Photochemistry of Carbonyltrinitrosylmanganese in Frozen Gas Matrices at 20 K. Infrared Spectroscopic Evidence for Trinitrosylmanganese, (Dinitrogen)trinitrosylmanganese, and a Species formed by Metal-to-Nitrosyl Photoelectron Transfer

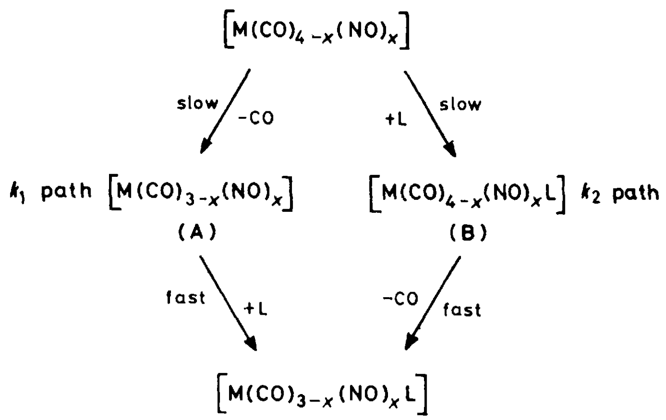
By **Oliver Crichton** and **Antony J. Rest**,*† University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EP

Infrared evidence is presented for the formation of a three-co-ordinate species, [Mn$(NO)_3$], on u.v. photolysis of [Mn(CO)$(NO)_3$] in argon matrices, and for the formation of a four-co-ordinate species, [Mn$(N_2)(NO)_3$], in nitrogen matrices at 20 K. Infrared evidence, including ^{15}NO data, is also presented for the formation of [Mn(CO)$(NO)_2$(NO*)], where the asterisk denotes a nitrosyl group having an unusually low value of ν(NO), on photolysis of [Mn(CO)$(NO)_3$] with visible radiation in both argon and nitrogen matrices. It is concluded that [Mn(CO)$(NO)_2$(NO*)] belongs to a class of complexes in which photoelectron transfer has occurred, with the nitrosyl ligand (NO*) accepting additional electron density to leave an electron-deficient metal centre. The results are related to the postulate of co-ordinatively unsaturated and expanded co-ordination-shell species as intermediates in the thermal substitution reactions of [Mn(CO)$(NO)_3$].

THERMAL substitution reactions of the pseudo-Ni$(CO)_4$ series of complexes [M$(CO)_{4-x}(NO)_x$] in solution can be represented mechanistically by a scheme (Scheme 1) involving two paths, k_1 and k_2, corresponding to either a dissociative or an associative rate-determining process respectively. In contrast to the simple behaviour of [Ni$(CO)_4$], which undergoes substitution and exchange of CO by a dissociative mechanism (k_1 path),[1] the substitution reactions of [Co$(CO)_3$(NO)] [2,3] and [Fe$(CO)_2(NO)_2$] [4] follow a two-term rate law (1). For 'good'

$$\text{Rate} = (k_1 + k_2[\text{L}])[\text{nitrosyl complex}] \qquad (1)$$

ligands, *e.g.* PPh_3, the contribution from the ligand-independent path (k_1) is negligible, *i.e.* the k_2 path predominates, while 'poor' ligands, *e.g.* $AsPh_3$, react slowly with [Co$(CO)_3$(NO)] and [Fe$(CO)_2(NO)_2$] at a rate dependent only on the concentration of the nitrosyl complex, *i.e.* the k_1 path. The complex [Mn(CO)$(NO)_3$] is considerably less stable thermally [5] than its cobalt and iron analogues, and its lability has prevented a detailed study of its substitution reactions. However, both first- and second-order processes have been reported to occur rapidly.[6] The first-order rate constants (k_1) follow the order Ni > Co ≃ Fe < Mn, which has been correlated with the variation in M–C bond order as deduced from the variation in the C–O stretching force constants.[6] The availability of the second-order associative mechanism is generally ascribed [7] to the ability of the co-ordinated NO molecule to accept electron density from the metal atom, which can then in turn accept electron density from the extra ligand L to form an intermediate of type (B) (Scheme 1).



SCHEME 1

Recently we described i.r. evidence for the formation of [Co$(CO)_2$(NO)] [8] and [Fe(CO)$(NO)_2$],[9] *i.e.* type (A) species (Scheme 1), on u.v. photolysis of [Co$(CO)_3$(NO)] and [Fe$(CO)_2(NO)_2$] in inert matrices at 20 K. In this paper we describe the production of a variety of species formed from [Mn(CO)$(NO)_3$] in inert (argon) and reactive (nitrogen) matrices and we relate the findings to the substitution-reaction studies.[2-4,6] Preliminary results have been described elsewhere.[10]

EXPERIMENTAL

Details of the cryostat, the i.r. spectrometer, the photolysis lamp, matrix gases, and the preparation of gas mixtures with substrate : matrix gas ratios of between 1 : 5 000 and 1 : 20 000 have been given previously.[8] Infrared band positions are accurate to better than ±0.5 cm^{-1} but have been rounded to the nearest unit. Electronic spectra (u.v.–visible) were obtained with a modified Pye Unicam SP 1800B spectrometer.[11] Wavelength selection for photolysis was achieved by a combination of absorbing materials: filter A, $550 < \lambda < 640$ nm {solution cell (pathlength, 10 mm) containing AnalaR $K_2[Cr_2O_7]$ in water + solution cell (pathlength, 10 mm) containing AnalaR Ni[SO_4] in water with dilution-adjusted cut-on and cut-off points};

---

† *Present address:* Department of Chemistry, The University, Southampton SO9 5NH.

[1] J. P. Day, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, 1968, **90**, 6927.

[2] E. M. Thorsteinson and F. Basolo, *J. Amer. Chem. Soc.*, 1966, **88**, 3929.

[3] G. Cardaci, A. Foffani, G. Distefano, and G. Innorta, *Inorg. Chim. Acta*, 1967, **1**, 340.

[4] D. E. Morris and F. Basolo, *J. Amer. Chem. Soc.*, 1968, **90**, 2531, 2536.

[5] C. G. Barraclough and J. Lewis, *J. Chem. Soc.*, 1960, 4842.

[6] H. Wawersik and F. Basolo, *J. Amer. Chem. Soc.*, 1967, **89**, 4626.

[7] F. Basolo, *Chem. in Britain*, 1969, **5**, 505.

[8] O. Crichton and A. J. Rest, *J.C.S. Dalton*, 1977, 536.

[9] O. Crichton and A. J. Rest, *J.C.S. Dalton*, 1977, 656.

[10] O. Crichton and A. J. Rest, *Proc. 6th Internat. Conf. Organometallic Chem.*, Amherst, Massachusetts, 1973.

[11] O. Crichton and A. J. Rest, *J.C.S. Dalton*, 1977, 986.

filter B, $360 < \lambda < 460$ nm {solution cell (pathlength, 10 mm) containing AnalaR $Co[SO_4]$ in water + solution cell (pathlength, 10 mm) containing $[Cu(NH_3)_4][SO_4]$ in water with dilution-adjusted cut-on and cut-off points}; filter C, $220 < \lambda < 280$ nm {quartz gas cell (pathlength, 25 mm) containing 3 atm Cl_2 + quartz solution cells (pathlengths, 10 mm) containing AnalaR $Co[SO_4]$ in water and AnalaR $Ni[SO_4]$ in water with cut-on and cut-off points adjusted by dilution}; filter D, $\lambda > 410$ nm {quartz gas cell containing Cl_2 + soda-glass disc (thickness, 5 mm)}; filter E, $\lambda < 280$ nm and $\lambda > 410$ nm (quartz gas cell containing Cl_2 gas); and filter F, $\lambda > 330$ nm [soda-glass disc (thickness, 5 mm)].* In addition, because of the extreme sensitivity of the primary photoproducts (see below) to visible light, it was necessary to remove any visible light from the radiation emitted by the Nernst filament of the i.r. spectrometer. This was achieved using a germanium interference filter (Ocli Optical Coatings).[8]

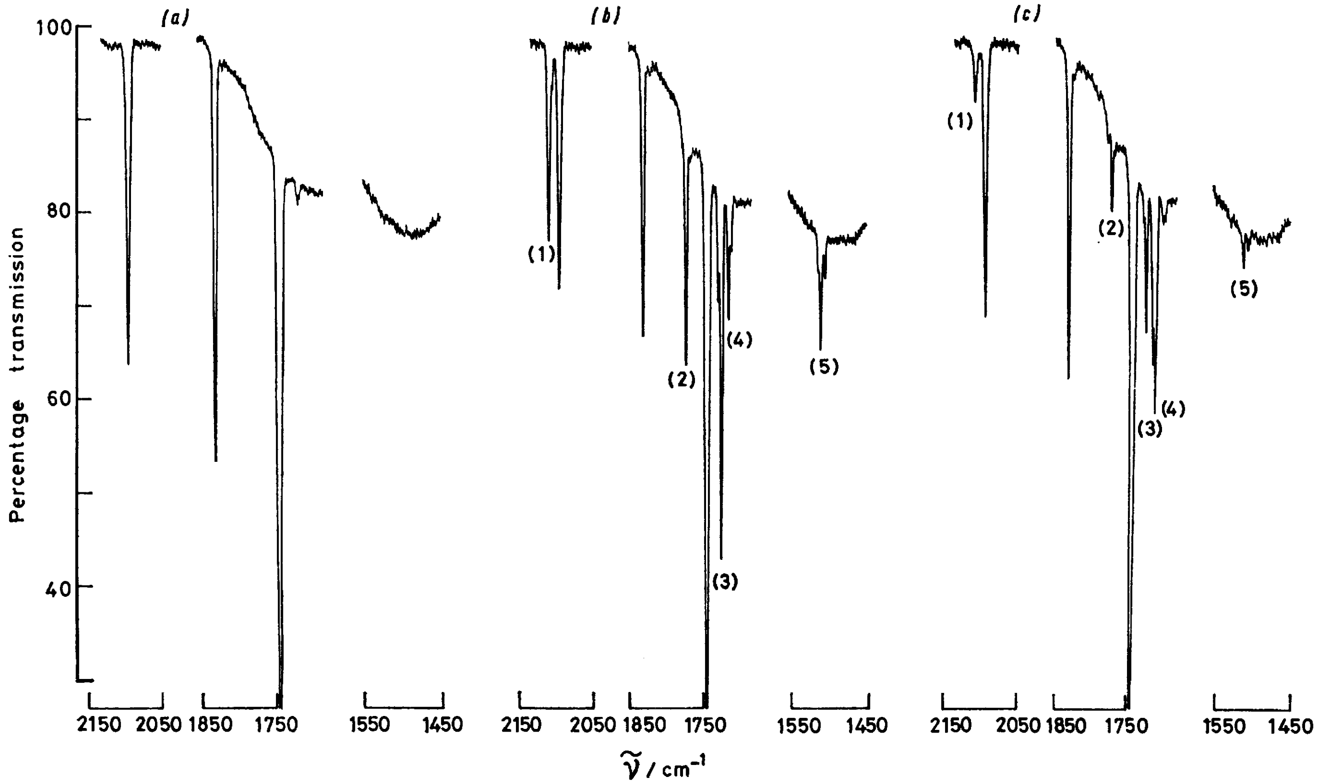


FIGURE 1 Infrared spectra from an experiment with $[Mn(CO)(NO)_3]$ isolated in an argon matrix: (*a*) after deposition; (*b*) after 10-min photolysis with filter A; (*c*) after photolysis for another 5 min with u.v. light (filter C). For an explanation of the numbering of the bands (1)—(5) see text

Preparation of $[Mn(CO)(NO)_3]$ *and* ^{15}NO*-enriched Samples.*—The complex $[Mn(CO)(NO)_3]$ is somewhat unstable [5] and was therefore prepared in small quantities, as required, by a convenient photochemical method.[12] This procedure was readily adapted to produce ^{15}NO-enriched $[Mn(CO)(NO)_3]$ by photolysing $[Mn(CO)_4(NO)]$ [13] (*ca.* 1 Torr) in the presence of 20 Torr of a mixture of ^{14}NO and ^{15}NO (B.O.C. Prochem, 95% ^{15}NO + 5% ^{14}NO) in the required ratio. Expansion of the product, $[Mn(CO)(NO)_3]$ or ^{15}NO-enriched $[Mn(CO)(NO)_3]$, into a bulb (1 l), followed by dilution with up to 250 Torr of matrix gas, gave mixtures suitable for immediate spray-on.

RESULTS AND DISCUSSION

Reactions.—Photolysis of $[Mn(CO)(NO)_3]$ *in argon matrices.* Infrared spectra from an experiment with $[Mn(CO)(NO)_3]$ in an argon matrix, using the germanium filter, are shown in Figure 1. At high dilution (1 : 10 000), the spectrum of the parent complex [Figure 1(*a*)] possesses three strong i.r. bands between 2 150 and 650 cm^{-1} corresponding to the terminal carbonyl- and two terminal nitrosyl-stretching modes expected for C_{3v} symmetry. At higher resolution the bands show splittings (Table 1) which are strikingly similar to those of the isostructural complex $[Co(CO)_3(NO)]$.†

Photolysis for a few minutes using orange light (filter A) corresponding to the weak band at 600 nm in the electronic-absorption spectrum (Figure 2) resulted in the appearance of a number of new bands [Figure 1(*b*)] in three regions of the i.r. spectrum: above 1 900 cm^{-1}, at 2 105 and 2 100 cm^{-1} (1); 1 900—1 600 cm^{-1}, at 1 772 cm^{-1} (2), 1 728 and 1 725 cm^{-1} (3), and 1 714 and 1 710 cm^{-1} (4); and below 1 600 cm^{-1}, at 1 505 and 1 499 cm^{-1} (5). Irradiation at shorter wavelengths (filter B)

---

* Throughout this paper: 1 atm = 101 325 Pa; 1 Torr = (101 325/760) Pa; 1 eV ≈ 1.60×10^{-19} J.

† The splittings for the series $[M(CO)_{4-x}(NO)_x]$ will be discussed in detail elsewhere.[14]

[12] O. Crichton and A. J. Rest, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 391.

[13] R. B. King, *Organometallic Synth.*, 1965, **1**, 164.

[14] O. Crichton and A. J. Rest, unpublished work.

caused a reduction in the intensity of most of the product bands [Figure 1(*c*)], although the doublet, designated (4), increased in contrast to the others and this band therefore belongs to a separate species. In a large number of experiments bands (1), (2), (3), and (5) all behaved analogously (growth and disappearance with different filtered photolyses) so that they are probably due to a single molecular species. Although the bands designated (1), (3), and (5) are apparently all doublets, the relative intensities of the components of each doublet remained constant under a variety of photolysis conditions so that each doublet probably corresponds to a single fundamental. The magnitude of the splittings are similar to those of $[Mn(CO)(NO)_3]$ (Table 1), which are typical of matrix effects (up to 10 cm^{-1}).

TABLE 1

Positions (cm^{-1}) of bands appearing in experiments with $[Mn(CO)(NO)_3]$ isolated in argon matrices; * bands in parentheses are from an experiment with ^{15}NO-enriched $[Mn(CO)(NO)_3]$

	$[Mn(CO)(NO)_3]$		$[Mn(CO)(NO)_2(NO^*)]$		$[Mn(NO)_3]$
$A_1[\nu(CO)]$	2 092 2 090	$\nu(CO)$	2 105 2 100		
$A_1[\nu(NO)]$	1 829	$\nu(NO)$	1 772		
$E[\nu(NO)]$	1 743 1 742 1 740	$\nu(NO)$	1 728 1 725	$E'[\nu(NO)]$	1 714 1 710
		$\nu(NO^*)$	1 505 (1 479) 1 499 (1 473)		

* Other weak bands appear at 1 788, 1 776, 1 706, and 1 699 cm^{-1}.

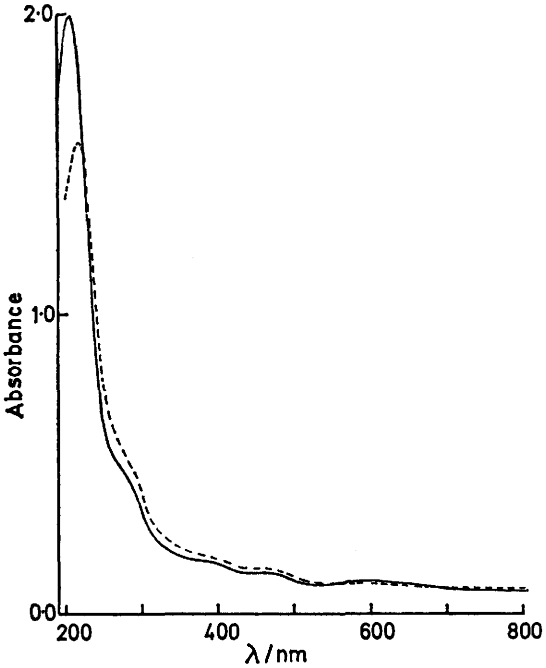


FIGURE 2 Electronic spectra from an experiment with $[Mn(CO)(NO)_3]$ isolated in an argon matrix, before (——) and after (– – – –) photolysis

Since the upper band [(1)] is obviously a terminal carbonyl-stretching mode, the product cannot have been formed by CO loss in contrast to the formation of $[Co(CO)_2(NO)]$ [8] and $[Fe(CO)(NO)_2]$.[9] The two fundamentals in the 1 700 cm^{-1} region [(2) and (3)] must be terminal nitrosyl-stretching bands and their relative intensity suggests a $[Mn(NO)_2]$ fragment. Whatever photochemical change has taken place must have involved the third nitrosyl ligand. This ligand cannot have been lost completely as there is no band at 1 880 cm^{-1} corresponding to free NO.[15] At 500 nm the photochemical energy per quantum is only *ca.* 2 eV so that energetic processes, such as dissociation of the nitrosyl ligand, can be ruled out because of the limited energy available. The remaining possibility for the unusually low wavenumber band [(5)] is that it is due to some type of NO ligand, although a bridging nitrosyl ligand (1 400—1 600 cm^{-1}) can also be eliminated because the species was formed at high dilution (1 : 5 000—1 : 15 000), and aggregation on brief photolysis is unlikely. The only plausible structure is $[Mn(CO)(NO)_2(NO^*)]$ where the NO* denotes a nitrosyl ligand with an altered coordination mode.

It is tempting to assign the remaining product band (4) in Figure 1(*b*) to a $[Mn(NO)_3]$ fragment analogous to $[Ni(CO)_3]$. A planar (D_{3h}) species would have only one i.r.-active terminal nitrosyl-stretching fundamental (E'), and the shift of *ca.* 30 cm^{-1} from the position of the E mode of $[Mn(CO)(NO)_3]$ is comparable with the shifts observed for ν(NO) on loss of CO from $[Co(CO)_3(NO)]$ [8] and $[Fe(CO)_2(NO)_2]$.[9] Further investigation, however, indicates that the situation is more complex. Photolysis using u.v. light (filter C) produces the spectrum shown in Figure 1(*c*). The bands due to $[Mn(CO)(NO)_2(NO^*)]$ have decreased in intensity while the lower-frequency component of band (4) (1 710 cm^{-1}) has increased substantially. At the same time, other weak new bands have appeared at 1 778, 1 706, and 1 699 cm^{-1}, together with a very weak band (not shown) due to liberated CO. The relative intensities of the two components of band (4) have also changed dramatically, indicating that the component at 1 714 cm^{-1} is unrelated to any of the other bands produced by u.v. photolysis since its intensity has increased only marginally.

Only the intensity of the absorption at 1 710 cm^{-1} has increased sufficiently to account for detectable absorption by liberated CO, which has a relatively low absorption coefficient. It is thus probable that this band is due to a $[Mn(NO)_3]$ fragment formed by ejection of a CO ligand. Quite possibly, both components of band (4) are due to spectroscopically distinct forms of $[Mn(NO)_3]$ resulting from minor differences in the local matrix environment favoured by the various photolysis sources used. Considering the vast difference in photochemical energy available at 280 and 550 nm this is by no means unlikely, *e.g.* the triplet pattern of the terminal

---

[15] W. A. Guillory and G. E. Hunter, *J. Chem. Phys.*, 1969, **50**, 3516.

nitrosyl absorption of [Ni(η-C_5H_5)(NO)] varies during the course of forward and reverse photolysis cycles.[11]

The assignment of bands (1), (2), (3), and (5) was confirmed by photolysis of ^{15}NO-enriched [Mn(CO)(NO)$_3$] in an argon matrix using filter A. The situation is complicated both by the presence of a number of bands due to isotopically substituted [Mn(CO)(NO)$_3$], and because some of the bands due to ^{15}NO-substituted [Mn(CO)(NO)$_2$(NO*)] apparently exhibit matrix splittings corresponding to those observed in the spectra of the naturally abundant complex. A simple force-constant calculation[16] did however account satisfactorily for the positions of the observed bands (Table 2).

Table 2

Observed and calculated positions (cm^{-1}) of bands due to [Mn(CO)(NO)$_2$(NO*)] generated from partially ^{15}NO-enriched [Mn(CO)(NO)$_3$] assuming k_{NO} = 1 344, $k_{\mathrm{NO^*}}$ = 996, $k_{\mathrm{NO,NO}}$ = 36, and $k_{\mathrm{NO,NO^*}}$ = 0.0 N m^{-1} [a]

	Position		
	obs.	calc.	Molecular species
ν(NO)	1 771.0	1 771.0	[Mn(CO)(^{14}NO)$_2$(NO*)]
	1 759.8	1 759.9	[Mn(CO)(^{14}NO)(^{15}NO)(NO*)]
	[b]	1 739.4	[Mn(CO)(^{15}NO)$_2$(NO*)]
	1 724.4 [c]	1 723.3	[Mn(CO)(^{14}NO)$_2$(NO*)]
	1 702.6	1 703.3	[Mn(CO)(^{14}NO)(^{15}NO)(NO*)]
	1 691.4	1 692.5	[Mn(CO)(^{15}NO)$_2$(NO*)]
ν(NO*)	1 505.0 [c]	1 505.0	[Mn(CO)(NO)$_2$(^{14}NO*)]
	1 478.2 [c]	1 478.2	[Mn(CO)(NO)$_2$(^{15}NO*)]

[a] Although $k_{\mathrm{NO,NO^*}}$ is unlikely to be exactly zero, this value was assumed as no splittings were observed which could be assigned to interaction between modes involving NO and NO* ligands. $k_{\mathrm{NO,NO^*}}$ may actually be quite significant and an upper limit of *ca.* ±20 N m^{-1} is consistent with the typical half-widths (*ca.* 3 cm^{-1}) observed for the NO stretching fundamentals. [b] This band is not observed, presumably because it is very close to a component at 1 740 cm^{-1} of a strong band due to [Mn(CO)(NO)$_3$]. [c] Since this band is split by interaction with the matrix, the position of the strongest component has been taken.

Confirmation of the assignment of [Mn(NO)$_3$] is more difficult, particularly for an essentially planar structure, since all the highest-frequency absorptions of the different isotopically substituted species are likely to be either forbidden or unobservably weak. Two additional bands were observed in a mixed-isotope experiment at 1 687 and 1 698 cm^{-1} which may be the lower-frequency A' modes of [Mn(^{14}NO)$_2$(^{15}NO)] and [Mn(^{14}NO)(^{15}NO)$_2$] respectively, but since their predicted positions are very insensitive to the frequency assumed for the highest-frequency band of [Mn(NO)$_3$] no further information can be obtained.

No assignment of the weak bands which appear on u.v. photolysis (filter C) can be made at this stage, although species such as [Mn(NO)$_2$(NO*)] may be involved.

Photolysis of [Mn(CO)(NO)$_3$] *in nitrogen matrices.** In a pure nitrogen matrix all the high-wavenumber i.r.-active fundamentals of [Mn(CO)(NO)$_3$] show fine splittings (Table 3), some obvious even under low resolution [Figure 3(*a*)]. Brief photolysis with visible light (filter D) produced four new bands [labelled (1)—(4) in Figure 3(*b*)]. Three of these bands [(1)—(3)] have closely similar positions to the three bands observed in argon experiments and which have been assigned to [Mn(CO)(NO)$_2$(NO*)]. On u.v. photolysis (filter C), bands (1) and (2) decreased in intensity [Figure 3(*c*)] while (3) and (4) grew significantly and a shoulder to low wavenumber of the parent nitrosyl band (at 1 828 cm^{-1}) became more pronounced. In argon (see above) the bands of [Mn(CO)(NO)$_2$(NO*)] grew on photolysis with visible light and decreased in intensity on u.v. photolysis. Bands (1) and (2) behave exactly as expected, but the third band (3) appeared to grow on irradiation with both visible and u.v. light. Under higher resolution, band (3) consisted of at least four components, two of which (at 1 725 and 1 720 cm^{-1}) behaved analogously to bands (1) and (2). It is probable, therefore, that one of the products is [Mn(CO)(NO)$_2$(NO*)], with a further unobserved band at *ca.* 1 500 cm^{-1} (Table 3).

Table 3

Positions (cm^{-1}) of bands appearing in experiments with [Mn(CO)(NO)$_3$] isolated in pure nitrogen matrices [a]

[Mn(CO)(NO)$_3$]		[Mn(CO)(NO)$_2$(NO*)]		[Mn(N$_2$)(NO)$_3$]	
$A_1[\nu$(CO)]	2 099 2 093	ν(CO)	2 115 2 108	$A_1[\nu$(NN)]	2 295 2 290
$A_1[\nu$(NO)]	1 828 1 826	ν(NO)	1 769	$A_1[\nu$(NO)]	1 826
$E[\nu$(NO)]	1 745 1 742 1 740	ν(NO)	1 725 1 720	$E[\nu$(NO)]	1 727 1 723
		ν(NO*)	*ca.* 1 500 [b]		

[a] Other weak bands appear at 1 780, 1 761, 1 712, 1 710, 1 693, 1 687, and 1 664 cm^{-1}. [b] Although this band was not actually observed in a N$_2$ matrix, its position may be estimated by analogy with experiments in argon.

Table 4

Positions (cm^{-1}) of the nitrosyl bands in [Mn(NO)$_3$L] complexes

L	Phase	ν(NO)	
		A_1	E
CO [a]	N$_2$ matrix	1 827	1 745 1 742 1 740
CO [b]	n-Pentane solution	1 821	1 735
PF$_3$ [c]	N$_2$ matrix	1 840	1 748 1 744 1 742
N$_2$ [a]	N$_2$ matrix	1 825	1 727 1 723
C$_2$H$_4$ [d]	n-Pentane solution	1 863	1 705
C$_2$H$_2$ [d]	n-Pentane solution	1 785	1 683
thf [d]	n-Pentane solution [e]	1 786	1 678

[a] This work. [b] Data from M. Herberhold and A. Razavi, *J. Organometallic Chem.*, 1974, **67**, 81. [c] Data from ref. 12. [d] Data from M. Herberhold, personal communication. [e] [Mn(CO)(NO)$_3$] + tetrahydrofuran (thf) (molar ratio 1 : 5) in n-pentane solution.

Spectra from an experiment in which more sample was

---

* The photolysis of [Mn(CO)(NO)$_3$] in matrices of pure nitrogen was investigated before there was any reason to believe that products having nitrosyl absorptions as low as 1 500 cm^{-1} might exist, and consequently no spectra from that region are available. It is still possible, however, to reach conclusions about the processes taking place, although some assignments must be rather tentative.

[16] L. M. Haines and M. K. B. Stiddard, *Adv. Inorg. Chem. Radiochem.*, 1969, **12**, 53.

deposited are shown in Figure 4. After photolysis with filter E [Figure 4(*a*)], substantial amounts of both $[Mn(CO)(NO)_2(NO^*)]$ and the species responsible for band (4) are present together with weak bands at 1 780 and 1 760 cm^{-1} and a band due to free CO (not shown). An extremely weak band (2 295 and 2 290 cm^{-1}) was detected in the high-wavenumber ν(NN) region,[17] which indicated that at least one species had been formed by replacement of CO by N_2. Since the shoulder on the $A_1[\nu(NO)]$ band of $[Mn(CO)(NO)_3]$ (at 1 826 cm^{-1}) and the other two components of band (3) (at 1 727 and 1 723 cm^{-1}) are in positions consistent with assignment to the A_1 and E modes of a C_{3v} $[Mn(NO)_3(L)]$ species (Table 4), the species containing the dinitrogen ligand is very probably $[Mn(N_2)(NO)_3]$.

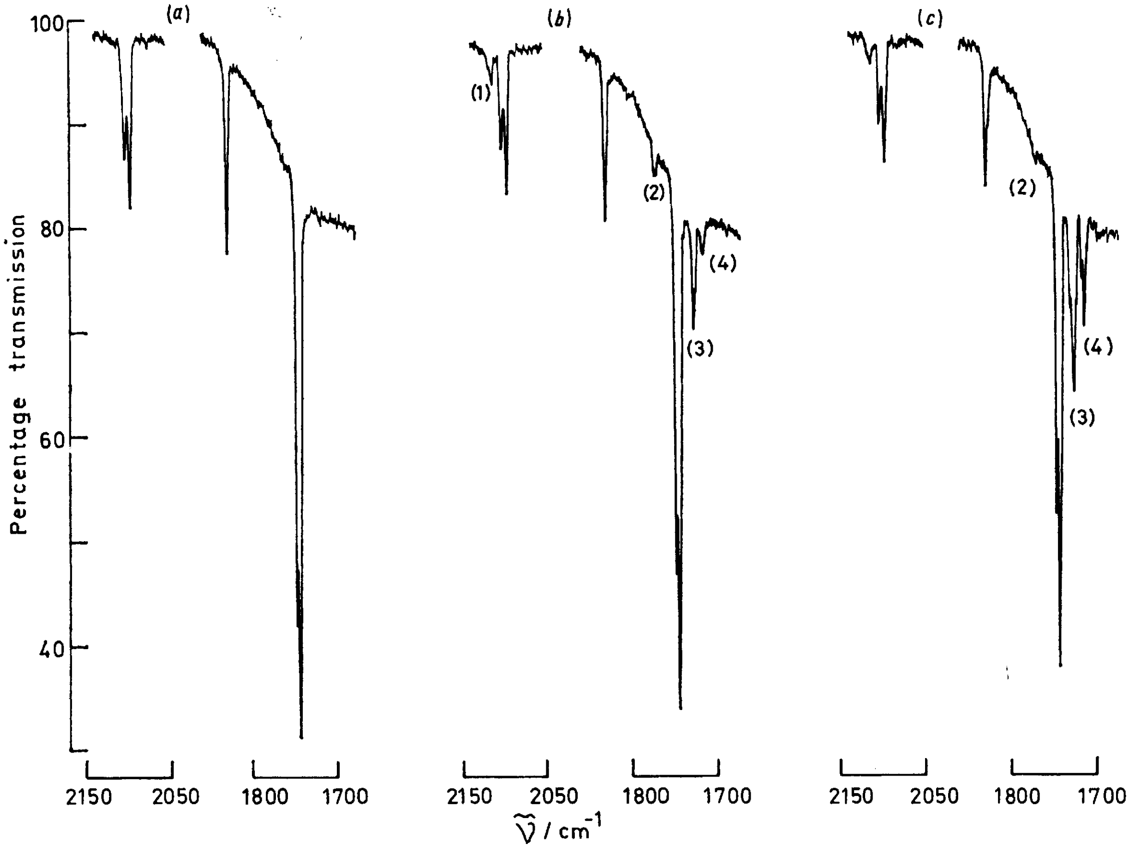


FIGURE 3 Infrared spectra from an experiment with $[Mn(CO)(NO)_3]$ isolated in a nitrogen matrix: (*a*) after deposition; (*b*) after photolysis for 1 min with filter D; (*c*) after photolysis for another 2 min with filter C. For an explanation of the numbering of bands (1)—(4) see text

Photolysis with filter E resulted in the spectrum shown in Figure 4(*b*). In addition to further growth of the weak bands mentioned above, the bands of $[Mn(N_2)(NO)_3]$ have become stronger than those of $[Mn(CO)(NO)_2(NO^*)]$. Photolysis with the unfiltered mercury lamp takes this process further [Figure 4(*c*)], and at the same time weak bands grow, notably those at 1 764, 1 761, 1 693, and 1 687 cm^{-1} (Table 3). Since the number of bands appearing in the region below 1 600 cm^{-1} is uncertain, no firm assignment of any of the weak bands can be made. Some possibilities are $[Mn(N_2)(NO)_2(NO^*)]$ {bands at 1 764 and 1 761, and 1 712 and 1 710 cm^{-1}, *cf.* $[Mn(CO)(NO)_2(NO^*)]$} and $[Mn(NO)_2(NO^*)]$ (bands at 1 693 and 1 687 cm^{-1}).

Mechanism.—The reactions of $[Mn(CO)(NO)_3]$ in argon matrices show that CO ejection can take place to give a co-ordinatively unsaturated species $[Mn(NO)_3]$ and additionally a species which is formed without loss of any ligands and which has a very low value of ν(NO). Evidence is accumulating that, in matrices, other nitrosyl complexes form species having a range of low values of ν(NO), *e.g.* $[Ni(\eta\text{-}C_5H_5)(NO^*)]$ (at 1 390 cm^{-1}),[11] $[Cr(NO)_3(NO^*)]$ (at 1 450 cm^{-1}),[18] and $[Mn(CO)_4(NO^*)]$ (at 1 465 cm^{-1}),[19] which suggests that one of the nitrosyl ligands can change its mode of co-ordination, as a result of photoelectron transfer from the metal to the nitrosyl, rather than form an ion pair $[Mn(CO)(NO)_2]^+,[NO]^-$. Likely consequences of electron transfer from metal to nitrosyl are: (*a*) the metal atom would be relatively electron deficient; and (*b*) the bound NO ligand presumably becomes progressively more bent * as more

---

* For a recent review, including discussion of linear *versus* bent co-ordination of the M–N–O group, see J. H. Enemark and R. D. Feltham, *Co-ordination Chem. Rev.*, 1974, **13**, 399.

[17] A. J. Rest, *J. Organometallic Chem.*, 1972, **40**, C76.

[18] O. Crichton, Ph.D. Thesis, Cambridge University, 1975.

[19] O. Crichton and A. J. Rest, following paper.

electron density is transferred to it. The reactivity of the primary photoproducts is demonstrated by the ready reversal of the reaction when the matrix is irradiated with light of different wavelengths and by the formation of the dinitrogen complex $[Mn(N_2)(NO)_3]$.

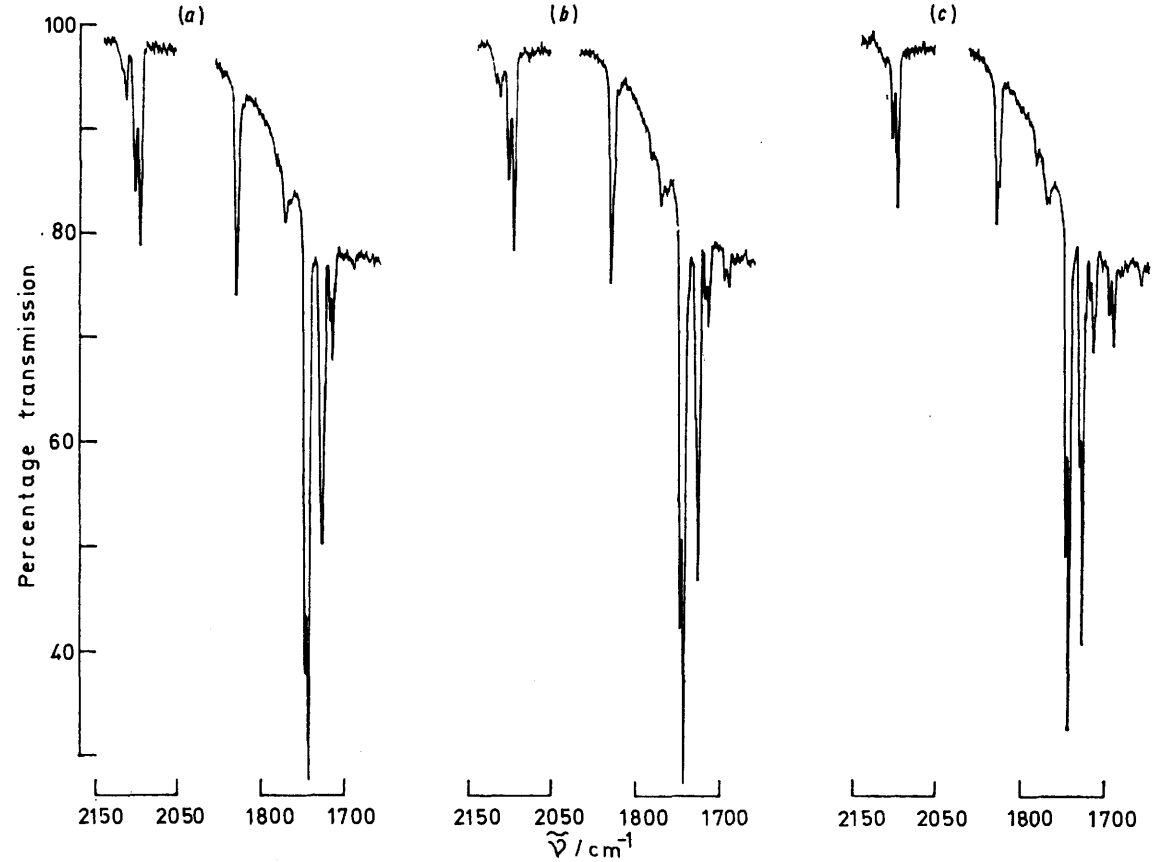
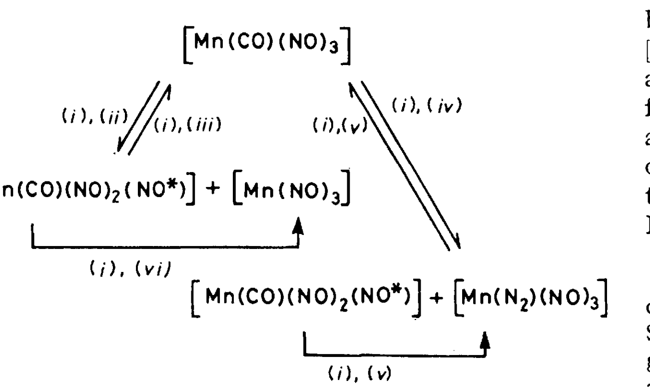


FIGURE 4 Infrared spectra from another experiment with $[Mn(CO)(NO)_3]$ in a nitrogen matrix: (*a*) after 2-min photolysis with filter E; (*b*) after photolysis for another 5 min with filter F; (*c*) after photolysis for another 20 min with the unfiltered mercury lamp

No evidence was obtained in this study for NO ejection. The reactions of $[Mn(CO)(NO)_3]$ in matrices are summarised in Scheme 2.



SCHEME 2 (*i*) $h\nu$; (*ii*) filter A, argon; (*iii*) filter B; (*iv*) filters D and E, nitrogen; (*v*) filters C and F; (*vi*) filter C

The production of $[Mn(NO)_3]$ in dilute argon matrices is analogous to the formation of $[Co(CO)_2(NO)]$ [8] and $[Fe(CO)(NO)_2]$ [9] and gives strong support to the species (A) in Scheme 1. The species formed by photoelectron transfer in argon and, very interestingly, in nitrogen matrices, $[Mn(CO)(NO)_2(NO^*)]$, can be considered as a precursor to (B) in Scheme 1, where electron transfer (metal to nitrosyl) leaves the metal susceptible to nucleophilic attack by the incoming ligand (L). The success in observing species in matrices corresponding to both the k_1 and k_2 paths for manganese, in contrast to $[Co(CO)_3(NO)]$ [8] and $[Fe(CO)_2(NO)_2]$,[9] can probably be attributed to the fact that electronic-absorption bands for manganese extend far out into the visible (Figure 2), allowing more selective long-wavelength photolysis to occur. Future work will attempt to investigate further the extent of the electron transfer and the nature of the M(NO*) bonding.

We thank the S.R.C. together with I.C.I. Ltd., Petrochemicals Division, Billingham, for the award of a C.A.P.S. Studentship (to O. C.), the Royal Society for support (a grant to purchase the Pye Unicam SP 1800B spectrometer) and for the award of a Pickering Research Fellowship (to A. J. R.), and Dr. M. Herberhold for permission to use the unpublished data for $[Mn(NO)_3(L)]$ complexes.

[7/123 *Received, 24th January,* 1977]