J. Am. Chem. Soc. **1981**, *103*, 7515–7520

Synthesis and Characterization of the Pentacarbonylmanganese(0) Radical, Mn(CO)$_5$, in Low-Temperature Matrices

Stephen P. Church, Martyn Poliakoff,* John A. Timney, and James J. Turner*

Contribution from the Department of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD, England. *Received April 17, 1981. Revised Manuscript Received June 11, 1981*

Abstract: Mn(CO)$_5$ has been synthesized by UV photolysis of HMn(CO)$_5$ in solid CO matrices at 10–20 K. The HCO radical is also produced. A combination of ^{13}CO enrichment and IR spectroscopy shows that Mn(CO)$_5$ has a square-pyramidal, C_{4v}, structure with an axial–equatorial bond angle of 96 ± 3°. Mn(CO)$_5$ has a weak visible absorption (λ_{max} = 798 nm), close to the absorption reported for Mn(CO)$_5$ generated in ethanol solution by pulse radiolysis. Photolysis with plane-polarized UV light has been used to unravel some of the complexities in the IR spectrum and to show that the UV absorption of Mn(CO)$_5$ in the region 300–340 nm has a transition moment of e symmetry.

There has long been interest in the radical species Mn(CO)$_5$, partly because of its importance as an intermediate in photochemical reactions[1] and partly because of its structural significance.[2]

Mn(CO)$_5$ is expected[2] to have a C_{4v} structure with a low-spin d^7 electronic distribution, giving an ESR signal near the free-spin value. There has been a considerable effort to obtain such ESR data: Fischer and co-workers[3] claimed that sublimation of Mn$_2$(CO)$_{10}$ onto a cold finger gave signals due to Mn(CO)$_5$ but Symons[4] et al. showed that these signals were actually due to O$_2$Mn(CO)$_5$. UV photolysis of Mn$_2$(CO)$_{10}$ in solution might seem the obvious way[1] to generate Mn(CO)$_5$. Unfortunately early claims to have observed Mn(CO)$_5$ by this route, using ESR detection,[5] were later shown to be misinterpreted because of the formation of Mn(II) species.[6] γ-irradiation of solid Mn$_2$(CO)$_{10}$ and Mn(CO)$_5$Br at 77 K gives rise to ESR signals assigned to uptake of an electron *without* bond fission,[7] i.e., formation of [Mn$_2$(CO)$_{10}$]$^-$ and [Mn(CO)$_5$Br]$^-$. At the moment there is no convincing ESR data for Mn(CO)$_5$ although CIDNP experiments[8] suggest the presence of a radical with $g \approx 2$ (Mn(CO)$_5$?) on hydrogenation of α-methylstyrene by HMn(CO)$_5$. Hence there is no structural information via this route.

Flash photolysis of Mn$_2$(CO)$_{10}$ in cyclohexane and THF solutions shows the instantaneous disappearance of Mn$_2$(CO)$_{10}$ and the reformation of this compound by a fast second-order process,[9] believed to involve 2Mn(CO)$_5$ → Mn$_2$(CO)$_{10}$. However, no UV/visible bands[38] could be assigned to Mn(CO)$_5$. More recently, in elegant pulse radiolysis studies of Mn$_2$(CO)$_{10}$ and Mn(CO)$_5$Br, Wojcicki, Dorfman, and colleagues[10] have generated a transient speceis with an absorption maximum at 830 nm. The reaction kinetics of this species are consistent with it being Mn(CO)$_5$, and, when we allow for solvent differences, the rates agree with the flash photolysis data. Unfortunately, the whole near-UV region of the spectrum ($\lambda < 440$ nm), was masked by absorption bands of Mn$_2$(CO)$_{10}$ and the α-ethanol radical. This meant that Wojcicki was unable to discover whether the transient species also had absorptions in this region. Although the evidence is strong that Wojcicki et al. did detect Mn(CO)$_5$, there is only sparse spectroscopic information and no structural data.

There is clearly scope for a conclusive structural and spectroscopic characterization of Mn(CO)$_5$. Matrix isolation is particularly well suited to the study of transition-metal carbonyls.[11] There is indeed some published work which claims to identify Mn(CO)$_5$ by IR spectroscopy following cocondensation of Mn atoms and CO/Ar mixtures.[12] However, it has been suggested that this work is incorrect[13,14] (although similar studies[15] with Re/Co mixtures certainly produce Re(CO)$_5$), and moreover this work[12] gave no UV/visible data for Mn(CO)$_5$.

This paper presents what we believe to be a definitive spectroscopic study of Mn(CO)$_5$. The radical is generated by UV photolysis of HMn(CO)$_5$ in solid CO; it is characterized by IR spectroscopy by using ^{13}CO isotope enrichment and is shown to have a C_{4v} structure; there is a visible band at 798 nm and a UV absorption, assigned to a transition of e symmetry by photolysis and spectroscopy by using plane-polarized light.

Experimental Section

The low-temperature apparatus, Air Products CS-202 Displex, has been previously described[16] but has since been permanently transported to the University of Nottingham. IR spectra were recorded on a modified Grubb-Parsons spectrometer[17] or a Perkin-Elmer Model 580 spectrometer fitted with a wire grid polarizer and interfaced to a Digico Micro 16-V computer for multiple scanning.[18] High-resolution IR spectra were obtained by using the Nicolet 7199A Fourier Transform interferometer in the laboratory of Professor I. M. Mills at Reading University and our own portable matrix isolation apparatus, essentially similar to our fixed

---

(1) Wrighton, M. *Chem. Rev.* **1974**, *74*, 401–430.

(2) Burdett, J. K. "Molecular Shapes"; Wiley-Interscience: New York; 1980.

(3) Fischer, E. O.; Offhaus, O.; Müller, J.; Nothe, D. *Chem. Ber.* **1972**, *105*, 3027–3035.

(4) Fieldhouse, S. A.; Fulham, B. W.; Neilson, G. W.; Symons, M. C. R. *J. Chem. Soc., Dalton Trans.* **1974**, 567–569.

(5) Hallock, S. A.; Wojcicki, A. *J. Organomet. Chem.* **1973**, *54*, C27–C29.

(6) Hudson, A.; Lappert, M. F.; Nicholson, B. K. *J. Organomet. Chem.* **1975**, *92*, C11–C14.

(7) Anderson, O. P.; Symons, M. C. R. *J. Chem. Soc., Chem. Commun.* **1972**, 1020–21 Anderson, O. P.; Fieldhouse, S. A.; Forbes, C. E.; Symons, M. C. R. *J. Chem. Soc., Dalton Trans.* **1976**, 1329–1336.

(8) Sweany, R. L.; Halpern, J. *J. Am. Chem. Soc.* **1977**, *99*, 8335–8337.

(9) Hughey, I. V. J. L.; Anderson, C. P.; Meyer, T. J. *J. Organomet. Chem.* **1977**, *125*, C49–C52.

(10) Waltz, W. L.; Hackelberg, O.; Dorfman, L. M.; Wojcicki, A. *J. Am. Chem. Soc.* **1978**, *100*, 7259–7264.

(11) Burdett, J. K.; Turner, J. J. "Cryochemistry"; Moskovits, M., Ozin, G. A., Eds.; Wiley: Toronto, 1976; Chapter 11, pp 493–523. Burdett, J. K. *Coord. Chem. Rev.* **1978**, *27*, 1–58.

(12) Hüber, H.; Kundig, E. P.; Ozin, G. A.; Poe, A. J. *J. Am. Chem. Soc.* **1975**, *97*, 308–314.

(13) Timney, J. A. *Inorg. Chem.* **1979**, *18*, 2502–2506; Ph.D. Thesis, University of Newcastle Upon Tyne, 1979.

(14) The frequencies of the ν_{C-O} vibrations of a series of transition-metal carbonyls usually decrease smoothly as the number of d electrons decreases. Thus, for the equivalent vibrations of M(CO)$_4$ species the ν_{C-O} frequencies are in the order Ni > Co > Fe > Cr. For M(CO)$_5$, however, the ν_{C-O} bands of "Mn(CO)$_5$"[12] are substantially lower in frequency than those of Cr(CO)$_5$. Similarly the ν_{C-O} frequencies of Cr(CO)$_5$ and W(CO)$_5$ are separated by only 9 cm^{-1}[30] while those of "Mn(CO)$_5$" and Re(CO)$_5$ are nearly 60 cm^{-1} apart—see Table I.

(15) Hüber, H.; Kundig, E. P.; Ozin, G. A. *J. Am. Chem. Soc.* **1974**, *96*, 5585–5586.

(16) See, for example: Perutz, R. N. Ph.D. Thesis, Cambridge University, 1974.

(17) Poliakoff, M.; Turner, J. J. *J. Chem. Soc., Dalton Trans.* **1974**, 2276–2285.

(18) Smith, K. P. Ph.D. Thesis, University of Newcastle upon Tyne, 1981.

Table I. Wavenumbers (cm^{-1}) of IR Bands of $Re(CO)_5$ and $Mn(CO)_5$

photolysis of $HRe(CO)_5$[a]	Re atoms + CO[15]
$Re(CO)_5$ Ar Matrix 10% CO	
2099	
1995.5	1995
1977.0	1977
$Mn(CO)_5$ CO Matrix	
photolysis of $HMn(CO)_5$[a]	Mn atoms + CO[12,d]
	2060
1992.7[b]	1938
1987.6[b]	
1978.4	1911
1956[c]	

[a] This work. [b] Matrix splitting–see text. [c] ^{13}C satellite, very weak. [d] This species was claimed to be $Mn(CO)_5$, but, in view of ref 14 and the experiments in this paper, the bands must be due to some other $Mn(CO)_x$ fragment.

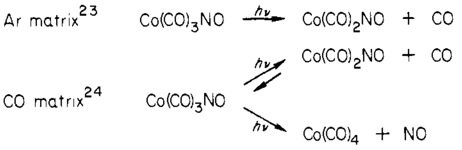
equipment. UV/visible spectra were recorded on a Perkin-Elmer 356 double wavelength spectrometer with the use of a Polacoat 105 UV WMR polarizer on a quartz substrate in polarization experiments.[19]

The photolysis source was a 125-W medium-pressure Hg arc, either focussed with *f*/4 quartz optics on the entrance slit of an Applied Photophysics M300 high-radiance monochromator or unfocussed and filtered with a 4-cm quartz water cell, when high-intensity illumination was required. Polarized irradiations were carried out with monochromated light passed through a Polacoat 105 UV WMR polarizer.

$HMn(CO)_5$ was prepared by a standard route,[20] and and CO (BOC Grade X) and ^{13}CO (Prochem 90%) were used without further purification.

Results

Metal carbonyls readily lose CO on photolysis, although other ligands may also be photoejected.[1] It is to be expected that $HMn(CO)_5$ will have a high quantum yield for CO ejection and a much lower one for H ejection. This is confirmed by photolysis of $HMn(CO)_5$ in an Ar matrix,[21] which yielded $HMn(CO)_4$, as the only product detected by IR spectroscopy. However, unpublished ESR experiments[22] suggest that $Mn(CO)_5$ may be formed as a minor product. Nevertheless, in a solid CO matrix the CO ejection will be readily reversed and hence the ejection of H might perhaps be promoted. We have previously used a variation of this technique to generate $Co(CO)_4$.



Synthesis of $Mn(CO)_5$. Because of the disagreement[14] about the IR spectrum of $Mn(CO)_5$, we first photolyzed *$HRe(CO)_5$* in solid CO since there is no argument about the expected product $Re(CO)_5$. Indeed the IR spectrum of the photolysis products of $HRe(CO)_5/CO$ agrees very closely with that obtained by cocondensation of Re atoms and CO (Table I). Thus

$$HRe(CO)_5 \xrightarrow[\text{CO matrix}]{h\nu} Re(CO)_5$$

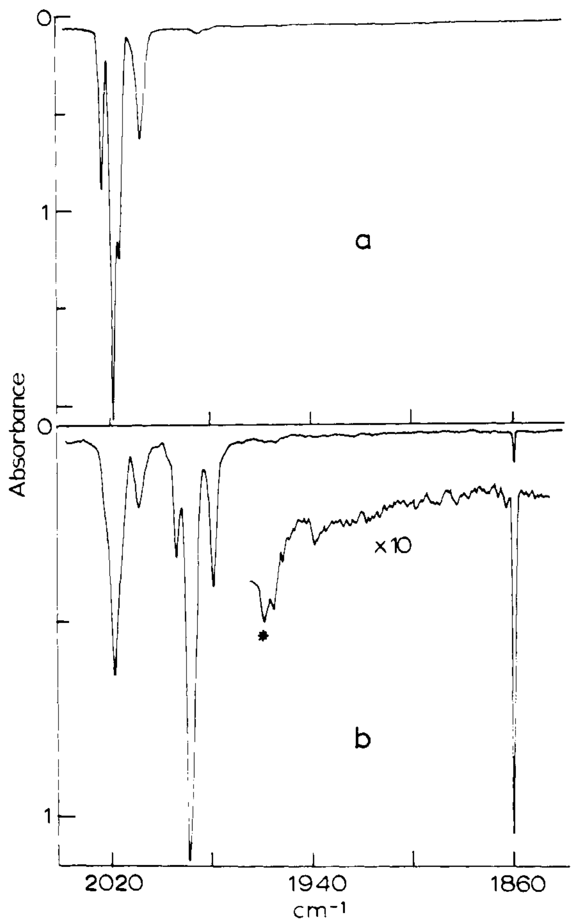


Figure 1. IR absorption spectra in the C–O stretching region of a CO matrix containing $HMn(CO)_5$ ($CO/HMn(CO)_5$, 3000:1) at 20 K: (a) after deposition; (b) after 80-min UV photolysis, showing the formation of a new $Mn(CO)_x$ species and the HCO radical at 1860 cm^{-1}. Note that spectrum b is drawn with a X2 ordinate expansion relative to spectrum a, and the inset spectrum is expanded a further 10 times. The weak band marked with an asterisk is a ^{13}CO satellite of the $Mn(CO)_x$ species. Spectra were recorded on the Nicolet 7199A interferometer at 0.5-cm^{-1} resolution; no further detail was revealed at 0.06-cm^{-1} resolution.

UV photolysis of $HMn(CO)_5$ in solid CO generates a carbonyl species X *and* the radical HCO (ν_{C-O} = 1860 cm^{-1})[25,26] (Figure 1).

$$HMn(CO)_5 \xrightarrow[+CO]{h\nu} X + HCO$$

The product X has an IR spectrum (Figure 1b), which is strikingly similar to that of $HMn(CO)_5$ but shifted to somewhat lower frequencies. By analogy with the photolysis of $HRe(CO)_5$, one would expect X to be $Mn(CO)_5$. Furthermore X cannot contain hydrogen as it can also be generated by UV photolysis of $Mn(CO)_4NO$ in a CO matrix.[24,27]

$$Mn(CO)_4NO \xrightarrow[\text{CO matrix}]{\text{UV}} X + NO$$

The detailed interpretation of the IR spectra of matrix-isolated metal carbonyls is often made more difficult by so-called "matrix splittings" which give rise to extra IR bands.[28] Thus $HMn(CO)_5$, with C_{4v} symmetry, would be expected to have three IR-active

---

[19] Baird, M. S.; Dunkin, I. R.; Hacker, N.; Poliakoff, M.; Turner, J. J. *J. Am. Chem. Soc.* **1981**, *103*, 5190–5195.

[20] Eisch, J. J.; King, R. B. "Organometallic Syntheses"; Academic Press: New York, 1965; Vol. 1, pp 158–160.

[21] Rest, A. J.; Turner, J. J. *J. Chem. Soc., Chem. Commun.* **1969**, 375–377.

[22] Sweany, R. L., private communication, 1979. This result is in sharp contrast to the photolysis of $HCo(CO)_4$, which in an Ar matrix yields $Co(CO)_4$ as the major product. Sweany, R. L. *Inorg. Chem.* **1980**, *19*, 3512–3516.

[23] Crichton, O. Ph.D. Thesis, Cambridge University, 1974.

[24] Crichton, O.; Poliakoff, M.; Rest, A. J.; Turner, J. J. *J. Chem. Soc., Dalton Trans.* **1973**, 1321–1324.

[25] Milligan, D. E.; Jacox, M. E. *J. Chem. Phys.* **1964**, *41*, 3032–3036; **1969**, *51*, 277–288.

[26] Sweany[22]) has independently observed the ESR spectrum of HCO on UV photolysis of $HMn(CO)_5$ in a CO matrix and a second ESR signal which may be due to $Mn(CO)_5$.

[27] The IR spectra in the case of $Mn(CO)_4NO$ are not so easy to interpret as with $HMn(CO)_5$ since the 1978-cm^{-1} band of X overlaps an absorption of $Mn(CO)_4NO$ itself. This meant that it was difficult to decide which $Mn(CO)_x$ species had been formed.

[28] E.g.: Poliakoff, M.; Turner, J. J. *J. Chem. Soc., Dalton Trans.* **1973**, 1351–1357.

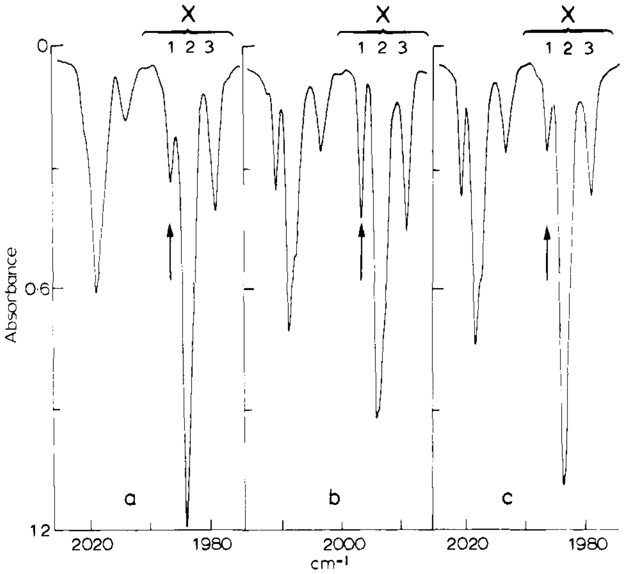
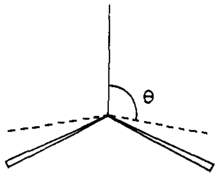


Figure 2. IR absorption spectra showing the effects of annealing and irradiation of the CO matrix. The three bands labeled X are due to the $Mn(CO)_x$ species and the unlabeled bands are those of $HMn(CO)_5$ (all spectra run at 20 K): (a) after UV photolysis—a repeat of spectrum 1b; (b) after annealing the matrix to 33 K; (c) after 20-min irradiation with light, $\lambda > 375$ nm. Note the behavior of the arrowed band, 1, of X.

C–O stretching vibrations, $2a_1 + e$. Although one of the a_1 modes, 2122 cm^{-1} in a CO matrix, lies outside the range of Figure 1a, $HMn(CO)_5$ has at least four bands in the part of the spectrum shown in the Figure. During UV photolysis the spectrum changes substantially and the two broad bands in Figure 1b are easily identifiable as the e and a_1 modes. Such photolytic changes in IR spectra are very common with other metal carbonyls, although the mechanism is not entirely clear.[16,28]

In Figure 1b, the photoproduct X has three IR bands. Before deciding whether X is indeed $Mn(CO)_5$, it is important to know which bands, if any, are spurious matrix splittings. This can be done by monitoring the behavior of the bands during annealing or irradiation of the matrix. On the basis of such experiments, Figure 2, it can be shown that band 1 (arrowed) is a matrix splitting of the strong band 2, while band 3 is due to a different fundamental mode of X. Thus band 1 grows in intensity when the matrix is annealed to 33 K (note similar changes in the bands of $HMn(CO)_5$) and decreased on irradiation with light, $\lambda > 375$ nm, corresponding to a visible absorption of X (see below). In fact, prolonged irradiation at this wavelength will almost remove band 1 completely. Throughout these changes, the combined areas of bands 1 + 2 remained constant and the ratio of the areas (1 + 2)/3 also remained constant. In a later section, we confirm our assignment by showing that both bands 1 and 2 have transition moments of the same symmetry, while band 3 has a transition moment of different symmetry. Thus X has two fundamentals in this region of the spectrum, and the similarity of the spectra of X and $HMn(CO)_5$ suggest that X is probably $Mn(CO)_5$, with a C_{4v} structure (**1**). Such a molecule should have another C–O stretching band to higher frequency, but, by analogy with $HMn(CO)_5$, this band may be very weak and perhaps hidden by the strong absorptions of the CO matrix itself.



1

Structure of $Mn(CO)_5$. The use of ^{13}CO and IR spectroscopy to determine the structure of metal carbonyls has been described at length elsewhere.[29,30] In essence, the spectrum observed for a carbonyl partially enriched with ^{13}CO is compared, both in frequency and relative absorbance, with spectra calculated for possible structures of the carbonyl by using an energy-factored force field. The calculations for $Mn(CO)_5$ are identical with those already described for $Cr(CO)_5$, (apart, of course, from the numerical values of force constants etc.). Figure 3a shows the spectrum of X, produced by UV photolysis of $HMn(CO)_5$ in a CO matrix containing 45% ^{13}CO. It can be seen that the spectrum calculated for C_{4v} $Mn(CO)_5$ (Figure 3b and Table II, is in excellent agreement with the observed spectrum. This confirms our tentative identification of X as $Mn(CO)_5$.

Table II. Observed and Calculated Wavenumbers of the IR Bands of Different $Mn(^{12}CO)_{5-x}(^{13}CO)_x$ Species in a CO Matrix

molecule[a]	symmetry	obsd[e]	calcd
$Mn(^{12}CO)_5$ C_{2v}	a_1	*b*	2105.3
	b_2	*c*	2017.6
	e	1987.6	1987.6
	a_1	1978.4	1978.1
$Mn(^{12}CO)_4(^{13}CO)$ C_s	a′	*b*	2097.6
	a′	*d*	2011.5
	a″	1987.6	1987.6
	a′	*d*	1978.7
	a′	1956	1955.7
$Mn(^{12}CO)_3(^{13}CO)_2$ C_s–eq,eq (cis)	a′	*b*	2088.6
	a″	*d*	2007.1
	a′	*d*	1979.4
	a′	1957.3	1957.6
	a″	1953.5	1953.5
$Mn(^{12}CO)_2(^{13}CO)_3$ C_s–eq,eq,eq	a′	*b*	2078.7
	a′	1992.7	1992.7
	a′	1971.0	1971.3
	a′	*d*	1955.1
	a″	1943.2	1943.2
$Mn(^{12}CO)_2(^{13}CO)_3$ C_s–ax,eq,eq (cis)	a′	*b*	2083.7
	a″	*d*	2007.1
	a′	1962.9	1962.9
	a″	1953.5	1953.5
	a′	*d*	1934.6
$Mn(^{13}CO)_5$ C_{4v}	a_1	*b*	2058.4
	b_1	*c*	1972.7
	e	1943.4	1943.3
	a_1	1934.0	1934.0

10 frequencies, root-mean-square error 0.2 cm^{-1}, maximum error 0.33 cm^{-1}

force constants (for definition, see ref 29, 30): $k_{ax} = 1604$, $k_{eq} = 1650.9$, $k_{ax,eq} = 33$, $k_{eq,eq}(cis) = 30.69$, $k_{eq,eq}(trans) = 54.94$ N m^{-1}

[a] Since the number of observed frequencies was relatively small, it was not necessary to include all of the 12 possible $Mn(^{12}CO)_{5-x}(^{13}CO)_x$ molecules in the least-squares refinement, although all the molecules were, of course, used to predict the spectrum in Figure 3. [b] Predicted to be weak. [c] IR inactive. [d] Not observed, predicted to be overlapped or obscured by bands of $HMn(^{12}CO)_{5-x}(^{13}CO)_x$ or $Mn(^{12}CO)_{5-x}(^{13}CO)_x$ species. [e] Each observed frequency was only entered once into the least-squares refinement.

The calculations predict that the "missing" a_1 band of $Mn(CO)_5$ should occur at 2105.3 cm^{-1}, which is in a region quite close to the absorptions of ^{13}CO and $C^{18}O$ in the matrix. The relative intensities of the two a_1 modes and the e mode of a C_{4v} pentacarbonyl fragment can be used to calculate the bond angle and dipole derivative ratio, μ'_{ax}/μ'_{eq}, for the equatorial and axial groups.[30] This method works successfully for $HMn(CO)_5$ (calculated 96.5°, observed 97°).[29] Since we have not observed the high frequency a_1 band of $Mn(CO)_5$, any bond angle calculation must involve approximations. If we assume that $\mu'_{ax}/\mu'_{eq} = 1$ (the ratio is 1.04 for $HMn(CO)_5$) then the bond angle is given by[29,30]

$$\sin^2\theta = 1.25R_3/(1 + R_3)$$

---

(29) Burdett, J. K.; Dubost, H.; Poliakoff, M.; Turner, J. J. "Advances in Infrared and Raman Spectroscopy"; Clark, R. J. H., Hester, R. E., Eds.; Heyden: London, 1976; Vol. 2, pp 1–52.

(30) Perutz, R. N.; Turner, J. J. *Inorg. Chem.* **1975**, *14*, 262–270.

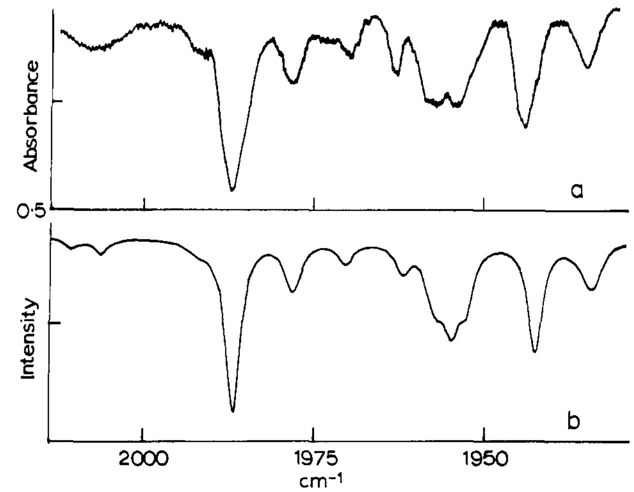


Figure 3. (a) IR absorption spectrum obtained by prolonged UV photolysis *of* $\mathrm{HMn(CO)_5}$ *in* a CO m*atrix containing* ^{12}CO *(55%) and* ^{13}CO (45%). (b) Spectrum predicted for C_{4v} $\mathrm{Mn(CO)_5}$ with an axial-equatorial bond angle of 96° and with the assumption of a uniform line width of 2.5 cm^{-1} (fwhm) by using the force constants in Table II and the method described in ref 29.

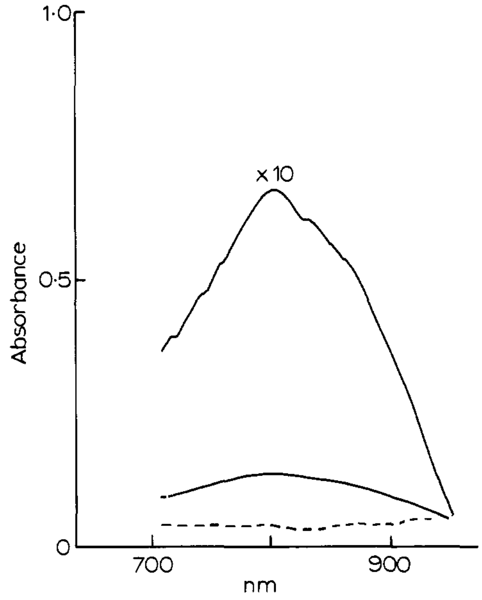


Figure 4. Visible absorption spectra of $\mathrm{Mn(CO)_5}$ in a CO matrix at 20 K: broken line (---), spectrum after deposition of a $\mathrm{HMn(CO)_5/CO}$ mixture; solid line (—), spectrum after UV photolysis.

where $R_3 = I_e/(I_{a_1\,\mathrm{high}} + I_{a_1\,\mathrm{low}})$. Since $I_{a_1\,\mathrm{high}}$ is unknown but presumably small, we must also assume that $R_3 = I_e/I_{a_1\,\mathrm{low}}$. For $\mathrm{Mn(CO)_5}$, the measured value of $I_e/I_{a_1\,\mathrm{low}}$ is 3.8 ± 0.15 which gives a value for the axial–equatorial bond angle 96 ± 3°. This approximate bond angle is consistent with the bond angles, ~98°, predicted by simple MO calculations.[31,32] More interestingly it is similar to the axial equatorial bond angle 96° of the $\mathrm{Mn(CO)_5}$ moiety[32] in $\mathrm{Mn_2(CO)_{10}}$.

Mechanism of Formation of $\mathrm{Mn(CO)_5}$. The generation of $\mathrm{Mn(CO)_5}$ in solid CO and $\mathrm{HMn(CO)_4}$ in solid argon suggests the following photochemical processes.

$$\text{major}\quad \mathrm{HMn(CO)_5} \underset{h\nu,\,\Delta}{\overset{h\nu}{\rightleftarrows}} \mathrm{HMn(CO)_4} + \mathrm{CO}$$

$$\text{minor}\quad \mathrm{HMn(CO)_5} \xrightarrow{h\nu} \underset{\mathrm{HCO}}{\underset{\downarrow\,\mathrm{CO}}{\mathrm{H}}} + \mathrm{Mn(CO)_5}$$

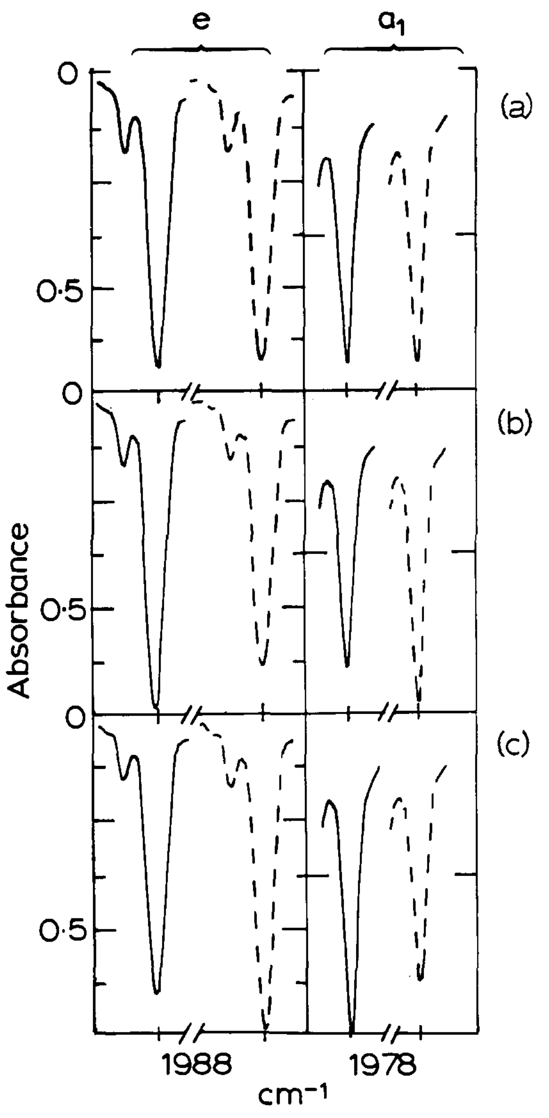


Figure 5. Photochemistry and spectroscopy with plane-polarized light. The solid and broken lines represent IR spectra of the same matrix, recorded under the same conditions with light polarized vertically (—) and horizontally (---). The two columns of the diagram show the following absorptions of $\mathrm{Mn(CO)_5}$ in a CO matrix: e mode (1987.6 cm^{-1}), the a_1 mode (1978.4 cm^{-1}). (a) Spectrum of $\mathrm{Mn(CO)_5}$, after generation from $\mathrm{HMn(CO)_5}$ with *unpolarized* UV light. Note that, for each mode, the bands recorded for the two positions of the polarizer (broken and solid lines) have the same intensities. (b) Spectra after prolonged irradiation with light (330 ± 10 nm) polarized horizontally (corresponding to spectra drawn in broken lines). Note that there is now a difference in intensity between spectra recorded with the two positions of the polarizer. (c) Spectra after further irradiation with light (330 nm) polarized vertically. Note that the intensity difference has been reversed. The IR spectra were recorded on the Perkin-Elmer 580 spectrometer with a computer average over five scans. The a_1 mode is plotted with X3 ordinate expansion relative to the e mode.

This scheme is supported by our experiment with $\mathrm{HMn(CO)_5}$ in a mixed $^{12}\mathrm{CO}/^{13}\mathrm{CO}$ matrix, (see preceding section), which clearly showed that formation of $\mathrm{HMn(^{12}CO)_{5-x}(^{13}CO)_x}$ species was much faster than formation of the corresponding $\mathrm{Mn(CO)_5}$ species. Thus it would seem that the CO matrix is increasing the rate at which $\mathrm{HMn(CO)_4}$ recombines with CO rather than the rate at which $\mathrm{HMn(CO)_5}$ loses H. This is consistent with our earlier quantum yield measurements[33] with $\mathrm{Mo(CO)_6}$.

UV/Visible Spectra of $\mathrm{Mn(CO)_5}$. UV photolysis of $\mathrm{HMn(CO)_5}$ in CO matrices also produced changes in the UV/visible spectrum (Figure 4). In a CO matrix, $\mathrm{Mn(CO)_5}$ has an absorption $(\lambda_{\max}$

---

(31) Burdett, J. K. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 1599–1613.
(32) Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058–1076.
(33) Poliakoff, M. *J. Chem. Soc., Faraday Trans. 2* **1977**, *73*, 569–573.

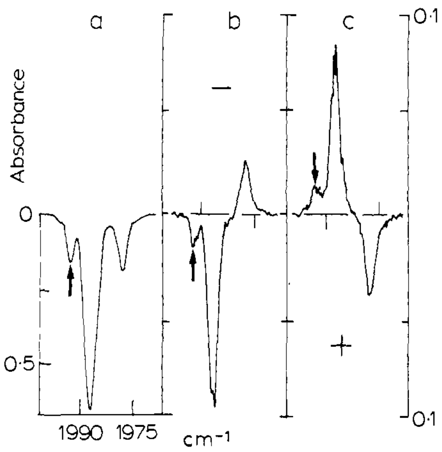
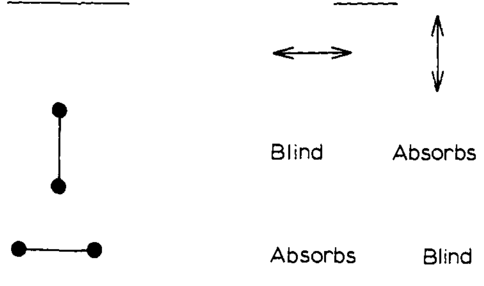


Figure 6. (a) Normal absorbance spectrum of $Mn(CO)_5$ in a CO matrix at 20 K. (b and c) Linear dichroism spectra, each generated by computer subtraction of the two polarized IR spectra illustrated in parts b and c, respectively, of Figure 5 (vertical polarization minus horizontal polarization). Note that the a_1 mode (1978 cm^{-1}) has the opposite dichroism from the other two bands.

= 798 nm) and a continuous UV absorption at $\lambda < 340$ nm, which increases in intensity toward shorter wavelengths but reaches no maximum $\lambda > 240$ nm. Wojcicki and Dorfman reported only one absorption (λ_{max} = 830 nm (ϵ_{max} = 800 ± 80 M^{-1} cm^{-1})) for $Mn(CO)_5$ in ethanol solution, but the UV region was obscured by the absorptions of other species.[10] Extinction coefficients of matrix isolated molecules are notoriously difficult to measure, because of uncertainties in the exact amount of material frozen on to the cold window of the apparatus. However, it is probable that the extinction coefficient of the 798-nm band is in the range 400–1000 M^{-1} cm^{-1}. Since the absorption bands, both in solution and matrix, are relatively broad, the shift from 830 to 798 nm may not be significant and it is probable that the species observed in solution and the matrix are the same.

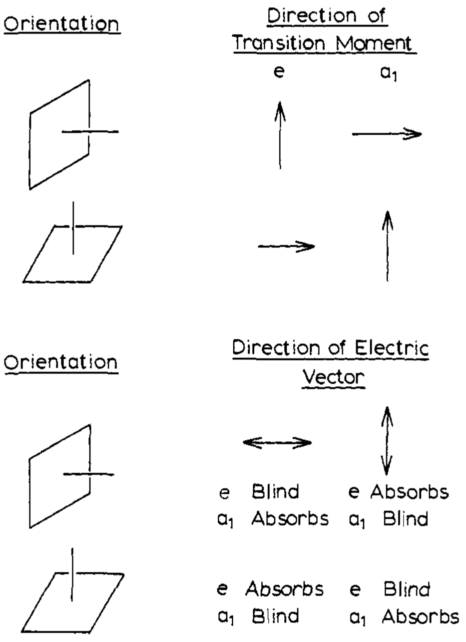
Photolysis with Plane-Polarized Light. We have previously shown that photolysis and spectroscopy with plane-polarized light provided valuable information[34] about the photochemistry of $Cr(CO)_5$. Here we show that similar techniques can be used with $Mn(CO)_5$. Although the quantitative interpretation of polarized photochemistry is complicated, the basic principles are relatively straightforward.

In any molecule with noncubic symmetry, the transition moment associated with a particular absorption band will have a definite direction with respect to the geometry of the molecule and the way in which this transition moment interacts with plane-polarized light depends on the orientation of the molecule. Imagine a diatomic molecule with a transition moment along the internuclear axis. This molecule can absorb light polarized in a plane, parallel to this axis but *cannot* absorb light polarized perpendicular to it (see **2**). Thus, in a matrix irradiated by plane polarized light, there will be two extreme orientations for the rigidly trapped molecule, "maximum absorption" and "blind", depending on the orientation of the internuclear axis relative to the plane of polarization. Normally, matrix-isolated molecules do not have sufficient thermal energy to rotate in the matrix, but suppose now that each time a molecule absorbs a photon of light, it undergoes a rotation. In our experience, such rotation never occurs by an ordinary thermal process but only when a specific photochemical pathway is opened. If, following the "rotation", the molecule is held rigidly once more by the matrix, then prolonged irradiation with polarized light will eventually lead to an accumulation of molecules in the "blind" orientation. This preferential orientation can be detected as a difference in absorbance between two spectra recorded with light polarized (i) in a plane parallel and (ii) in a plane perpendicular to the irradiating beam, so-called *linear dichroism.*



2

The case of a C_{4v} molecule such as $Mn(CO)_5$ is more complicated as the direction of the a_1 transition moment is perpendicular to that of the e transition moment (see **3**). This means that in a sample with preferentially oriented molecules, the a_1 and *e* transitions will show dichroism of opposite signs (i.e., with one polarization, the spectrum will have a_1 transitions stronger and *e* transitions weaker than in a spectrum taken with unpolarized light, while with the perpendicular polarization the a_1 transition will be weaker and the e transition stronger). Thus, given the symmetry of the transition associated with only *one* UV or IR absorption band of the molecule, the symmetries of all of the other transitions, UV and IR, can be assigned from the sign of the dichroism of the corresponding bands.



3

The results of photolysis of $Mn(CO)_5$ with plane-polarized UV light are shown in Figure 5. The following points are clear from the figure. (1) Before irradiation with polarized light, none of the bands display any dichroism. That is the bands have the same intensity for both polarizations of the spectrometer beam (Figure 5a). (2) After irradiation, definite dichroism develops in the IR bands. As expected, the IR bands display dichroism of opposite signs, confirming their assignment to a_1 and e modes (Figure 5b,c). Unfortunately, the visible band at 798 nm was too weak for us to obtain convincing polarization data, and the symmetry remains unassigned. On the other hand, we can deduce that the transition moment of the photoactive UV absorption has e symmetry. After UV irradiation (either at 330 or 313 nm), the e IR absorption was less intense in the plane *parallel* to the plane of polarization of the UV light. It is not clear whether this UV absorption is due to a charge transfer or ligand field transition (see, e.g., ref 35 and

---

[34] Burdett, J. K.; Gryzbowski, J. M.; Perutz, R. N.; Poliakoff, M.; Turner, J. J.; Turner, R. F. *Inorg. Chem.* **1978**, *17*, 147-154.

36 for spectra of isoelectronic d^7 Co^{II} species).

It is less clear from the spectra in Figure 5 how the weak IR band on the side of the e mode is polarized. This uncertainty is completely removed by the difference spectra illustrated in Figure 6. These spectra, obtained by computer subtraction, show that this weak band, arrowed, is polarized in the same direction as the e mode and opposite to the a$_1$ mode. This supports our original assignment of this band to a matrix splitting of the e mode (qv).

Conclusions

These experiments have finally ended the search for the elusive Mn(CO)$_5$ radical and it is clear that earlier attempts[12] to synthesize Mn(CO)$_5$ in matrices were unsuccessful.[37] Mn(CO)$_5$ has a C_{4v} structure with a probable bond angle of 96 ± 3°. This structure is not wholly unexpected as a d^7 D_{3h} M(CO)$_5$ species would be Jahn–Teller unstable. The IR spectrum of Mn(CO)$_5$ is similar to that of Re(CO)$_5$ and, as expected, the ν_{C-O} bands lie at frequencies between those of the d^6 and d^8 M(CO)$_5$ molecules, Cr(CO)$_5$ and Fe(CO)$_5$, in the matrix.

Acknowledgment. We thank the Science Research Council and Perkin-Elmer Ltd for supporting this research. Some of the experiments were carried out in the Department of Inorganic Chemistry of the University of Newcastle upon Tyne. We are indebted to Professor I. M. Mills, Dr. P. H. Turner, and Miss C. M. Deeley for their help and for allowing us to work in their laboratory. We thank Professor M. C. R. Symons, Mr. C. S. Maclean, and Mr. N. Woodhead for their advice and Professor R. L. Sweany for sending us his unpublished results.

---

(35) Alexander, J. J.; Gray, H. B. *J. Am. Chem. Soc.* **1967**, *89*, 3356–3357.

(36) Endicott, J. F.; Lilie, J.; Kuszaj, J. M.; Ramaswamy, B. S.; Schomnsees, W. G.; Simic, M. G.; Glick, M. D.; Rillema, P. D. *J. Am. Chem. Soc.* **1977**, *99*, 429–439.

(37) G. A. Ozin (private communication, 1981) has pointed out that Mn atoms dimerize very easily, even in highly dilute matrices, and that the species thought to be Mn(CO)$_5$ in ref 12 may well have been an Mn$_2$(CO)$_x$ fragment.

(38) **Note Added in Proof**: An absorption, 600–900 nm, assigned to Mn(CO)$_5$ has now been observed during the flash photolysis of Mn$_2$(CO)$_{10}$. Yasufuku, K.; Yesaka, H.; Kobayashi, T.; Yamazaki, H.; Nagakura, S., Proceedings of the 10th International Conference on Organometallic Chemistry, Toronto, 1981.

Palladium-Catalyzed Cyclocarbonylation of Acetylenic Alcohols to Methylene Lactones. Scope and Synthesis of Appropriate Substrates

Timothy F. Murray,[1a] Edward G. Samsel,[1a,b] Vijaya Varma,[1a] and Jack R. Norton*[1a-c]

Contribution from the Departments of Chemistry, Princeton University, Princeton, New Jersey 08540, and Colorado State University, Fort Collins, Colorado 80523.

Received April 27, 1981

Abstract: Methylene lactones are available by catalytic cyclocarbonylation of the ethynyl alcohols resulting from epoxidation and ethynylation of olefins. Dimethylethynylaluminum etherate in toluene is useful for the ethynylation of base-sensitive epoxides. Trans cycloalkanols can be converted to their cis isomers either by oxidation and stereoselective reduction or by epimerization of the corresponding tosylate. The best cyclocarbonylation catalyst system has proved to be PdCl$_2$, anhydrous SnCl$_2$, and 2 equiv of a tertiary phosphine in CH$_3$CN. A wide variety of methylene lactones, including both cis and trans fused-ring systems, can be made from the appropriate ethynyl alcohol precursors if the substrate concentration is kept sufficiently low to favor cyclization over intermolecular reaction. Incipient ring strain, although it lowers the yield of methylene lactone, does not affect the rate of consumption of starting material, as demonstrated by the competitive cyclocarbonylation of **3c** and **5c**. This observation suggests that the formation of a carboalkoxy intermediate from the catalyst and the substrate alcohol is irreversible.

Interest in synthetic methods for the α-methylene lactone unit has arisen because of the wide spectrum of physiological activity shown by natural products containing it.[2] The unit generally occurs as an α-methylene γ-lactone, most commonly fused to six-, seven-, or ten-membered rings, with both cis and trans stereochemistry observed at the ring junction. A few α-methylene δ-lactones are also found in natural products, fused cis to six-membered rings. A wide variety of other functional groups occur along with the methylene lactone moiety.[2]

Many methods have been developed for the synthesis of the α-methylene lactone unit.[3] Methods involving the introduction of α-methylene group onto a preformed lactone ring[4] have been most widely employed, e.g., in the recent total syntheses of vernolepin,[5a-d] frullanolide,[5e] and eriolanin.[5f,g] These methods necessarily use strongly basic conditions to attack the α position of the lactone—conditions not easily reconciled with the highly functionalized nature of many of the natural-product target molecules. The other approaches which have been suggested[6,7]

---

(1) (a) Princeton University. (b) Colorado State University. (c) Alfred P. Sloan Fellow, 1977-1981.

(2) Geissman, T. A.; Irwin, M. A. *Pure Appl. Chem.* **1970**, *21*, 167. Kupchan, S. M.; *Ibid.* **1970**, *21*, 227. Lee, K.-H.; Piantadosi, C.; Huang, E.-S.; Panago, J. S.; Geissman, T. A. *Cancer Res.* **1971**, *31*, 1649.

(3) (a) Grieco, P. . *Synthesis* **1975**, 67. (b) Gammill, R. B.; Wilson, C. A.; Bryson, T. *Synth. Commun.* **1975**, *5*, 245. (c) Newaz, S. S. *Aldrichimica Acta* **1977**, *10*, 64.

(4) (a) Martin, J.; Watts, P. C.; Johnson, F. *J. Chem. Soc. D.* **1970**, 27. (b) Grieco, P. A.; Hiroi, K. *J. Chem. Soc., Chem. Commun.* **1972**, 1317. (c) Grieco, P. A.; Hiroi, *Ibid.* **1973**, 500. (d) Parker, W. L.; Johnson, F. *J. Org. Chem.* **1973**, *38*, 2489. (e) Grieco, P. A.; Miyashita, M. *Ibid.* **1974**, *39*, 120. (f) Danishefsky, S.; Kitahara, T.; McKee, R.; Schuda, P. F. *J. Am. Chem. Soc.* **1976**, *98*, 6715. (g) Minato, H.; Horibe, I. *J. Chem. Soc. C.* **1967**, 1575. (h) Harmon, A. D.; Hutchinson, C. R. *Tetrahedron Lett.* **1973**, 1293; *J. Org. Chem.* **1975**, *40*, 3474. (i) Ronald, R. C. *Tetrahedron Lett.* **1973**, 3831.

(5) (a) Grieco, P. A.; Nishizawa, M.; Oguri, T.; Burke, S. D.; Marinovic, N. *J. Am. Chem. Soc.* **1977**, *99*, 5773. (b) Danishefsky, S.; Schuda, P. F.; Kitahara, T.; Etheredge, S. J. *Ibid.* **1977**, *99*, 6066. (c) Kieczykowski, G. R.; Quesada, M. L.; Schlessinger, R. H. *Ibid.* **1980**, *102*, 782. (d) Iio, H.; Isobe, M.; Kawai, T.; Goto, T. *Ibid.* **1979**, *101*, 6076. (e) Kido, F.; Tsutsumi, K.; Maruta, R.; Yoshikoshi, A. *Ibid.* **1979**, *101*, 6420. (f) Grieco, P. A.; Oguri, T.; Gilman, S. J. *Ibid* **1980**, *102*, 5886. (g) Roberts, M. R.; Schlessinger, R. H. *Ibid.* **1981**, *103*, 724.