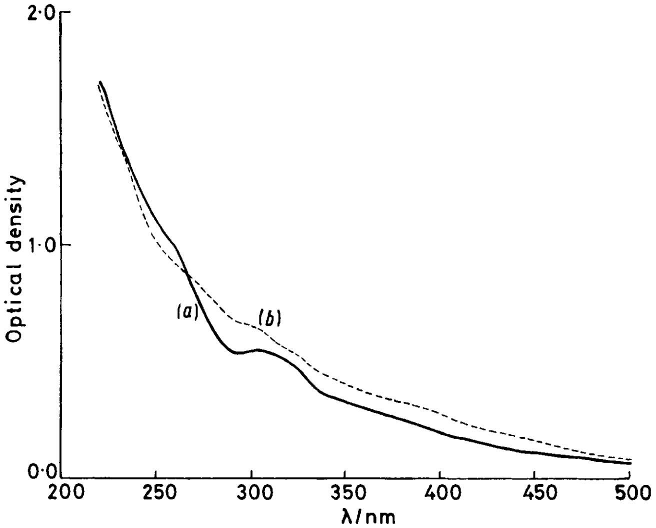
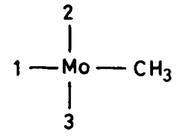


FIGURE 2 Ultraviolet–visible spectra from an experiment with $[Mo(\eta^5\text{-}C_5H_5)(CO)_3(CH_3)]$ isolated at high dilution in a CH_4 matrix at 12 K: (*a*) after deposition, and (*b*) after 30 min photolysis using filter A

Photolysis of $[Mo(\eta^5\text{-}C_5H_5)(CO)_3(CH_3)]$ *in* N_2 *Matrices*.—The i.r. spectrum of $[Mo(\eta^5\text{-}C_5H_5)(CO)_3(CH_3)]$ isolated in a pure N_2 matrix in the terminal CO-stretching region [Figure 4 (*a*), Table 1] is very similar to that in Ar, CO, and CH_4 matrices [Figure 1(*a*)]. The two terminal CO-stretching bands correspond to the A' (2 028.6 cm^{-1}) and coincident ($A' + A''$) (1 941.4 cm^{-1}) modes as before. A period of photolysis, using the medium-pressure mercury arc (filter A), produced new i.r. bands [Figure 4 (*b*)] at 2 190.8, 2 138.0, 1 972.8, 1 969.7, 1 913.7, and 1 884.4 cm^{-1}, of which the band at 2 138.0 cm^{-1} corresponds to CO liberated by photolysis. All these bands increased with a constant relative intensity. Irradiation with long-wavelength light from the mercury lamp (filter B) or annealing the matrix for 2 min and then re-cooling to 12 K produced increases in bands at 2 190.8, 1 969.7, and 1 913.7 cm^{-1} with corresponding decreases in bands at 1 972.8 and 1 884.4 cm^{-1} and with little or no change in the intensity of parent bands [Figure 4(*c*)].

TABLE 2

Observed and calculated [a] band positions (cm^{-1}) of terminal CO-stretching bands in an experiment with a ^{13}CO-enriched sample of $[Mo(\eta^5\text{-}C_5H_5)(CO)_3(CH_3)]$ in a CH_4 matrix at 12 K



i.e. 1 ≠ 2 = 3

Complex (symmetry)		ν(CO)	Observed	Calculated
$[Mo(\eta^5\text{-}C_5H_5)(^{12}CO)_3(CH_3)]$		A'	2 025.4	2 025.5
(C_s)		$A' + A''$	1 940.1	1 939.9
$[Mo(\eta^5\text{-}C_5H_5)(^{12}CO)_2(^{13}CO)(CH_3)]$	*b*	A'	2 016.0	2 016.3
(C_s)		A'	1 939.2 [c]	1 939.9
		A''	1 906.6 [d]	1 905.4
	e	A'	2 013.2	2 013.8
		A'	1 939.2 [c]	1 939.9
		A''	1 906.6 [d]	1 907.8
$[Mo(\eta^5\text{-}C_5H_5)(^{12}CO)(^{13}CO)_2(CH_3)]$	*f*	A'	2 001.0 [g]	2 002.3
(C_s)		A'	1 918.4	1 918.7
		A''	*h*	1 896.7
	i	A'	1 998.9	1 998.9
		A'	1 921.4	1 922.0
		A''	*h*	1 896.8
$[Mo(\eta^5\text{-}C_5H_5)(^{13}CO)_3(CH_3)]$		A'	1 980.6	1 980.5
(C_s)		$A' + A''$	1 896.5	1 896.7
$[Mo(\eta^5\text{-}C_5H_5)(^{12}CO)_2(CH_3)]$		A'	1 965.9	1 965.3
(C_s)		A''	1 879.6	1 879.1
$[Mo(\eta^5\text{-}C_5H_5)(^{12}CO)(^{13}CO)(CH_3)]$		A	1 947.8	1 948.5
(C_1)		A	1 852.7	1 853.2
$[Mo(\eta^5\text{-}C_5H_5)(^{13}CO)_2(CH_3)]$		A'	*h*	1 921.6
(C_s)		A''	1 836.8	1 837.3

[a] Refined energy-factored force constants for $[Mo(\eta^5\text{-}C_5H_5)(CO)_3(CH_3)]$: K_1 = 1 559.5, K_2 = 1 569.3, k_{12} = 43.8, and k_{23} = 49.0 N m^{-1} as defined by the numbering in the diagram above. Refined energy-factored force constants for $[Mo(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)]$: K = 1 493.5 and k_i = 67.0 N m^{-1}. [b] ^{13}CO in position 1. [c] Band obscured by bands of $[Mo(\eta^5\text{-}C_5H_5)(CO)_3(CH_3)]$. [d] Broad band arising probably from two components at 1 905 and 1 908 cm^{-1}. [e] ^{13}CO in position 2. [f] ^{12}CO in position 2. [g] Component of broad band centred at 2 000 cm^{-1}. [h] Band obscured by bands of ^{13}CO-enriched $[Mo(\eta^5\text{-}C_5H_5)(CO)_3(CH_3)]$. [i] ^{12}CO in position 1.

Taking into account the dilution and the subsequent reversibility (filter B) of the primary photolysis step, these bands can be assigned to two mononuclear species. The bands at 1 972.8 and 1 884.4 cm^{-1} can be assigned to the terminal CO-stretching modes of $[Mo(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)]$ species by comparison of the band positions to those for CH_4, Ar, and CO matrices (Table 1) together with their analogous reversal behaviour. The band at 2 190.8 cm^{-1} may be assigned to a $^{14}N{-}^{14}N$ stretching mode and the bands at 1 969.7 and 1 913.7 cm^{-1} may be assigned to the terminal CO-stretching modes of $[Mo(\eta^5\text{-}C_5H_5)(CO)_2(N_2)(CH_3)]$ (see below). Long-wavelength irradiation (filter B) or annealing the matrix and re-cooling to 12 K failed to reverse the bands of $[Mo(\eta^5\text{-}C_5H_5)(CO)_2(N_2)(CH_3)]$ in contrast to the ready reversal of the bands due to $[Mo(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)]$. The non-reversibility complex of the $[Mo(\eta^5\text{-}C_5H_5)(CO)_2(N_2)(CH_3)]$ is analogous to observations of

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[*] Strictly speaking, the ratio $I_{sym}/I_{antisym}$ gives the angle between the CO oscillating dipoles, which may or may not coincide with the CO bond direction vectors. In practice, estimations of bond angles using such a ratio have been supported by other structural measurements.

other dinitrogen complexes, $[Co(\eta^5\text{-}C_5H_5)(CO)(N_2)]$ [18] and $[Mn(\eta^5\text{-}C_5H_5)(CO)_2(N_2)]$,[20] which have ν(NN) in the 2 160 cm^{-1} region, and is in contrast to the behaviour of $[Fe(\eta^4\text{-}C_4H_4)(CO)_2(N_2)]$ [20] and other matrix-isolated dinitrogen complexes, *e.g.* $[Ni(CO)_3(N_2)]$,[21] [Rh(tfa)(CO)(N_2)] (tfa = 1,1,1-trifluoroacetylacetonate),[22] which have ν(NN) above 2 200 cm^{-1}.

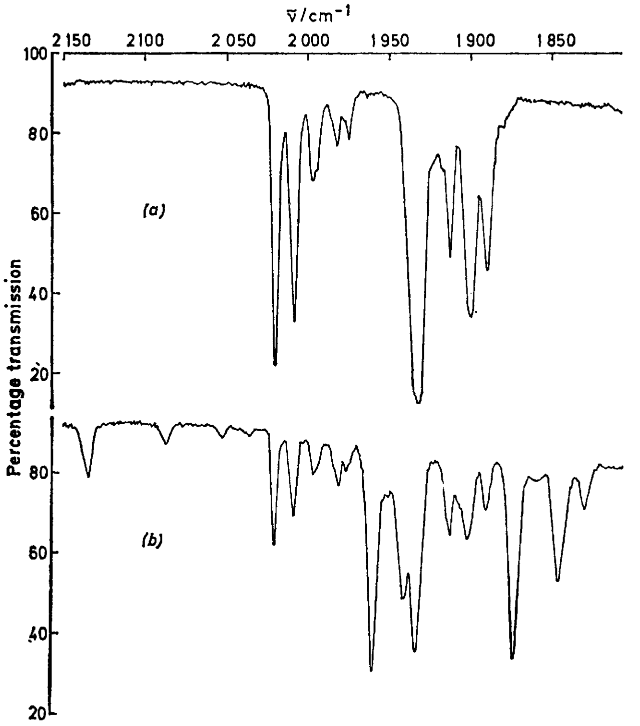


FIGURE 3 Infrared spectra from an experiment with ^{13}CO-enriched $[Mo(\eta^5\text{-}C_5H_5)(CO)_3(CH_3)]$ isolated at high dilution in a CH_4 matrix at 12 K: (*a*) after deposition, and (*b*) after 75 min photolysis using filter A

Photolysis of ^{13}*CO-enriched* $[Mo(\eta^5\text{-}C_5H_5)(CO)_3(CH_3)]$ *in* N_2 *Matrices*.—A period of photolysis (1 h) of ^{13}CO-enriched $[Mo(\eta^5\text{-}C_5H_5)(CO)_3(CH_3)]$ isolated in a pure N_2 matrix using a medium-pressure mercury arc (filter A) gave the bands for the ^{12}CO species at 1 969.7 and 1 913.7 cm^{-1} (Table 1) and new ^{13}CO-enriched product bands at 1 955.3, 1 924.5, 1 886.0, and 1 871.4 cm^{-1}. These bands were observed in addition to the bands due to complexes $[Mo(\eta^5\text{-}C_5H_5)(^{12}CO)_{3-n}(^{13}CO)_n(CH_3)]$ (n = 0—3) and $[Mo(\eta^5\text{-}C_5H_5)(^{12}CO)_{2-m}(^{13}CO)_m(CH_3)]$ (m = 0—2). Irradiation with long-wavelength light from the mercury lamp (filter B) or annealing the matrix for 2 min and then re-cooling to 12 K produced increase of bands at 1 955.3, 1 924.5, 1 886.0, 1 871.4, and 2 190.8 [ν(NN)] cm^{-1} with corresponding decrease of bands of $[Mo(\eta^5\text{-}C_5H_5)(^{12}CO)_{2-m}(^{13}CO)_m(CH_3)]$ (m = 0—2) complexes. Using an energy-factored force-field fitting, a good correspondence was obtained between the observed and calculated bands of a C_s $Mo(CO)_2$ fragment (Table 3). Therefore, the photoproduct obtained in the N_2 matrices (see above) corresponding to the bands at 2 190.8, 1 969.7, and 1 913.7 cm^{-1} can conclusively be assigned to the species $[Mo(\eta^5\text{-}C_5H_5)(CO)_2(N_2)(CH_3)]$. Two structures (I and II) can be drawn for the $Mo(CO)_2(N_2)(CH_3)$ fragment of this complex. On the basis of a comparison of k_i obtained for this complex (43.3 N m^{-1}) with k_i values for $[Mo(\eta^5\text{-}C_5H_5)(CO)_3(CH_3)]$ ($k_{12} = k_{cis}$ = 43.8 and $k_{23} = k_{trans}$ = 49.0 N m^{-1}), it seems likely that $[Mo(\eta^5\text{-}C_5H_5)(CO)_2(N_2)(CH_3)]$ adopts structure I.

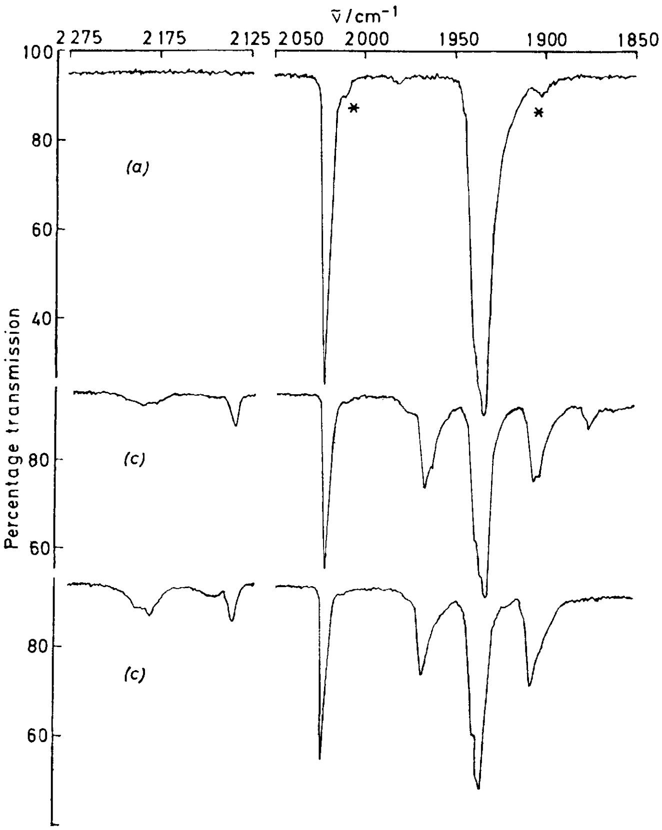
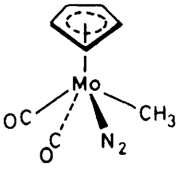
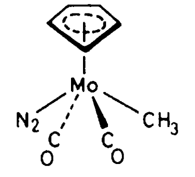


FIGURE 4 Infrared spectra from an experiment with $[Mo(\eta^5\text{-}C_5H_5)(CO)_3(CH_3)]$ isolated at high dilution in a N_2 matrix at 12 K: (*a*) after deposition, (*b*) after 50 min photolysis using filter A, and (*c*) after annealing the matrix. Bands marked (*) are due to $[Mo(\eta^5\text{-}C_5H_5)(^{12}CO)_2(^{13}CO)(CH_3)]$ in natural abundance



I (*cis*)

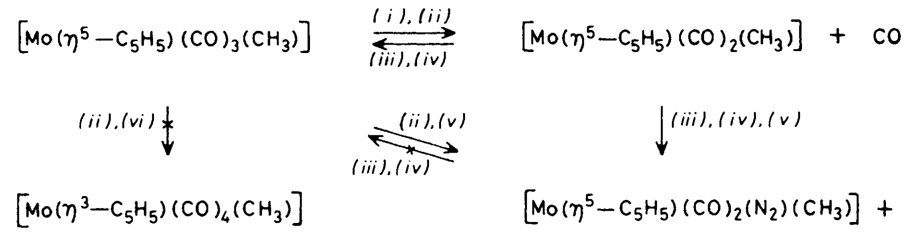


II (*trans*)

DISCUSSION

The photoreactions of $[Mo(\eta^5\text{-}C_5H_5)(CO)_3(CH_3)]$ at high dilution in CH_4, Ar, CO, and N_2 matrices are summarised in the Scheme.

The observation of the co-ordinatively unsaturated 16-electron species, $[Mo(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)]$, even in a CO matrix, is consistent with the dissociative mechanism proposed[1-7] for ligand substitution reactions of $[Mo(\eta^5\text{-}C_5H_5)(CO)_3(CH_3)]$. In the CO matrix, no evidence was obtained for the formation of expanded co-ordination number species $[Mo(\eta^3\text{-}C_5H_5)(CO)_4(CH_3)]$, possibly for steric reasons, in contrast to the expanded co-ordination number species $[Co(\eta^3\text{-}C_5H_5)(CO)_3]$ and $[Fe(\eta^3\text{-}C_5H_5)(CO)_3(CH_3)]$ produced from the complexes $[Co(\eta^5\text{-}C_5H_5)(CO)_2]$ [18] and $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)]$ [23] respectively.



SCHEME (*i*) CH_4, Ar, CO, or N_2; (*ii*) $h\nu$ (filter A); (*iii*) $h\nu$ (filter B); (*iv*) annealing; (*v*) N_2; (*vi*) CO

TABLE 3

Observed and calculated* band positions (cm^{-1}) of terminal CO-stretching bands for ^{13}CO-enriched $[Mo(\eta^5\text{-}C_5H_5)(CO)_2(N_2)(CH_3)]$ in a N_2 matrix at 12 K

Complex	ν(CO)	Observed	Calculated
$[Mo(\eta^5\text{-}C_5H_5)(^{12}CO)_2(N_2)(CH_3)]$	A'	1 969.7	1 969.0
	A''	1 913.7	1.913.8
$[Mo(\eta^5\text{-}C_5H_5)(^{12}CO)(^{13}CO)(N_2)(CH_3)]$	A	1 955.3	1 954.6
	A	1 886.0	1 885.1
$[Mo(\eta^5\text{-}C_5H_5)(^{13}CO)_2(N_2)(CH_3)]$	A'	1 924.5	1 925.2
	A''	1 871.4	1 871.3

* Refined energy-factored constants for $[Mo(\eta^5\text{-}C_5H_5)(CO)_2(N_2)(CH_3)]$: $K = 1\,523.0$ and $k_t = 43.3$ N m^{-1}.

In CH_4, Ar, and CO gas matrices at 12 K, no evidence was obtained for the homolysis of the Mo–CH_3 bond, forming radicals, whereas in solution evidence for a radical pathway comes from the formation of the dimer $[\{Mo(\eta^5\text{-}C_5H_5)(CO)_3\}_2]$.[6,7,9] Interestingly, in the ^{13}CO exchange reaction (see Experimental section) the dimer complex was obtained in addition to the ^{13}CO-enriched species. Other evidence for the importance of a primary photoprocess involving radicals comes from e.s.r. studies of the photolysis of $[M(\eta^5\text{-}C_5H_5)(CO)_3(CH_3)]$ (M = Cr, Mo, and W) complexes in hydrocarbon solvents.[11] In this work the e.s.r. spectra were interpreted as being most consistent with a radical anion species $[Mo(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)]^{\cdot -}$, rather than the expected radical species $[Mo(\eta^5\text{-}C_5H_5)(CO)_3]^{\cdot}$, although this species was postulated as possibly being the primary photoproduct in a reaction scheme. In contrast to the gas matrix observations described above, in a pvc polymer matrix at 12—293 K both CO dissociation and Mo–CH_3 bond-cleavage reactions occur.[13] The evidence for the latter process comes from the disappearance of bands due to $[Mo(\eta^5\text{-}C_5H_5)(CO)_3(CH_3)]$ together with the growth of bands due to $[Mo(\eta^5\text{-}C_5H_5)(CO)_3Cl]$.[13] One of the reasons for the failure to observe radical species in gas matrices could be that unlike the polymer matrix there are no secondary reaction processes, *e.g.* Cl abstraction, that can lead to product stabilisation. Additionally, the small gas matrix molecules can pack tightly around a substrate molecule to create a 'tight cage' [24] in which the radicals produced on photolysis are unable to diffuse far enough apart to prevent a thermal back reaction. In contrast, the bulky polymer chains form a 'loose cage' from which the $CH_3^{\cdot}$ can escape. Support for the latter explanation can also be drawn from the fact that trapping of a radical species following photolysis of an organometallic compound in gas matrices has only been observed [12,25] when H· has been ejected (see below).

$$[CoH(CO)_4] \xrightarrow[Ar]{h\nu} [Co(CO)_4]^{\cdot} + H^{\cdot} + [CoH(CO)_3] + CO$$

$$[CoH(CO)_4] \xrightarrow[CO]{h\nu} [Co(CO)_4]^{\cdot} + HCO^{\cdot}$$

The formation of $[Mo(\eta^5\text{-}C_5H_5)(CO)_2(N_2)(CH_3)]$ in nitrogen matrices could be envisaged to occur *via* the 16-electron species $[Mo(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)]$ which can add a N_2 molecule. The observation of $[Mo(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)]$ as well as $[Mo(\eta^5\text{-}C_5H_5)(CO)_2(N_2)(CH_3)]$ on photolysis of $[Mo(\eta^5\text{-}C_5H_5)(CO)_3(CH_3)]$ in N_2 matrices suggests that $[Mo(\eta^5\text{-}C_5H_5)(CO)_2(N_2)(CH_3)]$ may be very difficult to prepare in a conventional reaction. This is in contrast to the complexes $[Mn(\eta^5\text{-}C_5H_5)(CO)_2(N_2)]$ and $[Cr(\eta^6\text{-}C_6H_6)(CO)_2(N_2)]$ which have been produced by photolysis in N_2 matrices [20] and also characterised by elemental analysis following reactions in solution.[26] Other contraindications for the preparation of $[Mo(\eta^5\text{-}C_5H_5)(CO)_2(N_2)(CH_3)]$ are the relatively high value of ν(NN) (2 190.8 cm^{-1}) compared to values of 2 175.3 and 2 148.4 cm^{-1} for $[Mn(\eta^5\text{-}C_5H_5)(CO)_2(N_2)]$ and $[Cr(\eta^6\text{-}C_6H_6)(CO)_2(N_2)]$ respectively, and the formation in solution of radicals leading to $[\{Mo(\eta^5\text{-}C_5H_5)(CO)_3\}_2]$ (see above).

CONCLUSION

The photoreactions of $[Mo(\eta^5\text{-}C_5H_5)(CO)_3(CH_3)]$ in Ar, CH_4, CO, and N_2 matrices at 12 K indicate that the principal reactive intermediate in the thermal and photochemical solution substitution reactions is probably the co-ordinatively unsaturated species $[Mo(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)]$. The reactions, therefore probably involve dissociative mechanisms rather than associative mechanisms, *cf.* $[Co(\eta^5\text{-}C_5H_5)(CO)_2] + CO \rightleftharpoons [Co(\eta^3\text{-}C_5H_5)(CO)_3]$.[18] Evidence for a contribution from a radical pathway has been obtained in a separate study [13] using pvc matrices.

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