Photochemistry of some Manganese and Chromium Dinuclear Metal Carbonyl Complexes in Frozen Gas Matrices at *ca.* 12 K

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Infrared spectroscopic evidence is presented to show that photolysis of the non-metal–metal bonded dimers $[Mn_2(\mu\text{-}\eta^5\text{:}\eta^{5'}\text{-}C_{10}H_8)(CO)_6]$, $[Mn_2(\mu\text{-}\eta^5\text{:}\eta^{5'}\text{-}C_5H_4CH_2C_5H_4)(CO)_6]$, $[Cr_2(\mu\text{-}\eta^6\text{:}\eta^{6'}\text{-}C_{12}H_{10})(CO)_6]$, and $[Cr_2(\mu\text{-}\eta^6\text{:}\eta^{6'}\text{-}C_{14}H_{14})(CO)_6]$ together with its mononuclear analogue $[Cr(\eta^6\text{-}C_7H_8)(CO)_3]$ in gas matrices at *ca.* 12 K results in CO ejection to yield $[M(CO)_2]$ molecular fragments rather than detachment of polyene rings or the formation of new M–M linkages *via* M–M bonding and/or CO bridging. The reactivity of the resultant $[M(CO)_2]$ molecular fragments is demonstrated by the recombination with CO when matrices (Ar, CH_4) were irradiated with light of a longer wavelength and by the reactions with N_2 and ^{13}CO (5% in Ar or CH_4) to afford $[M(CO)_2(N_2)]$ and $[M(^{12}CO)_n(^{13}CO)_{3-n}]$ fragments, respectively. The failure to form new M–M linkages is attributed to the isolation of the dimers in pseudo-*trans* configurations in the matrix cages such that even the excess photochemical energy is insufficient to both cleave M–CO bonds and supply the energies required to rotate the bulky fragments in the rigid matrix cages. These findings are discussed in relation to solution photochemical reactions.

The photochemistry of organometallic species which have direct metal–metal bonds, *e.g.* $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ and $[M_2(CO)_{10}]$ (M = Mn or Re), has been extensively studied.[1–3] In contrast, the photochemical behaviour of dinuclear organometallics without a metal–metal bond such as (**1**)—(**4**) has not been widely investigated, although the mononuclear analogues, *i.e.* (**5**)—(**7**), have been studied in some detail.[3–10]

Herrmann *et al.*[11] have recently shown that photolysis of $[Mn_2(\mu\text{-}\eta^5\text{:}\eta^{5'}\text{-}C_{10}H_8)(CO)_6]$ (**1**), in benzene in the presence of π-donor ligands, gave monosubstituted derivatives of composition $[Mn_2(\mu\text{-}\eta^5\text{:}\eta^{5'}\text{-}C_{10}H_8)(CO)_5L]$ (L = ethylene, cyclooctene, or 2-butyne) whilst σ-donor ligands yielded disubstituted complexes $[Mn_2(\mu\text{-}\eta^5\text{:}\eta^{5'}\text{-}C_{10}H_8)(CO)_4L_2]$ [L = tetrahydrofuran (thf), PPh_3, or C_5H_5N; $L_2 = Ph_2PCH_2PPh_2$, (**8**)]. Solution photochemical studies[12] of (**2**) in the presence of thf resulted only in the production of the monosubstituted complex (**9**). Bitterwolf[13] has shown that photolysis of $[Cr_2(\mu\text{-}\eta^6\text{:}\eta^{6'}\text{-}C_{12}H_{10})(CO)_6]$ (**3**), in benzene in the presence of $Ph_2PCH_2PPh_2$, resulted in the production of (**10**), containing a bridging phosphine ligand, as the major photoproduct. Substantial quantities of compound (**11**) were also found in the reaction mixture indicating that loss of a chromium tricarbonyl moiety during u.v. irradiation is possibly an alternative photoprocess for (**3**) and one which might be possible for other similar dinuclear species.

Recently flash photolysis and time-resolved i.r. spectroscopy have been used[14] to show that on photolysis of $[Mn(\eta^5\text{-}C_5H_5)(CO)_3]$ (**5**), in room-temperature alkane solutions, two transient species are formed. One of the species was identified as $[Mn(\eta^5\text{-}C_5H_5)(CO)_2(solv)]$ (solv = cyclohexane or n-heptane) from both its kinetic behaviour and its i.r. spectrum. The second transient species $[Mn_2(\eta^5\text{-}C_5H_5)(CO)_5]$, (**12**), was formed by the reaction of $[Mn(\eta^5\text{-}C_5H_5)(CO)_2(solv)]$ with unphotolysed (**5**). The experimental data suggested that the dinuclear species had a single bridging CO group and a metal–metal bond. It seems possible that photolysis of the dimanganese species (**1**) and (**2**) could also lead to the production of transient species, similar to (**12**), although the cyclopentadienyl rings would clearly be held in a *cis* configuration, *i.e.* (**13**) and (**14**). Any such short-lived, thermally unstable species may possibly be isolable in low-temperature gas matrices.

In this paper the results of matrix-isolation studies of compounds (**1**)—(**4**) and (**7**) are described as a means of probing the mechanistic photochemistry of such complexes and comparing them with mononuclear analogues and metal–metal bonded dimers.

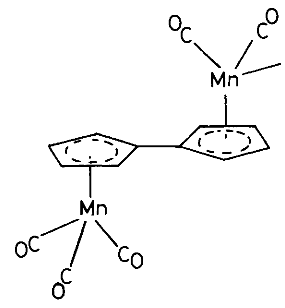
Experimental

The equipment for matrix-isolation studies at 12 K together with the photolysis lamp, matrix gases, and spectrometers have been described elsewhere.[15]

Wavelength-selective photolyses were achieved as follows: filter A, $\lambda < 280$, > 550 nm, quartz gas cell (pathlength 27 mm) containing Cl_2 gas (2 atm, *ca.* 2×10^5 Pa) + quartz gas cell (pathlength 27 mm) containing Br_2 (300 Torr, *ca.* 4×10^5 Pa); filter B, $290 < \lambda < 370$, > 550 nm, quartz gas cell (pathlength 27 mm) containing Br_2 (300 Torr) + Pyrex disc (2 mm thick); filter C, $\lambda > 300$ nm, soda glass disc (3 mm thick); filter D, $320 < \lambda < 390$ nm, Corning glass filter no. 5874; filter F, $\lambda > 415$ nm, Corning glass filter, no. 9689; filter K, $\lambda > 475$ nm, Corning glass filter, no. 3385.

Compounds were kindly supplied by Professor T. E. Bitterwolf and Dr. N. J. Fitzpatrick and used without further purification.

Matrices were prepared by the slow spray-on method[16] holding the samples at constant temperatures [(**1**), 70; (**2**), 75; (**3**), 55; (**7**), 50; and (**4**), 52 °C] while spraying on an excess of matrix gas.



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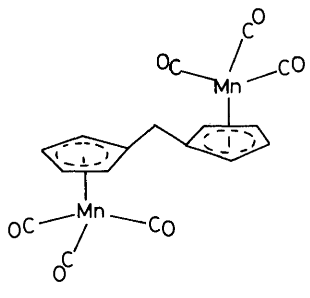

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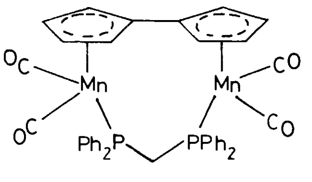

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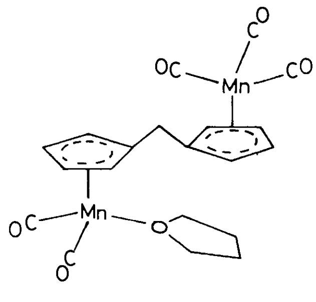

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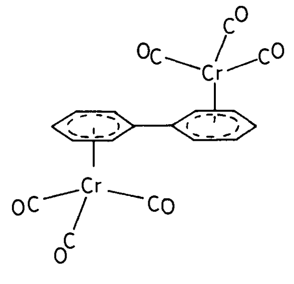

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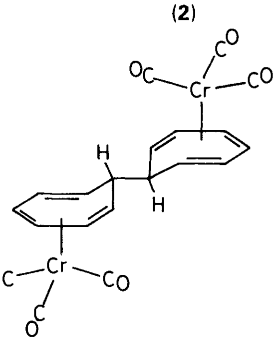

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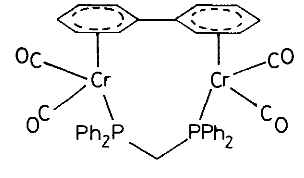

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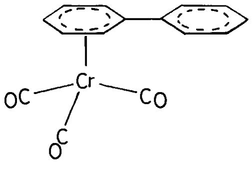

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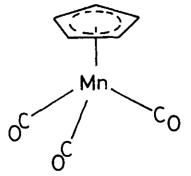

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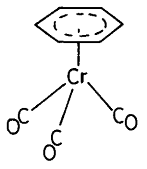

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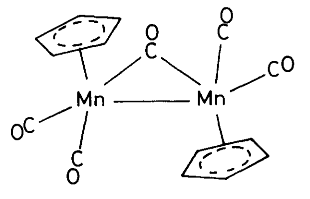

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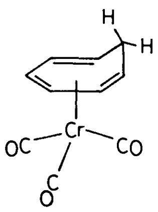

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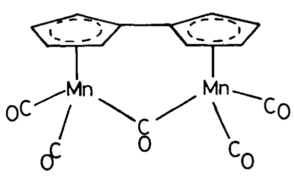

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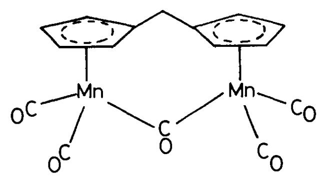

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Results

Photolyses of the complexes studied were carried out at various wavelengths corresponding to the electronic absorption bands of each species. The electronic absorption spectra are summarised in Table 1 and are discussed briefly as each species is considered.

(*a*) *Photolysis of* $[Mn_2(\mu\text{-}\eta^5:\eta^{5'}\text{-}C_{10}H_8)(CO)_6]$ **(1)** *and* $[Mn_2(\mu\text{-}\eta^5:\eta^{5'}\text{-}C_5H_4CH_2C_5H_4)(CO)_6]$ **(2)** *in Frozen Gas Matrices at* ca. 12 K.—The electronic absorption spectrum of compound **(1)** in iso-octane solution at 298 K has a well defined u.v. transition band at 335 nm, with a tail below 385 nm. This band position is very similar to those seen for a variety of $[Mn(\eta^5\text{-}Y)(CO)_3]$ species ($Y = C_5H_5$ or C_5H_4Me,[17] $C_5H_4COCH_2Ph$,[18] or C_5H_4COMe[19]). These lowest observable transitions in the $[Mn(\eta^5\text{-}Y)(CO)_3]$ species have been interpreted as charge-transfer transitions with substantial $Mn \longrightarrow (\eta^5\text{-}Y)$ character but with additional $Mn \longrightarrow (CO)$ charge-transfer contributions.[3,17,18] A very similar spectrum for compound **(2)** leads to an analogous interpretation of its u.v.–visible transitions (Table 1). Aside from a slight band sharpening, little change is noted between solution and gas matrix spectra (Table 1). This is consistent with the little change observed in the electronic spectrum of **(5)** when solutions were cooled to 77 K.[17]

The i.r. spectrum (CO-stretching region) of compound **(1)** isolated at high dilution in a methane matrix at 12 K is shown in Figure 1(*a*). The spectrum shows two strong matrix-split absorptions centred at 2 023.8 and 1 946.7 cm^{-1}. These bands agree with solution (2 025 and 1 956 cm^{-1} in n-hexane)[11] and KBr disc (2 000 and 1 925 cm^{-1})[20] data and may be assigned to the expected two i.r.-active terminal carbonyl-stretching modes, if the metal centres are considered to have local C_{3v} symmetry. Weak bands are seen at 2 015.3, 1 939.9, and 1 912.3 cm^{-1} which agree well with those seen in methane matrices for $[Mn(\eta^5\text{-}C_5H_5)(^{12}CO)_2(^{13}CO)]$ (2 014.7, 1 940.7, and 1 907.0 cm^{-1}),[8] and are therefore assigned to the naturally abundant ^{13}CO-substituted species of **(1)**. The i.r. spectrum after deposition is very similar to that observed for **(5)** in gas matrices[8,21] and hence the respective metal-centre environ-

Table 1. Observed electronic absorption bands ($\lambda_{max.}$/nm) for the species (1)—(7) in solution at 298 K and in argon matrices at 12 K

Compound	Solution (298 K)[a]	Argon matrix (12 K)
(1)	335	335
	255[b]	260[b]
	220	225
(2)	337	340
	260[b]	255[b]
	220	220
(3)	390[b]	385[b]
	325	325
	260	265
	220	220
(4)	485	490[c]
	350	355
	270[b]	270[b]
	230	225
(5)[d]	330	—
	220	—
(6)[e]	320	—
	265	—
	220	—
(7)	480	485[c]
	350	350
	270[b]	265[b]
	230	230

[a] In MeOH. [b] Shoulder band. [c] Very weak absorption. [d] Solution spectrum recorded in iso-octane.[17] [e] Solution spectrum recorded in cyclohexane.[25]

ments, as reflected by CO-stretching frequencies, are clearly little affected by the presence of the second metal centre on the adjacent, bonded ring system.

Photolysis (filter D) into the lowest-energy electronic absorption band resulted in the parent i.r. bands decreasing in intensity with two new bands being produced at 1 963.6 and 1 896.0 cm^{-1} along with a band due to 'free' CO (2 138.8 cm^{-1}). Continued photolysis at this wavelength saw further CO production and the two new bands growing together along with a new very weak band at 1 861.4 cm^{-1}, all at the expense of the parent i.r. bands [Figure 1(*b*)]. Low-energy photolysis (filter F) rapidly caused regeneration of the parent bands at the expense of the product absorptions [Figure 1(*c*) and (*d*)]. No clear changes were observed in the electronic spectrum of the matrix-isolated sample on photolysis at all wavelengths. In separate experiments higher-energy photolysis (filters B and A) of (1) yielded rapid decomposition of the parent but no new i.r. bands were observed; presumably any photoproducts are similarly destroyed by the high-energy radiation.

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 species. The photoproduct is also clearly a product of CO loss from the parent species. Comparison of the new i.r. bands with data for the fragment [Mn(η^5-C_5H_5)(CO)$_2$] (Table 3) allows the assignment of the photoproduct (ν_{CO} at 1 963.6 and 1 896.0 cm^{-1}) as having a co-ordinatively unsaturated metal centre with 16 valence electrons and two i.r.-active CO stretching modes. The reversal on longer-wavelength irradiation is consistent with a CO-loss species having been produced. The i.r. data provide evidence for at least one manganese metal centre having undergone photoejection of a CO ligand to produce a species such as (**15**). However the parent molecule could lose a CO ligand from both metal centres to produce (**16**).

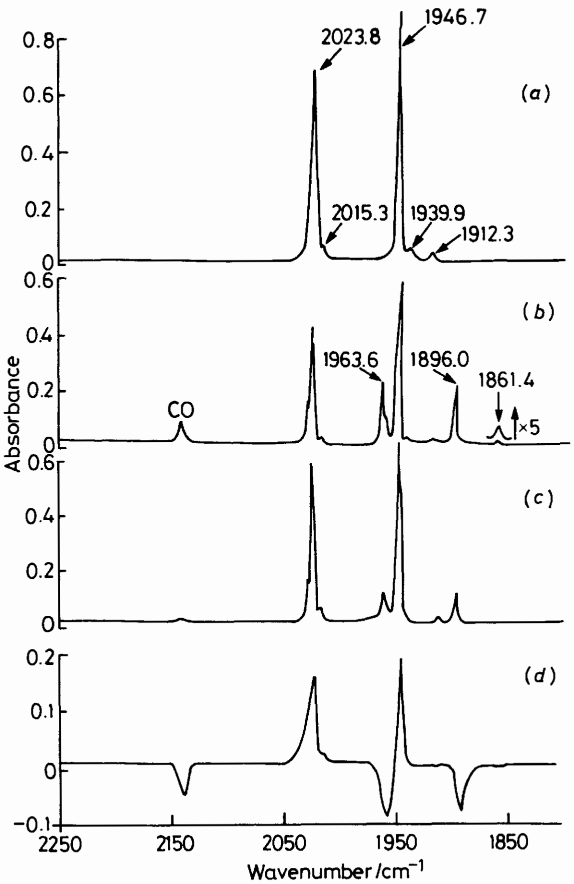


Figure 1. Infrared spectra (Nicolet 7199, resolution 1 cm^{-1}) from an experiment with [Mn$_2$(μ-η^5:$\eta^{5'}$-$C_{10}H_8$)(CO)$_6$] isolated at high dilution in a methane matrix: (*a*) after deposition, (*b*) after 60 min of irradiation using filter D, (*c*) after 30 min of irradiation using filter F, and (*d*) subtraction spectrum [(*c*) − (*b*)]

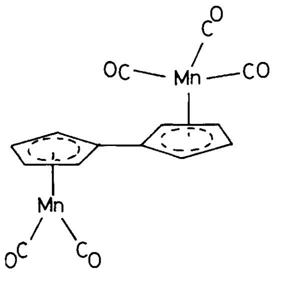
The i.r. spectrum alone could not distinguish between compound (**15**) and (**16**), unless the stoicheiometric loss of CO from (**1**) could be determined. The absorption coefficients for CO and (**1**) in the gas matrix would be required to allow *quantitative* measures of the increase in CO absorption and decrease in absorption due to (**1**). During the photochemical production of [Mn(η^5-C_5H_5)(CO)$_2$] in methylcyclohexane glasses at 100 K, Hill and Wrighton[10] were able to show a net loss of one CO molecule for each molecule of the parent species, (**5**), consumed. The experimental conditions allowed quantitative measurements by using known solution concentrations, i.r. cells of known pathlength, and a previously experimentally measured value[22] for the absorption coefficient of uncomplexed CO in methlycyclohexane at 100 K. Unfortunately the slow spray-on technique required in the present gas matrix study prevents quantitative measurements of CO loss from compound (**1**). To enable the clear presentation of the matrix-isolation results, from this point onwards it will be assumed that photoejection of a CO ligand only occurs at one metal centre for each molecule, and the two-ring system and second metal centre will be represented by η^5-X, thus (**15**) will have the formula, [Mn(η^5-X)(CO)$_2$] [X = $C_{10}H_8Mn(CO)_3$].

On extended photolysis of (**1**) a further species with a very weak i.r. band at 1 861.4 cm^{-1} was observed. Prolonged photolysis of (**5**) in glasses at 77 K produced[6] a weak new i.r. band at 1 857 cm^{-1} which was attributed to the monocarbonyl species [Mn(η^5-C_5H_5)(CO)]. This species was not observed on photolysis of (**5**) in methane and argon matrices.[21] However, the lower-energy i.r. band of [Mn(η^5-C_5H_5)(^{12}CO)(^{13}CO)] was observed at 1 861.5 cm^{-1} in ^{13}CO-doped methane matrices[8] and this is in agreement with the unassigned weak

Table 2. Observed positions (cm^{-1}) of terminal CO-stretching bands and mean positions of band centres for compounds (**1**) and (**2**) and their photoproducts in frozen gas matrices

Compound	CH_4	Ar	N_2	CO
(**1**)[a]	2 023.8	2 028.9	2 032.8	2 026.8
	1 946.7	1 952.7	1 949.1	1 940.8
(**15**)	1 963.6	1 971.9	*b*	*b*
	1 896.0	1 903.6		
(**18**)	—	—	1 979.8[c]	—
	—	—	1 928.9	—
(**2**)[d]	2 024.8	2 026.4	2 028.6	2 026.9
	1 946.5	1 950.4	1 947.3	1 941.4
(**19**)	1 962.3	1 970.0	*b*	*b*
	1 893.8	1 899.6		
(**20**)	—	—	1 977.9[e]	—
	—	—	1 922.8	—

[a] ν_{CO} at 2 025 and 1 956 cm^{-1} in n-hexane at 298 K. [b] Not observed. [c] ν_{NN} at 2 172.8 cm^{-1}. [d] ν_{CO} at 2 022 and 1 941 cm^{-1} in CH_2Cl_2 at 298 K. [e] ν_{NN} at 2 175.9 cm^{-1}.



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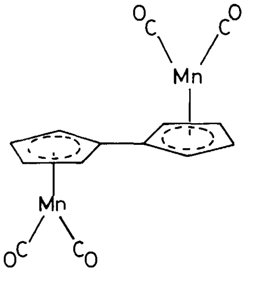

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band seen in the present study at 1 861.4 cm^{-1}. It seems reasonable that small amounts of [Mn(η^5-X)(^{12}CO)(^{13}CO)] have been isolated in the matrix on photolysis of naturally abundant [Mn(η^5-X)($^{12}CO)_2$(^{13}CO)].

Allowing for matrix shifts, experiments in argon matrices produced identical results to those seen in methane matrices (Table 2).

Infrared spectra from an experiment with compound (**1**) isolated in a nitrogen matrix using filter D are shown in Figure 2. The spectrum of the parent complex [Figure 2(*a*)] is very similar to that in argon and methane matrices with matrix splittings under high resolution (Table 2). Weak bands (marked with an asterisk) are due to natural-abundance [Mn(η^5-X)-($^{12}CO)_2$(^{13}CO)] fragments.

A period of photolysis (filter D) produced a spectrum [Figure 2(*b*)] containing four new bands at 2 172.8, 2 138.0, 1 979.8, and 1 928.9 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 in the region of the ν_{NN} position of [Mn(η^5-C_5H_5)$(CO)_2(N_2)$] (**17**) (ν_{NN} at 2 169 cm^{-1} in n-hexane,[23] 2 175.3 cm^{-1} in a nitrogen matrix[21]). The other two bands at 1 979.8 and 1 928.9 cm^{-1} are in good agreement with the ν_{CO} of the same species (**17**) (ν_{CO} at 1 980 and 1 923 cm^{-1} in n-hexane,[23] 1 978.7 and 1 927.0 cm^{-1} in a nitrogen matrix[21]) and so the assignment of the photoproduct as the species [Mn(η^5-X)$(CO)_2(N_2)$], (**18**), seems reasonable. On irradiation at longer wavelengths compound (**18**) did not undergo photoreversal as was seen for (**17**).[19] Higher-energy photolyses only resulted in decomposition of all species.

Photolysis of compound (**1**) in a pure CO matrix failed to cause any observable photoreaction. However, an experiment with a ^{13}CO-doped (5%) methane matrix showed that photolysis (filter D) resulted in isotopic enrichment of (**1**) and the production of [Mn(η^5-X)($^{12}CO)_2$(^{13}CO)], [Mn(η^5-X)(^{12}CO)-($^{13}CO)_2$], and even some [Mn(η^5-X)($^{13}CO)_3$]. Prolonged photolysis resulted in the formation of the co-ordinatively unsaturated species [Mn(η^5-X)($^{12}CO)_2$] and [Mn(η^5-X)-(^{12}CO)(^{13}CO)]. All assignments were confirmed by the excellent agreement of the observed band positions with those previously observed and calculated for the enriched mononuclear species (**5**)[8] (Table 4).

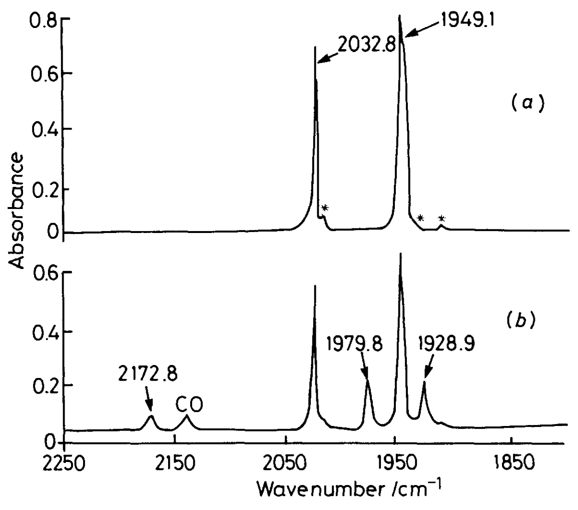
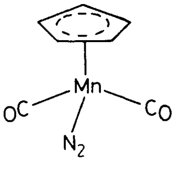


Figure 2. Infrared spectra (Nicolet 7199, resolution 1 cm^{-1}) from an experiment with [Mn_2(μ-η^5:$\eta^{5'}$-$C_{10}H_8$)$(CO)_6$] isolated at high dilution in a pure nitrogen matrix: (*a*) after deposition, (*b*) after 60 min of irradiation using filter D. Bands marked with * arise from ^{13}CO-substituted species present in natural abundance



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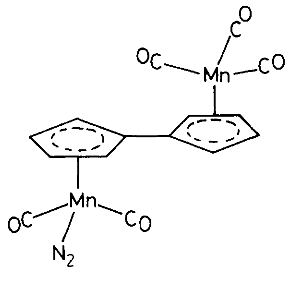

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The i.r. spectra obtained on isolation of compound (**2**) in frozen gas matrices were in good agreement with previous solution spectra.[24] These matrix i.r. data are summarised in Table 2. Photolysis (filter D) led to similar results to those found on photolysis of (**1**) in gas matrices: (*i*) in argon and methane matrices the reversible photoejection of a CO ligand resulted in the production of compound (**19**); (*ii*) in nitrogen matrices photolysis afforded (**20**); (*iii*) isotopic enrichment of (**2**) was observed in ^{13}CO-doped methane matrices. These results are represented in Scheme 1 and the i.r. data are summarised in Tables 2 and 4.

(*b*) *Photolysis of* [Cr_2(μ-η^6:$\eta^{6'}$-$C_{12}H_{10}$)$(CO)_6$], (**3**), *in Frozen Gas Matrices at* ca. 12 K.—The electronic absorption spectrum of compound (**3**) in methanol solution at 298 K shows a sharp, intense band at 325 nm, with a low-energy shoulder near 390 nm and two further high-energy transitions at 260 and 220 nm. The spectrum is very similar to that found[25,26] for [Cr(η^6-C_6H_6)-$(CO)_3$] (**6**) (see Table 1) and by comparison to this assigned[27] spectrum the lower-energy bands at 325 and 390 nm are attributed to charge-transfer transitions from chromium to the

Table 3. Carbonyl stretching bands (cm^{-1}) of compound (**5**) and its carbonyl-loss photoproduct in various media at low temperatures

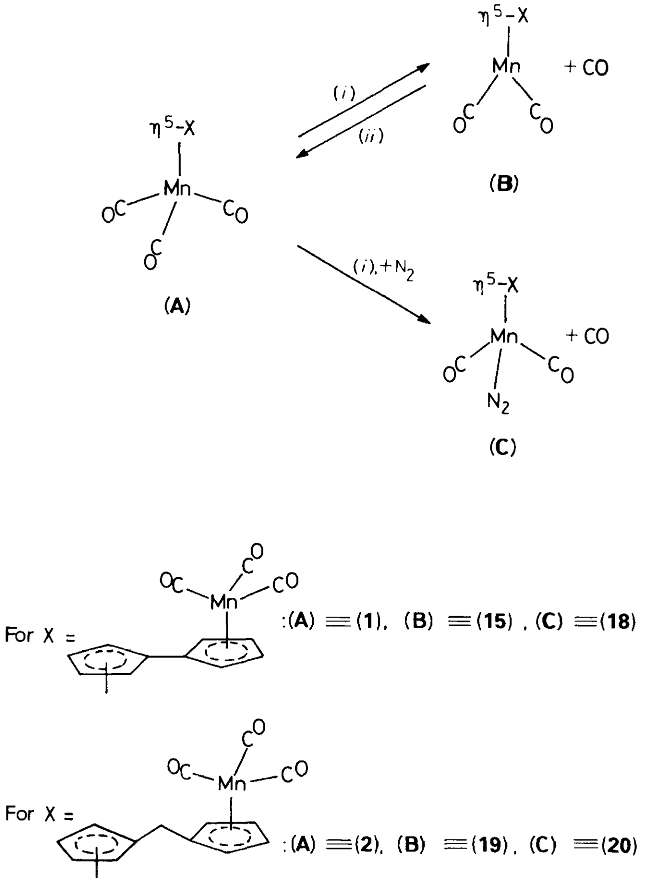
Medium and temperature	$[Mn(\eta^5\text{-}C_5H_5)(CO)_3]$	$[Mn(\eta^5\text{-}C_5H_5)(CO)_2]$
Argon matrix at 12 K[a]	2 032.6	1 972.0
	1 951.0	1 903.2
Methane matrix at 12 K[a]	2 028.5	1 961.4
	1 943.0	1 892.8
Methylcyclohexane–isopentane glass (4:1) at 77 K[b]	2 026	1 955
	1 938	1 886
Methylcyclohexane glass at 100 K[c]	2 027	1 950
	1 942	1 880

[a] From ref. 21. [b] From ref. 6. [c] From ref. 10.

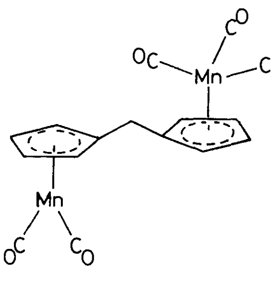
Table 4. Observed band positions (cm^{-1}) of terminal CO-stretching modes in ^{13}CO enrichment experiments for compounds (**5**),[a] (**1**),[b] and (**2**)[b] isolated in ^{13}CO-doped methane matrices at 12 K

Fragment	(**5**)[c]	(**1**)[d]	(**2**)[e]
$[Mn(\eta^5\text{-}X)(^{12}CO)_3]$	2 025.8	2 023.2	2 024.8
	1 940.7	1 942.2	1 942.1
$[Mn(\eta^5\text{-}X)(^{12}CO)_2(^{13}CO)]$	2 014.7	2 015.1	2 015.3
	1 940.7	1 942.2	1 942.1
	1 907.0	1 910.0	1 909.6
$[Mn(\eta^5\text{-}X)(^{12}CO)(^{13}CO)_2]$	2 001.6	1 999.7	2 000.3
	1 920.5	1 919.2	1 920.4
	1 895.9	1 894.7	1 896.4
$[Mn(\eta^5\text{-}X)(^{13}CO)_3]$	1 979.8	1 978.9	1 980.1
	1 895.9	1 894.7	1 896.4
$[Mn(\eta^5\text{-}X)(^{12}CO)_2]$	1 959.2	1 960.6	1 960.3
	1 889.2	1 890.1	1 891.2
$[Mn(\eta^5\text{-}X)(^{12}CO)(^{13}CO)]$	*f*	*f*	*f*
	1 861.5	1 861.4	1 860.3

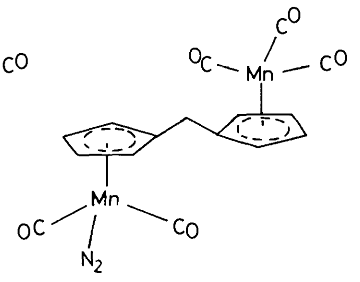
[a] From ref. 8. [b] This work. [c] $X = C_5H_5$. [d] $X = C_5H_4[C_5H_4Mn(CO)_3]$. [e] $X = C_5H_4CH_2[C_5H_4Mn(CO)_3]$. [f] Band obscured by overlap.



Scheme 1. (*i*) $h\nu$, $320 < \lambda < 390$ nm; (*ii*) $h\nu$, $\lambda > 420$ nm



(**19**)



(**20**)

rings and, to a lesser extent, to the carbonyl groups, while the high-energy transitions are assigned to charge transfers from the chromium and the rings to the carbonyls.

The i.r. spectrum (CO-stretching region) of compound (**3**) isolated at high dilution in a methane matrix is shown in Figure 3(*a*). The spectrum shows two strong i.r. absorptions at 1 978.8 and 1 910.4 cm^{-1} (matrix split) which agree with previous solution data.[13] Three weak bands (marked with an asterisk) are due to the naturally abundant ^{13}CO-substituted species of (**3**).

Irradiation (filter B) produced a spectrum [Figure 3(*b*)] with three new i.r. bands at 2 136.9 ('free' CO), 1 922.7, and 1 869.8 cm^{-1}, all at the expense of the parent absorptions. Continued photolyses at this wavelength saw the two strong bands at 1 922.7 and 1 869.8 cm^{-1} grow together. Rapid photochemical reversal was observed on subsequent lower-energy irradiation (filter F) [Figure 3(*c*) and (*d*)], although no clear new electronic absorption bands were seen throughout the experiment. Higher-energy photolysis (filter A) caused a rapid growth in the product bands, but prolonged photolysis led to general decomposition. Annealing the matrices to 30 K after photolysis also afforded some reversal of the photoreaction.

By comparison with i.r. data for matrix-isolated $[Cr(\eta^6\text{-}C_6H_6)(CO)_2]$ fragments (ν_{CO} at 1 925.0 and 1 870.0 cm^{-1} in a methane matrix)[21] it is possible to assign the two new bands as due to the related species (**21**). This assignment is supported by the concurrent production of 'free' CO, and the observed photochemical and thermal recombination with CO to reproduce the parent species.

Results in argon matrices were consistent with the same photochemistry having occurred (Table 5).

By comparison with i.r. data for $[Cr(\eta^6\text{-}C_6H_6)(CO)_2(N_2)]$,[21,28] the results in nitrogen matrices were consistent with the production of compound (**22**) on photolysis of (**3**). No photoreactions were observed in carbon monoxide matrices

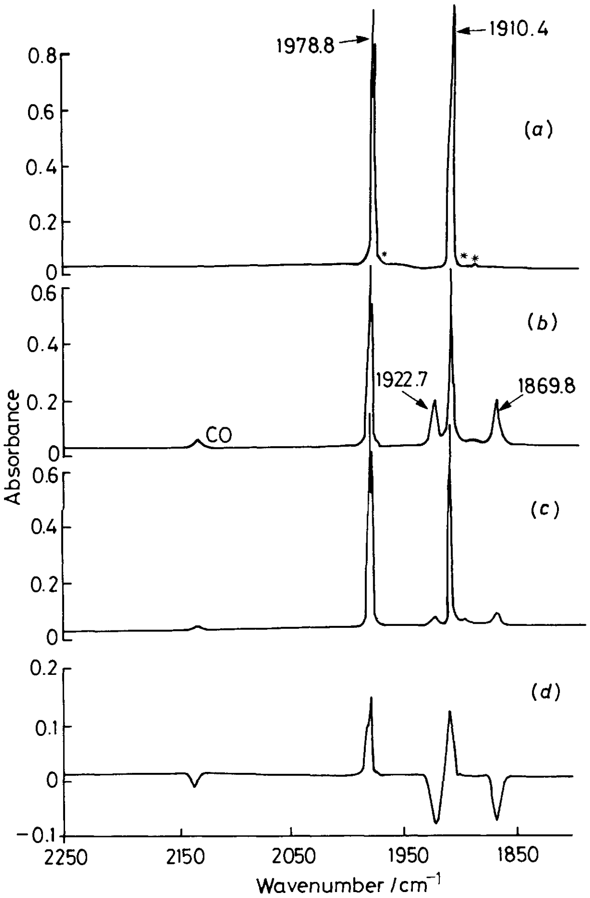
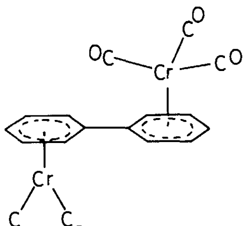
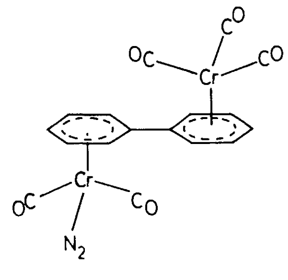


Figure 3. Infrared spectra (Nicolet 7199, resolution 1 cm^{-1}) from an experiment with [$Cr_2(\mu$-$\eta^6:\eta^{6'}$-$C_{12}H_{10})(CO)_6$] isolated at high dilution in a methane matrix: (*a*) after deposition, (*b*) after 45 min of irradiation using filter B, (*c*) after 30 min of irradiation using filter F, and (*d*) subtraction spectrum [(*c*) − (*b*)]. Bands marked with * arise from ^{13}CO-substituted species present in natural abundance



(21)



(22)

and experiments with ^{13}CO-doped (5%) methane matrices showed that on photolysis some very limited isotopic enrichment took place. These results are represented in Scheme 2 and the i.r. data summarised in Table 5.

(*c*) *Photolysis of* [$Cr(\eta^6$-$C_7H_8)(CO)_3$], **(7)** *and* [$Cr_2(\mu$-$\eta^6:\eta^{6'}$-$C_{14}H_{14})(CO)_6$], **(4)**, *in Frozen Gas Matrices at* ca. 12 K.—The electronic absorption spectra of compounds **(7)** and **(4)** are fairly similar to those seen for **(3)** and **(6)**; although the spectra remain unassigned, it seems likely that as for **(3)** and **(6)**, they are dominated by metal–ligand charge-transfer reactions.

The i.r. spectrum (CO-stretching region) of compound **(7)** isolated at high dilution in a methane matrix is shown in Figure 4(*a*). It shows three strong absorptions at 1 987.0, 1 923.8, and 1 901.8 cm^{-1} which are the three i.r.-active terminal-CO stretching modes for the C_s symmetry-group molecule, and are in good agreement with solution data.[29,30,*] Weak bands (marked with an asterisk) are due to naturally abundant [$Cr(\eta^6$-$C_7H_8)(^{12}CO)_2(^{13}CO)$] species.

Table 5. Observed positions (cm^{-1}) of terminal CO-stretching bands and mean positions of band centres for compounds (3), (7), and (4) and their photoproducts in frozen gas matrices

Compound	CH_4	Ar	N_2	CO
(3)[a]	1 978.8	1 981.8	1 982.0	1 980.6
	1 910.4	1 918.0	1 916.1	1 913.6
(21)	1 922.7	1 931.2	*b*	*b*
	1 869.8	1 882.3		
(22)	—	—	1 941.0[c]	—
	—	—	1 898.2	—
(7)[d]	1 987.0	1 991.3	1 993.4	1 992.0
	1 923.8	1 927.2	1 929.3	1 925.3
	1 901.8	1 899.6	1 901.7	1 900.6
(23)	1 943.9	1 944.6	*b*	*b*
	1 864.0	1 868.1		
(24)	—	—	1 957.9[e]	—
	—	—	1 886.3	—
(25)[f]	—	—	—	2 038.0
	—	—	—	1 952.0
	—	—	—	1 933.0
(4)[g]	1 984.0	1 994.1	1 995.2	1 987.2
	1 921.9	1 933.8	1 934.3	1 928.6
	1 899.8	1 909.8	1 902.7	1 903.4
(26)	1 933.2	1 940.7	*b*	*b*
	1 860.7	1 872.4		
(27)	—	—	1 958.2[h]	—
	—	—	1 887.2	—

[a] ν_{CO} at 1 970 and 1 900 cm^{-1} in $CDCl_3$ at 298 K.[13] [b] Not observed. [c] ν_{NN} at 2 151.1 cm^{-1}. [d] ν_{CO} at 1 980, 1 920, and 1 895 cm^{-1} in CH_2Cl_2 at 298 K. [e] ν_{NN} at 2 153.4 cm^{-1}. [f] Bands for molybdenum analogue at 2 040, 1 954, and 1 926 cm^{-1}.[33] [g] ν_{CO} at 1 982, 1 924, and 1 894 cm^{-1} in $CDCl_3$ at 298 K.[33] [h] ν_{NN} at 2 154.4 cm^{-1}.

Irradiation (filter C) afforded a decrease in the parent i.r. bands and produced two new weak bands at 1 943.9 and 1 864.0 cm^{-1}, as well as some 'free' CO (2 138.8 cm^{-1}). Continued photolyses at this wavelength saw the two weak bands and the band due to 'free' CO grow together, at the continued expense of the parent i.r. bands [Figure 4(*b*)]. Subsequent low-energy photolysis (filter K) afforded reversal of the photoreaction [Figure 4(*c*) and (*d*)], as did annealing the matrix to about 30 K. In separate experiments higher-energy photolyses (filter A) afforded the same photoproduct, but prolonged photolysis resulted only in decomposition of all species.

The two new bands are clearly due to a single species produced *via* photochemical loss of CO. By comparison with i.r. data for the co-ordinatively unsaturated fragments [$Cr(\eta^6$-$C_6H_6)(CO)_2$] and **(21)**, the new i.r. bands are attributed to the co-ordinatively unsaturated species [$Cr(\eta^6$-$C_7H_8)(CO)_2$] **(23)**. This assignment is supported by the observed photochemical and thermal reversal to the parent tricarbonyl species (Scheme 2).

Experiments in argon matrices produced identical results to those seen in CH_4 (Table 5).

Results obtained on photolysis of compound **(7)** in nitrogen matrices were consistent with the production of the previously

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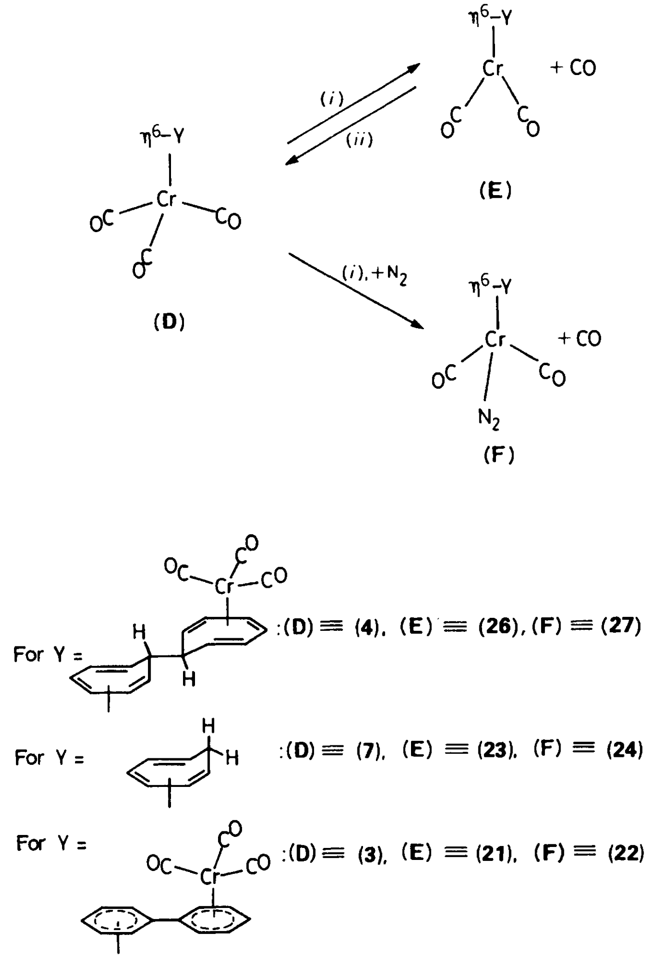
* Thermal rearrangement in the gas phase of the molybdenum analogue of (7), *i.e.* [$Mo(\eta^7$-$C_7H_8)(CO)_3$], to produce the metal hydride complex [$(Mo(\eta^6$-$C_7H_7)(CO)_3H$], has previously been observed in CO matrices.[31] However, no evidence was found in the present study for a similar product being isolated on deposition of (7) in gas matrices.



Scheme 2. (*i*) $h\nu$, $\lambda > 300$ nm; (*ii*) $h\nu$, $\lambda > 475$ nm

unreported species [Cr(η^6-C_7H_8)$(CO)_2(N_2)$] (**24**), which was assigned by comparison with data for the similar species [Cr(η^6-C_6H_6)$(CO)_2(N_2)$] and (**22**). The observation of dinitrogen co-ordination further supports the assignment of (**23**). Photoreactions of (**7**) have been observed[32] in solution where a single carbonyl ligand was substituted by phosphines and it seems likely that these reactions may proceed through the intermediacy of the observed species (**23**).

Photolysis of (**7**) in pure CO matrices (filter C) leads to a change in the relative intensities of the parent bands together with the appearance of weak bands at 2 038.0, 1 952.0, and 1 933.0 cm^{-1}. Longer irradiation and spectral subtraction revealed that there was a single band at 1 986.4 cm^{-1} under the highest-wavenumber parent band. The latter band can be assigned to [$Cr(CO)_6$] while the former set may be assigned to [Cr(η^4-C_7H_8)$(CO)_4$] (**25**) by analogy with the behaviour of [Mo(η^6-C_7H_8)$(CO)_3$] in CO matrices.[33] Experiments with compound (**7**) in ^{13}CO-doped (5%) methane matrices showed some limited enrichment on photolysis.

Experiments with the dinuclear species, (**4**), in all gas matrices produced similar results to those seen for its mononuclear analogue, (**7**). The i.r. spectra on isolation in the matrices were consistent with solution data.[34] The observed matrix photochemistry is represented in Scheme 2 and the i.r. data summarised in Table 5. The similarity between the results obtained for (**4**) and (**7**) was consistent with that observed for the three dinuclear species (**1**)—(**3**) and their mononuclear analogues.

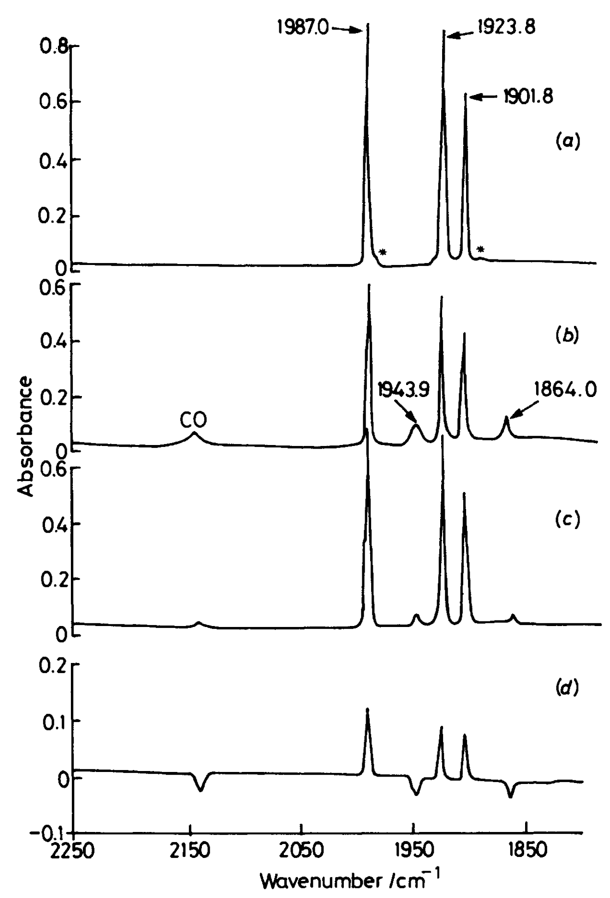
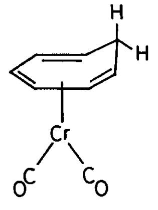
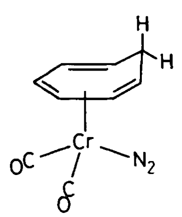


Figure 4. Infrared spectra (Nicolet 7199, resolution 1 cm^{-1}) from an experiment with [Cr(η^6-C_7H_8)$(CO)_3$] isolated at high dilution in a methane matrix: (*a*) after deposition, (*b*) after 60 min of irradiation using filter C, (*c*) after 120 min of irradiation using filter K, and (*d*) subtraction spectrum [(*c*) − (*b*)]. Bands marked with * arise from [Cr(η^6-C_7H_8)$(^{12}CO)_2(^{13}CO)$] present in natural abundance



(**23**)



(**24**)

Discussion

The observed matrix photochemistry of each of the dinuclear species (**1**)—(**4**) and that of the mononuclear species (**7**) is represented in the Schemes 1 and 2. For each species photolysis resulted in photochemical ejection of a CO ligand to produce co-ordinatively unsaturated metal dicarbonyl centres. This is not unexpected as the electronic transitions, into which irradiation took place, all involved some metal to carbonyl charge transfer, and excited-state species thus formed could readily lose a carbonyl ligand.

Recently Poliakoff and co-workers[14] studied the photochemistry of compound (**5**) *via* flash photolysis in alkane solutions. A transient dicarbonyl species was produced and addition of carbon monoxide to the solution reduced its lifetime but had little effect on its overall yield. Also relatively small rate constants were measured for the reaction of the transient dicarbonyl species with CO, N_2, and PPh_3 compared to those reported for the reaction of $[Cr(CO)_5]$ with CO in cyclohexane.[35] Measurements at different temperatures showed that the reaction of $[Mn(\eta^5\text{-}C_5H_5)(CO)_2]$ with PPh_3 leading to the formation of the known compound $[Mn(\eta^5\text{-}C_5H_5)(CO)_2(PPh_3)]$[36] had a significant activation barrier. Thus it was concluded that it was unlikely that $[Mn(\eta^5\text{-}C_5H_5)(CO)_2]$ existed as a co-ordinatively unsaturated species in the hydrocarbon solvents. Rather, as in the case of $[Cr(CO)_5]$,[35] a molecule of solvent was probably acting as a weakly co-ordinated token ligand to give a $[Mn(\eta^5\text{-}C_5H_5)(CO)_2(solv)]$ species. Therefore the possibility of the matrix gases acting in a similar fashion as the solvent must be considered.

The matrix shift of the photoproduct bands for methane relative to argon matrices (Tables 2 and 5) was very similar to that of the parent molecule and this suggests that the photoproducts are probably $[M(CO)_2]$ fragments in methane matrices rather than $[M(CO)_2 \cdots CH_4]$, *cf.* $[Fe(CO)_4 \cdots CH_4]$.[37] However, comparison of i.r. matrix shifts as a means of identifying very weak interactions of carbonyl fragments with a matrix such as methane must be treated cautiously because this method while identifying $[Fe(CO)_4 \cdots CH_4]$[37] would not identify $[Cr(CO)_5 \cdots CH_4]$ which was only detected[38] using electronic spectroscopy and mixed matrices. Hence the possibility of the observed dicarbonyl fragments having host matrix gas molecules as token ligands cannot be ruled out, though no clear new electronic absorption bands were seen in the matrix experiments, in contrast to the band observed ($\lambda_{max.}$ = *ca.* 580 nm) for the intermediate $[Mn(\eta^5\text{-}C_5H_5)(CO)_2(solv)]$.[14]

There was no evidence for bridging species being formed on photolysis of any of the studied compounds in any of the gas matrices. Complexes (**1**) and (**2**) seemed to be the most likely candidates to produce a bridging species, *i.e.* (**13**) and (**14**), forming in the same way as (**12**) was formed in alkane solutions,[14] as the two metal centres are held in close proximity by the ring linkage. Photolysis of (**1**) and (**2**) only resulted in the production of co-ordinatively unsaturated metal centres which did not react with the second fully co-ordinated metal centre of each molecule to form bridged species. The complexes are probably isolated in the matrix cages in pseudo-*trans* configurations, with the metal centres as far apart as possible, as depicted in the structures presented in this study. The excess energy provided by the irradiating source beyond that needed for the M–CO band cleavage is unlikely to be sufficient to allow M–M bond formation because of the large energies required to rotate the bulky fragments against the effects of the very rigid matrix cages.

Early reports on $[M(\eta^6\text{-arene})(CO)_3]$ (M = Cr, Mo, or W) complexes claimed reactions according to equations (1)[39] and (2)[40] as general photoreactions. More recent studies[41,42] have shown that the quantum yield for equation (1) (M = Cr) is very high, and if reaction according to (2) obtains at all it is very inefficient.

$$[\mathrm{M}(\eta^6\text{-arene})(\mathrm{CO})_3] \xrightarrow[\mathrm{L}]{h\nu} [\mathrm{M}(\eta^6\text{-arene})(\mathrm{CO})_2\mathrm{L}] + \mathrm{CO} \qquad (1)$$

$$[\mathrm{M}(\eta^6\text{-arene})(\mathrm{CO})_3] \xrightarrow[\text{arene*}]{h\nu} [\mathrm{M}(\eta^6\text{-arene*})(\mathrm{CO})_3] + \text{arene} \qquad (2)$$

The observed matrix photochemistry of compound (**3**) exclusively involves CO loss, although $[Cr(CO)_3]$ loss during irradiation of room-temperature solutions of (**3**) has been reported. Thermal reactions of (**6**) readily result in arene ligand exchange.[43,44]

There was no evidence in this study for the ejection of ring systems in the dimer complexes to yield $[M(CO)_3]$ fragments, *cf.* $[Cr(CO)_3]$[45] and $[Mn(CO)_3]$[46] which have been separately characterised by matrix-isolation spectroscopy. However, the mononuclear complex $[Cr(\eta^6\text{-}C_7H_8)(CO)_3]$ did afford $[Cr(\eta^4\text{-}C_7H_8)(CO)_4]$ and $[Cr(CO)_6]$ in agreement with a previous study on its molybdenum analogue.[33]

Overall it appears that the dinuclear species studied follow similar photochemical pathways in gas matrices as their mononuclear analogues with the exceptions, in some cases, of reactions in CO matrices. In the configurations trapped in the gas matrices the metal centres show no significant interaction. The lengthening of the linkage between the rings, as in (**2**) compared to (**1**), the loss of delocalisation between the rings, as in (**4**) compared to (**3**), and the change in metal centres and ring sizes seem to have no significant effect on the observed matrix photochemistry of each of the dinuclear species studied.

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