Photochemistry of Chloro-, Bromo-, and Iodo-pentacarbonylmanganese in Frozen Gas Matrices at 12 K. Infrared Spectroscopic Evidence for Tetracarbonylhalogenomanganese Species with a C_{2v} Trigonal-bipyramidal Structure

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Infrared spectroscopic evidence, including ^{13}CO labelling and energy-factored force-field fitting for $[Mn(CO)_5Cl]$ and $[Mn(CO)_4Cl]$, is presented to show that on photolysis of $[Mn(CO)_5X]$ (X = Cl, Br, or I) complexes at high dilutions in Ar and CH_4 matrices at 12 K new species $[Mn(CO)_4X]$, with the X ligand occupying an equatorial position in a trigonal-bipyramidal structure and having C_{2v} symmetry, are produced. The observations of CO ejection, the formation of a co-ordinatively unsaturated species, and the *reversibility* of the reaction (i) are interpreted as

$$[Mn(CO)_5X] \underset{h\nu'}{\overset{h\nu}{\rightleftharpoons}} [Mn(CO)_4X] + CO \qquad (i)$$

confirming the existence of a co-ordinatively unsaturated species as the intermediate in the substitution reactions of $[Mn(CO)_5X]$ complexes; *i.e.* the reaction follows the dissociative path proposed from previous kinetic studies.

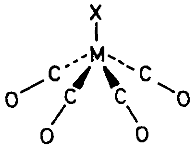
THE CO-exchange and ligand-substitution reactions of the Group 7A pentacarbonylhalogenometal complexes have been extensively studied and it is generally agreed that the rate-determining step is CO dissociation in both cases [equation (1)].[1-8] Some early work[1,2] has

$$[M(CO)_5X] \overset{slow}{\rightleftharpoons} [M(CO)_4X] + CO \xrightarrow[+L]{fast} [M(CO)_4(L)X] \qquad (1)$$

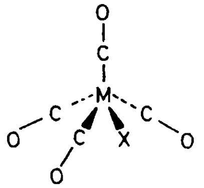
M = Mn or Re; X = Cl, Br, or I; L = ^{13}CO, $C^{18}O$, PR_3 *etc.*

indicated that the rate constant for dissociation of the radial CO ligands, *cis* to the halide ligand, is greater than that for dissociation of the axial CO ligand, although this difference was found to depend on the nature of X.[3] Experiments with $C^{18}O$, however, showed[4] that for $[Mn(CO)_5Cl]$ and $[Mn(CO)_5Br]$ the five CO ligands exchange at approximately the same rate, in agreement with the results of Hieber and Wollmann[3] for these two compounds. Later work[5-7] has clearly demonstrated the preference for labilisation of the radial CO ligands to form the co-ordinatively unsaturated intermediate $[Mn(CO)_4X]$. Discussions of the details of the reaction mechanism have assumed that the co-ordinatively unsaturated intermediate adopts either a square-pyramidal or trigonal-bipyramidal structure and have recognised that such a species could be fluxional.[4-7] Additionally, it has been pointed out[9] that there might be a non-dissociative exchange of radial and axial CO ligands in $[M(CO)_5X]$ compounds. Of the four possible structures (I—IV), it has been proposed[7] that the instantaneous structure is either (I) or (III). Generalised molecular-orbital calculations favoured structures (I) or (II) for $[M(CO)_4X]$ fragments.[10,11] A more recent calculation, however, has shown that the lowest energy form of $[Mn(CO)_4Br]$ is the C_{2v} structure (IV).[12]

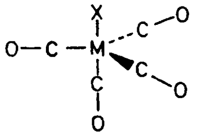
The matrix-isolation technique lends itself well to establishing the existence and geometry of unstable metal carbonyl species,[13-15] including those of $[Mn(CO)_4H]$[16] and $[Mn(CO)_4(CH_3)]$.[17] In this paper we present i.r. spectroscopic evidence for the formation of $[Mn(CO)_4X]$ species on photolysis of $[Mn(CO)_5X]$ complexes in Ar and CH_4 matrices and we relate the results to previous kinetic studies;[1-8] a preliminary report of the results has been made.[18]



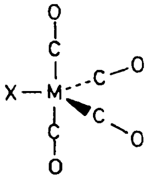
(I)(C_{4v})



(II)(C_s)



(III)(C_{3v})



(IV)(C_{2v})

EXPERIMENTAL

Cryogenic temperatures (*ca.* 12 K) were obtained using a Displex CSA-202 closed-cycle helium refrigeration system (Air Products and Chemicals Inc.). The $[Mn(CO)_5X]$ complexes are intermediate between those which are volatile enough to give gas mixtures for ' pulsed ' deposition[19] and those which need high temperatures to sublime them onto the cold window. A glass spray-on system was designed[20] to co-condense the vapour evaporating from the cooled solid (*ca.* 10 °C) with host matrix gas onto the cold CsI or LiF 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 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 2 200 to 1 850 cm^{-1} region were recorded on a Grubb–Parsons Spectromajor grating spectrometer modified to suppress the grating change to 1 850 cm^{-1}. Calibration in the terminal CO stretching 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 medium-pressure mercury arc lamp (Philips HPK 125 W). Wavelength-selective photolysis was achieved using the following filters: A, $200 < \lambda < 280$ nm, quartz gas cell (pathlength 25 mm) containing Cl_2 gas (2 atm *); B, $\lambda > 380$ nm, quartz gas cell containing Cl_2 gas and a soda glass disc (thickness 5 mm).

Matrix gases (Ar, CH_4) were B.O.C. ' Grade X ' purity and ^{13}CO (95% enriched) was obtained from B.O.C. Prochem Ltd. Samples of $[Mn(CO)_5X]$ (X = Cl, Br, and I) were prepared from freshly sublimed $[Mn_2(CO)_{10}]$ (Strem Chemicals Inc.) by standard procedures.[21] Samples of ^{13}CO-enriched $[Mn(CO)_5Cl]$ were obtained by stirring a solution of the complex (*ca.* 20 mg) in CH_2Cl_2 (10 cm^3; Koch-Light, used after further purification) at 25 °C for 36 h in a closed vessel under a ^{12}CO–^{13}CO atmosphere of known composition. The solid was obtained by pumping off the gas and solvent and was purified by sublimation (50 °C at 10^{-3} Torr).

RESULTS

The Isotropic Spectra of $[Mn(CO)_5Cl]$.—The Group 7A pentacarbonylhalogenometal complexes all belong to the C_{4v} symmetry point group and are expected to show three $(2A_1 + E)$ i.r.-active terminal CO stretching fundamentals.[22,23] The i.r. spectrum of $[Mn(CO)_5Cl]$ is typical of that for $[Mn(CO)_5X]$ complexes in Ar or CH_4 matrices at 12 K [Figure 1(*a*)]. As expected, three groups of bands are observed with splittings arising from matrix effects as demonstrated by the different patterns for the same fundamental in Ar and CH_4 (Table 1). In Figure 1(*a*) the band marked with an asterisk is due to $[Mn(^{12}CO)_4(^{13}CO)Cl]$ occurring in natural abundance while those marked with a dagger are due to a small amount of $[Mn_2(CO)_{10}]$ impurity.† In order to assign the structures of photolysis products arising from $[Mn(CO)_5X]$ complexes it was necessary to demonstrate the ability of the force-field fitting procedure to analyse the i.r. spectra of ^{13}CO-enriched $[Mn(CO)_5Cl]$, *e.g.* Figure 2(*a*). The choice of $[Mn(CO)_5Cl]$ for this exercise was made on the basis of a faster rate of ^{14}CO incorporation for this complex (Cl : Br : I = 200 : 8 : 1).[1] Use of the energy-factored CO stretching and interaction force constants for $[Mn(CO)_5Cl]$ in solution [23] allowed the band positions and the relative band intensities of all the possible $[Mn(^{12}CO)_{5-n}(^{13}CO)_nCl]$ molecules to be calculated. This

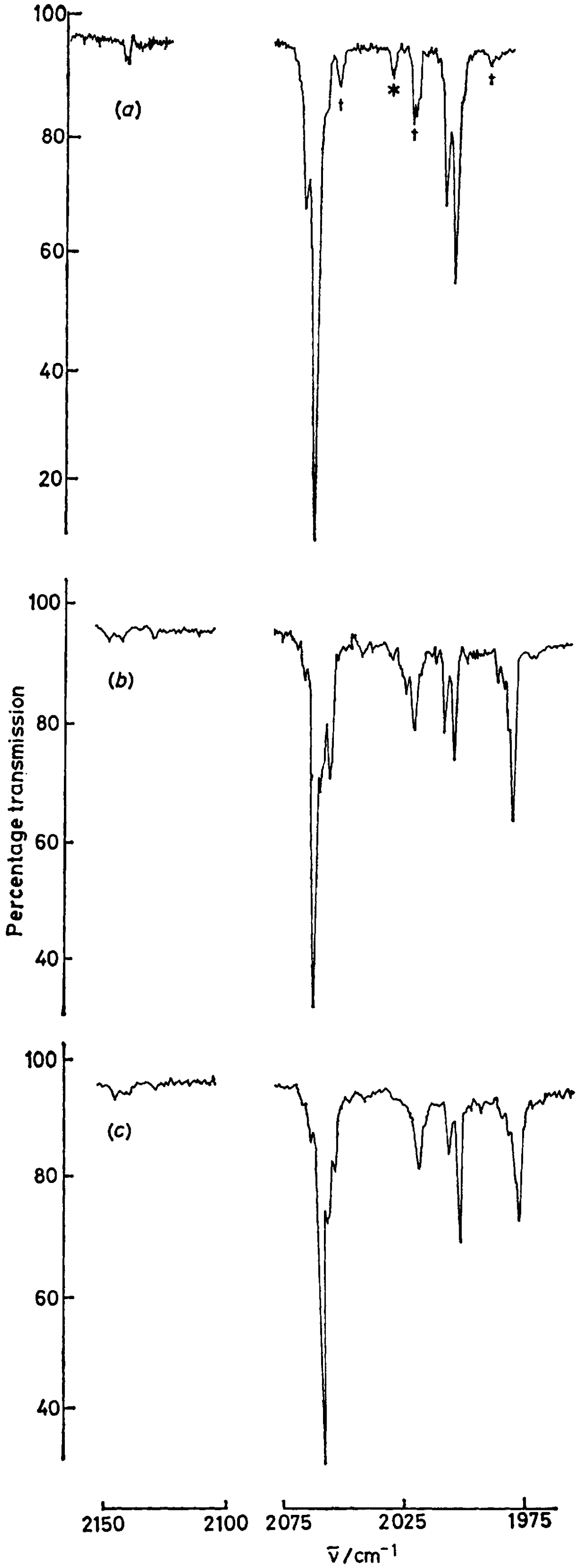


FIGURE 1 Infrared spectra from an experiment with $[Mn(CO)_5Cl]$ isolated at high dilution in a CH_4 matrix at 12 K: (*a*) after deposition, (*b*) after 4 min photolysis using filter A, and (*c*) after another 15 min photolysis using filter B. See text for an explanation of the bands marked * and †

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

† It is difficult to get the reaction of $[Mn_2(CO)_{10}]$ with Cl_2 to go to completion and, since $[Mn(CO)_5Cl]$ and $[Mn_2(CO)_{10}]$ have similar solubilities in organic solvents and also similar volatilities, it was impossible to remove the last traces of $[Mn_2(CO)_{10}]$ (*ca.* 2%) from the sample of $[Mn(CO)_5Cl]$.

calculation * gave predicted bands and relative band intensities which were sufficiently similar to the observed spectra with varying degrees of ^{13}CO enrichment to enable the observed bands to be assigned. Refinement of the energy-factored force field gave calculated wavenumbers which compare well with the observed wavenumbers † as shown in Table 2. The refined force constants obtained in this work agree well with those for a cyclohexane solution [23] (Table 2). Once accurately established, the energy-factored force field allowed relative band intensities to be calculated *via* dipole moment derivatives (see Appendix), and these were compared with the observed relative band intensities. The 'in-phase' solution gave a OC$_{ax.}$–Mn–CO$_{rad.}$ bond angle of 87 ± 2° which compares reasonably well with the value of 89.8° obtained previously.[22]

TABLE 1

Band positions (cm^{-1})* for [Mn(CO)$_5$X] complexes and their photoproducts in the terminal CO stretching region for argon and methane matrices at 12 K

Complex	Point group	ν(CO)	Ar	CH$_4$
[Mn(CO)$_5$Cl]	C_{4v}	A_1	2 142.1w	2 141.8vw
		E	2 064.0mw 2 058.4s	2 060.8mw 2 056.8s
		A_1	2 006.6mw 2 002.1m	2 002.3mw 1 997.8m
[Mn(CO)$_4$Cl]	C_{2v}	A_1	2 126.0vw	2 123.7vw
		B_1	2 055.3s 2 051.0s	2 054.5s 2 050.6s
		A_1	2 018.9mw	2 014.5mw
		B_2	1 977.4s	1 973.1s
[Mn(CO)$_5$Br]	C_{4v}	A_1	2 139.5vw	2 137.8vw
		E	2 060.8mw 2 054.9s	2 058.1mw 2 050.0s
		A_1	2 009.0w 2 004.3m	2 004.6w 2 000.7m
[Mn(CO)$_4$Br]	C_{2v}	A_1	2 118.3vw	2 118.1vw
		B_1	2 046.7s	2 048.4s 2 046.1s
		A_1	2 018.9mw 2 016.8w	2 017.7mw
		B_2	1 979.5ms 1 977.7mw	1 980.9mw 1 978.8ms 1 974.9ms
Mn(CO)$_5$I]	C_{4v}	A_1	2 132.7w 2 130.0w	2 129.9w 2 127.6w
		E	2 056.9mw 2 053.3s 2 050.7m 2 047.5s	2 049.6s 2 046.7m 2 045.4s
		A_1	2 006.8m 2 005.8m	2 002.4s
[Mn(CO)$_4$I]	C_2	A_1	2 106.6w	2 108.4vw 2 106.7vw
		B_1	2 036.7s 2 035.7s	2 040.9m 2 034.9s
		A_1	2 016.6mw	2 016.6m 2 012.5m
		B_2	1 978.9s	1 975.0s

* Relative intensities: vw = very weak, mw = medium weak, w = weak, m = medium, ms = medium strong, s = strong. Bands bracketed together arise from a single fundamental with matrix splitting.

Photolysis of [Mn(CO)$_5$Cl] *in* Ar *and* CH$_4$ *Matrices*.—Irradiation of [Mn(CO)$_5$Cl] isolated at high dilution in CH$_4$ matrices with u.v. light (filter A) produced new bands [Figure 1(*b*)] at 2 138.0 cm^{-1}, due to 'free' CO, and at 2 123.7vw, 2 054.5 and 2 050.6s (doublet), 2 014.5mw, and 1 973.1ms cm^{-1} (Table 1). Subsequent irradiation with long-wavelength light (filter B) regenerated the parent bands [Figure 1(*c*)] at the expense of the new ones. Moreover, the relative intensities of the new bands remained constant on varying the forward and reverse photolysis times and this behaviour indicates that one species is responsible for the four new bands. Since 'free' CO was produced in the forward photolysis step, the experiments were carried out at high dilutions, and the primary step was reversible, which might not have been the case if Cl atoms had been produced, the likely identity of the primary photoproduct is the mononuclear species [Mn(CO)$_4$Cl].

Two of the simple structures [(II)(C_s) and (IV)(C_{2v})] can give rise to four i.r.-active fundamentals, one of which is expected to be very weak and to occur above 2 100 cm^{-1} because it is a symmetric CO stretching mode of a pair of approximately co-linear CO ligands. In order to distinguish between the two possibilities it was necessary to produce ^{13}CO enriched [Mn(CO)$_4$Cl] with various levels of ^{13}CO incorporation. Photolysis (filter A) of ^{13}CO-enriched [Mn(CO)$_5$Cl] in a CH$_4$ matrix produced a large number of bands [Figure 2(*b*)]. Attempts were made to fit the observed patterns using the C_s(II) and C_{2v}(IV) model geometries for the ^{13}CO-enriched [Mn(CO)$_4$Cl] species.

The C_s model, although allowing considerable flexibility through having seven force constants, failed to predict the positions of all the observed bands for the various ^{13}CO-enriched isomers. It also consistently predicted bands, with relatively high intensities, which were not observed. Additionally, the relative band-intensity pattern expected for a C_s [Mn(^{12}CO)$_4$Cl] species, *e.g.* [Cr(CO)$_4$(CS)][2 070.4w and 2 069.3w (A'), 2 011.3s (A'), 1 977.7vs and 1 975.6vs (A''), and 1 949.3s (A') cm^{-1}],[30] is very different from that observed (Table 1). In contrast, the C_{2v} model refined satisfactorily although the fit of the band positions (Table 3) was not quite as good as for [Mn(CO)$_5$Cl] (Table 2), the mean errors ‡ being ±0.4 and ±0.2 respectively. The relative band intensities predicted (see Appendix) for [Mn(^{12}CO)$_4$Cl] using this model [A_1 (0.025), B_1 (0.93), A_1 (0.20), and B_2 (0.66)] correlate well with observed relative intensities [A_1 (0.028), B_1 (0.86), A_1 (0.20), and B_2 (0.66); CH$_4$ matrix at 12 K] and also with those of other matrix-isolated C_{2v} species: *e.g.* [Mn(CO)$_4$(NO)][A_1 (0.08), B_1 (0.88), A_1 (0.20), and B_2 (0.78); N$_2$ matrix at 12 K] [31] and [Fe(CO)$_4$ · · · CH$_4$][A_1 (0.04), B_1 (0.70), A_1 (0.20), and B_2 (0.90); CH$_4$ matrix at 10 K].[28] It seems probable, therefore, that [Mn(CO)$_4$Cl] adopts structure (IV). For such a structure the bond dipole-moment derivatives gave values for the OC$_{eq.}$–Mn–CO$_{eq.}$ and OC$_{ax.}$–Mn–CO$_{ax.}$ angles of 119 ± 2 and 179 ± 2° respectively on the basis of the 'out-of-phase' solution, *cf.* [Fe(CO)$_4$] and [Fe(CO)$_4$ · · · CH$_4$].[28]

Analogous results were obtained on photolysis of [Mn(CO)$_5$Cl] in Ar matrices (Table 1), although the matrix splittings were different and the overall yield of the [Mn(CO)$_4$Cl] product species was lower.

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* In order to refine calculated and observed spectra interactively on the University of Southampton PDP-11 computer it was necessary to re-cast equations and condense procedures used previously [24–29] to reduce the core store required. Details are given in an Appendix which can be obtained in Supplementary Publication No. SUP 22890 (6 pp.). See Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

† In the event of matrix-split fundamentals, a weighted average of wavenumbers was used in the calculations.

‡ Mean errors calculated as (σ^2/n^2).

Long irradiation times for both Ar and CH_4 matrices caused appreciable conversion into lower carbonyl fragments $[Mn(CO)_nCl]$ ($n < 4$), which will be the subjects of further work.

TABLE 2

Observed and calculated[a] wavenumbers (cm^{-1}) of terminal CO stretching bands of ^{13}CO-enriched $[Mn(CO)_5Cl]$ in a CH_4 matrix at 12 K

Complex	Point group	$\nu(CO)$	Observed	Calculated
$[Mn(^{12}CO)_5Cl]$	C_{4v}	A_1	2 141.8	2 142.0
		B_2	*b*	2 087.9
		E	2 057.1	2 057.2
		A_1	1 999.2	1 999.7
$[Mn(^{12}CO)_4(^{13}CO)Cl]$ (rad. ^{13}CO)	C_s	A'	2 134.5	2 134.5
		A'	2 081.5	2 081.3
		A''	2 057.3	2 057.2
		A'	2 025.9	2 025.8
		A'	1 998.8	1 998.8
(ax. ^{13}CO)	C_{4v}	A_1	*c*	2 140.8
		B_2	*b*	2 087.9
		E	2 057.3	2 057.3
		A_1	1 956.3	1 956.3
$[Mn(^{12}CO)_3(^{13}CO)_2Cl]$ (*cis* rad. ^{13}CO, rad. ^{13}CO)	C_s	A'	2 124.9	2 124.9
		A''	2 077.1	2 077.1
		A'	2 029.5	2 029.4
		A''	2 021.4	2 021.9
		A'	*c*	1 998.1
(*trans* rad. ^{13}CO, rad. ^{13}CO)	C_{2v}	A_1	*d*	2 127.5
		B_1	2 057.3	2 057.2
		A_1	*c*	2 056.7
		B_2	2 011.6	2 011.5
		A_1	*c*	1 998.4
(ax. ^{13}CO, rad. ^{13}CO)	C_s	A'	*c*	2 133.3
		A'	2 081.5	2 081.3
		A''	2 057.3	2 057.2
		A'	*c*	2 025.3
		A'	1 956.3	1 956.0
$[Mn(^{12}CO)_2(^{13}CO)_3Cl]$ (ax. ^{12}CO, rad. ^{12}CO)	C_s	A'	2 114.8	2 114.7
		A'	*c*	2 056.7
		A'	*c*	2 024.2
		A''	2 011.6	2 011.5
		A'	*c*	1 997.8
(*cis* rad. ^{12}CO, rad. ^{12}CO)	C_s	A'	*c*	2 123.5
		A''	2 077.1	2 077.1
		A'	*c*	2 028.6
		A''	2 021.4	2 021.9
		A'	*c*	1 955.7
(*trans* rad. ^{12}CO, rad. ^{12}CO)	C_{2v}	A_1	*d*	2 126.3
		B_1	2 057.3	2 057.2
		A_1	*c*	2 056.0
		B_2	2 011.6	2 011.5
		A_1	*c*	1 955.7
$[Mn(^{12}CO)(^{13}CO)_4Cl]$ (ax. ^{12}CO)	C_{4v}	A_1	2 097.5	2 096.6
		B_2	*b*	2 041.5
		E	2 011.6	2 011.5
		A_1	*c*	1 997.5
(rad. ^{12}CO)	C_s	A'	*c*	2 113.2
		A'	*c*	2 056.2
		A'	*c*	2 024.0
		A''	2 011.6	2 011.5
		A'	*c*	1 955.5
$[Mn(^{13}CO)_5Cl]$	C_{4v}	A_1	2 094.8	2 094.4
		B_2	*b*	2 041.5
		E	2 011.6	2 011.5
		A_1	*c*	1 955.2

[a] Refined energy-factored CO force constants: $K_{ax.} = 1\,623.4$, $K_{rad.} = 1\,756.6$, $k_t = 46.8$, $k_c = 21.3$, and $k_l = 21.2$ N m^{-1}; *cf.* force constants for cyclohexane solution:[23] $K_{ax.} = 1\,624$, $K_{rad.} = 1\,751$, $k_t = 45.2$, $k_c = 23.1$, and $k_l = 21.3$ N m^{-1}. [b] Infrared-inactive band. [c] Predicted band obscured by other bands. [d] Not observed.

Photolysis of $[Mn(CO)_5Br]$ *and* $[Mn(CO)_5I]$ *in* Ar *and* CH_4 *Matrices.*—An extensive series of experiments showed that the behaviour of the other two members of the series in Ar and CH_4 matrices was similar to that of $[Mn(CO)_5Cl]$ in that analogous band patterns and intensities were observed (Table 1). Although isotope-enrichment studies were not carried out for these complexes,* it seems reasonable to

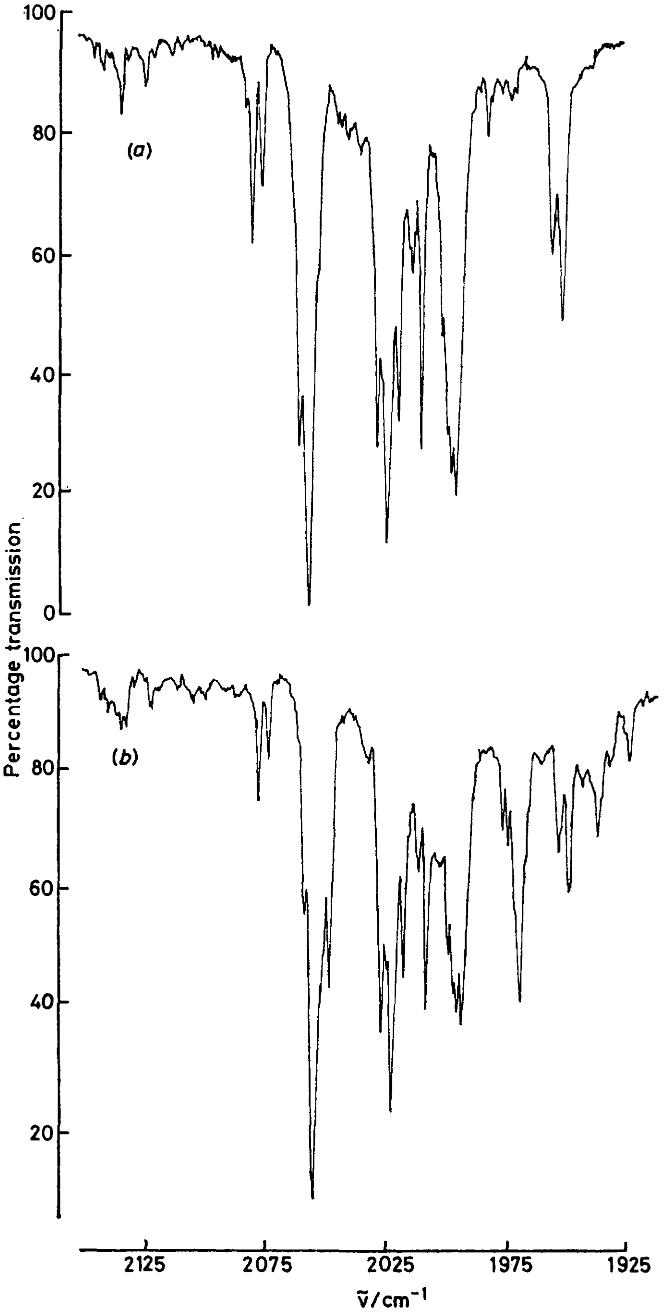

FIGURE 2 Infrared spectra from an experiment with ^{13}CO-enriched $[Mn(CO)_5Cl]$ isolated at high dilution in a CH_4 matrix: (*a*) after deposition and (*b*) after 4 min photolysis using filter A

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* The rates of incorporation of ^{14}CO into $[Mn(CO)_5X]$ complexes are in the ratio Cl : Br : I = 200 : 8 : 1.[1] Although $[Mn(CO)_5Br]$ has been shown to incorporate ^{13}CO on a spectroscopic scale,[5,6] our attempts to do this on a preparative scale using a hexane solution were unsuccessful. Isotope enrichment calculations were, therefore, carried out solely with $[Mn(CO)_5Cl]$ and $[Mn(CO)_4Cl]$.

conclude, on the basis of similarity to [$Mn(CO)_4Cl$], that the species formed are [$Mn(CO)_4Br$] and [$Mn(CO)_4I$], both with structures of type (IV).

DISCUSSION

The photoreactions of [$Mn(CO)_5X$] complexes in Ar and CH_4 matrices can be summarised as in equation (2).

$$[Mn(CO)_5X] \underset{h\nu'}{\overset{h\nu}{\rightleftarrows}} [Mn(CO)_4X] + CO \qquad (2)$$

The observation of CO ejection, the formation of a co-ordinatively unsaturated species, and the reversibility of the reaction are consistent with the dissociative mechanism and the co-ordinatively unsaturated intermediate proposed in kinetic studies.[1-8] It should be noted, however, that in the ^{13}CO exchange in [$Mn(CO)_5Br$] no site preference was found for the photochemical reaction, in contrast to the thermal reaction, and this led the authors[5] to propose that there were different intermediates for the two reactions (see below).

Unfortunately the proposed fluxionality[4-7,9] of the [$Mn(CO)_4X$] species could not be tested directly because specifically labelled ^{13}CO-enriched [$Mn(CO)_5Cl$] could not be prepared. However, in a separate study of the photolysis of [$Mn(CO)_5(CH_3)$] in frozen gas matrices at 12 K it was found[32] that, after a cycle of forward and reverse photolysis, an appreciable amount of *trans*-[$Mn(^{12}CO)_4(^{13}CO)(CH_3)$] had been produced in an experiment which started with exclusively the *cis* isomer. This result is analogous to the detection of *cis*-[$Cr(^{12}CO)_4(^{13}CO)(CS)$] in a frozen gas matrix after a photolysis cycle starting with the *trans* isomer and where fluxionality of the five-co-ordinate intermediate was proposed.[30] It seems probable, therefore, that the [$Mn(CO)_4X$] species are also fluxional. It is interesting to note that the trigonal-bipyramidal structure (IV) proposed for [$Mn(CO)_4X$] species is in accordance with the molecular-orbital study[12] for the lowest-energy configuration of [$Mn(CO)_4Br$]. A square-pyramidal geometry of type (II) was found to be the next lowest-energy configuration,[12] but the energy separation between (IV) and (II) was not so large as to prevent Berry-type interconversion[33] between the two structures. The other possibility for fluxionality is intramolecular rearrangement of the [$Mn(CO)_5X$] complexes.[9] This possibility has recently been demonstrated for $^{13}C^{18}O$-enriched [$W(CO)_5\{P(OCH_3)_3\}$], where stereochemical non-rigidity was found to occur by a process which did not involve loss of either CO or $P(OCH_3)_3$ ligands. This result together with the fluxionality of [$Mn(CO)_4X$] species suggests that the stereochemical aspects of CO exchange and replacement mechanisms will need to be reinvestigated.

The C_{2v} structure of [$Mn(CO)_4X$] in this work is in contrast with earlier matrix-isolation studies of [$Mn(CO)_4H$][16] and [$Mn(CO)_4(CH_3)$];[17] structures of type (III) were assigned to these species on the basis of the observation of *three* i.r.-active terminal CO stretching bands. Experience with [$Mn(CO)_4(NO)$], which also has ' apparently ' three i.r.-active terminal CO stretching bands in solution, consistent with structure (III), but *four* such bands in a N_2 matrix, has shown that there can be band overlaps which lead to incorrect conclusions. The C_{2v} structure of [$Mn(CO)_4(NO)$] in the N_2 matrix was established[31] by ^{13}CO substitution together with energy-factored force-field fitting of the observed and calculated spectra and is consistent with the *X*-ray crystallographic study of the compound. A ^{13}CO-labelling study[32] of [$Mn(CO)_4(CH_3)$] has also shown that energy-factored force-field fitting of observed and calculated spectra is only possible for the C_{2v} structure of type (IV). It seems possible, therefore, that [$Mn(CO)_4H$] also has a structure of type (IV) rather than of type (III);[16] *i.e.* the [$Mn(CO)_4X$] (X = Cl, Br, I, H, or CH_3) series of species has a common structure of type (IV).

TABLE 3

Observed and calculated[a] wavenumbers (cm^{-1}) of terminal CO stretching bands of ^{13}CO-enriched [$Mn(CO)_4Cl$] in a CH_4 matrix at 12 K

Complex	Point group	ν(CO)	Observed	Calculated
[$Mn(^{12}CO)_4Cl$]	C_{2v}	A_1	2 123.7	2 123.6
		B_1	2 052.3	2 052.5
		A_1	2 014.5	2 014.5
		B_2	1 973.1	1 973.1
[$Mn(^{12}CO)_3(^{13}CO)Cl$] (eq. ^{13}CO)	C_s	A'	*b*	2 121.4
		A'	2 052.3	2 052.5
		A'	*b*	2 003.0
		A''	1 942.1	1 942.3
(ax. ^{13}CO)	C_s	A'	2 108.9	2 109.2
		A'	2 030.2 [c]	2 029.1
		A'	2 006.0 [d]	2 006.0
		A''	1 973.1	1 973.3
[$Mn(^{12}CO)_2(^{13}CO)_2Cl$] (eq. ^{13}CO, eq. ^{13}CO)	C_{2v}	A_1	*e*	2 119.3
		A_1	2 052.3	2 052.5
		B_1	1 974.0	1 973.8
		B_2	1 929.3	1 929.3
[$Mn(^{12}CO)_2(^{13}CO)_2Cl$] (ax. ^{13}CO, ax. ^{13}CO)	C_{2v}	A_1	*b*	2 085.4
		A_1	2 007.0 [d]	2 006.9
		B_1	2 006.0 [d]	2 005.8
		B_2	1 973.1	1 973.1
[$Mn(^{12}CO)_2(^{13}CO)_2Cl$] (ax. ^{13}CO, eq. ^{13}CO)	C_1	A	2 106.5	2 106.6
		A	*b*	2 026.1
		A	*b*	1 998.2
		A	1 942.1	1 942.1
[$Mn(^{12}CO)(^{13}CO)_3Cl$] (ax. ^{12}CO)	C_s	A'	2 104.5	2 104.1
		A'	*b*	2 023.9
		A'	1 971.0 [c]	1 971.3
		A''	1 929.3	1 929.3
(eq. ^{12}CO)	C_s	A'	*b*	2 080.8
		A'	2 007.0 [d]	2 006.9
		A'	*b*	1 997.1
		A''	1 942.1	1 942.0
[$Mn(^{13}CO)_4Cl$]	C_{2v}	A_1	*b*	2 076.4
		B_1	2 007.0 [d]	2 006.9
		A_1	1 976.0 [c]	1 969.7
		B_2	1 929.3	1 929.3

[a] Refined energy-factored force constants: $K_{ax.} = 1\,750.4$, $K_{eq.} = 1\,617.7$, $k_t = 48.5$, $k_c = 30.3$, and $k_i = 44.9$ N m^{-1}. [b] Band obscured by others including those of the [$Mn(CO)_5Cl$] parent. [c] Band partially obscured by other bands, estimated position given. [d] Estimated position of unresolved band. [e] Band predicted to have very low intensity.

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