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Manganese Carbonyl Nitrosyls: Comparison with Isoelectronic Iron Carbonyl Derivatives

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The manganese carbonyl nitrosyls $Mn(NO)(CO)_4$, $Mn_2(NO)_2(CO)_n$ ($n = 7, 6, 5, 4$), and $Mn_3(NO)_3(CO)_9$ have been studied by density functional theory (DFT) using the B3LYP and BP86 methods for comparison of their predicted structures with those of isoelectronic iron carbonyl derivatives. DFT predicts a trigonal bipyramidal structure for $Mn(NO)(CO)_4$ with an equatorial NO group very close to the experimental structure. The predicted lowest energy structure for $Mn_2(NO)_2(CO)_7$ has two bridging NO groups in contrast to the known structure of the isoelectronic $Fe_2(CO)_9$, which has three bridging CO groups. The structures for the unsaturated binuclear $Mn_2(NO)_2(CO)_n$ ($n = 6, 5, 4$) derivatives are similar to those of the corresponding binuclear iron carbonyls $Fe_2(CO)_{n+2}$ derivatives but always with a preference of bridging NO groups over bridging CO groups. The trinuclear $Mn_3(NO)_3(CO)_9$ is predicted to have a structure analogous to the known structure for $Fe_3(CO)_{12}$ but with two bridging NO groups rather than two bridging CO groups across one of the metal–metal edges of the M_3 triangle. The dark red solid photolysis product of $Mn(NO)(CO)_4$ characterized by its $\nu(CO)$ and $\nu(NO)$ frequencies ~45 years ago is suggested by these DFT studies not to be the originally assumed $Mn_2(NO)_2(CO)_7$ analogous to $Fe_2(CO)_9$. Instead, this photolysis product appears to be $Mn_2(NO)_2(CO)_5$ with a Mn≡Mn formal triple bond analogous to $(\eta^5\text{-}C_5H_5)_2V_2(CO)_5$ obtained from the photolysis of $(\eta^5\text{-}C_5H_5)V(CO)_4$.

1. Introduction

A number of metal carbonyl nitrosyls are known which are isoelectronic with homoleptic metal carbonyl derivatives, particularly for the less oxophilic transition metals with at least six valence electrons. Thus, the compounds in the sequence $Co(NO)(CO)_3 \rightarrow Fe(NO)_2(CO)_2 \rightarrow Mn(NO)_3CO \rightarrow Cr(NO)_4$ are all tetrahedral molecules isoelectronic and isostructural with $Ni(CO)_4$ obtained by successively substituting NO groups for CO groups with reduction of the atomic number of the central metal atom by one for each NO → CO substitution to maintain the same number of total electrons. A less extensive series, $Mn(NO)(CO)_4 \rightarrow Cr(NO)_2(CO)_3$, is known to be isoelectronic with $Fe(CO)_5$. In all cases, the NO groups are linear three-electron donors rather than bent one-electron donors.[1,2]

The series of metal carbonyl nitrosyls isoelectronic with $Fe(CO)_5$ is particularly interesting since the stable homoleptic carbonyls of iron include not only $Fe(CO)_5$ but also $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$. Furthermore, $Mn(NO)(CO)_4$, isoelectronic with $Fe(CO)_5$, is a stable compound, first prepared in 1961 by nitrosylation of $HMn(CO)_5$ with *N*-nitroso-*N*-methyl-*p*-toluenesulfonamide (Diazald).[3] A subsequent low-temperature (−110 °C) crystallographic study[4] on $Mn(NO)(CO)_4$ showed a trigonal bipyramidal structure analogous to the known structure of $Fe(CO)_5$. The NO group occupies one of the equatorial positions of the trigonal bipyramid, reducing the actual symmetry of the trigonal bipyramid from the ideal D_{3h} to C_{2v}.

Manganese carbonyl nitrosyl analogues of the other stable iron carbonyls, namely $Mn_2(NO)_2(CO)_7$ analogous to $Fe_2(CO)_9$ and $Mn_3(NO)_3(CO)_9$ analogous to $Fe_3(CO)_{12}$, have not

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yet been characterized. However, in 1961 the original discoverers[3] of $Mn(NO)(CO)_4$ photolyzed it in an attempt to prepare $Mn_2(NO)_2(CO)_7$ analogous to the well-known irradiation of $Fe(CO)_5$ to give $Fe_2(CO)_9$. The product was a "very air-sensitive" deep red solid, assumed to be $Mn_2(NO)_2(CO)_7$ by analogy with iron carbonyl chemistry. However, this product was not obtained pure and was characterized only by its ν(CO) and ν(NO) frequencies with no analytical data or structural information. As far as can be determined, no subsequent work has been done on this substance in the 45 years since this report, so that its identity remains obscure.

This paper describes the use of density functional theory (DFT) to examine possible structures for mononuclear, binuclear, and trinuclear manganese carbonyl nitrosyls having one NO group per manganese atom, so that they are isoelectronic with homoleptic iron carbonyl derivatives. This work has the following more specific objectives:

(1)Prediction of the structures of $Mn_2(NO)_2(CO)_7$ analogous to $Fe_2(CO)_9$ and $Mn_3(NO)_3(CO)_9$ analogous to $Fe_3(CO)_{12}$.

(2)Comparing CO and NO groups as bridging groups in binuclear and trinuclear manganese carbonyl nitrosyls.

(3)Comparing unsaturated binuclear manganese carbonyl nitrosyls $Mn_2(NO)_2(CO)_n$ ($n = 6, 5, 4$) with the corresponding unsaturated homoleptic binuclear iron carbonyls $Fe_2(CO)_n$ ($n = 8, 7, 6$) studied previously.[5]

(4)Providing some clues as to the nature of the dark red solid obtained by photolysis of $Mn(NO)(CO)_4$.

Theoretical methods related to those used in this work are well-established in metal carbonyl chemistry.[6-13]

2. Theoretical Methods

For carbon, nitrogen, and oxygen, the double-ζ plus polarization (DZP) basis set used here (9s5p/4s2p) adds one set of pure spherical harmonic d functions with orbital exponents $\alpha_d(C) = 0.75$, $\alpha_d(N) = 0.80$, and $\alpha_d(O) = 0.85$ to the Huzinage−Dunning standard contracted DZ sets.[14,15] For Mn, in our loosely contracted DZP basis set, the Wachters' primitive set is used, but it is augmented by two sets of p functions and one set of d functions and contracted following Hood et al. and designated (14s11p6d/10s8p3d).[16,17] For $MnNO(CO)_4$, there are 199 contracted Gaussian basis functions. For the binuclear manganese carbonyl nitrosyls $Mn_2(NO)_2(CO)_7$, $Mn_2(NO)_2(CO)_6$, $Mn_2(NO)_2(CO)_5$, and $Mn_2(NO)_2(CO)_4$, there are 368, 338, 308, and 278 contracted Gaussian basis functions, respectively. For the trinuclear $Mn_3(NO)_3(CO)_9$, there are 507 contracted Gaussian basis functions.

Two DFT methods were used in this study. The first functional is the hybrid B3LYP method, which incorporates Becke's three-parameter exchange functional (B3)[18] with the Lee, Yang, and Parr (LYP) correlation functional.[19] The second approach is the BP86 method, which marries Becke's 1988 exchange functional (B)[20] with Perdew's 1986 correlation functional.[21] The geometries of all of the structures were fully optimized using both the DZP B3LYP and DZP BP86 methods. The vibrational frequencies were determined at the same levels by evaluating analytically the second derivatives of the energy with respect to the nuclear coordinates. The corresponding infrared intensities were evaluated analytically as well. All of the computations were carried out with the Gaussian 94 program[22] in which the fine grid (75, 302) is the default for evaluating integrals numerically and the tight (10^{-8} hartree) designation is the default for the energy convergence.

In the search for minima, low-magnitude imaginary vibrational frequencies are suspect because the numerical integration procedures used in existing DFT methods have significant limitations. Thus, an imaginary vibrational frequency of magnitude less than $100i$ cm^{-1} should imply that there is a minimum with energy very similar to that of the stationary point in question. In most cases, we do not follow the eigenvectors corresponding to imaginary frequencies less than $100i$ cm^{-1} in search of another minimum.[23]

The optimized geometries from these computations are depicted in Figures 1−6 with all bond distances given in angstroms.

3. Results and Discussion

3.1. Molecular Structures. 3.1.1 $Mn(NO)(CO)_4$. Our DFT theory studies predict two trigonal bipyramidal structures for $Mn(NO)(CO)_4$ (Figure 1 and Table 1). Both structures are genuine minima without any imaginary frequencies and have linear Mn−C−O and Mn−N−O bonds. In the more stable structure, **Ia**, the NO group is in an equatorial position of the trigonal bipyramid corresponding to the structure found experimentally.[4] The alternative C_{3v} structure, **Ib**, with the NO group in an axial position of the trigonal bipyramid, lies 11.1 (B3LYP) or 9.1 kcal/mol (BP86) above **Ia**. The calculated bond lengths for structure **Ia** agree within ±0.03 Å with those found experimentally for $Mn(NO)(CO)_4$ except for the calculated Mn−N bond distance, which is about 0.1 Å longer than the experimental value.

3.1.2. $Mn_2(NO)_2(CO)_7$. The global minimum structure **IIa** of $Mn_2(NO)_2(CO)_7$ (Figure 2 and Table 2) has C_s symmetry and two bridging NO groups. A C_2 isomer, **IIb**, of $Mn_2(NO)_2(CO)_7$ lies above **IIa** by 16.2 (B3LYP) or 6.7 kcal/mol (BP86). Both isomers have real harmonic vibrational frequencies. The Mn−Mn bond distances of 2.671 (B3LYP) or 2.644 Å (BP86) in **IIa** and 2.778 (B3LYP) or 2.725 Å (BP86) in **IIb** are reasonable for the single bonds required by the 18-electron rule assuming the bridging NO groups and linear terminal NO groups to be three-electron donors. An attempt to optimize a tribridged structure for $Mn_2(NO)_2$-

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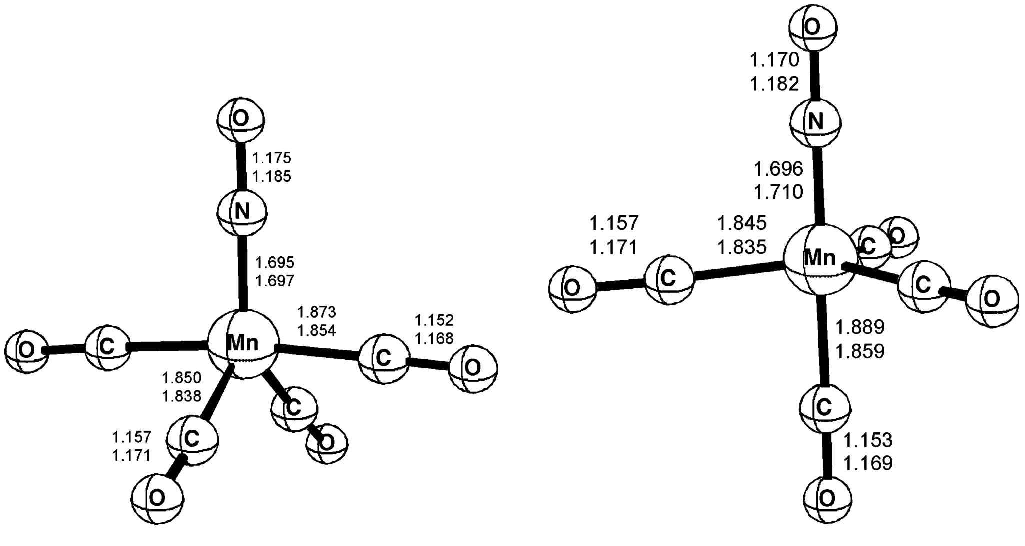


Ia (C_{2v}) **Ib** (C_{3v})

Figure 1. Optimized geometries for $Mn(NO)(CO)_4$.

Table 1. Bond Distances (in Å), Total Energies (E in Hartree), and Relative Energies (ΔE in kcal/mol) for $Mn(NO)(CO)_4$

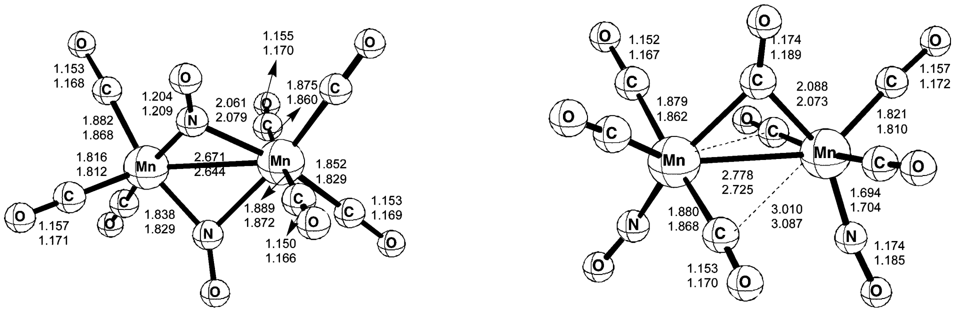
	Ia (C_{2v})		**Ib** (C_{3v})		
	B3LYP	BP86	B3LYP	BP86	exptl[4]
M−N/C(ax)	1.695/1.850	1.697/1.838	1.696/1.889	1.710/1.859	1.797/1.886
N−O(ax)	1.175	1.185	1.170	1.182	1.152
C−O(ax)	1.157	1.171	1.153	1.169	1.167
M−C(eq)	1.873	1.854	1.845	1.835	1.851
C−O(eq)	1.152	1.168	1.157	1.171	1.135
M−N/C−O(ax)	180.0/179.1	180.0/178.4	180.0	180.0	180.0
M−C−O(eq)	176.7	177.8	178.0	178.4	179.3
N−M−C	93.6/124.5	97.7/121.0	94.6	95.4	90.2/120.6
$-E$	1734.45331	1734.70919	1734.43565	1734.69469	
ΔE	0.0	0.0	11.08	9.10	
imaginary frequencies	none	none	none	none	

$(CO)_7$ analogous to the known structure for the isoelectronic $Fe_2(CO)_9$ led instead to **IIb** with a single bridging CO group.

3.1.3. $Mn_2(NO)_2(CO)_6$. Four different structures were studied for $Mn_2(NO)_2(CO)_6$ (Figure 3 and Table 3). The C_{2v} structure, **IIIa**, with two bridging NO groups is the most stable and has only a very small imaginary vibrational frequency, namely $5i$ (B3LYP) or $4i$ (BP86) cm^{-1}, showing this structure to be a genuine minimum. The C_s structure, **IIIc**, with two bridging CO groups lies 24.1 (B3LYP) or 12.1 kcal/mol (BP86) higher in energy than structure **IIIa** with two bridging NO groups and has only a very small imaginary vibrational frequency ($5i$ cm^{-1}) by BP86 but a significant imaginary vibrational frequency of $161i$ by B3LYP (Table 3). The energy of the C_{2v} unbridged structure, **IIId**, is higher than that of either structure **IIIa** or structure **IIIc** at 27.7 (B3LYP) or 21.9 kcal/mol (BP86) above structure **IIIa**. The structure **IIId** has two imaginary frequencies, namely $55i$ and $22i$ (B3LYP) or $58i$ and $20i$ (BP86) cm^{-1}. Following the highest imaginary frequency of **IIId** leads to a completely unsymmetrical dibridged structure (**IIIb**) with one bridging NO group and one bridging CO group. The energy of structure **IIIb** is 20.3 (B3LYP) or 18.8 kcal/mol (BP86) lower than **IIId** but still 7.4 (B3LYP) or 4.0 kcal/mol (BP86) above the global minimum **IIIa**.

The manganese−manganese distances in all four isomers of $Mn_2(NO)_2(CO)_6$ can be interpreted to imply the Mn═Mn double bonds required to give both manganese atoms the favored 18-electron configurations. Thus, the Mn═Mn bonds in the dibridged isomers **IIIa**, **IIIb**, and **IIIc** fall in the range 2.48−2.55 Å. However, the Mn═Mn bond in the unbridged isomer **IIId** is significantly longer, namely 2.665 (B3LYP) or 2.635 Å (BP86), in accord with the previously observed effect of bridging CO (and presumably bridging NO) groups in shortening metal−metal bonds of a given order by 0.1−0.2 Å.

3.1.4. $Mn_2(NO)_2(CO)_5$. Two energetically low-lying $Mn_2(NO)_2(CO)_5$ isomers were found (Figure 4 and Table 4). Both isomers have C_s symmetry and small imaginary vibrational frequencies well below the $100i$ cm^{-1} threshold. Structure **IVa** has two semibridging NO groups, whereas structure **IVb** has a weakly semibridging CO group and an unusual bridging NO group bonding to one manganese atom (the "right" manganese atom) both through the nitrogen and oxygen atoms, as indicated by a relatively short Mn−O distance of



IIa (C_s) **IIb** (C_2)

Figure 2. Optimized geometries for the $Mn_2(NO)_2(CO)_7$ isomers.

Table 2. Bond Distances (in Å), Total Energies (E in Hartree), and Relative Energies (ΔE in kcal/mol) for $Mn_2(NO)_2(CO)_7$ Isomers

	IIa (C_s)		**IIb** (C_2)	
	B3LYP	BP86	B3LYP	BP86
Mn−Mn	2.671	2.644	2.778	2.725
Mn−C(bridge)	−	−	2.088	2.073
Mn−N(bridge)	2.061/1.838	2.079/1.829	−	−
Mn−N(terminal)	−	−	1.694	1.704
Mn−N−O	144.1/129.3	144.7/129.0	172.3	172.2
−E	−3355.54939	−3356.05204	3355.52353	3356.04137
ΔE	0.0	0.0	16.2	6.7
imaginary frequencies	none	none	none	none

2.172 (B3LYP) or 2.237 Å (BP86). The energies of the two $Mn_2(NO)_2(CO)_5$ isomers **IVa** and **IVb** are very similar so that the relative energies are method dependent. Thus, isomer **IVa** lies 1.7 kcal/mol below isomer **IVb** using the B3LYP method but 5.3 kcal/mol above **IVb** using the BP86 method. An attempt to optimize a structure for $Mn_2(NO)_2(CO)_5$ with two bridging CO groups led to structure **IVb**.

The metal−metal distances in the $Mn_2(NO)_2(CO)_5$ isomers **IVa** and **IVb** are consistent with the 18-electron rule. Thus, the manganese−manganese distance of 2.411 (B3LYP) or 2.372 Å (BP86) in **IVa** is consistent with the Mn≡Mn triple bond required to give both metal atoms the favored 18-electron configurations assuming the CO and NO groups to be the usual two- and three-electron donors, respectively. However, the unusual bridging η^2-μ-NO group in **IVb** can be considered to be a formal five-electron donor to the pair of metal atoms since it bonds to one of the metal atoms as a normal three-electron donor linear NO ligand and to the other metal atom through an electron pair from an N−O π bond. Therefore, in **IVb** only a Mn═Mn double bond is required to give both manganese atoms the 18-electron configurations in accord with the longer metal−metal distance of 2.638 (B3LYP) or 2.573 Å (BP86) in **IVb** relative to **IVa**. A similar five-electron donor bridging η^2-μ-NO group has previously been reported[24] in $[(\eta^5\text{-}C_5H_5)Mo(NO)(\mu\text{-}\eta^1\text{:}\eta^2\text{-}NO)(\mu\text{-}CHCMe_3)][(\eta^5\text{-}C_5H_5)Mo({=}CHCMe_3)]$.

3.1.5. $Mn_2(NO)_2(CO)_4$. Two optimized structures for $Mn_2(NO)_2(CO)_4$ were found (Figure 5 and Table 5). The global minimum, **Va**, has two bridging NO groups and no imaginary vibrational frequencies. The second $Mn_2(NO)_2(CO)_4$ isomer, **Vb**, lies 29.3 (B3LYP) or 19.7 kcal/mol (BP86) above the global minimum **Va**. An attempt to optimize a $Mn_2(NO)_2(CO)_4$ structure with bridging CO groups led to the unbridged structure **Vb**.

The metal−metal bond distance in the unbridged isomer, **Vb**, of $Mn_2(NO)_2(CO)_4$ is very short, namely 2.010 (B3LYP) or 2.035 Å (BP86), consistent with the Mn−Mn quadruple bond required to give both metal atoms the favored 18-electron configuration. The metal−metal bond distance of 2.450 (B3LYP) or 2.451 Å (BP86) in the lower energy $Mn_2(\mu\text{-}NO)_2(CO)_4$ isomer with two bridging NO groups (**Va**) corresponds to a Mn═Mn double bond when allowance is made for the metal−metal distance shortening effect of the two NO bridges. Since the Mn−O distances to the bridging NO groups of 2.612 (B3LYP) or 2.702 Å (BP86) are too long for these NO groups to serve as five-electron donors such as the bridging NO group in isomer **IVb** of $Mn_2(CO)_5(NO)_2$, the manganese atoms in **Va** each appear to have 16-electron configurations. This is consistent with the vacancy in the coordination sphere in each manganese atom trans to the bridging NO group.

3.1.6. $Mn_3(NO)_3(CO)_9$. The C_s structure **VIa** with a Mn_3 triangle bridged by two NO groups on one of its edges was found to be the most stable structure for $Mn_3(NO)_3(CO)_9$ without any imaginary vibrational frequencies (Figure 6 and Table 6). This structure is analogous to the experimentally known structure for $Fe_3(CO)_{12}$. The three Mn−Mn distances in **VIa** are consistent with the single bonds required to give each manganese atom in **VIa** the favored 18-electron rare gas configuration. The dibridged Mn−Mn bond distance in **VIa** is 2.500 (B3LYP) or 2.529 Å (BP86), which is shorter by 0.090 (B3LYP) or 0.043 Å (BP86) than the corresponding

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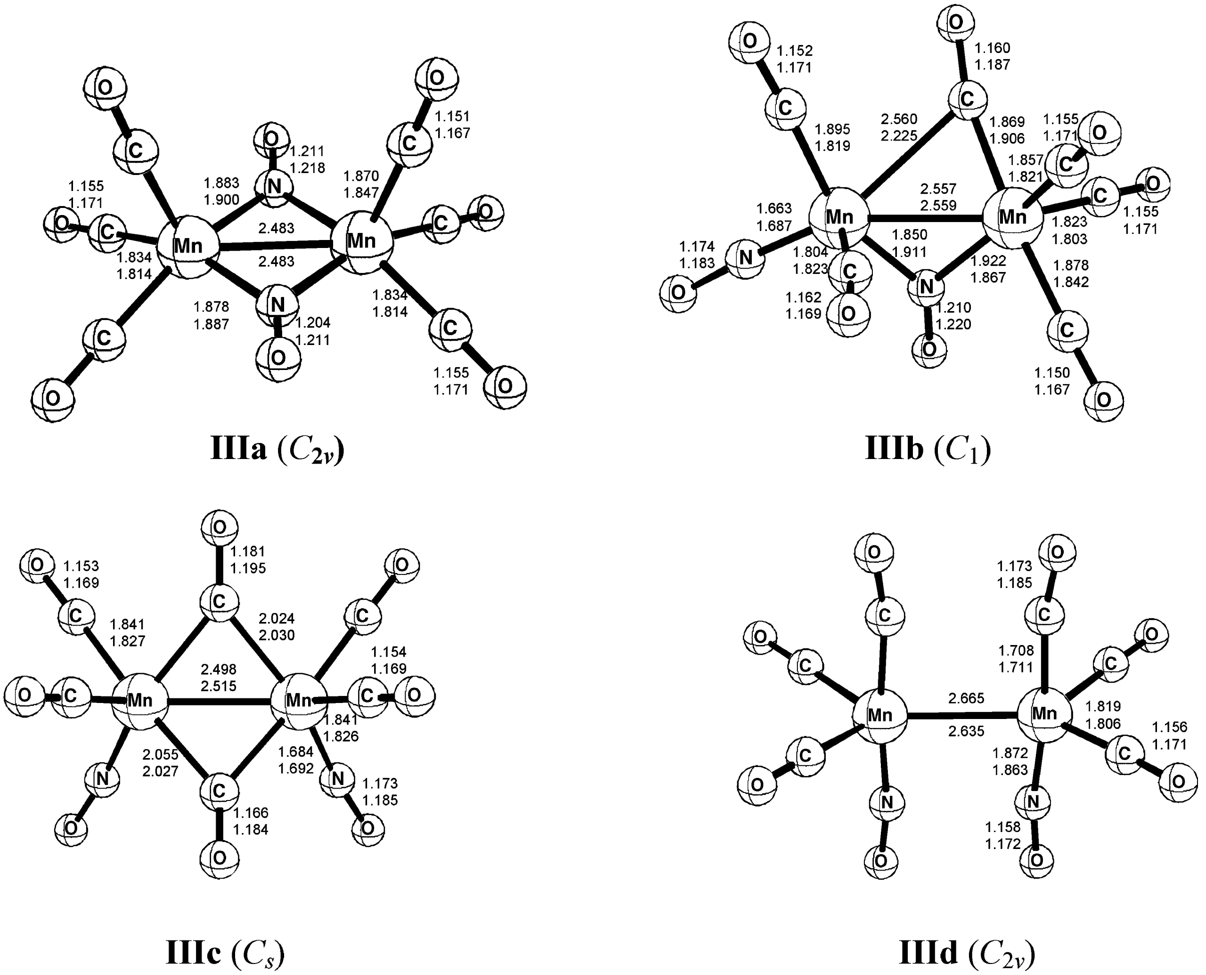


IIIa (C_{2v}) **IIIb** (C_1)

IIIc (C_s) **IIId** (C_{2v})

Figure 3. Optimized geometries for the $Mn_2(NO)_2(CO)_6$ isomers.

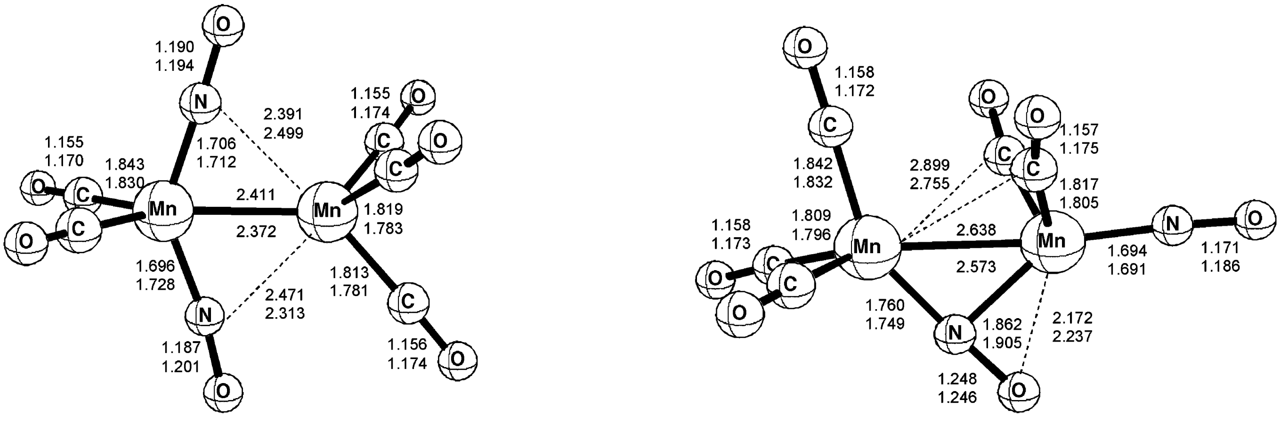
Table 3. Bond Distances (in Å), Total Energies (*E* in Hartree) and Relative Energies (Δ*E* in kcal/mol) for $Mn_2(NO)_2(CO)_6$ Isomers

	IIIa (C_{2v})		**IIIb** (C_1)		**IIIc** (C_s)		**IIId** (C_{2v})	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
Mn−Mn	2.483	2.483	2.557	2.559	2.498	2.515	2.665	2.635
Mn−C(bridge)	−	−	2.560 1.869	2.225 1.906	2.024 2.055	2.030 2.027	−	−
Mn−N(bridge)	1.883 1.878	1.900 1.887	1.850 1.922	1.911 1.867	−	−		
Mn−N(terminal)	−	−	1.663	1.687	1.684	1.692	1.872	1.863
Mn−N−O	138.8 138.6	139.2 138.9	138.9 171.2	133.9 173.5	174.1	174.7	170.5	170.4
−*E*	3242.18693	3242.68939	3242.17514	3242.68295	3242.14854	3242.67007	3242.14281	3242.65456
Δ*E*	0.0	0.0	7.4	4.0	24.1	12.1	27.7	21.9
imaginary frequencies	5*i*	4*i*	none	none	161*i*	5*i*	55*i*,22*i*	58*i*, 20*i*

dibridged Fe−Fe bond in $Fe_3(CO)_{12}$. The two unbridged Mn−Mn bond distances are significantly longer than the dibridged Mn−Mn distance, namely 2.998 and 2.918 Å (B3LYP) or 2.883 and 2.827 Å (BP86) in accord with the edge shortening expected for two bridging groups. These unbridged Mn−Mn distances in **VIa** are significantly longer than the corresponding unbridged Fe−Fe distances in $Fe_3(CO)_{12}$ by 0.262 and 0.182 Å (B3LYP) or 0.182 and 0.114 Å (BP86).

A C_s structure, **VIb**, was also found for $Mn_3(NO)_3(CO)_9$ with an NO bridge and two CO bridges in the trigonal Mn_3 plane at an energy of 11.1 (B3LYP) or 8.7 kcal/mol higher than that of **VIa**. The structure **VIb** is a genuine minimum with only real vibrational frequencies. The Mn−Mn bond distances are 2.821, 2.869, and 3.023 Å, corresponding to the Mn−Mn single bonds required for 18-electron configurations for each manganese atom. In addition, an unbridged structure, **VIc**, having essentially C_{3v} symmetry, was also found for $Mn_3(NO)_3(CO)_9$ at 11.4 (B3LYP) or 10.3 kcal/mol (BP86) above the global minimum, **VIa**. Structure **VIc** has small imaginary frequencies, namely 30*i* and 7*i* (B3LYP) or 34*i* and 16*i* (BP86) cm^{-1}.

3.2. Vibrational Frequencies. The harmonic vibrational frequencies and their infrared intensities for all of the



IVa (C_s)

IVb (C_s)

Figure 4. Optimized geometries for the $Mn_2(NO)_2(CO)_5$ isomers.

Table 4. Bond Distances (in Å), Total Energies (E in Hartree) and Relative Energies (ΔE in kcal/mol) for $Mn_2(NO)_2(CO)_5$ Isomers

	IVa (C_s)		**IVb** (C_s)	
	B3LYP	BP86	B3LYP	BP86
Mn−Mn	2.411	2.372	2.638	2.573
Mn−C(bridge)	−	−	1.817/2.899	1.805/2.755
Mn−N(bridge)	1.706/2.391 1.696/2.471	1.712/2.499 1.728/2.313	1.760/1.862	1.749/1.905
Mn−N(terminal)	−	−	1.694	1.691
Mn−N−O	172.3/172.3	176.8/170.0	173.2/179.7	176.6/177.2
$-E$	3128.80345	3129.29409	3128.80073	3129.30248
ΔE	0.0	0.0	1.7	−5.3
imaginary frequencies	3i	9i	77i	42i

structures have been calculated by the B3LYP and BP86 methods. Complete reports of the vibrational frequencies and their infrared intensities are given in the Supporting Information.

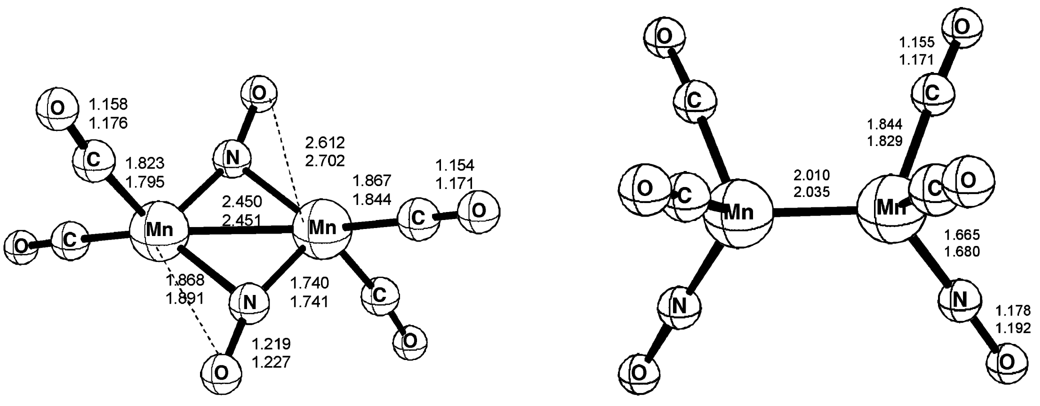
The relatively strong ν(CO) and ν(NO) frequencies are useful for characterizing metal carbonyl nitrosyls. Table 7 compares the ν(CO) and ν(NO) frequencies calculated for both isomers of $Mn(NO)(CO)_4$ (**Ia** and **Ib** in Figure 1) with those found experimentally for $Mn(NO)(CO)_4$, shown by X-ray diffraction to have structure **Ia**. The ν(CO) and ν(NO) frequencies calculated by the BP86 method are found to be much closer to the experimental values than those calculated by the B3LYP method. Thus the calculated ν(CO) frequencies for **Ia** by the BP86 method are found to be within 30 cm^{-1} of the experimental values (assuming that the calculated frequencies of 1998 and 1993 are not resolved in the experiment). The deviation is somewhat larger for the ν(NO) where the calculated value (BP86) of 1818 cm^{-1} for **Ia** lies 59 cm^{-1} above that of the experimental ν(NO) frequency of 1759 cm^{-1}.

Table 8 lists the infrared ν(CO) and ν(NO) frequencies for the binuclear manganese carbonyl nitrosyls $Mn_2(NO)_2(CO)_n$ (n = 7, 6, 5, and 4) obtained with the BP86 method that generally gives ν(CO) and ν(NO) frequencies closer to the experimental values than the B3LYP method. These frequencies fall into the expected pattern. Thus terminal ν(CO) frequencies occur the range 2065−1950 cm^{-1} and shift slightly downward as the number of CO groups decreases in accord with the greater metal electron density per CO group for back-bonding reducing the carbon−oxygen bond order. Bridging ν(CO) frequencies and terminal ν(NO) frequencies occur in the range 1855−1760 cm^{-1} with the bridging ν(CO) frequencies typically at the upper end of this range and the terminal ν(NO) frequencies at the lower end of this range. However, in a compound with both bridging ν(CO) and terminal ν(NO) groups, notably isomer **IIIc** of $Mn_2(NO)_2(CO)_6$ with two bridging ν(CO) groups and two terminal ν(NO) groups, assignment of the frequencies in this region on the basis solely of their numerical values can be ambiguous. In this case, it was necessary to check the actual vibrations of the frequencies in this region to make the assignments.

Still lower ν(NO) frequencies, typically in the range 1650−1569 cm^{-1}, are found for bridging ν(NO) groups. The lowest ν(NO) frequency found in this work, namely 1488 cm^{-1}, arises from the unusual η^2-μ-NO formal five-electron donor bridging NO group in isomer **IVb** of $Mn_2(NO)_2(CO)_5$ in which the N≡O π bond is involved in the bonding to one of the manganese atoms. Such π-bonding is expected to lower the effective nitrogen−oxygen bond order, thereby leading to an unusually low ν(NO) frequency.

Table 9 lists the ν(CO) and ν(NO) frequencies for the three isomers of $Mn_3(NO)_3(CO)_9$. These follow the same pattern as the corresponding infrared frequencies of the binuclear $Mn_2(NO)_2(CO)_n$ (n = 7, 6, 5, and 4) listed in Table 8 except that the two bridging ν(CO) frequencies in isomer **VIb** occur at the relatively high values of 1926 and 1917 cm^{-1}. Nevertheless, these bridging ν(CO) frequencies in **VIb** are at least 48 cm^{-1} below the lowest terminal ν(CO) frequencies in any of the $Mn_2(NO)_2(CO)_6$ isomers, which have the same Mn/NO/CO ratio as $Mn_3(NO)_3(CO)_9$ and thus should have similar electron density on the metal atoms for back-bonding to the CO and NO groups.

3.3. Comparison of Manganese Carbonyl Nitrosyls with Their Isoelectronic Iron Carbonyl Derivatives. Table 10 compares the structures of isoelectronic manganese carbonyl



Va (C_i)

Vb (C_s)

Figure 5. Optimized geometries for $Mn_2(NO)_2(CO)_4$ isomers.

Table 5. Bond Distances (in Å), Total Energies (*E* in Hartree) and Relative Energies (Δ*E* in kcal/mol) for $Mn_2(NO)_2(CO)_4$ Isomers

	Va (C_i)		**Vb** (C_s)	
	B3LYP	BP86	B3LYP	BP86
Mn−Mn	2.450	2.451	2.010	2.035
Mn−N(bridge)	1.868/1.740	1.891/1.741	−	−
Mn−C(terminal)	1.867/1.823	1.844/1.795	1.844	1.829
Mn−N(terminal)	−	−	1.665	1.680
Mn−N−O	159.0/113.9	154.8/118.6	179.4	179.1
−*E*	3015.43061	3015.91785	3015.38392	3015.88649
Δ*E*	0.0	0.0	29.3	19.7
imaginary frequencies	none	none	8*i*	8*i*

nitrosyls and iron carbonyls with respect to the number and types of CO and/or NO bridges, the metal−metal distances and implied formal bond orders, and the M−C/N and C/N−O distances to the CO and NO ligands. Only the global minima are compared except for two isomers of $Mn_2(NO)_2(CO)_4$ where both the dibridged global minima with formal metal−metal double bonds and slightly higher energy unbridged structures with formal metal−metal quadruple bonds are compared.

3.3.1. Mononuclear Derivatives. The Mn−N(equatorial) bond distance is shorter by 0.121 (B3LYP) or 0.108 Å (BP86) in $Mn(NO)(CO)_4$ as compared with the Fe−C(equatorial) bond distances in $Fe(CO)_5$.[25] However, the Mn−C(axial) bond distance in $Mn(NO)(CO)_4$ is longer by 0.050 (B3LYP) or 0.049 Å (BP86) than the corresponding Fe−C(axial) bond distance in $Fe(CO)_5$. The significantly shorter Mn−N bond in $Mn(NO)(CO)_4$ relative to the corresponding Fe−C bond in $Fe(CO)_5$ can be related to the fact that NO is a stronger π-acceptor than CO.

3.3.2. Binuclear Derivatives. Our work predicts that binuclear manganese carbonyl nitrosyl structures with bridging NO groups are energetically preferred over those with bridging CO groups. Thus, the global minimum structure for $Mn_2(NO)_2(CO)_7$ (**IIa**) has two bridging NO groups (**IIa**) and is thus very different than the experimentally observed structure of $Fe_2(CO)_9$ with three bridging CO groups. However, the two NO bridges in **IIa** donate six electrons to the pair of metal atoms similar to the three CO bridges in $Fe_2(CO)_9$.

The structures of the binuclear unsaturated $Mn_2(NO)_2(CO)_n$ ($n = 6$, 5, and 4) derivatives parallel rather closely those of the isoelectronic $Fe_2(CO)_{n+2}$ derivatives again with a preference for bridging NO groups over bridging CO groups. Thus, the lowest energy predicted isomer for $Mn_2(NO)_2(CO)_6$ (**IIIa**) has two bridging NO groups similar to the lowest energy isomer predicted[5] for the isoelectronic $Fe_2(CO)_8$ with two bridging CO groups. Similarly the lowest energy predicted isomer for $Mn_2(NO)_2(CO)_5$ (**IVa**) has two highly unsymmetrical bridging NO groups similar to the lowest energy structure predicted for $Fe_2(CO)_7$ with two highly unsymmetrical bridging CO groups.

Both isomers found for $Mn_2(NO)_2(CO)_4$, namely **Va** and **Vb**, have their counterparts in $Fe_2(CO)_6$ isomers found in our earlier work.[5] Thus, the lowest lying $Mn_2(NO)_2(CO)_4$ isomer has two bridging NO groups and an Mn═Mn distance suggesting a double bond analogous to the global minimum previously found for $Fe_2(CO)_6$ with two bridging CO groups and an Fe═Fe distance likewise suggesting a double bond. The higher lying unbridged $Mn_2(NO)_2(CO)_4$ isomer, **Vb**, with a very short metal−metal distance suggesting a quadruple bond has its iron counterpart in an unbridged $Fe_2(CO)_6$ isomer[5] with a similar very short metal−metal distance suggested originally to be a quadruple bond.

3.3.3. Trinuclear Derivatives. The lowest energy isomer found for the trinuclear derivative $Mn_3(NO)_3(CO)_9$ with two bridging NO groups across one of the Mn−Mn bonds (**VIa**) is very similar to the experimentally known structure of the isoelectronic $Fe_3(CO)_{12}$ with two bridging CO groups across one of the Fe−Fe bonds. However, the Mn_3 triangle in $Mn_3(NO)_3(CO)_9$ is a scalene triangle with all three edges nonequivalent in contrast to the Fe_3 triangle in $Fe_3(CO)_{12}$, which is an isoceles triangle with the two unbridged Fe−Fe edges equivalent and 0.141 Å longer than the unique dibridged edge. In the scalene Mn_3 triangle of $Mn_3(NO)_3(CO)_9$, the average length of the unbridged edges, namely 2.855 Å, is longer than the unique dibridged edge by 0.326 Å.

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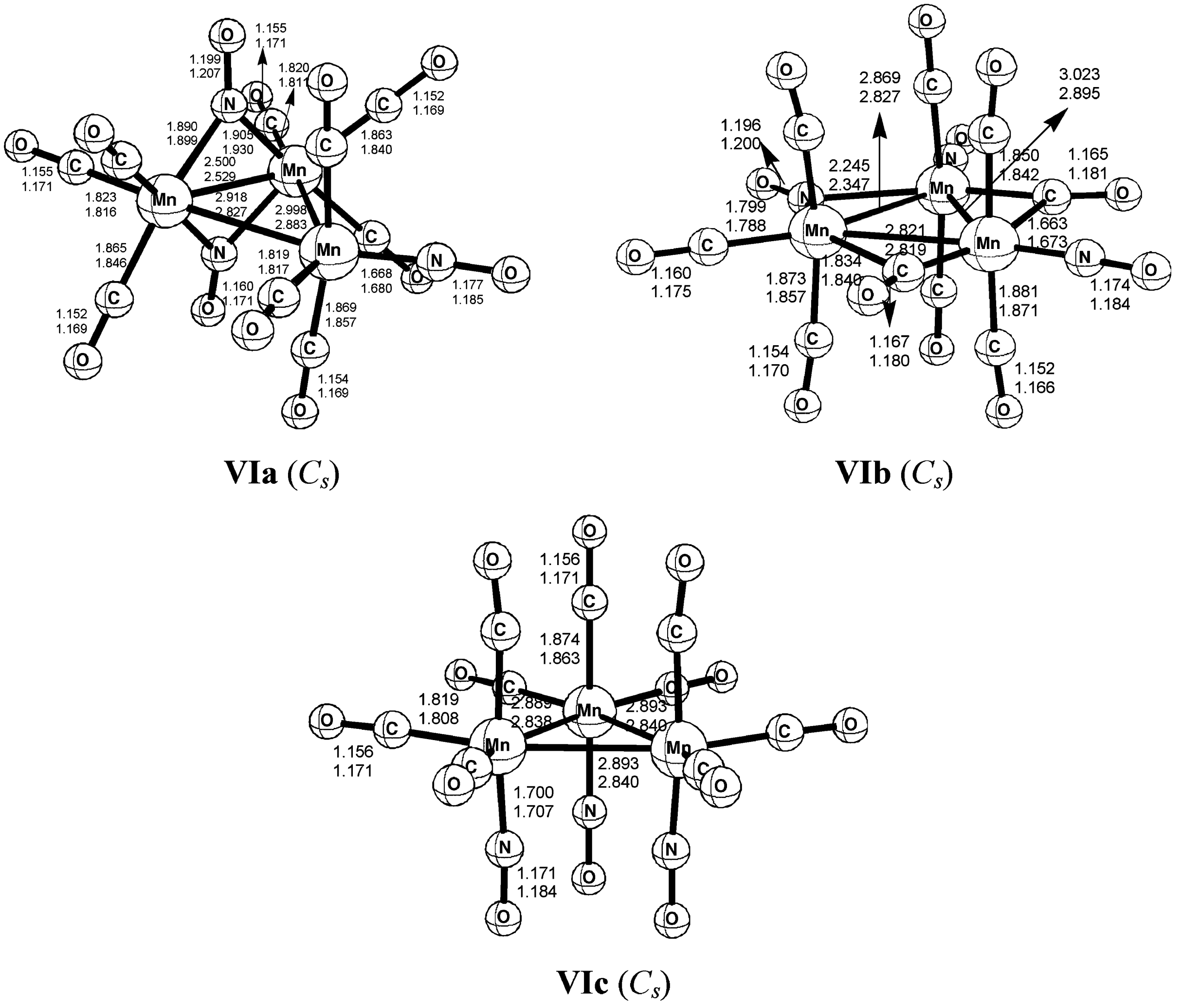

VIa (C_s)

VIb (C_s)

VIc (C_s)

Figure 6. Optimized geometries for $Mn_3(NO)_3(CO)_9$ isomers.

Table 6. Bond Distances (in Å), Total Energies (E in Hartree) and Relative Energies (ΔE in kcal/mol) for $Mn_3(NO)_3(CO)_9$ Isomers

	VIa (C_s)		**VIb** (C_s)		**VIc** (C_{3v})	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
Mn1−Mn2	2.500	2.529	2.869	2.827	2.892	2.838
Mn1−Mn3	2.918	2.827	2.821	2.819	2.892	2.840
Mn2−Mn3	2.998	2.883	3.023	2.895	2.892	2.840
Mn−C(bridge)	−	−	1.850	1.842	−	−
Mn−N(bridge)	1.890/1.905	1.899/1.930	2.245	2.347	−	−
Mn−N(terminal)	−	−	1.663	1.673	1.700	1.707
Mn−N−O	170.9/139.2	174.0/137.8	174.6/175.2	176.1/176.8	174.1	174.0
$-E$	4863.26861	4864.03463	4863.25090	4864.02075	4863.25047	4864.01821
ΔE	0.0	0.0	11.1	8.7	11.4	10.3
imaginary frequency	none	none	none	none	30*i*, 7*i*	34*i*, 16*i*

3.4. Nature of the Photolysis Product of $Mn(NO)(CO)_4$. The original discoverers[3] of $Mn(NO)(CO)_4$ in 1961 reported its photolysis to give an air-sensitive dark red solid that could be sublimed in a vacuum. Because of the similarity of its volatility to that of $Mn_2(CO)_{10}$, also produced in this reaction, this dark red solid was not obtained pure. Its infrared frequencies were reported to be 2101(w), 2042(vs), 2006(vs), 1995(w), 1976(s), 1743(m), 1735(m), 1731(w), 1726(w), and 1710(m) in tetrachloroethane solution. By analogy with the well-known photolysis of $Fe(CO)_5$ to give $Fe_2(CO)_9$, this red solid was assumed to be $Mn_2(NO)_2(CO)_7$ isoelectronic with $Fe_2(CO)_9$. Apparently, in the 45 years since this report, no one has made any attempt to isolate this volatile dark red solid in pure form and to characterize it by other methods including X-ray diffraction.

The calculations reported in this paper predict the structure of $Mn_2(NO)_2(CO)_7$ to be very different from that of $Fe_2(CO)_9$, namely with two bridging NO groups rather than three bridging CO groups. More significantly, the ν(NO) frequencies of these two bridging NO groups in $Mn_2(NO)_2(CO)_7$ are predicted by the BP86 method to have ν(NO) frequencies of 1648 and 1626 cm^{-1}, which is more than 80 cm^{-1} below the experimentally observed ν(NO) frequencies of the red solid. In fact, the experimentally observed ν(NO)

Table 7. Infrared ν(CO) and ν(NO) Frequencies for the $Mn(NO)(CO)_4$ Isomers (Calculated Infrared Intensities Are Given in Parentheses in km/mol)

	infrared ν(CO) and ν(NO) frequencies, cm^{-1}	
isomer	B3LYP	BP86
Ia (calcd)	2154(95), 2090 (1530), 2081(250), 2055(1320), 1865(1200)[a]	2067(98), 1998(1340), 1993(122), 1974(1230), 1818(977)[a]
exptl		2095(m), 2019(s), 1972(s), 1759(s)[a]
Ib (calcd)	2144(175), 2088(415), 2058(1350), 1889 (1240)[a]	2058(125), 1997(366), 1978(1170), 1837(938)[a]

[a] ν(NO) frequency.

Table 8. Infrared ν(CO) and ν(NO) Frequencies Calculated for Binuclear Manganese Carbonyl Nitrosyls Using the BP86 Method (Calculated Infrared Intensities Are Given in Parentheses in km/mol)

compound	infrared ν(CO) and ν(NO) frequencies, cm^{-1} (BP86)
$Mn_2(NO)_2(CO)_7$ (**IIa**)	2065(66), 2020(1920), 2002(611), 1993(947), 1985(1350), 1984(368), 1971(56), 1648(170),[a] 1626(677)[a]
$Mn_2(NO)_2(CO)_7$ (**IIb**)	2060(137), 2015(1140), 1992(2060), 1984(49), 1978(448), 1972(429), 1852(57),[b]1814(1450),[c] 1806(503)[c]
$Mn_2(NO)_2(CO)_6$ (**IIIa**)	2053(3), 2020(2060), 1999(1070), 1994(26), 1983(1730), 1974(0), 1631(158),[a]1589(620)[a]
$Mn_2(NO)_2(CO)_6$ (**IIIb**)	2052(280), 2016(1580), 1995(408), 1985(1590), 1974(95), 1872(251),[b]1830(1110),[c]1590(425)[a]
$Mn_2(NO)_2(CO)_6$ (**IIIc**)	2045(264), 2010(1800), 1992(1400), 1987(1), 1888(566),[b]1825(569), 1812(1140), 1802(360)
$Mn_2(NO)_2(CO)_6$ (**IIId**)	2045(165), 2005(2280), 1985(600), 1977(1760), 1974(0), 1950(91), 1834(1290),[c]1766(90)[c]
$Mn_2(NO)_2(CO)_5$ (**IVa**)	2035(8), 2007(1733), 1981(1090), 1959(725), 1954(613), 1757(293),[d]1706(622)[d]
$Mn_2(NO)_2(CO)_5$ (**IVb**)	2034(590), 1985(1230), 1968(1290), 1964(225), 1819(1240),[c]1488(352)[e]
$Mn_2(NO)_2(CO)_4$ (**Va**)	2016(0), 1981(2330), 1952(1820), 1951(0), 1596(0),[a]1569(789)[a]
$Mn_2(NO)_2(CO)_4$ (**Vb**)	2031(453), 1982(1200), 1976(1790), 1963(0), 1798(1300),[c] 1774(779)[c]

[a] Bridging ν(NO) frequency. [b] Bridging ν(CO) frequency. [c] Terminal ν(NO) frequency. [d] Semibridging ν(NO) frequency. [e] η^2-μ-NO bridging ν(NO) frequency. All other listed frequencies are terminal ν(CO) frequencies.

Table 9. Infrared ν(CO) and ν(NO) Frequencies Calculated for $Mn_3(NO)_3(CO)_9$ Isomers Using the BP86 Method (Calculated Infrared Intensities Are Given in Parentheses in km/mol)

isomer	infrared ν(CO) and ν(NO) frequencies, cm^{-1} (BP86)
VIa	2057(53), 2013(2460), 2004(1510), 2001(1745), 1989(0), 1982(14), 1978(507),1974(77), 1968(72), 1814(810),[c]1648(179),[a]1623(529)[a]
VIb	2065(26), 2013(549), 2011(2410), 2008(979), 1975(10), 1963(199), 1960(119),1926(322),[b] 1917(779),[b] 1833(543),[c] 1828(1148),[c] 1704(430)[a]
VIc	2057(278), 2009(2360), 2008(2420), 2004(731), 1978(248), 1977(302), 1969(13),1966(14), 1966(0), 1854(1460),[c] 1782(43),[c] 1781(42)[c]

[a] Bridging ν(NO) frequency. [b] Bridging ν(CO) frequency. [c] Terminal ν(NO) frequency. All other listed frequencies are terminal ν(CO) frequencies.

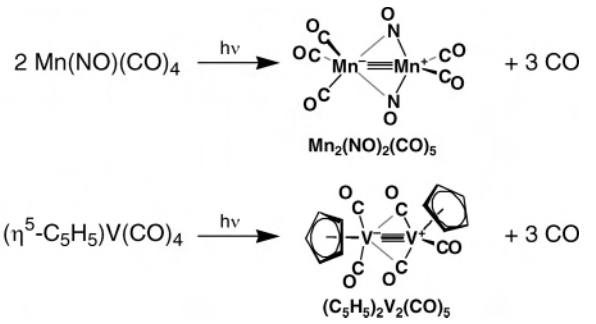

Figure 7. Comparison of the suggested photolysis pathway of $Mn(NO)(CO)_4$ to give $Mn_2(NO)_2(CO)_5$ with the known photolysis of $(\eta^5\text{-}C_5H_5)V(CO)_4$ to give $(\eta^5\text{-}C_5H_5)_2V_2(CO)_5$.

frequencies for the $Mn(NO)(CO)_4$ photolysis product in the 1743−1710 cm^{-1} region appear to be too low for terminal NO groups but too high for symmetrically bridging NO groups, as suggested by our calculations on the binuclear and trinuclear manganese carbonyl nitrosyls. This suggests that the $Mn(NO)(CO)_4$ photolysis product has unsymmetrical semibridging NO groups.

One of the binuclear manganese carbonyl nitrosyl derivatives, namely the lowest energy isomer, **IVa**, of $Mn_2(NO)_2(CO)_5$ (Figure 4), has the type of semibridging NO groups suggested by the ν(NO) frequencies in the dark red $Mn(NO)(CO)_4$ photolysis product and has a predicted infrared spectrum in the ν(CO) and ν(NO) regions quite close to that of the photolysis product. Thus, considering only the strongest ν(CO) and ν(NO) frequencies, the calculated infrared spectrum for **IVa** of 2007, 1981, 1959, 1954, 1757, and 1706 cm^{-1} matches quite well to the observed infrared spectrum of 2042, 2006, 1976, 1743, 1735, and 1710 cm^{-1} for the $Mn(NO)(CO)_4$ photolysis product.

The suggested formulation of the $Mn(NO)(CO)_4$ photolysis product as $Mn_2(NO)_2(CO)_5$ means that the photolysis of $Mn(NO)(CO)_4$ is analogous to the photolysis of $(\eta^5\text{-}C_5H_5)V(CO)_4$ to give $(\eta^5\text{-}C_5H_5)_2V_2(CO)_5$ rather than that of $Fe(CO)_5$ to give $Fe_2(CO)_9$ (Figure 7).[26] This is quite plausible since an MnNO moiety is isoelectronic not only with an FeCO moiety but also with a $(\eta^5\text{-}C_5H_5)V$ moiety. The structure[27,28] of the central portion of $(\eta^5\text{-}C_5H_5)_2V_2(CO)_5$ is quite similar to that predicted for $Mn_2(NO)_2(CO)_5$ but with two semibridging CO groups rather than two semibridging NO groups. Both $(\eta^5\text{-}C_5H_5)_2V_2(CO)_5$ and $Mn_2(NO)_2(CO)_5$ require M≡M triple bonds for the metal atoms to attain the favored 18-electron rare gas configurations. In this connection, the experimental V≡V distance is 2.462 Å in $(\eta^5\text{-}C_5H_5)_2V_2(CO)_5$ which is close to our predicted Mn≡Mn distance of 2.411 (B3LYP) or 2.372 Å (BP86) in $Mn_2(NO)_2(CO)_5$ (**IVa**).

4. Summary

The DFT methods in this paper were first tested on the known[3,4] mononuclear $Mn(NO)(CO)_4$ where geometrical parameters and infrared ν(CO) and ν(NO) frequencies close to the experimental values were obtained. Binuclear and trinuclear manganese carbonyl nitrosyls were found to prefer structures with bridging NO groups rather than bridging CO groups. Thus, the predicted lowest energy structure for $Mn_2(NO)_2(CO)_7$ was found to have two bridging NO groups in contrast to the known structure of the isoelectronic $Fe_2(CO)_9$, which has three bridging CO groups. The structures for the unsaturated binuclear $Mn_2(NO)_2(CO)_n$ (n = 7, 6, 5, 4) derivatives are similar to those of the corresponding binuclear iron carbonyls $Fe_2(CO)_{n+2}$. The trinuclear $Mn_3(NO)_3(CO)_9$

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Table 10. Bond Distances (in Å) and Formal Metal−Metal Bond Orders for the Lowest Energy Manganese Carbonyl Nitrosyl and Their Isoelectronic Iron Carbonyl Structures (BP86 Results)

	symmetry	no. of bridges	M−M distance	M−C/N(b) distances	C/N−O(b) distances	bond order
$Mn(NO)(CO)_4$ (**Ia**)	C_{2v}	0	−	1.697 (eq Mn−N) 1.854 (ax Mn−C)	1.185 (eq) 1.168 (ax)	−
$Fe(CO)_5$	D_{3h}	0	−	1.805(X-ray)	1.167	−
$Mn_2(NO)_2(CO)_7$ (**IIa**)	C_s	2(NO)	2.644	2.079/1.829	1.209	1
$Fe_2(CO)_9$	D_{3h}	3(CO)	2.519	2.007	1.186	1
$Mn_2(NO)_2(CO)_6$ (**IIIa**)	C_{2v}	2(NO)	2.483	1.900/1.887	1.211	2
$Fe_2(CO)_8$	C_{2v}	2(CO)	2.447	1.976	1.190	2
$Mn_2(NO)_2(CO)_5$ (**IVa**)	C_s	2(NO)	2.372	1.712/1.728	1.194/1.201	3
$Fe_2(CO)_7$	C_s	2(CO)	2.235	1.806/1.841	1.173/1.177	3
$Mn_2(NO)_2(CO)_4$ (**Va**)	C_i	2(NO)	2.451	1.891/1.741	1.227	2
$Fe_2(CO)_6$	C_{2h}	2(CO)	2.434	1.792	1.171	2
$Mn_2(NO)_2(CO)_4$ (**Vb**)	C_s	0	2.035	1.829/1.680	1.171/1.192	4
$Fe_2(CO)_6$	D_{3h}	0	2.029	1.786	1.171	4
$Mn_3(NO)_3(CO)_9$ (**VIa**)	C_s	2(NO)	2.529/2.883/2.827	1.930/1.899	1.207	1
$Fe_3(CO)_{12}$	C_{2v}	2(CO)	2.572/2.713	1.996	1.187	1

is predicted to have a structure analogous to the known structure for $Fe_3(CO)_{12}$ but with two bridging NO groups rather than two bridging CO groups across one of the metal−metal edges of the M_3 triangle. The dark red solid photolysis product of $Mn(NO)(CO)_4$, characterized by its ν(CO) and ν(NO) frequencies ∼45 years ago, is suggested by these DFT studies not to be the originally assumed $Mn_2(NO)_2(CO)_7$ analogous to $Fe_2(CO)_9$. Instead, this photolysis product appears to be $Mn_2(NO)_2(CO)_5$ with a Mn≡Mn formal triple bond analogous to $(\eta^5\text{-}C_5H_5)_2V_2(CO)_5$ obtained from the photolysis of $(\eta^5\text{-}C_5H_5)V(CO)_4$.

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Supporting Information Available: Tables S1−S15: Harmonic vibrational frequencies for $Mn(NO)(CO)_4$ (two isomers), $Mn_2(NO)_2(CO)_7$ (two isomers), $Mn_2(NO)_2(CO)_6$ (four isomers), $Mn_2(NO)_2(CO)_5$ (two isomers), $Mn_2(NO)_2(CO)_4$ (two isomers), and $Mn_3(NO)_3(CO)_9$ (three isomers); Table S16: Cartesian coordinates for the 15 structures; complete ref 22. This material is available free of charge via the Internet at http://pubs.acs.org.

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