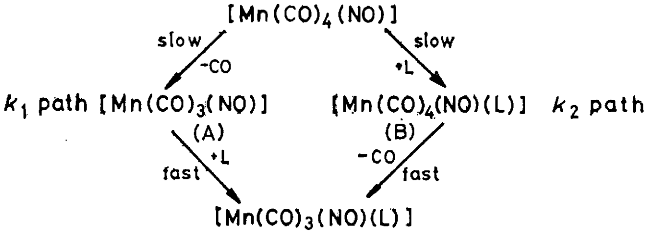
Photochemistry of Tetracarbonylnitrosylmanganese in Frozen Gas Matrices at 20 K. Infrared Spectroscopic Evidence for Tricarbonylnitrosylmanganese, Tricarbonyl(dinitrogen)nitrosylmanganese, and a Species formed by Metal-to-nitrosyl Photoelectron Transfer

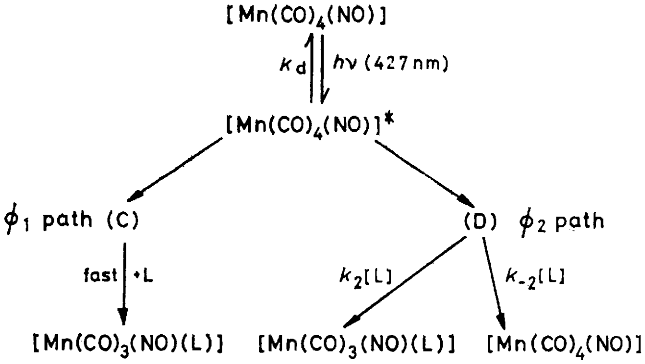
By **Oliver Crichton** and **Antony J. Rest**,*† University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EP

Infrared evidence is presented for the formation of a four-co-ordinate species $[Mn(CO)_3(NO)]$, apparently capable of existing in two distinct structural modifications, on u.v. photolysis of $[Mn(CO)_4(NO)]$ in argon and methane matrices, and for the formation of a five-co-ordinate species $[Mn(CO)_3(N_2)(NO)]$ in nitrogen matrices at 20 K. Further loss of CO probably gives $[Mn(CO)_2(NO)]$ and $[Mn(CO)(NO)]$ in methane and $[Mn(CO)_2(N_2)_2(NO)]$ in nitrogen matrices. Infrared evidence is also presented for the formation of a species $[Mn(CO)_4(NO^*)]$, where the asterisk denotes a nitrosyl group having an unusually low value of ν(NO) (at *ca.* 1 460 cm^{-1}), on photolysis of $[Mn(CO)_4(NO)]$ with visible radiation in both argon and methane matrices. It is concluded that $[Mn(CO)_4(NO^*)]$ belongs to a class of compounds in which photoelectron transfer has occurred with the nitrosyl ligand (NO^*) accepting additional electron density from the metal atom. The results are related to the postulates of co-ordinatively unsaturated and expanded-co-ordination-shell species as intermediates in the thermal and photochemical substitution reactions of $[Mn(CO)_4(NO)]$ in solution.

TETRACARBONYLNITROSYLMANGANESE is unique among metal nitrosyl complexes because there have been detailed studies of the thermal[1] and photochemical[2] substitution reactions it can undergo. The thermal substitution reactions take place[1] by a second-order process, *i.e.* an associative mechanism (k_2 path in Scheme 1), although for ligands which are poor nucleophiles, *e.g.* $AsPh_3$, there is a contribution from the dissociative process (k_1 path in Scheme 1). Further substitution to give $[Mn(CO)_2(NO)L_2]$ is dominated by a dissociative process, a rather surprising result. At 427 nm the photochemical substitution reaction also showed[2] a dependence on the nature of the incoming nucleophile, *e.g.* $AsPh_3$ replaced CO with a concentration-independent quantum yield of *ca.* 0.15 whereas PPh_3, a better nucleophile, had a higher quantum yield which increased with increasing ligand concentration. Scheme 2, where poor nucleophiles follow the ϕ_1 path and good nucleophiles follow mainly the ϕ_2 path, illustrates the mechanism proposed to explain these results. A proportion of the primary photoproduct $\{[Mn(CO)_4(NO)]^*\}$ decays *via* CO loss to give (C), *i.e.* $[Mn(CO)_3(NO)]$, which reacts rapidly with the entering ligand. In addition, a species (D) is formed, perhaps by rearrangement to give an altered co-ordination geometry, for which deactivation by collision with L (represented as $k_{-2}[L]$) to give $[Mn(CO)_4(NO)]$ competes with capture of L (represented as $k_2[L]$) to give the substituted complex perhaps *via* a relatively stable intermediate with an expanded co-ordination shell, *i.e.* $[Mn(CO)_4(NO)(L)]$ (E). The remaining process in Scheme 2 is thermal deactivation of $[Mn(CO)_4(NO)]^*$ (represented as k_d).



SCHEME 1



SCHEME 2

The matrix-isolation technique affords one approach to the identification of unstable species postulated as intermediates in reaction mechanisms. Recently we described i.r. spectroscopic evidence for the formation of $[Co(CO)_2(NO)]$[3] and $[Fe(CO)(NO)_2]$,[4] *i.e.* type (A) (Scheme 1) and (C) species (Scheme 2), on 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 $[Mn(CO)_4(NO)]$ in inert (argon and methane) and reactive (nitrogen) matrices ‡ and we relate the findings to the thermal and photochemical substitution studies.[1,2] The formation of unsaturated complexes {assigned as $[Mn(CO)_3(NO)]$ and $[Mn(CO)_2(NO)]$} on *brief* photolysis of $[Mn(CO)_4(NO)]$ in an argon matrix was first reported by Rest,[6] although the dilutions used $\{[Mn(CO)_4(NO)] : argon = 1 : 200\}$ do

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

‡ $[Mn(CO)_4(NO)]$ is also known to react with CO when photolysed in pure carbon monoxide matrices.[5]

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

[2] D. P. Keeton and F. Basolo, *Inorg. Chim. Acta*, 1972, **6**, 33.

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

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

[5] O. Crichton, M. Poliakoff, A. J. Rest, and J. J. Turner, *J.C.S. Dalton*, 1973, 1321.

[6] A. J. Rest, *Chem. Comm.*, 1970, 345.

not eliminate the possibility of aggregation. Poliakoff[7] examined the effect of *prolonged* photolysis and annealing on the spectrum of [Mn(CO)$_4$(NO)] in argon (1 : 2 000) as a model for [Fe(CO)$_5$], and found a number of bands not observed by Rest. Since very different photolysis conditions were used in the two studies it is not surprising that apparently contradictory results were obtained. A preliminary account of the work described in this paper has been presented elsewhere.[8]

EXPERIMENTAL

Details of the cryostat, the i.r. spectrometer, the photolysis lamp, matrix gases, and the preparation and deposition of gas mixtures with substrate : matrix gas ratios of between 1 : 5 000 and 1 : 20 000 have been given previously.[3] Infrared band positions are accurate to better than ± 0.5 cm^{-1} but have been rounded to the nearest unit. The complex [Mn(CO)$_4$(NO)] was prepared by the literature method[9] and stored at 253 K in a deep freeze. Wavelength selection for photolysis was achieved using a combination of absorbing materials: filter A, $\lambda < 280$, $\lambda > 550$ nm [quartz gas cell (pathlength, 25 mm) containing 3 atm Cl_2 + quartz gas cell (pathlength, 25 mm) containing 150 Torr Br_2]; filter B, $450 < \lambda < 600$ nm {solution cell (pathlength, 10 mm) containing AnalaR Cu[SO$_4$] in water + solution cell (pathlength, 10 mm) containing K$_2$[CrO$_4$] with cut-on and cut-off points adjusted by dilution}; filter C, $350 < \lambda < 510$ nm {solution cell (pathlength, 10 mm) containing AnalaR Cu[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 D, $\lambda > 610$ nm {solution cell (pathlength, 10 mm) containing AnalaR K$_2$[Cr$_2$O$_7$] in water + solution cell (pathlength, 10 mm) containing K[MnO$_4$] in water with dilution-adjusted cut-on and cut-off points}; filter E, $\lambda > 400$ nm [quartz gas cell containing Cl_2 and soda-glass disc (thickness, 5 mm)]; and filter F, $\lambda < 280$, $\lambda > 400$ nm (quartz gas cell containing Cl_2).* Because of the extreme sensitivity of some of the primary photoproducts (see below) to visible light, it also was necessary to remove any visible light from the radiation emitted by the Nernst filament of the i.r. spectrometer. This was achieved using germanium interference filters (Ocli Optical Coatings).[3]

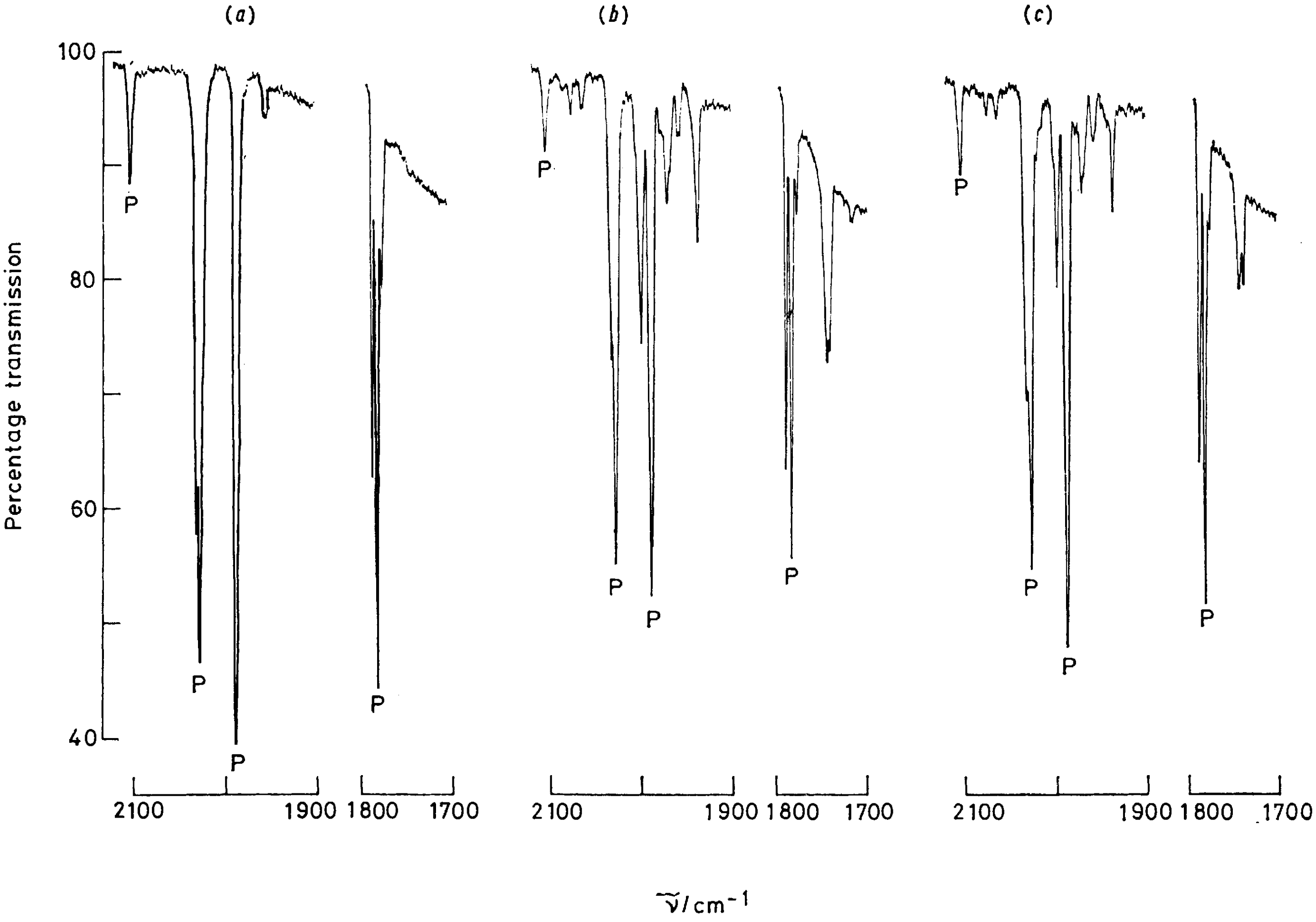

FIGURE 1 Infrared spectra from an experiment with [Mn(CO)$_4$(NO)] (bands marked P) isolated in an argon matrix: (*a*) after deposition; (*b*) after 5-min photolysis with the unfiltered mercury lamp; (*c*) after annealing the matrix from stage (*b*)

RESULTS AND DISCUSSION

Reactions.—Photolysis of [Mn(CO)$_4$(NO)] *in argon matrices.* Infrared spectra from an experiment with

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

[7] M. Poliakoff, Ph.D. Thesis, Cambridge University, 1972.

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

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

$[Mn(CO)_4(NO)]$ in an argon matrix, using the germanium filter, are shown in Figure 1. At high dilution (*ca.* 1 : 10 000) the spectrum of the parent complex [Figure 1(*a*)] includes four strong bands (P) at high wavenumbers, corresponding to three terminal carbonyl- and one terminal nitrosyl-stretching modes, as well as a weak band (1 955 and 1 951 cm^{-1}) due to $[Mn(^{12}CO)_3(^{13}CO)(NO)]$ present at natural abundance. At sufficiently high resolution, all these bands exhibit typical matrix splittings (Table 1) and, in particular, the band at *ca.* 2 020 cm^{-1} has at least four components spread over 11 cm^{-1}. In the crystalline state $[Mn(CO)_4(NO)]$ has a trigonal-bipyramidal structure with an equatorial nitrosyl group and C_{2v} symmetry.[10] For this structure four terminal C–O stretching fundamentals are expected $(2A_1 + 2B_1 + B_2)$, but in an earlier solution study only three terminal absorptions were observed and a C_{3v} solution structure with an axial nitrosyl ligand was postulated.[11] It seems probable that the apparent inconsistency of *X*-ray diffraction and solution i.r. studies results from an accidental near degeneracy of two i.r. modes, thus explaining the broadness and complexity of the corresponding bands in the vicinity of 2 020 cm^{-1} in argon as well as in methane and nitrogen matrices (Tables 2 and 3).

TABLE 1

Positions (cm^{-1}) of observed bands between 2 150 and 650 cm^{-1} in experiments with $[Mn(CO)_4(NO)]$ isolated in argon matrices; bands in parentheses are from $[Mn(^{12}CO)_3(^{13}CO)(NO)]$ in natural abundance

	$[Mn(CO)_4(NO)]$ Before photolysis		Products: Brief photolysis	Products: Prolonged photolysis
ν(CO)	2 102	(1) [a]	2 072	2 074
	2 106		1 994	2 072
	2 097(sh)		1 939	2 060 [b]
			1 734(sh)	2 051 [c]
ν(CO)	2 029		1 732	1 998 [d]
	2 024			1 994
	2 022	(2) [e]	2 060	1 992 [d]
	2 018		1 998	1 976 [b]
			1 996	1 966 [b]
ν(CO)	1 986		1 969	1 963
	1 984		1 966	1 943 [c]
	1 983(sh)		1 963	1 939
			1 737	1 925
	(1 955)			1 920
	(1 951)	(3) [f]	2 017	1 741
			1 972	1 734
ν(NO)	1 782		1 465	1 732
	1 776			
	1 770			
		Others:	2 012	
			1 953	
			1 712 [g]	

[a] Bands produced rapidly by u.v. photolysis and readily destroyed by annealing or photolysis with filter B. [b] Intensity decreased reversibly during annealing. [c] Intensity increased irreversibly during annealing. [d] Intensity increased reversibly during annealing. [e] Bands produced in small amounts by u.v. photolysis and partially destroyed by annealing or photolysis with filter C. [f] Bands growing on photolysis with filter C. [g] Weak band observed after u.v. photolysis and destroyed by annealing or exposure to visible light.

Brief photolysis with the unfiltered mercury lamp [Figure 1(*b*)] produces, in addition to a band due to liberated CO (not shown), a large number of new bands and some minor changes in the splitting pattern of the spectrum of the parent complex. On annealing the

TABLE 2

Positions (cm^{-1}) of bands observed between 2 150 and 650 cm^{-1} in experiments with $[Mn(CO)_4(NO)]$ isolated in methane matrices; bands in parentheses are from $[Mn(^{12}CO)_3(^{13}CO)(NO)]$ in natural abundance

	$[Mn(CO)_4(NO)]$		Products
ν(CO)	2 102(sh)	(1)	2 072
	2 099		1 998
	2 097(sh)		1 994
			1 934 [a]
ν(CO)	2 028		1 930
	2 026		1 731
	2 023		1 727
	2 021		
	2 017	(2)	2 056
			[b]
ν(CO)	1 983		1 964
	1 979		1 961
			[b]
	(1 951)		
	(1 947)	(3)	2 012
			2 010
ν(NO)	1 773		1 966
	1 768		1 460
	1 763		
		(4)	1 991 [c]
			1 934 [a]
			1 701 [c]
			1 697 [c]
		Others:	1 986
			1 952
			1 912
			1 891
			1 673

[a] This absorption behaves anomalously on u.v. photolysis and seems to result from overlap of two bands (see text). [b] One carbonyl and one nitrosyl band of (2) are apparently obscured by other bands at *ca.* 1 990 and *ca.* 1 730 cm^{-1}. [c] Grew on u.v. photolysis and was readily destroyed by annealing or long-wavelength photolysis.

TABLE 3

Positions (cm^{-1}) of bands observed between 2 500 and 650 cm^{-1} in experiments with $[Mn(CO)_4(NO)]$ isolated in pure nitrogen matrices

	$[Mn(CO)_4(NO)]$		$[Mn(CO)_3(N_2)(NO)]$		$[Mn(CO)_2(N_2)_2(NO)]$
		ν(NN)	2 264	ν(NN)	[a]
ν(CO)	2 102				
	2 098	ν(CO)	2 063	ν(NN)	[a]
ν(CO)	2 037	ν(CO)	2 004		
	2 034		2 000	ν(CO)	*ca.* 2 020 [b]
	2 032				
	2 030	ν(CO)	1 969	ν(CO)	1 950
	2 020		1 965		1 946
ν(CO)	1 980	ν(NO)	1 757	ν(NO)	1 739
	1 978		1 754		1 732
			1 751		1 728
ν(NO)	1 778		1 748		
	1 774				
	1 772				
	1 767				

[a] Too weak to be observed. [b] Coincident with a parent band which behaves anomalously during forward photolysis.

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[10] B. A. Frenz, J. H. Enemark, and J. A. Ibers, *Inorg. Chem.*, 1969, **8**, 1288.

[11] P. M. Treichel, E. Pitcher, R. B. King, and F. G. A. Stone, *J. Amer. Chem. Soc.*, 1961, **83**, 2593; I. S. Butler and G. Barna, *Canad. Spectroscopy*, 1972, **17**, 2.

matrix (increasing the temperature to 30 K, by applying a back pressure to the liquid-hydrogen reservoir, for a few minutes and then cooling to 20 K before recording a spectrum) most of the product peaks decrease in intensity to varying extents and the [Mn(CO)$_4$(NO)] bands grow [Figure 1(*c*)], indicating that the effects of photolysis are at least partially, reversible thermally.

In other experiments (not illustrated) the effects of photolysis using various filters were examined. Forward photolysis using filter A caused some of the original product bands to grow while long-wavelength photolysis using filter B selectively reconverts some of the species responsible for these bands into [Mn(CO)$_4$(NO)]. Further photolysis using filter C caused further regeneration of [Mn(CO)$_4$(NO)] at the expense of a different set of product bands while, at the same time, weak bands also grew at 2 017, 1 972, and 1 465 cm^{-1}.

As was noted by Poliakoff,[7] prolonged photolysis (>1 h) with an unfiltered mercury lamp produces a large number of bands, some of which apparently correspond to bands observed after short periods of photolysis. Table 1 lists the positions of bands appearing during experiments with [Mn(CO)$_4$(NO)] in argon matrices as a result of both short and long periods of photolysis, together with notes on their behaviour when the matrices were subsequently annealed or photolysed.

Despite the complexity of these results, it is possible to reach some definite conclusions about the behaviour of [Mn(CO)$_4$(NO)] in argon matrices, at least for short photolysis times. Depending on their behaviour, the bands appearing during short periods of photolysis may be divided into four principal groups [labelled (*a*), (*e*), (*f*), and others in Table 1]. Apart from those in group (*f*), which will be discussed in the section dealing with methane-matrix experiments, all the bands increase in intensity with liberation of CO on u.v. photolysis and the products responsible for them can be at least partially reconverted into [Mn(CO)$_4$(NO)] on annealing or by longer-wavelength photolysis. In view of the high dilution and hence the low probability of aggregate formation, this behaviour implies the presence of a number of co-ordinatively unsaturated mononuclear fragments.

The bands in group (*a*) [2 072, 1 994, 1 939, 1 734 (sh), and 1 732 cm^{-1}] increase and decrease together under a variety of conditions and therefore probably belong to a single molecular species (1). These bands may be assigned as three terminal carbonyl and one (split) nitrosyl fundamentals as expected for a low-symmetry [Mn(CO)$_3$(NO)] species and in agreement with one of the products assigned by Rest {[Mn(CO)$_3$(NO)]: ν(CO) at 2 072, 1 994, and 1 932 cm^{-1}; ν(NO) at 1 733 cm^{-1}}.[6]

The second group of bands (*e*) may also be assigned as four fundamentals belonging to a single molecular species (2) (*i.e.* 2 060 cm^{-1}; 1 998 and 1 996 cm^{-1}; 1 969, 1 966, and 1 963 cm^{-1}; and 1 737 cm^{-1}), and if this is so the previous assignment [6] of bands at 1 999, 1 967, and 1 739 cm^{-1} is incorrect. Loss of a further CO ligand from [Mn(CO)$_3$(NO)] should produce a species with a much lower nitrosyl absorption than 1 737 cm^{-1}, and indeed the position and behaviour of the very weak band (*g*) at 1 712 cm^{-1} is much more consistent with assignment as [Mn(CO)$_2$(NO)] (see next section). With three terminal carbonyl and one terminal nitrosyl fundamentals, (2) is thus probably also [Mn(CO)$_3$(NO)], differing in structure from (1) above.

Photolysis of [Mn(CO)$_4$(NO)] *in methane matrices*. Photolysis of [Fe(CO)$_5$] in methane matrices results in enhanced yields of lower fragments, *e.g.* [Fe(CO)$_3$],[12] as well as evidence for [Fe(CO)$_4 \cdots$ CH$_4$].[7,13] Similar experiments were undertaken with [Mn(CO)$_4$(NO)] in methane matrices to help with characterisation of lower fragments such as [Mn(CO)$_2$(NO)] and [Mn(CO)(NO)].

Infrared spectra from an experiment with [Mn(CO)$_4$(NO)] isolated at high dilution in methane matrices are illustrated in Figures 2 and 3. As in argon, the low-resolution spectrum [Figure 2(*a*)] shows four bands in the 1 400—2 100 cm^{-1} region, although the detailed high-resolution pattern is different (Table 2). Photolysis with filter C produces the spectrum shown in Figure 2(*b*) in which some of the bands (2 072, 1 998, 1 994, 1 934, 1 731, and 1 727 cm^{-1}) correspond closely to those observed in argon which were attributed to [Mn(CO)$_3$(NO)] (1).

The remaining product bands in Figure 2(*b*) at 2 010 and 1 966 cm^{-1} as well as one at 1 460 cm^{-1} (weak; not illustrated) resemble those observed at 2 017, 1 972, and 1 465 cm^{-1} in argon experiments [group (*f*) in Table 1], implying the formation in both matrices of a species (3) with several unusual properties: (*i*) one of its bands is at rather low frequency for a terminal nitrosyl ligand; (*ii*) growth and decay of (3) on photolysis does not seem to be associated with corresponding changes in the intensity of the absorption due to free CO; and (*iii*) in both matrices, (3) is produced by visible light and destroyed by u.v. light. These features are quite consistent with the behaviour of other mononuclear species detected following photolysis of [Ni(η-C$_5$H$_5$)(NO)] [ν(NO) at 1 390 cm^{-1}] [14] and [Mn(CO)(NO)$_3$] [ν(NO) at 1 505 cm^{-1}].[15] The most satisfactory explanation for these low-wavenumber bands, which shift appropriately on ^{15}NO substitution, is that photoelectron transfer from the metal to the nitrosyl ligand has taken place. In this case the species (3) formed from [Mn(CO)$_4$(NO)] without loss of CO may be formulated as [Mn(CO)$_4$(NO*)] where NO* denotes a terminal nitrosyl ligand with an altered co-ordination mode.

The effects of further photolysis using filter A (principally u.v. light) are illustrated in Figure 2(*c*). The absorptions due to (3) have decreased in intensity while bands corresponding to those of species (2), and in particular (1), in argon experiments have grown. There are two important differences between this spectrum and its argon counterparts: (*a*) although the absorptions at

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[12] M. Poliakoff, *J.C.S. Dalton*, 1974, 210.

[13] M. Poliakoff and J. J. Turner, *J.C.S. Dalton*, 1974, 2276.

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

[15] O. Crichton and A. J. Rest, preceding paper.

1 934 and 1 930 cm^{-1} apparently correspond to the band of (1) at 1 939 cm^{-1} in argon, the component at 1 934 cm^{-1} is anomalously intense (see below); (*b*) the strong nitrosyl band at 1 701 and 1 697 cm^{-1} and the weak band at 1 673 cm^{-1} now present imply that CO loss proceeds further in methane than in argon.

Further photolysis with the unfiltered mercury lamp [Figure 3(*a*)] causes most product bands to grow but most striking of all is that the band at 1 934 cm^{-1} becomes the most intense in the spectrum. At the same time the nitrosyl band at 1 701 and 1 697 cm^{-1} becomes nearly as intense as the nitrosyl band of the primary product (1 731 and 1 727 cm^{-1}) and a weak absorption at 1 991 cm^{-1} becomes stronger. Annealing the matrix at this stage [Figure 3(*b*)] causes the absorptions at 1 991, 1 934, 1 701, and 1 697 cm^{-1} to decrease greatly, while the remaining bands of [Mn(CO)$_3$(NO)] (1) and those of [Mn(CO)$_4$(NO)] increase in intensity. Long-wavelength photolysis [filter D; Figure 3(*c*)] results in more regeneration of [Mn(CO)$_4$(NO)] at the expense of all the product bands.

The related behaviour of the bands at 1 991, 1 701, and 1 697 cm^{-1} implies that they belong to a single molecular species (4) which evidently also absorbs at 1 934 cm^{-1}, accounting for the anomalous behaviour of the 1 934-cm^{-1} component of this band of [Mn(CO)$_3$(NO)] (1) in methane compared with the argon counterpart. The behaviour of (4), both on long-wavelength photolysis and on annealing, when [Mn(CO)$_3$(NO)] (1) is formed as well as [Mn(CO)$_4$(NO)], suggests that it is the lower fragment [Mn(CO)$_2$(NO)]. The steady shift to lower wavenumbers of the nitrosyl vibration as more CO ligands are removed {[Mn(CO)$_4$(NO)], ν(NO) at *ca.* 1 768 cm^{-1}; [Mn(CO)$_3$(NO)], ν(NO) at *ca.* 1 730 cm^{-1}; [Mn(CO)$_2$(NO)], ν(NO) at 1 700 cm^{-1}} suggests that the weak band at 1 673 cm^{-1}, which appears on photolysis with the unfiltered mercury lamp, may be due to [Mn(CO)(NO)].

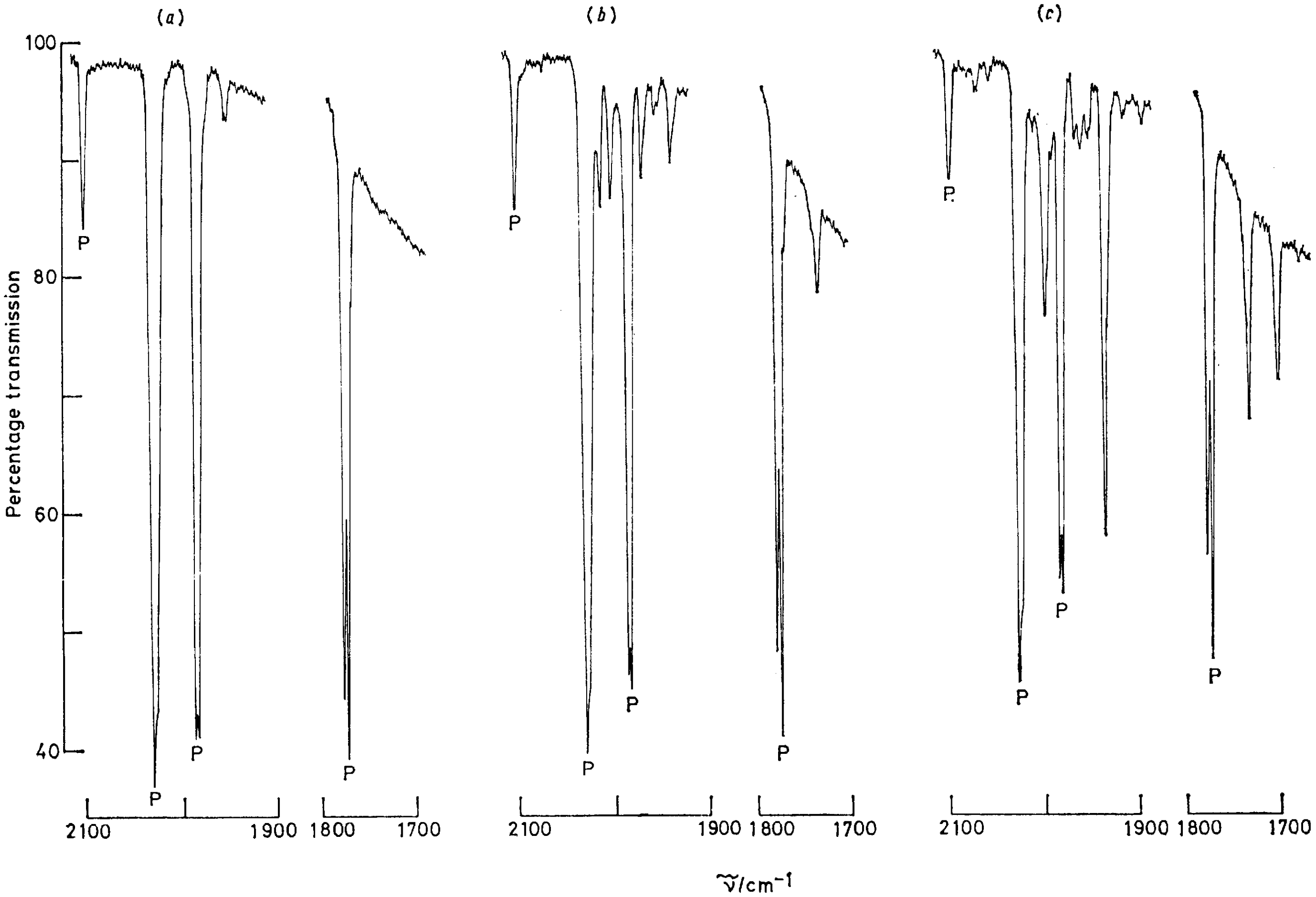

FIGURE 2 Infrared spectra from an experiment with [Mn(CO)$_4$(NO)] (bands marked P) isolated in a methane matrix: (*a*) after deposition; (*b*) after 10-min photolysis with filter C; (*c*) after photolysis for another 10 min with filter A

Comparison of band positions in argon and methane matrices (Tables 1 and 2 respectively) reveals variable small shifts in band positions, generally to lower wavenumber in methane. It seems more likely that these shifts (usually less than 5 cm^{-1} except for nitrosyl vibrations) are due to non-specific 'solvation' rather than to formation of discrete methane complexes because, relative to [Fe(CO)$_4$], the spectrum of [Fe(CO)$_4$ $\cdots$ CH$_4$] showed much greater changes with band shifts of up to 16 cm^{-1}.[13]

Photolysis of [Mn(CO)$_4$(NO)] *in nitrogen matrices.** Infrared spectra from an experiment with [Mn(CO)$_4$(NO)] isolated at high dilution in a pure nitrogen matrix are illustrated in Figure 4. As in argon and methane matrices, the spectrum of [Mn(CO)$_4$(NO)] includes four strong bands at high wavenumber [Figure 4(*a*)], although the broadness and extensive splitting of the band between 2 040 and 2 020 cm^{-1} (Table 3) is quite consistent with the presence of two distinct fundamentals.[16]

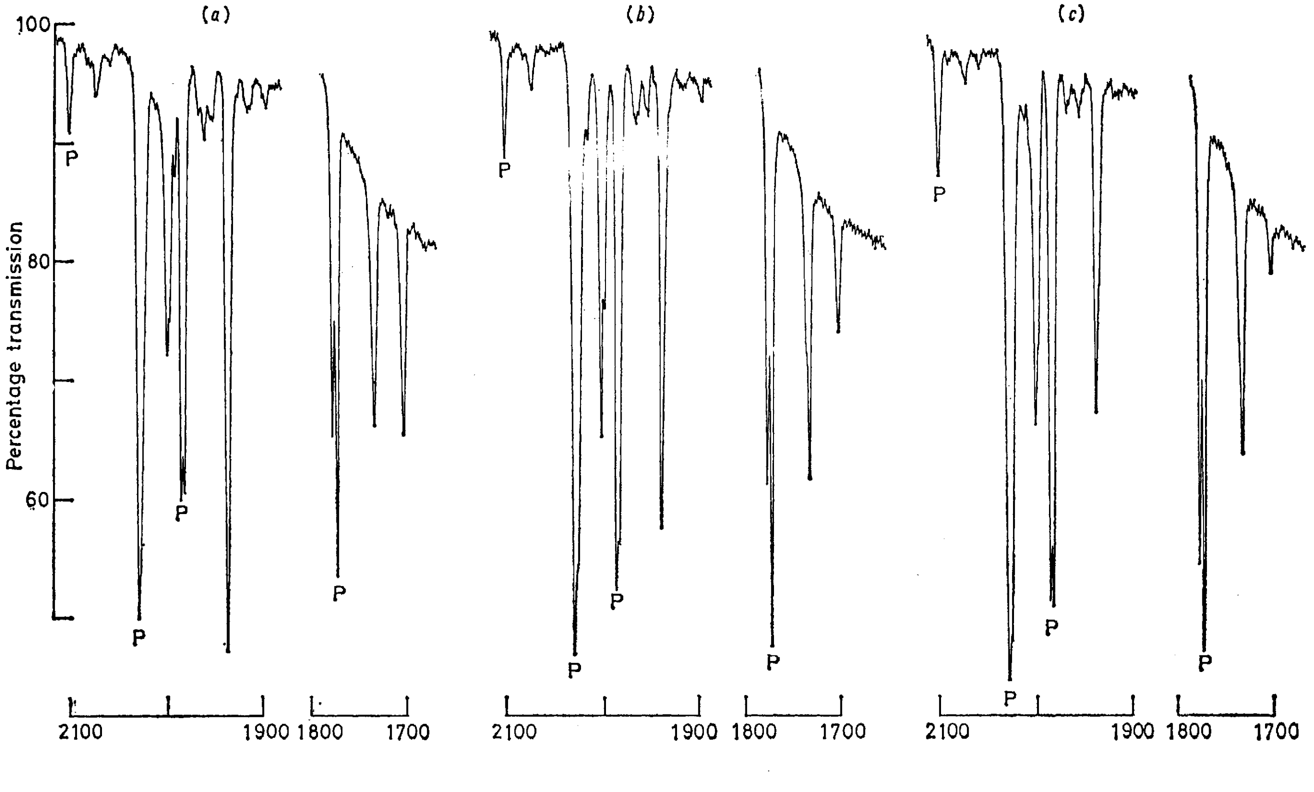

FIGURE 3 Further i.r. spectra from the same experiment as in Figure 2 with [Mn(CO)$_4$(NO)] (bands marked P) isolated in a methane matrix: (*a*) after 5-min photolysis with the unfiltered mercury lamp; (*b*) after annealing the matrix from stage (*a*); (*c*) after photolysis for another 20 min with filter D

Photolysis with visible light (filter E) causes four new bands of significant intensity [labelled Y in Figure 4(*b*)] to appear together with an absorption due to liberated CO (not illustrated). Exposure to the unfiltered mercury lamp, even for a short period of time, causes marked changes in the spectrum [Figure 4(*c*)]. In addition to the increasing intensity of bands Y and that of free CO, a large number of other product absorptions have appeared and there has been a considerable decrease in the total integrated intensity of the bands in the 'carbonyl' region (1 900—2 150 cm^{-1}). At this stage in the experiment several very weak bands above 2 150 cm^{-1} (not illustrated) were present which may be assigned to co-ordinated N$_2$.[17]

In other experiments (not illustrated) photolysis using u.v. and visible light produced a spectrum in which both bands Y, and a second set [labelled Z in Figure 4(*c*)] were reasonably strong and a weak band was present at 2 264 cm^{-1}. Further photolysis with visible radiation (filter E) causes regeneration of [Mn(CO)$_4$(NO)] at the expense of bands Z but there was little change in bands Y or the band at 2 264 cm^{-1}; photolysis with the unfiltered mercury lamp then caused both sets of bands to increase again at the expense of [Mn(CO)$_4$(NO)].

The behaviour described above indicates that two principal product species are formed. The major product (5), produced both by u.v. photolysis and by visible light, has three terminal carbonyl bands as well as bands due to co-ordinated NO and N$_2$ and hence must be [Mn(CO)$_3$(N$_2$)(NO)] (Table 3). Only two bands (at 1 950 and 1 946 and 1 739, 1 732, and 1 728 cm^{-1}) can be definitely assigned to the second principal product (6), but this species probably also has weak high-wavenumber absorptions [ν(NN)] and is probably also responsible for the peculiar behaviour of the [Mn(CO)$_4$(NO)] absorption at 2 020 cm^{-1} [marked with an asterisk in Figure 4(*b*) and (*c*)] which does not decrease in intensity to the same extent as the other parent bands. Species (6) may be either [Mn(CO)$_2$(N$_2$)(NO)] or [Mn(CO)$_2$(N$_2$)$_2$(NO)] but the latter is more probable because: (*i*) it

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* No germanium filter was used in these experiments so that the formation of co-ordinatively unsaturated fragments is very unlikely.

[16] A. J. Rest and D. J. Taylor, *J.C.S. Chem. Comm.*, 1977, 717.

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

is stable to radiation from the Nernst glowbar of the i.r. spectrometer whereas co-ordinatively unsaturated species in argon and methane matrices took up CO in the absence of the germanium filter; (*ii*) the shift of its nitrosyl band compared to that of $[Mn(CO)_3(N_2)(NO)]$ (20 cm^{-1}) is more consistent with the replacement of a CO ligand by N_2 as in $[Mn(CO)_4(NO)] \longrightarrow [Mn(CO)_3(N_2)(NO)]$ (Table 3) rather than the 30 cm^{-1} shift for $[Mn(CO)_3(NO)] \longrightarrow [Mn(CO)_2(NO)]$ (Table 2).

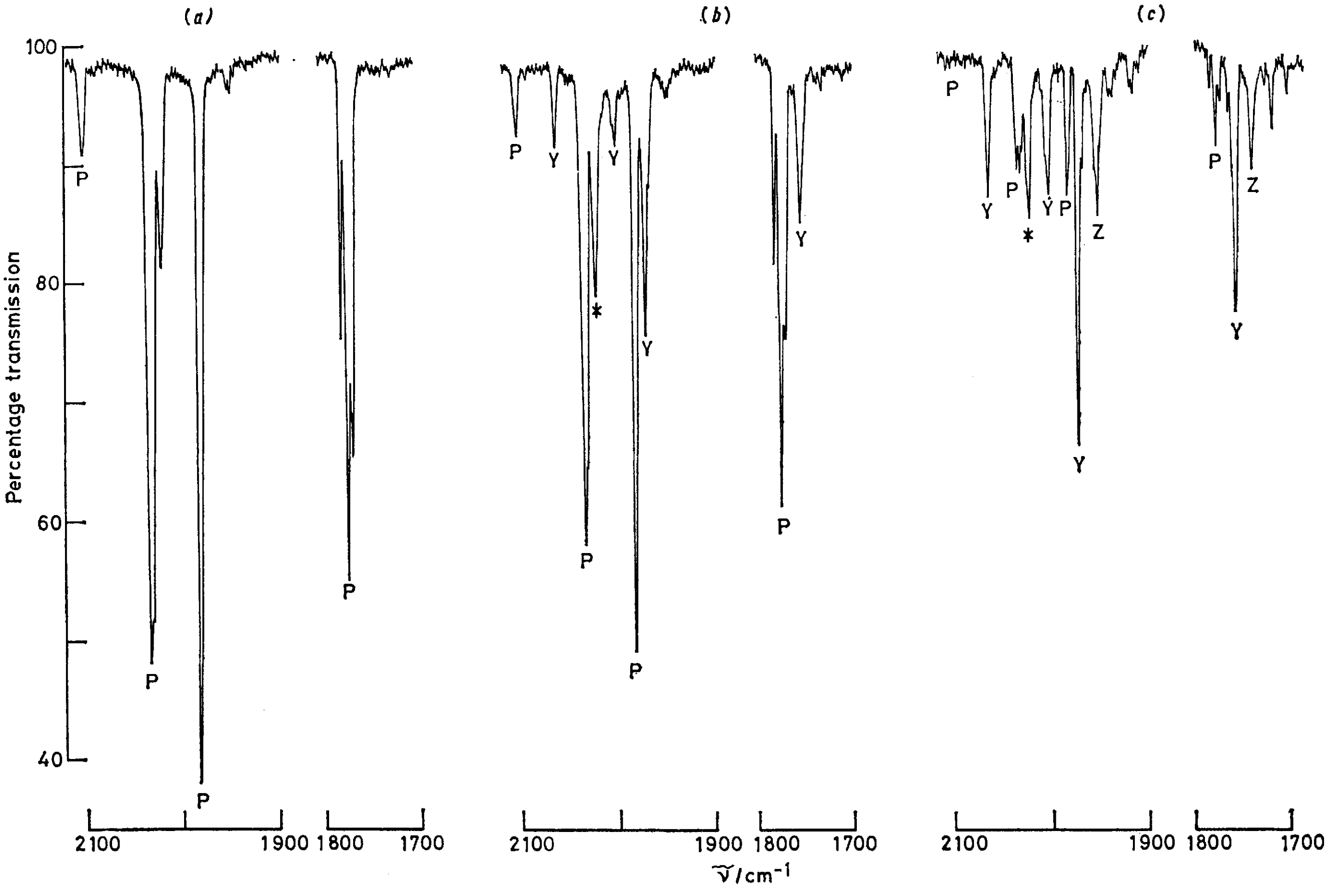
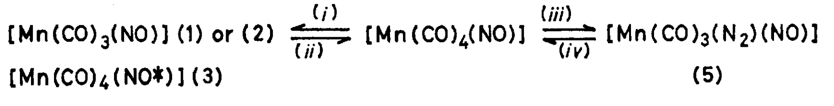


FIGURE 4 Infrared spectra from an experiment with $[Mn(CO)_4(NO)]$ (bands marked P) isolated in a pure nitrogen matrix: (*a*) after deposition; (*b*) after 30-min photolysis with filter E; (*c*) after photolysis for another 5 min with the unfiltered mercury lamp. For an explanation of bands marked *, Y, and Z see text

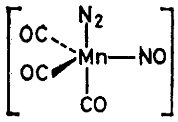
The succession of nitrosyl bands produced by photolysis with the unfiltered mercury lamp [Figure 4(*c*)] indicates that further substitution of CO by N_2 can take place, but although bands were visible in the 2 150—2 300 cm^{-1} region they were too weak for satisfactory correlation with lower-wavenumber bands.

Structural and Mechanistic Conclusions.—The results presented show that photochemical CO ejection proceeds readily in argon and methane matrices to give co-ordinatively unsaturated $[Mn(CO)_3(NO)]$, evidently in two structural modifications, and in methane matrices further loss of CO produces $[Mn(CO)_2(NO)]$ and possibly $[Mn(CO)(NO)]$. In both matrices another species, $[Mn(CO)_4(NO^*)]$, is formed without loss of any ligand but with a very low value of ν(NO). Photochemical CO substitution also occurs readily in nitrogen matrices giving high yields of $[Mn(CO)_3(N_2)(NO)]$ in addition to smaller amounts of more highly substituted species. The principal reactions of $[Mn(CO)_4(NO)]$ in matrices are summarised in Scheme 3.



SCHEME 3 (*i*) Argon on methane, *h*ν; (*ii*) *h*ν′ or annealing; (*iii*) nitrogen, *h*ν; (*iv*) *h*ν″

The disappointingly low yields of $[Mn(CO)_4(NO^*)]$ obtained preclude firm structural conclusions, although it seems reasonable to speculate that the low value of ν(NO) is a consequence of increased electron density on the nitrosyl ligand and is presumably associated with bending of the M–N–O linkage.[18] The geometry of the $[Mn(CO)_3(NO)]$ fragment in (1), (2), and (5) can only be definitely established by ^{13}CO enrichment, but in view of the complexity of the spectra, even of the naturally abundant species, and the low symmetry of the products, mixed-isotope experiments may be exceedingly difficult to interpret. The species $[Mn(CO)_3(N_2)(NO)]$ (5) actually has a very similar spectrum to a model compound {$[Mn(CO)_3(CH_3OPF_2)(NO)]$: ν(CO) at 2 064m, 2 005m, and 1 960s cm^{-1} in hexane[19] with an axial CH_3OPF_2 ligand and an equatorial NO ligand in a trigonal-bipyramidal structure} and may have a similar structure (I). The two spectroscopically distinguishable forms of $[Mn(CO)_3(NO)]$, (1) and (2), may arise from the existence of both singlet and triplet states. {The isoelectronic tetracarbonyl $[Fe(CO)_4]$ has been observed only in a C_{2v} structure[15] which is consistent with theoretical predictions for a triplet state.[20]}



(I)

The results of experiments with $[Mn(CO)_4(NO)]$ in argon and methane matrices are particularly interesting because of their direct relation to photochemical substitution studies. The ϕ_1 path (Scheme 2), involving an intermediate (C) which reacts indiscriminately with an entering ligand (L) and which is proposed[2] to be co-ordinatively unsaturated, is supported by identification of (1) and (2). [Although (1) seems to be the favoured modification under matrix conditions, it is not possible to say which form is thermodynamically more stable.] The ϕ_2 path involves an intermediate (D) which is quite stable in the dark; *e.g.* with L = PPh_3 the intermediate has a half-life of minutes at 20 °C.[2] Electron transfer from metal to nitrosyl would leave the metal relatively electron deficient and susceptible to attack by a good nucleophile, *e.g.* PPh_3. The isolation of $[Mn(CO)_4(NO^*)]$ (3), which has a very low value of ν(NO) (at *ca.* 1 460 cm^{-1}) supports formulation of (D) as the co-ordinatively expanded species $[Mn(CO)_4(NO^*)L]$ with the nitrosyl ligand acting formally as a one- instead of a three-electron donor as in $[Mn(CO)_4(NO)]$. One might thus expect formation of $[Mn(CO)_4(N_2)(NO^*)]$ in experiments in nitrogen matrices, but since this species may well be sensitive to long-wavelength radiation (*e.g.* from a Nernst source) it may only be observed in experiments with a germanium filter. Alternatively, it is conceivable that (3) (formed by irradiation with $350 < \lambda < 510$ nm) is actually the species $[Mn(CO)_4(NO)]^*$ in Scheme 2.

The formation of (1) and (2) also gives strong support to participation of species (A) in the thermal reactions of $[Mn(CO)_4(NO)]$ (Scheme 1). It is possible that (B) in the non-dissociative path is produced by slow reaction of an entering ligand with a low equilibrium concentration of $[Mn(CO)_4(NO^*)]$ formed by rapid thermal rearrangement of $[Mn(CO)_4(NO)]$. A more likely mechanism resulting in second-order kinetics involves formation of $[Mn(CO)_4(NO^*)L]$ by a genuine associative process (k_2 path) in which incorporation of L and electron transfer are simultaneous.

Future work will attempt to determine the geometry of $[Mn(CO)_3(NO)]$, $[Mn(CO)_4(NO^*)]$, and $[Mn(CO)_3(N_2)(NO)]$ species by ^{13}CO incorporation and will also seek to isolate $[Mn(CO)_4(NO^*)L]$ (L = CO or N_2) species.

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