Photochemistry of Tricarbonyl(1—6-η-cycloheptatriene)-molybdenum in Frozen Gas Matrices at 12 K. Photodissociation of Cycloheptatriene and Carbon Monoxide Ligands†

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Infrared spectroscopic studies reveal that u.v. irradiation of [Mo(η^6-C_7H_8)(CO)$_3$] (1) in CH_4 and Ar matrices at 12 K results in the reversible formation of [Mo(η^6-C_7H_8)(CO)$_2$] *via* photodissociation of CO. Energy-factored force field fittings show that the species [Mo(η^6-C_7H_8)(CO)$_{3-n}$(^{13}CO)$_n$] (*n* = 1—3) and [Mo(η^6-C_7H_8)(CO)$_{2-m}$(^{13}CO)$_m$] (*m* = 0—2) are produced on prolonged irradiation of (1) in a ^{13}CO doped (5%) CH_4 matrix at 12 K. Photolysis of (1) in a N_2 matrix at 12 K leads to photoproducts of the type [Mo(η^6–C_7H_8)(CO)$_{3-x}$(N_2)$_x$] (*x* = 1—3). Stepwise photoelimination of cycloheptatriene in a CO matrix at 12 K results in the conversion of (1) to [Mo(CO)$_6$] *via* the intermediate species [Mo(η^4-C_7H_8)(CO)$_4$].

Thermal reactions of cycloheptatriene–metal complexes of the type [M(η^6-C_7H_8)(CO)$_3$] (M = Cr, Mo, or W) are known to involve substitution of the cycloheptatriene ring by neutral ligands. Such reactions have been used extensively in the preparation of new compounds of the type *fac*-[M(CO)$_3$L$_3$] (*e.g.* where L = phosphines, arsines, or MeCN).[1–3] The ease of cycloheptatriene displacement from the starting complexes has been found to depend very much on the central metal in the following order: Mo ≫ W > Cr. Results of kinetic studies of the reaction, in solution, of acetonitrile with [Mo(η^6-C_7H_8)(CO)$_3$] to give [Mo(CO)$_3$(MeCN)$_3$] have indicated that the mechanism probably involves successive attack by acetonitrile with stepwise loss of the cyclic olefin.[4] The photochemical exchange of cycloheptatriene in the chromium and molybdenum complexes by ^{14}C-labelled cycloheptatriene (C_7H_8*) has also been studied [5a] [equation (1)].

$$[M(\eta^6\text{-}C_7H_8)(CO)_3] + C_7H_8^* \rightleftharpoons [M(\eta^6\text{-}C_7H_8^*)(CO)_3] + C_7H_8\ (\text{solvent}) \quad (1)$$
$$(M = \text{Cr or Mo})$$

Only one thermal reaction in which direct substitution of CO in [M(η^6-C_7H_8)(CO)$_3$] (M = Cr or Mo) occurs has been reported.[6] Other studies, however, have shown that photosubstitution of CO in the complex [Cr(η^6-C_7H_8)(CO)$_3$] by ligands without loss of cycloheptatriene occurs in solution. For example, irradiation of [Cr(η^6-C_7H_8)(CO)$_3$] in the presence of triphenylphosphine or triphenyl phosphite in tetrahydrofuran (thf) using light of wavelength 366 nm leads to the formation of [Cr(η^6-C_7H_8)(CO)$_2$(PPh$_3$)] and [Cr(η^6-C_7H_8)(CO)$_2${P(OPh)$_3$}] respectively.[7] More recently the photochemical preparation of the compounds [Cr(η^6-C_7H_8)(CO)$_2$L] [L = PMe$_3$, AsMe$_3$, and P(OCH$_3$)$_3$] and [Cr(η^6-C_7H_8)(CO)L$_2$] [L = P(OCH$_3$)$_3$] was achieved.[8] Similar reactions of the molybdenum or tungsten complexes have not been reported. As part of our matrix isolation studies of reactive species involved in thermal and photochemical reactions of organometallic compounds, we report here the photochemistry of [Mo(η^6-C_7H_8)(CO)$_3$] observed in low temperature gas matrices at 12 K.

Experimental

The complex [Mo(CO)$_6$] was refluxed with cycloheptatriene[9,10] in light petroleum (b.p. 100—120 °C) under N_2 for 16 h. After cooling to room temperature the reaction mixture was filtered under N_2 and the filtrate cooled to −78 °C. The crude product which separated was filtered off and purified by first volatilising unreacted [Mo(CO)$_6$] at 25 °C/0.05 mmHg and then subliming the residue at 70 °C/0.05 mmHg giving [Mo(η^6-C_7H_8)(CO)$_3$] as red crystals. Samples were sublimed at 30—40 °C/10^{-6} mmHg ‡ and co-condensed onto a CaF_2 cold window (*ca.* 12 K) with a large excess of host matrix gas, ensuring monomer isolation. Cryogenic temperatures were obtained using a Displex CSA-202 closed-cycle refrigerator (Air Products and Chemical Inc.).

Intensities of i.r. bands were monitored in between deposition and photolysis periods using either a Grubb Parsons Spectromajor grating spectrometer (resolution ⩽1 cm^{-1}) or a Nicolet 7199 FT-IR system (resolution <0.25 cm^{-1}). A water cooled mercury-arc lamp (Philips HPK 125 W) was used as the photolysis source and irradiation into specific wavelength bands was achieved using the following filters: filter A, $\lambda < 280$ and >550 nm, quartz gas cell (pathlength 25 mm) containing Br_2 (300 Torr) + quartz gas cell (pathlength 25 mm) containing Cl_2 (2 atm); filter B, $290 < \lambda < 370$ nm, quartz gas cell (pathlength 25 mm) containing Br_2 (300 Torr) + Pyrex disc (thickness 3 mm); filter C, $\lambda > 320$ nm, soda glass disc (thickness 4 mm); filter D, $\lambda > 400$ nm, quartz gas cell (pathlength 25 mm) containing Cl_2 (2 atm) + Pyrex disc (thickness 3 mm). Matrix gases used (CH_4, Ar, CO, and N_2) were of grade ' X ' purity and obtained from B.O.C. Prochem. Ltd. together with ^{13}CO (95% enriched). Cycloheptatriene (source) was purified by removing dissolved gases and gas mixtures (1 : 1 000) were made up manometrically.

Results

Photolysis of [Mo(η^6-C_7H_8)(CO)$_3$] *in* CH_4 *and* Ar *Matrices at* 12 K.—Figure 1(*a*) shows the i.r. spectrum of [Mo(η^6-C_7H_8)(CO)$_3$] (1) isolated at high dilution in a CH_4 matrix at 12 K after deposition. The three terminal carbonyl stretching bands seen centred at 1 993.6 (*A′*), 1 928.3 (*A′*), and *ca.* 1 900 cm^{-1} (*A″*) (the lowest energy band is matrix split into a doublet) are characteristic of the cycloheptatriene–metal complex[9] which has C_s symmetry. The u.v.-visible spectrum obtained for the same matrix is shown in Figure 2(*a*). After a period of u.v. photolysis (filter A) two new carbonyl bands were seen at 1 939.3 and 1 860.4 cm^{-1} together with a broad band at

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† *Non-S.I. units employed:* 1 mmHg ≈ 13.6 × 9.8 Pa; 1 Torr = (101 325/760) Pa; 1 atm = 101 325 Pa.

‡ Higher temperature sublimation resulted in partial conversion to [MoH(η^5-C_7H_7)(CO)$_3$].[11]

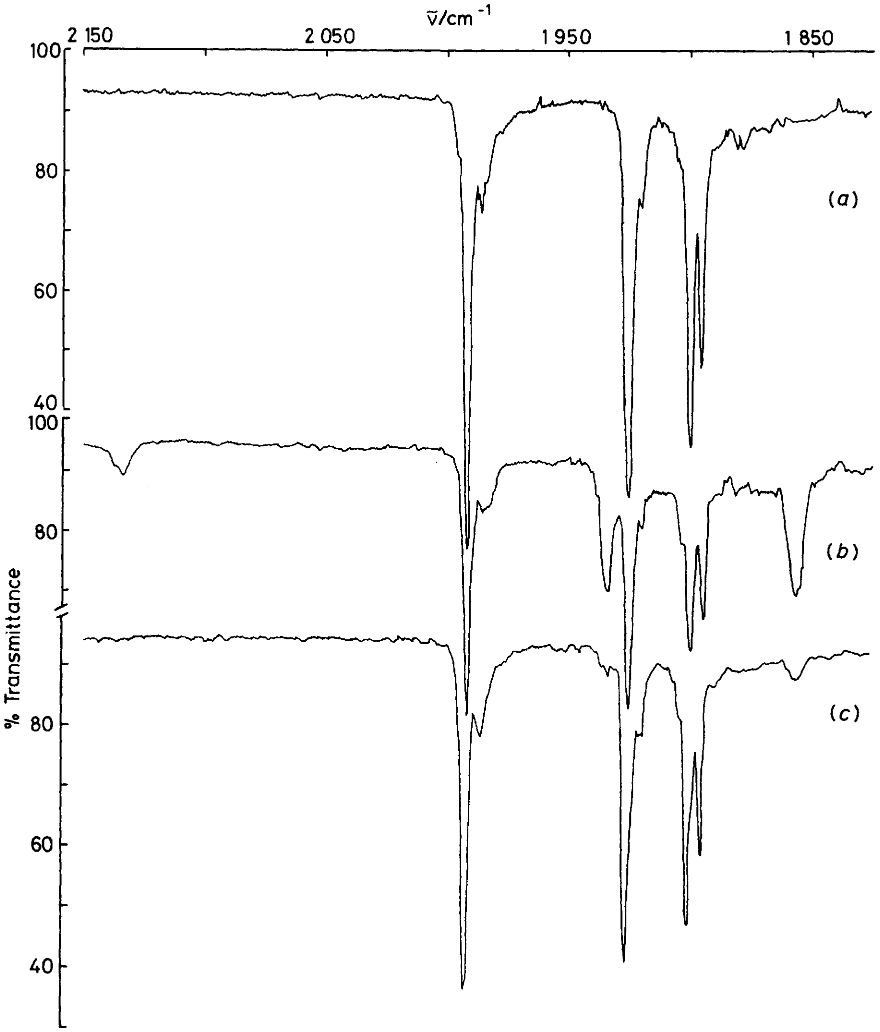

Figure 1. Infrared spectra from an experiment with [Mo(η^6-C_7H_8)(CO)$_3$] isolated at high dilution in a CH_4 matrix at 12 K: (*a*) after deposition, (*b*) after 15 min photolysis using filter A, and (*c*) after further 30 min photolysis using filter D (Grubb Parsons Spectromajor spectrometer)

2 136 cm^{-1} and a reduction in the bands associated with (1) [Figure 1(*b*)]. Figure 2(*b*) shows the u.v.–visible spectrum of the matrix after photolysis. Either annealing the matrix or a subsequent period of irradiation in the visible region (filter D) results in a reversal of the photoreaction with a reduction in the new bands and corresponding increases in the parent band intensities [Figure 1(*c*)]. The forward photoreaction was seen to occur at a much slower rate on photolysis using filter B, giving light corresponding to the intense band at 320 nm shown in Figure 2(*a*). The band seen at 2 136 cm^{-1} can be assigned to free CO trapped in the matrix whilst the positions of the two other new bands are consistent with a metal dicarbonyl fragment formed by photodissociation of CO from (1). The reversibility of the reaction supports the view that a species of lower co-ordination, [Mo(η^6-C_7H_8)(CO)$_2$], is formed which recombines with CO to give (1) on irradiation with light of wavelength 400 nm [see Figure 2(*b*)]. A matrix of (1) in Ar at 12 K gave a similar i.r. spectrum [Figure 3(*a*); Table 1]. A much longer period of irradiation (filter A) was required before a similar change to that seen for the CH_4 matrix was obtained in the spectrum [Figure 3(*b*)]. An identical reversal of bands was seen after subsequent long-wavelength photolysis [Figure 3(*c*)]. Using the ratio of the upper and lower terminal carbonyl stretching band intensities ($I_{sym}/I_{antisym}$) and the formula [12] $I_{sym}/I_{antisym} = \cot^2(\theta/2)$, a OC–Mo–CO bond angle (θ) of 97 ± 1 and 94 ± 1° was

Table 1. Positions of i.r. bands (cm^{-1}) in the terminal carbonyl stretching region for [Mo(η^6-C_7H_8)(CO)$_3$] and its photoproducts in CH_4, Ar, and N_2 matrices at 12 K

Complex	CH_4	Ar	N_2
[Mo(η^6-C_7H_8)(CO)$_3$]	1 993.6	2 002.7	1 998.6
	1 928.3	1 938.0	1 929.6
	^{a} 1 903.4	1 912.1	1 908.4
	1 898.1		
[Mo(η^6-C_7H_8)(CO)$_2$]	1 939.3	1 948.9	
	1 860.4	1 873.5	
[Mo(η^6-C_7H_8)(CO)$_2$(N_2)]			2 173 ^{b}
			1 949.5
			1 889.7
[Mo(η^6-C_7H_8)(CO)(N_2)$_2$]			2 181 ^{b}
			2 150 ^{b}
			1 918.7

^{a} Matrix splitting. ^{b} ν(NN).

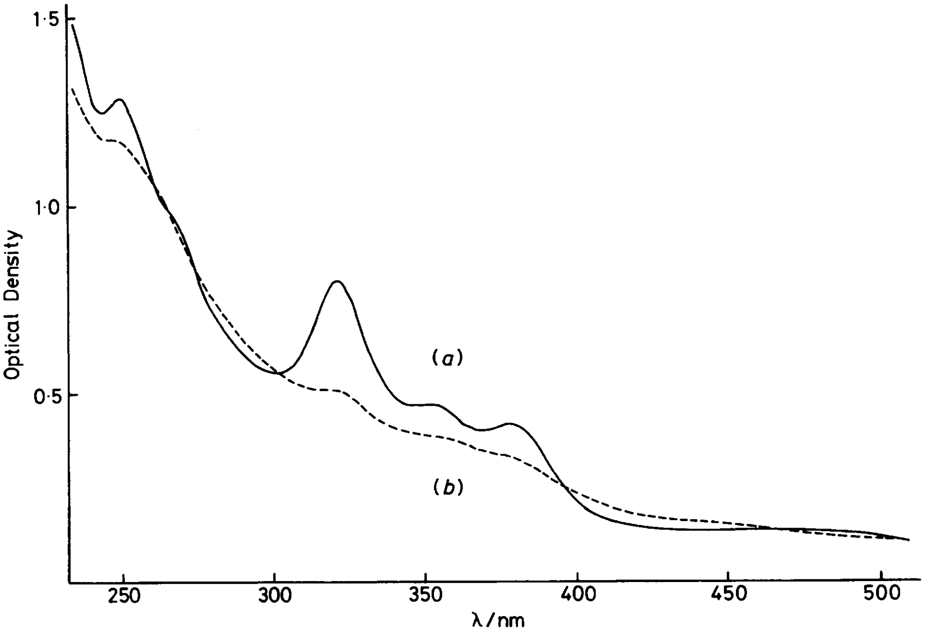

Figure 2. Ultraviolet–visible spectra from an experiment with [Mo(η^6-C_7H_8)(CO)$_3$] isolated at high dilution in a CH_4 matrix at 12 K: (*a*) after deposition and (*b*) after 15 min photolysis using filter A

calculated for the unsaturated species produced in CH_4 and Ar respectively.

Photolysis of [Mo(η^6-C_7H_8)(CO)$_3$] *in* ^{13}CO *Doped* CH_4 *Matrices at* 12 K.—The i.r. spectrum of [Mo(η^6-C_7H_8)(CO)$_3$] isolated at high dilution in a ^{13}CO doped (5%) CH_4 matrix at 12 K is shown in Figure 4(*a*). Parent carbonyl bands are seen at 1 991.0, 1 925.2, and 1 898.2 cm^{-1}. After photolysis (filter B) these bands were reduced with the production of new bands (together with a band at 2 136 cm^{-1}) in the terminal carbonyl stretching region [Figure 4(*b*)]. The latter bands increased considerably after further irradiation (filter A) as shown in Figure 4(*c*). Two of these bands seen at 1 936.6 and 1 858.6 cm^{-1} are analogous to the product bands seen on photolysis of (1) in CH_4 and Ar and are assigned to [Mo(η^6-C_7H_8)(CO)$_2$]. After subsequent irradiation (filter C) these two bands decreased in intensity while the other new bands increased further [Figure 4(*d*)]. After further u.v. photolysis (filter A) the product bands increased at the expense of the parent bands, with further photoejection of CO [Figure 4(*e*)]. The new i.r. bands seen can be assigned to the species [Mo(η^6-C_7H_8)(^{12}CO)$_{3-n}$(^{13}CO)$_n$] (n = 1—3) and [Mo(η^6-C_7H_8)(^{12}CO)$_{2-m}$(^{13}CO)$_m$] (m = 0—2) on the basis of energy-factored force field fittings for C_s Mo(CO)$_3$ and C_s Mo(CO)$_2$ fragments.[12] Although several bands are obscured by each other or by parent bands, the agreement between observed and calculated band positions is very good (Table 2). Enriched parent molecules are formed by rapid photosubstitution of ^{12}CO by ^{13}CO and subsequent photoelimination of CO results in the formation of metal dicarbonyl species in the matrix. Irradiation using filter C (λ > 320 nm) causes [Mo(η^6-C_7H_8)(CO)$_2$] to recombine with photoejected ^{12}CO or with ^{13}CO.

Photolysis of [Mo(η^6-C_7H_8)(CO)$_3$] *in* CO *Matrices at* 12 K.—The i.r. spectrum of [Mo(η^6-C_7H_8)(CO)$_3$] isolated at high dilution in a CO matrix at 12 K shows terminal carbonyl stretching bands at 1 993.7, 1 924.1, and 1 907.2 cm^{-1} (Figure 5(*a*)]. After irradiation of the matrix (filter C) these bands decreased with the production of two weak bands at *ca.* 2 040 and *ca.* 1 954 cm^{-1} and a shoulder band at 1 987.4 cm^{-1} [Figure 5(*b*)]. The spectrum obtained after further photolysis [Figure 5(*c*)] showed a significant increase in the band at 1 987.4 cm^{-1} and a reduction in all other bands. A further new band was revealed at *ca.* 1 926 cm^{-1} after a subtraction of spectra. The reaction was found to be irreversible and prolonged irradiation with either u.v. or visible light resulted in the formation of a species having one intense carbonyl i.r. band at 1 987.4 cm^{-1}. This band can be assigned to the complex [Mo(CO)$_6$][12] which is produced from (1) in the CO matrix. Indeed, photoejected cycloheptatriene was detected in the matrix by comparing spectra with that of a CO matrix doped with the cyclic olefin (Table 3). I.r. spectra showed new bands corresponding to ring C–H deformations after photolysis of (1) in CO at 12 K [Figures 6(*a*) and 6(*b*)] and are consistent with the release of the cycloheptatriene ligand. No bands which could be associated with [Mo(η^6-C_7H_8)(CO)$_2$] were seen on photolysis of (1) in this matrix. The less intense carbonyl bands seen after photolysis at 2 040, 1 954, and *ca.* 1 926 cm^{-1} can probably be assigned to species involved in the conversion of (1) to [Mo(CO)$_6$]. The observation of a band at 2 040 cm^{-1} suggests formation of the intermediate complex [Mo(η^4-C_7H_8)(CO)$_4$] * consistent with a mechanism proposed for the thermal substitution of cycloheptatriene in metal carbonyl complexes by other ligands.[4]

Photolysis of [Mo(η^6-C_7H_8)(CO)$_3$] *in* N_2 *Matrices at* 12 K.—The i.r. spectrum of [Mo(η^6-C_7H_8)(CO)$_3$] in a N_2 matrix at 12 K shows parent bands at 1 998.6, 1 929.6, and 1 908.4 cm^{-1} [Figure 7(*a*)]. After a short period of u.v. irradiation (filter A) new bands were seen in the terminal carbonyl stretching region at 1 949.5, 1 918.7, and 1 889.7 cm^{-1} with a corresponding reduction in the parent bands. Other new bands were observed at 2 173br, 2 144, and 2 136 cm^{-1} [Figure 7(*b*)]. All these new bands were seen in spectra after a longer period

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* For comparison, i.r. bands for the complex [MoL(CO)$_4$] (L = bicyclo[2.2.1]hepta-2,5-diene) isolated in a CO matrix at 12 K were seen at 2 044, 1 958br, and 1 906 cm^{-1}.[11]

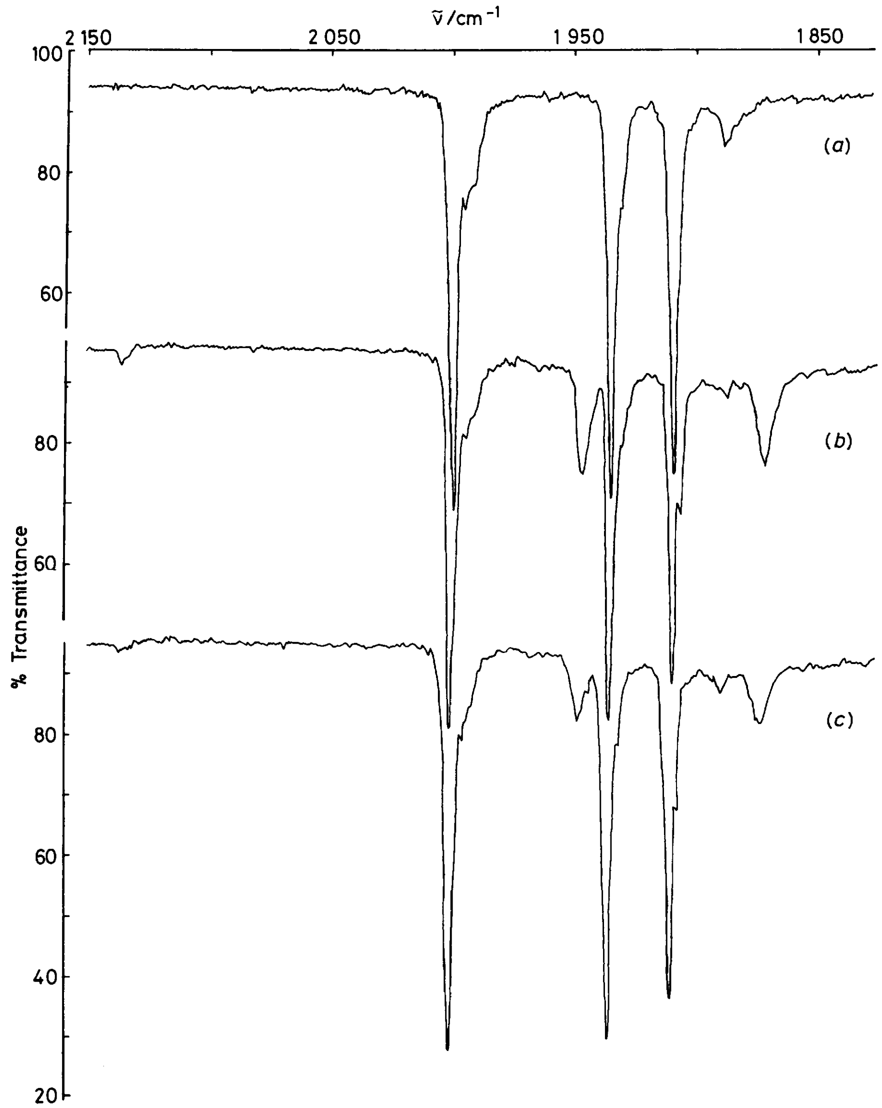

Figure 3. Infrared spectra from an experiment with $[Mo(\eta^6\text{-}C_7H_8)(CO)_3]$ isolated at high dilution in an Ar matrix at 12 K: (*a*) after deposition, (*b*) after 140 min photolysis using filter A, and (*c*) after further 120 min photolysis using filter D (Grubb Parsons Spectromajor spectrometer)

of irradiation using filter B. After further photolysis (filter A) all the product bands increased, with other bands appearing at *ca.* 2 181, 2 150(sh), and 2 096 cm^{-1}, together with a reduction in parent bands [Figure 7(*c*)]. Prolonged irradiation resulted in no further increase in the bands at 2 173, 1 949.5, and 1 889.7 cm^{-1} but other new bands at *ca.* 2 181, 2 150, 2 144, 2 136, and 1 918.7 cm^{-1} gained intensity. Further, the band at 2 096 cm^{-1} increased considerably and another new band appeared at 2 070 cm^{-1} [Figure 7(*d*)]. The band at 2 136 cm^{-1} indicates that photoelimination of CO from (1) occurs in N_2 matrices, while the new bands seen in the region 2 190—2 140 cm^{-1} can be assigned to $^{14}N-^{14}N$ stretching modes for metal–dinitrogen complexes.[13,14] We assign the new terminal carbonyl bands at 1 949.5 and 1 889.7 cm^{-1} (Table 1) and the band at 2 173 cm^{-1} to the species $[Mo(\eta^6\text{-}C_7H_8)(CO)_2(N_2)]$. This assignment is supported by the observation of the reactive species $[Mo(\eta^6\text{-}C_7H_8)(CO)_2]$ on photolysis of (1) in CH_4 and Ar matrices and comparison with previous work on $[M(\eta^n\text{-}C_nH_n)(CO)_2]$ and $[M(\eta^n\text{-}C_nH_n)(CO)_2(N_2)]$ species (M = Cr, *n* = 6; Mn, *n* = 5; M = Fe, *n* = 4).[13] It is interesting that $[Mo(\eta^6\text{-}C_7H_8)(CO)_2]$ was not observed in the reactive N_2 matrix even on using the same light filters. A OC–Mo–CO bond angle of 93 ± 1° was calculated for the dinitrogen–metal–carbonyl complex.

The new band seen at 1 918.7 cm^{-1}, which increases with the free CO band and other terminal nitrogen stretching bands on prolonged irradiation, is probably associated with the coordinatively saturated species $[Mo(\eta^6\text{-}C_7H_8)(CO)(N_2)_2]$, consistent with the production of dienriched tricarbonyl complexes on u.v. photolysis of (1) in a ^{13}CO doped CH_4 matrix. The broad bands seen at 2 181, 2 150, and 2 144 cm^{-1} may be tentatively assigned to symmetric and antisymmetric $^{14}N-^{14}N$ stretches of this bis(dinitrogen) complex and the species $[Mo(\eta^6\text{-}C_7H_8)(N_2)_3]$, also formed by further substitution of CO by N_2 [Figure 7(*d*)]. Since the parent molecule (1) is converted to $[Mo(CO)_6]$ on photolysis in the reactive CO matrix, it is quite possible that the new band seen at 2 096 cm^{-1}, which increases more rapidly than other bands after prolonged irradiation, is due to $[Mo(N_2)_6]$. The other new band seen at 2 070 cm^{-1} might similarly be assigned to $[Mo(\eta^4\text{-}C_7H_8)$-

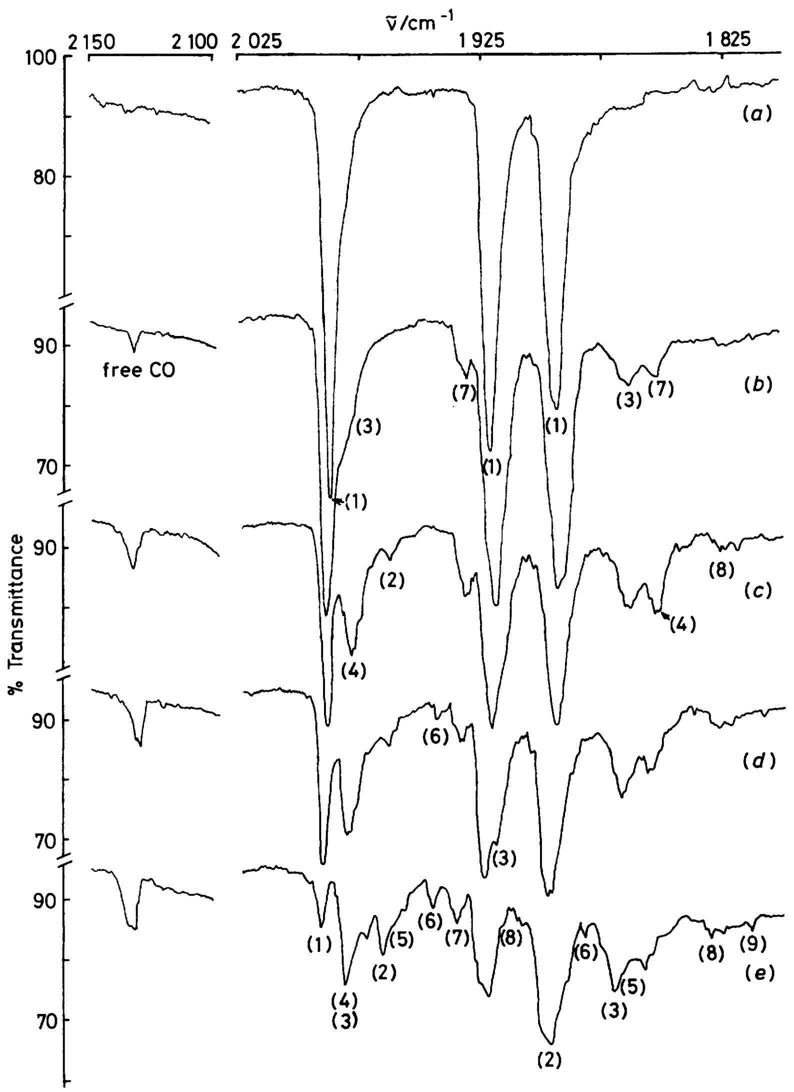

Figure 4. Infrared spectra from an experiment with [Mo(η^6-C_7H_8)(CO)$_3$] isolated at high dilution in a ^{13}CO doped CH_4 matrix at 12 K: (*a*) after deposition, (*b*) after 60 min photolysis using filter B, (*c*) after further 30 min photolysis using filter A, (*d*) after still further 30 min photolysis using filter C, and (*e*) after final 60 min photolysis using filter A (Grubb Parsons Spectromajor spectrometer). The numbering refers to the species as listed in Table 2 which give rise to these bands. Other very intense matrix bands due to isotopes of CO, seen in the region 2 100—2 025 cm^{-1}, are omitted from the spectra

$(N_2)_4$] or [Mo$(N_2)_5$]. Comparable i.r. band positions have been reported * for the unstable species [Cr$(N_2)_6$] and [Cr$(N_2)_5$] produced by co-condensing Cr atoms with N_2 at low temperatures.

Discussion

The proposed photoreactions seen on photolysis of [Mo(η^6-C_7H_8)(CO)$_3$] in various low temperature matrices are summarised in the Scheme (see later).

The primary photoprocess which is seen to occur in unreactive gas matrices at 12 K is dissociative loss of CO to give the species [Mo(η^6-C_7H_8)(CO)$_2$]. This is the reactive intermediate in other matrix photoreactions seen here where CO is substituted by other ligands (*e.g.* ^{13}CO and N_2). A further reaction involving photosubstitution of the cycloheptatriene ring by matrix molecules occurs in the reactive matrices. In contrast, this reaction, which is analogous to the facile thermal substitution of the cyclic olefin by three two-electron donor ligands, may proceed by a primary step involving the ' nucleophilic ' interaction by a ligand, as no evidence is seen for the formation of the unsaturated complexes [Mo(η^4-C_7H_8)(CO)$_3$], [Mo(η^2-C_7H_8)(CO)$_3$], or [Mo(CO)$_3$] on irradiation of (1) in CH_4 or Ar matrices at 12 K. Such highly reactive species might, however, not exist in these inert matrices for a long enough time to be observed. For example, [Mo(η^4-C_7H_8)(CO)$_3$], if formed, could react with CO in the CO matrices to give [Mo(η^4-C_7H_8)(CO)$_4$], followed by conversion to [Mo(CO)$_6$]. Production of [Mo(CO)$_3$] on photolysis of (1) in CH_4 or Ar would require the bulky cycloheptatriene ligand to move sufficiently far away from the metal through the very rigid matrix before a thermal back reaction reformed (1). Initial dissociation of the chromium analogue of (1) to give [Cr(CO)$_3$] and cycloheptatriene has been proposed as one possible pathway for the photochemical exchange of the cyclic olefin by solvent ^{14}C-labelled cyclo-

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* Most intense band [ν(NN)] for [Cr$(N_2)_5$] at 2 072 cm^{-1} and ν(NN) for [Cr$(N_2)_6$] at 2 112 cm^{-1} (ref. 15).

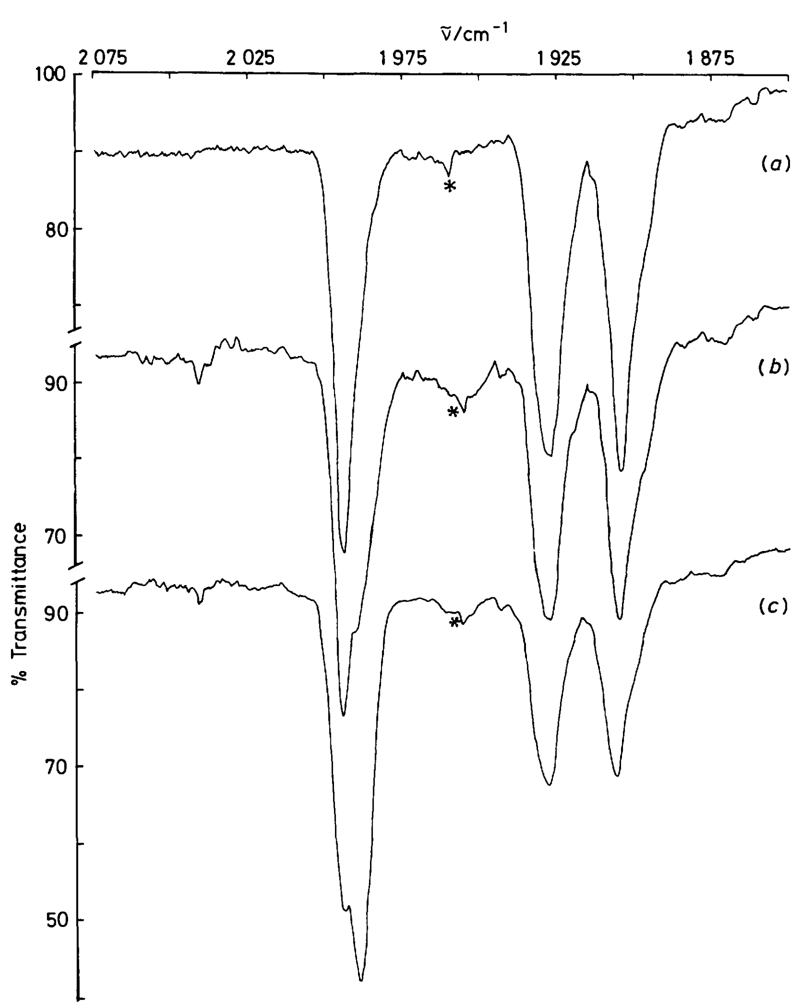


Figure 5. Infrared spectra from an experiment with [Mo(η^6-C_7H_8)(CO)$_3$] isolated at high dilution in a CO matrix at 12 K: (*a*) after deposition, (*b*) after 25 min photolysis using filter C, and (*c*) after further 60 min photolysis using filter C (Nicolet 7199 FT-IR system). Band marked (*) is due to [MoH(η^5-C_7H_7)(CO)$_3$] (ref. 11)

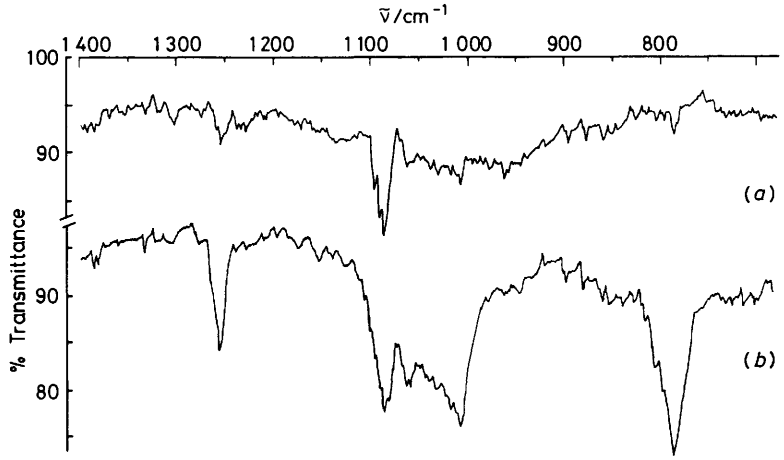


Figure 6. Infrared spectra from an experiment with [Mo(η^6-C_7H_8)(CO)$_3$] isolated at high dilution in a CO matrix, showing the region 1 400—700 cm^{-1}: (*a*) after deposition and (*b*) after 120 min photolysis using filter C (Nicolet 7199 FT-IR system)

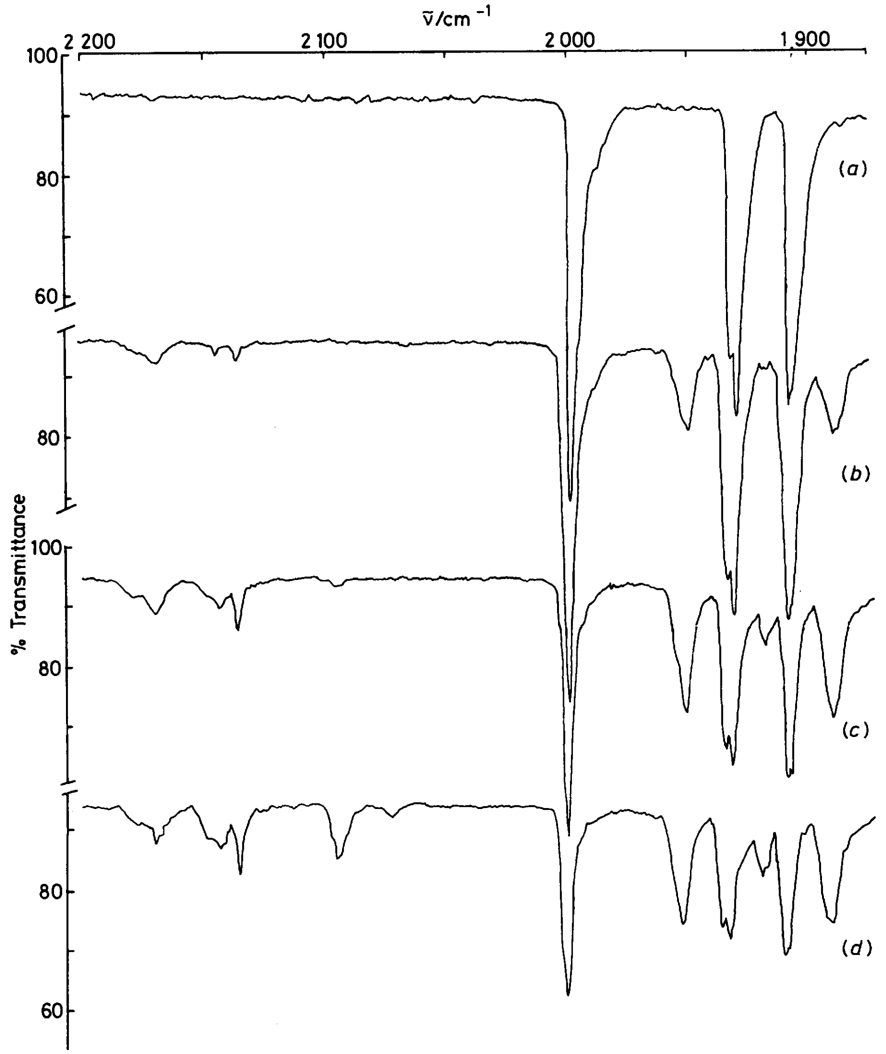


Figure 7. Infrared spectra from an experiment with [Mo(η^6-C_7H_8)(CO)$_3$] isolated at high dilution in a N_2 matrix at 12 K: (*a*) after deposition, (*b*) after 6 min, (*c*) after 20 min, and (*d*) after 40 min photolysis using filter A (Grubb Parsons Spectromajor spectrometer)

heptatriene [equation (2)], as has the formation of a transition state [5b] [equation (3)].

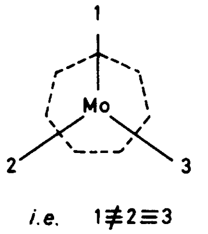
$$[Cr(\eta^6\text{-}C_7H_8)(CO)_3] \xrightarrow{h\nu} [Cr(CO)_3] + C_7H_8 \qquad (2)$$

$$[Cr(\eta^6\text{-}C_7H_8)(CO)_3] + C_7H_8{}^* \xrightarrow{h\nu} [Cr(C_7H_8)(CO)_3 \cdots C_7H_8{}^*] \qquad (3)$$

As mentioned earlier, the observation of the intermediate species [Mo(η^4-C_7H_8)(CO)$_4$] in the CO matrix supports the view that substitution of cycloheptatriene (probably thermal [4] and photochemical) in these complexes by two-electron donor ligands involves stepwise decreases in the hapticity of the cyclic olefin. The solution photochemistry of [Cr(η^6-C_7H_8)(CO)$_3$] involving direct substitution of CO (for λ = 366 nm)[7,8] is analogous to that seen on u.v. irradiation of the molybdenum complex in our gas matrices.

Future matrix isolation studies with the chromium and tungsten complexes are expected to reveal the intermediacy of [Cr(η^6-C_7H_8)(CO)$_2$] and [W(η^6-C_7H_8)(CO)$_2$] in the solution reactions. Use of ^{15}N labelling will be made to assist in the identification of dinitrogen complexes. From Fourier-transform i.r. studies of a variety of [M(polyene)(CO)$_n$] complexes isolated in low temperature matrices we hope to be able to establish a means of characterising the hapticity of the polyene ligand from ν(CH), ν(CC), and ν(metal-ring) vibrations.

Table 2. Observed [a] and calculated [b] band positions (cm^{-1}) of i.r. terminal carbonyl stretching bands for $[Mo(\eta^6\text{-}C_7H_8)(CO)_3]$ and its photoproducts in a ^{13}CO doped CH_4 matrix at 12 K



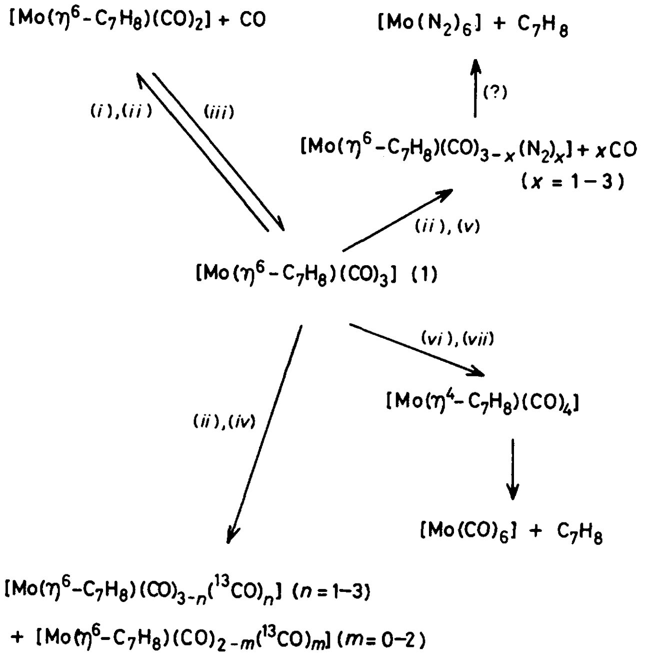
Complex	Symmetry		ν(CO)	
			Observed	Calculated
(1) $[Mo(\eta^6\text{-}C_7H_8)(^{12}CO)_3]$	C_s	A'	1 991.0	1 990.7
		A'	1 925.2	1 925.0
		A''	1 898.2	1 898.4
(2) $[Mo(\eta^6\text{-}C_7H_8)(^{12}CO)_2(^{13}CO)]$ [c]	C_s	A'	1 969.1	1 969.1
		A'	1 903 [d]	1'902.8
		A''	*e*	1 898.5
(3) $[Mo(\eta^6\text{-}C_7H_8)(^{12}CO)_2(^{13}CO)]$ [f]	C_1	A	1 984 [g]	1 985.4
		A	1 918.1	1 917.9
		A	1 868.3	1 868.0
(4) $[Mo(\eta^6\text{-}C_7H_8)(^{12}CO)(^{13}CO)_2]$ [h]	C_s	A'	1 980.6	1 981.1
		A'	1 893 [d]	1 892.5
		A''	1 856 [i]	1 856.0
(5) $[Mo(\eta^6\text{-}C_7H_8)(^{12}CO)(^{13}CO)_2]$ [j]	C_1	A	1 960 [g]	1 959.7
		A	*e*	1 901.8
		A	1 866 [g]	1 866.8
(6) $[Mo(\eta^6\text{-}C_7H_8)(^{13}CO)_3]$	C_s	A'	1 946.6	1 946.3
		A'	1 882.1	1 882.2
		A'	*e*	1 856.3
(7) $[Mo(\eta^6\text{-}C_7H_8)(^{12}CO)_2]$	C_s	A'	1 936.6	1 936.5
		A''	1 858.6	1 858.8
(8) $[Mo(\eta^6\text{-}C_7H_8)(^{12}CO)(^{13}CO)]$	C_1	A	1 920	1 920.4
		A	1 832.4	1 932.5
(9) $[Mo(\eta^6\text{-}C_7H_8)(^{13}CO)_2]$	C_s	A'	*e*	1 893.5
		A''	1 817.3	1 817.2

[a] In the case of matrix-split bands, the mean position was used in force constant calculations. [b] Refined energy-factored force constants using notation for $[Mo(\eta^6\text{-}C_7H_8)(CO)_3]$ (see diagram above): $K_1 = 1\,564.8$, $K_2 = K_3 = 1\,494.7$, $k_{12} = k_{13} = 35.0$, $k_{23} = 38.6$ N m^{-1}. Refined energy-factored force constants for $[Mo(\eta^6\text{-}C_7H_8)(CO)_2]$: $K = 1\,455.4$ and $k_t = 59.8$ N m^{-1}. [c] ^{13}CO in position 1. [d] Band obscured by band of $[Mo(\eta^6\text{-}C_7H_8)(CO)_3]$. [e] Hidden by more prominent bands. [f] ^{13}CO in position 2. [g] Band occurs as shoulder. [h] ^{12}CO in position 1. [i] Band obscured by band of $[Mo(\eta^6\text{-}C_7H_8)(CO)_3]$. [j] ^{12}CO in position 2.

Table 3. Position of i.r. bands (cm^{-1}) in the ring C–H deformation region for cycloheptatriene (C_7H_8) in CO matrices at 12 K

δ(C–H) [a]/cm^{-1}	δ(C–H) [b]/cm^{-1}
1 434	1 430w
1 394	
1 260	1 261
1 048	1 065, 1 045br, 1 010
795	790

[a] From an experiment with C_7H_8 isolated (1 : 1 000) in a CO matrix at 12 K. [b] Photoejected C_7H_8 from an experiment with $[Mo(\eta^6\text{-}C_7H_8)(CO)_3]$ isolated in a CO matrix at 12 K.



Scheme. (*i*) CH_4, Ar; (*ii*) *h*ν (filter A); (*iii*) *h*ν (filter D); (*iv*) $^{13}CO/CH_4$; (*v*) N_2; (*vi*) CO; (*vii*) *h*ν (filter C)

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