DOI: 10.1002/ejic.200900621

(Cyclopentadienyl)nitrosylmanganese Compounds: The Original Molecules Containing Bridging Nitrosyl Groups

Bing Yan,*[a,b] Yaoming Xie,[b] R. Bruce King,*[b] and Henry F. Schaefer III[b]

Dedicated to Yitzak Apeloig on the occasion of his 65th birthday

Keywords: Manganese / Nitrosyl ligands / Cyclopentadienyl ligands / Density functional calculations / Bridging ligands / Carbonyl ligands / Structure elucidation

The (cyclopentadienyl)nitrosylmanganese derivatives $Cp_2Mn_2(NO)_2(CO)_n$ (n = 2, 1, 0), $Cp_2Mn_2(NO)_3X$ (X = NO_2, σ-C_5H_5), $CpMn(NO)_2$, $Cp_2Mn_2(NO)_4$, and $Cp_3Mn_3(NO)_4$ have been investigated by using density functional theory. Six structures are found for $Cp_2Mn_2(NO)_2(CO)_2$ with various combinations of terminal and bridging carbonyl and nitrosyl groups within ca. 3 kcal/mol of each other indicating a highly fluxional system. A triplet-state triply bridged structure is predicted to be the global minimum for $Cp_2Mn_2(NO)_2(CO)$, just as it is for the isoelectronic $Cp_2Fe_2(CO)_3$. For $Cp_2Mn_2(NO)_2$ a doubly bridged triplet structure is predicted to lie ca. 30 kcal/mol below the corresponding singlet structure, unlike the isoelectronic $Cp_2Fe_2(CO)_2$. The structures predicted for $Cp_2Mn(\mu\text{-}NO)_2(NO)X$ (X = NO_2 and η^1-C_5H_5) and $Cp_3Mn_3(\mu\text{-}NO)_3(\mu_3\text{-}NO)$ are close to the experimentally known structures. The monomer $CpMn(NO)_2$, with a favorable 18-electron configuration for the manganese atom, is predicted to be unstable with respect to dimerization to $Cp_2Mn_2(\mu\text{-}NO)_2(NO)_2$, for which two structures are found of similar energy. One $Cp_2Mn_2(\mu\text{-}NO)_2(NO)_2$ structure has a non-bonding Mn···Mn distance of ca. 3.1 Å and linear terminal MnNO units, whereas the other $Cp_2Mn_2(\mu\text{-}NO)_2(NO)_2$ structure has a single-bond Mn–Mn distance of ca. 2.5 Å and bent terminal MnNO units. In $Cp_2Mn(\mu\text{-}NO)_2(NO)(\eta^1\text{-}Cp)$ the $Mn_2(\mu\text{-}NO)_2$ unit is unsymmetrical, with significantly different (by ca. 0.2 Å) Mn–N bond lengths to each side. However, in $Cp_2Mn_2(NO)_2(CO)_n$ (n = 2, 1, 0) and $Cp_2Mn_2(\mu\text{-}NO)_2(NO)_2$ the $Mn_2(\mu\text{-}NO)_2$ units are symmetrical, with essentially the same Mn–N bond lengths to both sides.

1. Introduction

The landmark discovery of ferrocene, Cp_2Fe (Cp = η^5-C_5H_5), in 1951[1,2] was followed shortly by the synthesis of the other metallocenes of the first-row transition metals from vanadium to nickel. The availability of such metallocenes in quantity almost immediately led to a study of their chemical reactivity with simple inorganic ligating molecules, such as carbon monoxide and nitric oxide. The study of the reactions of metallocenes with carbon monoxide led to the discovery of a number of carbonyl(cyclopentadienyl)metal compounds such as $CpV(CO)_4$,[3] $CpMn(CO)_3$,[4,5] and $CpCo(CO)_2$,[5,6] which have become key molecules in transition metal organometallic chemistry during the past half century. Similar reactions of metallocenes with nitric oxide led to some interesting (cyclopentadienyl)nitrosylmetal compounds, notably the relatively stable CpNiNO from Cp_2Ni and NO.[5] Complexes such as CpNiNO with terminal nitrosyl ligands were not entirely unusual since such nitrosylmetal complexes with terminal nitrosyl ligands date back to the 19th century with species such as "nitroprusside," $Fe(CN)_5(NO)^{2-}$.

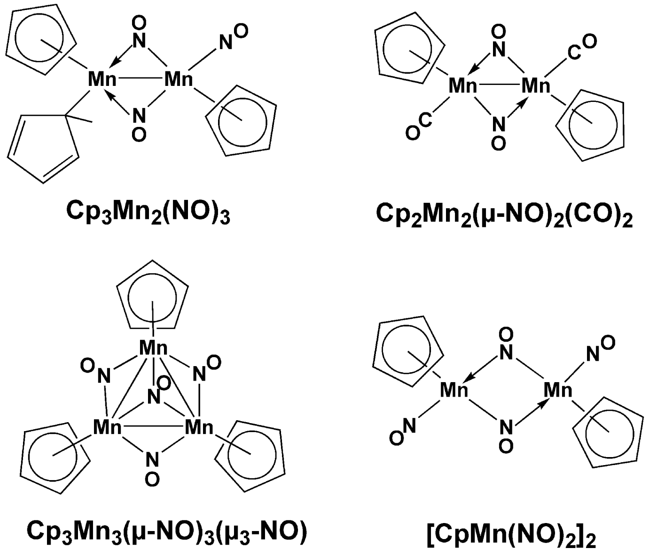
In the context of the early days of metallocene chemistry of the 1950s, mainly in the research groups of Wilkinson, then at Harvard University, and Fischer, then at the Technische Hochschule in Munich, Germany, the reaction of Cp_2Mn with nitric oxide was of particular interest. Already in 1956 this reaction was found by the Wilkinson group[7] to give a purple-black complex with the unusual composition $Cp_3Mn_2(NO)_3$. This complex was formulated as $(\eta^5\text{-}C_5H_5)_2$-$Mn_2(\mu\text{-}NO)_2(\eta^1\text{-}C_5H_5)(NO)$ (Figure 1) on the basis of ν(NO) frequencies assigned to both terminal and bridging nitrosyl groups. This structure, in which both manganese atoms have the favored 18-electron configuration, was particularly significant since no other examples of transition metal complexes with bridging nitrosyl groups were known at that time. Furthermore, no isoelectronic carbonylmetal

---

[a] Institute of Atomic and Molecular Physics, Jilin University,
Changchun 130012, P. R. China
E-mail: yanbing@jlu.edu.cn
[b] Department of Chemistry and Center for Computational Chemistry, University of Georgia,
Athens, Georgia 30602, USA
E-mail: rbking@chem.uga.edu

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.200900621.

analogues of $Cp_3Mn_2(NO)_3$ were known in 1956 or have been prepared in the subsequent half century. Since definitive structural elucidations by X-ray crystallography were rather difficult in the 1950s, no confirmation of this proposed structure for $Cp_3Mn_2(NO)_3$ became available until 1976.[8] Therefore, the ability of the nitrosyl group to serve as a bridging ligand as well as a terminal ligand remained in doubt until 20 years after the first report of $Cp_3Mn_2(NO)_3$.



$Cp_3Mn_2(NO)_3$ $Cp_2Mn_2(\mu\text{-}NO)_2(CO)_2$

$Cp_3Mn_3(\mu\text{-}NO)_3(\mu_3\text{-}NO)$ $[CpMn(NO)_2]_2$

Figure 1. Some early examples of (cyclopentadienyl)nitrosylmetal compounds (predating 1967).

Early in his career in the 1960s, while at the Mellon Institute (now Carnegie-Mellon University), one of the authors of this paper (R. B. K.) set out to prepare a dinuclear metal derivative with a bridging nitrosyl group directly analogous to a carbonylmetal derivative with a bridging carbonyl ligand.[9] This resulted in the synthesis of $Cp_2Mn_2(CO)_2(NO)_2$, which is isoelectronic with $Cp_2Fe_2(CO)_2(\mu\text{-}CO)_2$, one of the originally discovered carbonyl(cyclopentadienyl)metal derivatives.[5] The infrared spectrum of $Cp_2Mn_2(CO)_2(NO)_2$ showed both terminal and bridging ν(CO) and ν(NO) frequencies, suggesting an equilibrium mixture of isomers with bridging carbonyl and bridging nitrosyl groups (e.g., Figure 1). This work provided convincing evidence for the existence of bridging nitrosyl groups before X-ray structural determinations on key dinuclear nitrosylmetal derivatives became available.

One feature of the chemistry of $Cp_2Fe_2(CO)_2(\mu\text{-}CO)_2$ is its pyrolysis to give the green tetranuclear derivative $Cp_4Fe_4(\mu\text{-}CO)_4$.[10] A similar pyrolysis of $Cp_2Mn_2(CO)_2(NO)_2$ led to extensive decomposition to intractable mixtures. However, photolysis of $Cp_2Mn_2(CO)_2(NO)_2$ gave a curious black product, suggested by its ν(NO) frequencies to have nitrosyl groups bridging pairs of manganese atoms and other nitrosyl groups bridging three manganese atoms.[9] The original erroneous hexanuclear formulation of this black product arising from a faulty molecular weight determination was corrected to the trinuclear formulation $Cp_3Mn_3(\mu\text{-}NO)_3(\mu_3\text{-}NO)$ (Figure 1) by an X-ray structural determination.[11,12]

Another (cyclopentadienyl)nitrosylmanganese compound of interest is the mononuclear $CpMn(NO)_2$, which has the favored 18-electron configuration similar to the known isoelectronic $CpCo(CO)_2$. In this connection, ultraviolet irradiation of $[CpMn(CO)_2NO][PF_6]$ with sodium nitrite in aqueous solution was found to give a black precipitate, from which a substance of composition $CpMn(NO)_2$ could be isolated by extraction with polar organic solvents.[13] The solid nature of this "$CpMn(NO)_2$" in contrast to the liquid $CpCo(CO)_2$, as well as the presence of both bridging and terminal ν(NO) frequencies, indicate that this product is not the simple $CpMn(NO)_2$ monomer. Dimeric formulations, such as $Cp_2Mn_2(NO)_2(\mu\text{-}NO)_2$ (Figure 1) as well as higher oligomers were proposed for this product.[13] These observations suggest that monomeric $CpMn(NO)_2$, unlike monomeric $CpCo(CO)_2$, is unstable with respect to dimerization or higher oligomerization. Furthermore, this observation coupled with the 18-electron rule suggests that a pair of metal atoms bridged by a pair of nitrosyl groups does not require a metal–metal bond for stability, in contrast to a pair of metal atoms bridged by a pair of carbonyl groups.

More recent work has clarified the nature of some of this early (cyclopentadienyl)nitrosylmanganese chemistry. In particular, a variety of compounds of the type $Cp_2Mn_2(\mu\text{-}NO)_2(NO)X$ (X = Cl, Br, NO_2, and C_6H_5) are now known with structures closely related to the original[7] $(\eta^5\text{-}C_5H_5)_2Mn_2(\mu\text{-}NO)_2(\eta^1\text{-}C_5H_5)(NO)$ (Figure 1), in which the η^1-C_5H_5 ligand has been replaced by the X group.[14–16] Such compounds are readily formed from CpMn(CO)(NO)X derivatives by complete loss of the carbonyl groups and redistribution of the nitrosyl groups. The structures of these $Cp_2Mn_2(\mu\text{-}NO)_2(NO)X$ derivatives were found to be particularly interesting since one of the manganese atoms forms Mn–N bonds to the pair of bridging nitrosyl groups that are 0.2 Å longer than those formed by the other manganese atom.[8,14]

The experimental work discussed above suggests a number of unusual features of (cyclopentadienyl)nitrosylmanganese chemistry including the following:

(1) The unusual structure of the original (cyclopentadienyl)nitrosylmanganese compound,[7] namely $Cp_3Mn_2(NO)_3$, which historically is the first example of a bridging nitrosyl group.

(2) The indication of all combinations of bridging and terminal, carbonyl and nitrosyl groups[9] in $Cp_2Mn_2(CO)_2(NO)_2$.

(3) The unusual photolysis of $Cp_2Mn_2(CO)_2(NO)_2$ to $Cp_3Mn_3(\mu\text{-}NO)_3(\mu_3\text{-}NO)$, leading to the first example of a nitrosyl group bridging three metal atoms.[9]

(4) The tendency of $CpMn(NO)_2$ to oligomerize[10] in contrast to $CpCo(CO)_2$.

This paper reports density functional theory (DFT) studies with the objective of understanding some of the unusual features of the (cyclopentadienyl)nitrosylmanganese chemistry outlined above.

2. Theoretical Methods

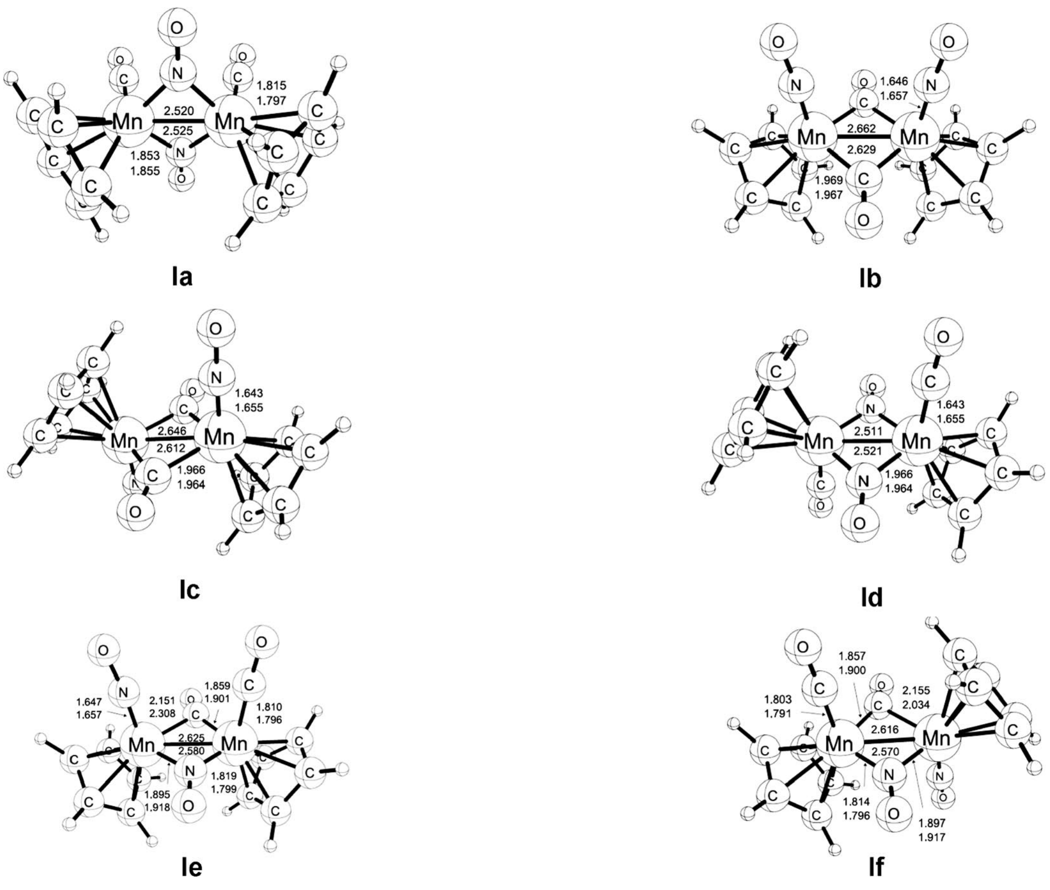
Electron correlation effects were included by employing density functional theory (DFT), which has been found to be a practical and effective computational tool, especially for organometallic compounds.[17–24] Two DFT methods were used in this study. The first one is B3LYP, which is a hybrid Hartree–Fock (HF)DFT method using a combination of Becke's three-parameter exchange functional (B3)[25] with the Lee, Yang, and Parr (LYP) generalized gradient correlation functional.[26] The second DFT method is BP86, which combines Becke's 1988 exchange functional (B)[27] with Perdew's 1986 generalized gradient correlation functional.[28]

For carbon, nitrogen, and oxygen, the double-ζ plus polarization (DZP) basis set used here, namely (9s5p/4s2p), adds one set of pure spherical harmonic d functions with orbital exponents $a_d(C) = 0.75$, $a_d(N) = 0.80$ and $a_d(O) = 0.85$ to the Huzinaga–Dunning standard contracted DZ sets.[29,30] For hydrogen, a set of polarization functions $a_p(H) = 0.75$ was added to the basis set. The loosely contracted DZP basis set for manganese is the Wachters primitive set augmented by two sets of p functions and one set of d functions, contracted following Hood, Pitzer, and Schaefer, designated (14s11p6d/10s8p3d).[31,32]

The geometries of all structures considered were fully optimized by 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 also evaluated analytically. All of the predicted ν(CO) and ν(NO) frequencies discussed explicitly in this paper were obtained by using the BP86 method, which has been shown to be more reliable than the B3LYP method for such spectral features. All of the computations were carried out by using the Gaussian 03[33] and Gaussian 94 programs[34] exercising the fine-grid option (75, 302) as the default for evaluating integrals numerically.[35] The tight (10^{-8} Hartree) designation is the default for the energy convergence. In some cases, where small imaginary vibrational frequencies were found, the ultrafine integration grid (99, 590) was used for their resolution.

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.[35] In many cases we do not follow the eigenvectors corresponding to imaginary frequencies less than 100*i* cm^{-1} in search of other minima.[36] In several cases studied here, the ultrafine grid causes small imaginary vibrational frequencies to become real; see below.

The geometries from these optimizations are depicted in Figures 2–10 with all bond lengths given in Å for both B3LYP (upper numbers) and BP86 (lower numbers).



Ia Ib Ic Id Ie If

Figure 2. Six optimized structures of $Cp_2Mn_2(NO)_2(CO)_2$.

Table 1. Bond lengths [Å], total energies *E* [Hartree], relative energies Δ*E* [kcal/mol], and numbers of imaginary vibrational frequencies for the six optimized $Cp_2Mn_2(NO)_2(CO)_2$ structures.

	Ia		**Ib** (C_{2v} $^1A_1$)	
	B3LYP (C_1 ^{1}A)	BP86 (C_2 ^{1}A)	B3LYP	BP86
Mn–Mn	2.520	2.525	2.662	2.629
Mn–C_{bridge}	–	–	1.969	1.967
Mn–$C_{terminal}$	1.815	1.797	–	–
Mn–N_{bridge}	1.853	1.855	–	–
Mn–$N_{terminal}$	–	–	1.646	1.657
E	–3175.87446	–3176.35281	–3175.85584	–3176.34844
Δ*E*	0.0	0.0	11.7	2.7
Imaginary frequency	none	none	none	10*i*
	Ic (C_i ^1A_g)		**Id** (C_{2h} ^1A_g)	
	B3LYP	BP86	B3LYP	BP86
Mn–Mn	2.646	2.612	2.511	2.521
Mn–C_{bridge}	1.966	1.964	–	–
Mn–$C_{terminal}$	–	–	1.807	1.791
Mn–N_{bridge}	–	–	1.849	1.852
Mn–$N_{terminal}$	1.643	1.655	–	–
E	–3175.86052	–3176.35415	–3175.87330	–3176.35457
Δ*E*	8.7	–0.8	0.7	–1.1
Imaginary frequency	none	none	none	none
	Ie (C_1 ^{1}A)		**If** (C_1 ^{1}A)	
	B3LYP	BP86	B3LYP	BP86
Mn–Mn	2.625	2.580	2.616	2.570
Mn–C_{bridge}	2.151/1.859	2.038/1.901	2.155/1.857	2.034/1.900
Mn–$C_{terminal}$	1.810	1.796	1.803	1.791
Mn–N_{bridge}	1.895/1.819	1.799/1.918	1.814/1.897	1.796/1.917
Mn–$N_{terminal}$	1.647	1.657	1.643	1.654
E	–3175.87042	–3176.35320	–3175.87234	–3176.35643
Δ*E*	2.5	–0.2	1.3	–2.3
Imaginary frequency	none	none	none	none

3. Results and Discussion

3.1 Molecular Structures

3.1.1 $Cp_2Mn_2(NO)_2(CO)_2$

Six energetically low-lying structures were found for $Cp_2Mn_2(NO)_2(CO)_2$ (Figure 2 and Table 1) representing all possible combinations of *cis* and *trans* arrangements of the two Cp rings and $Mn_2(\mu\text{-}NO)_2$, $Mn_2(\mu\text{-}NO)(\mu\text{-}CO)$, and $Mn_2(\mu\text{-}CO)_2$ configurations. These structures are essentially degenerate by the BP86 method within ca. 3 kcal/mol. This suggests that $Cp_2Mn_2(NO)_2(CO)_2$ in solution is likely to be an equilibrium mixture of these six isomers. This is consistent with the experimental observation[9] of all combinations of bridging and terminal ν(CO) and ν(NO) frequencies in solutions of $Cp_2Mn_2(NO)_2(CO)_2$. The predicted Mn–Mn distances increase upon replacing bridging nitrosyl groups with bridging carbonyl groups. This is indicated by Mn–Mn distances of 2.52 ± 0.01 Å for *cis*- and *trans*-$Cp_2Mn_2(\mu\text{-}NO)_2(CO)_2$ (**Ia** and **Id**), 2.60 ± 0.02 Å for *cis*- and *trans*-$Cp_2Mn_2(\mu\text{-}NO)(\mu\text{-}CO)(NO)(CO)$ (**Ie** and **If**), and 2.64 ± 0.03 Å for *cis*- and *trans*-$Cp_2Mn_2(\mu\text{-}CO)_2(NO)_2$ (**Ib** and **Ic**).

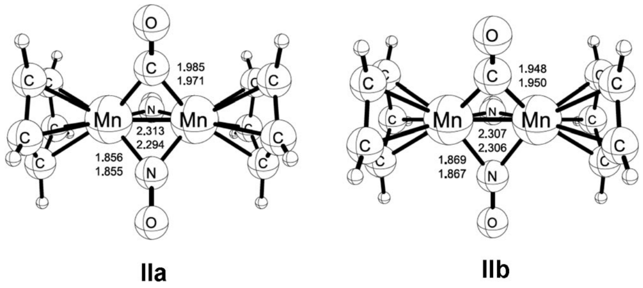
3.1.2 $Cp_2Mn_2(NO)_2(CO)$

Structures were optimized for $Cp_2Mn_2(NO)_2(CO)$ including both triply bridged and singly bridged structures. The global minimum was found to be the triplet-state triply bridged structure $Cp_2Mn_2(\mu\text{-}NO)_2(\mu\text{-}CO)$ (**IIa**) (Figure 3 and Table 2), which is isoelectronic with the known[37–39] $Cp_2Fe_2(\mu\text{-}CO)_3$. The Mn=Mn distance in **IIa** of 2.313 Å (B3LYP) or 2.294 Å (BP86) is very similar to the experimental Fe=Fe distance of 2.265 Å in $Cp_2Fe_2(\mu\text{-}CO)_3$ and corresponds to a $\sigma + {}^2\!/_2\pi$ triplet double bond similar to the double bond in isolated dioxygen. In such a formal double bond each of the orthogonal π orbitals contains a single electron leading to triplet-spin multiplicity.

A singlet-state triply bridged $Cp_2Mn_2(\mu\text{-}NO)_2(\mu\text{-}CO)$ structure (**IIb**) (Figure 3 and Table 2) was also found but at 24.7 kcal/mol (B3LYP) or 14.1 kcal/mol (BP86) above **IIa**. The Mn=Mn bond length in the singlet $Cp_2Mn_2(\mu\text{-}NO)_2\text{-}(CO)$ structure **IIb** (ca. 2.31 Å) is essentially the same as that in the corresponding triplet structure **IIa** indicating likewise a formal double bond. However, in the singlet structure **IIb** the double bond is of a (σ + π)-type with an electron pair in one of the orthogonal π orbitals and the other π orbital empty. The three singly bridged structures for $Cp_2Mn_2(NO)_2(CO)_2$ with either a bridging nitrosyl or a

Table 2. Bond lengths [Å], total energies *E* [Hartree] and relative energies Δ*E* [kcal/mol] for the two $Cp_2Mn_2(NO)_2(CO)$ structures of lowest energy.

	IIa (C_{2v} $^3B_1$)		**IIb** (C_{2v} $^1A_1$)	
	B3LYP	BP86	B3LYP	BP86
Mn–Mn	2.313	2.294	2.307	2.306
Mn–C_{bridge}	1.985	1.971	1.948	1.950
Mn–N_{bridge}	1.856	1.855	1.869	1.867
Mn–$N_{terminal}$	–	–	–	–
E	–3062.50088	–3062.96322	–3062.46151	–3062.94072
Δ*E*	0.0	0.0	24.7	14.1
Imaginary frequency	21*i*, 21*i*, (6*i*, 3*i*, when using ultrafine grid)	25*i*, 22*i*	17*i*, 16*i*	81*i*, 25*i*



IIa **IIb**

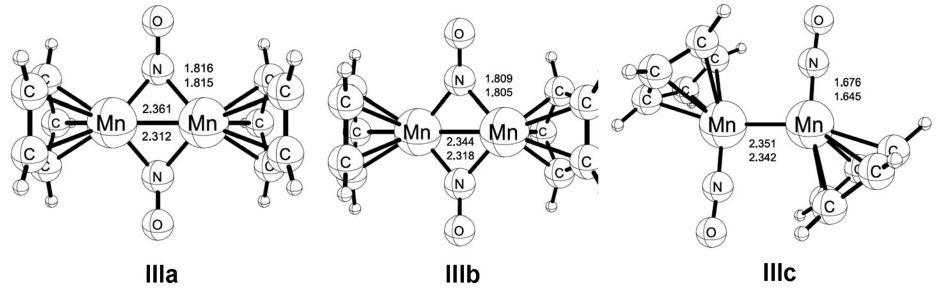
Figure 3. Global minimum optimized structure **IIa** of $Cp_2Mn_2(NO)_2(CO)$ and second structure **IIb** within 40 kcal/mol.

bridging carbonyl group were found to lie >40 kcal/mol above the global minimum **IIa** and therefore are not discussed in detail in this paper.

3.1.3 $Cp_2Mn_2(NO)_2$

Optimizations have been carried out on singlet and triplet $Cp_2Mn_2(NO)_2$ structures (Figure 4 and Table 3). Three $Cp_2Mn_2(NO)_2$ structures were found within 35 kcal/mol of the global minimum **IIIa**. Structures of $Cp_2Mn_2(NO)_2$ with bridging cyclopentadienyl rings were also investigated but found in all cases to lie >35 kcal/mol above the global minimum **IIIa**.

The $Cp_2Mn_2(NO)_2$ structure **IIIa** with the lowest energy is a triplet with two bridging nitrosyl groups (Figure 4). A similar singlet structure **IIIb** was also found but at 30.4 kcal/mol (B3LYP) or 11.1 kcal/mol (BP86) above **IIIa**. Structures **IIIa** and **IIIb** have similar Mn=Mn distances at 2.34 ± 0.03 Å. These Mn=Mn distances are very similar to the Mn=Mn distances in the singlet and triplet $Cp_2Mn_2(\mu\text{-}NO)_2(CO)$ structures **IIa** and **IIb** (Table 2). A formal double bond gives both manganese atoms in **IIIa** the 17-electron configurations required for a dinuclear triplet.



IIIa **IIIb** **IIIc**

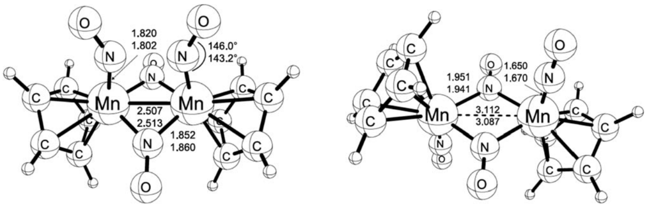
Figure 4. Three optimized structures of $Cp_2Mn_2(NO)_2$ within 35 kcal/mol of the global minimum **IIIa**.

Table 3. Bond lengths [Å], total energies *E* [Hartree] and relative energies Δ*E* [kcal/mol] for the three $Cp_2Mn_2(NO)_2$ structures within 35 kcal/mol of the global minimum **IIIa**.

	IIIa (C_{2v} $^3B_2$)		**IIIb** (C_s $^1A'$		**IIIc** (C_{2h} ^3B_u)	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
Mn–Mn	2.361	2.312	2.344	2.318	2.351	2.342
Mn–N_{bridge}	1.816	1.815	1.809	1.805	1.676	1.645
Mn–$N_{terminal}$	–	–	–	–	–	–
E	–2949.13743	–2949.57935	–2949.08893	–2949.56161	–2949.08387	–2949.53164
Δ*E*	0.0	0.0	30.4	11.1	33.6	29.9
Imaginary frequencies	32*i*, 29*i*, (8*i*, when using ultrafine grid)	6*i* (none, when using ultrafine grid)	11*i*	11*i*	82*i*	60*i*

Table 4. Bond lengths [Å], total energies *E* [Hartree], relative energies Δ*E* [kcal/mol], and imaginary vibrational frequencies for the two $Cp_2Mn_2(NO)_4$ structures.

	IVa (C_{2v}, $^1A_1$) B3LYP	BP86	**IVb** (C_{2h}, ^1A_g) B3LYP	BP86
Mn–Mn	2.507	2.513	3.112	3.087
$Mn–N_{bridge}$	1.852	1.860	1.951	1.941
$Mn–N_{terminal}$	1.820	1.802	1.650	1.670
$MnNO_{terminal}$	146.0	143.2	177.6	179.1
E	–3209.03622	–3209.55955	–3209.04532	–3209.54205
Δ*E*	5.7	0.0	0.0	11.0
Imaginary frequencies	16*i* (none, when using ultrafine grid)	18*i*	18*i*, 8*i* (none, when using ultrafine grid)	8*i*



IVa **IVb**

Figure 5. Two optimized structures of $Cp_2Mn_2(NO)_4$.

The third $Cp_2Mn_2(NO)_2$ structure **IIIc** within 35 kcal/mol of the global minimum **IIIa** is an unbridged triplet at 33.6 kcal/mol (B3LYP) or 29.9 kcal/mol (BP86) above **IIIa**. The Mn=Mn distance of 2.35 ± 0.01 Å is consistent with the formal double bond required to give both manganese atoms the 17-electron configurations required for a dinuclear triplet.

3.1.4 $Cp_2Mn_2(NO)_4$

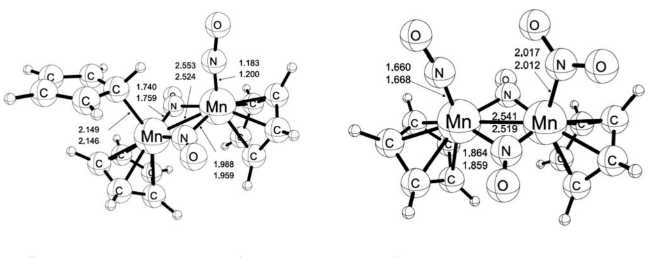
Two structures were optimized for $Cp_2Mn_2(NO)_4$ (Figure 5 and Table 4), namely, singlet *cis* and *trans* doubly bridged structures. The BP86 method predicts the singlet *cis* doubly bridged structure **IVa** to be 11.0 kcal/mol lower in energy than the singlet *trans* doubly bridged structure **IVb**. However, the B3LYP method predicts the reverse with structure **IVa** lying 5.7 kcal/mol above structure **IVb**.

A doubly bridged structure $Cp_2Mn_2(\mu\text{-}NO)_2(NO)_2$ does not require a metal–metal bond for both metal atoms to have the favored 18-electron configuration if all of the nitrosyl groups are the usual three-electron donors. In the *trans* doubly bridged structure **IVb** (Figure 5) the Mn···Mn distance is 3.112 Å (B3LYP) or 3.087 Å (BP86), which is ca. 0.5 Å longer than any of the Mn–Mn distances in the low-energy structures found in this work. This suggests that there is relatively little direct manganese–manganese interaction in **IVb** consistent with the 18-electron rule. Both of the terminal nitrosyl groups in **IVb** are the typical linear nitrosyl groups that function as formal three-electron donors.

The other $Cp_2Mn_2(\mu\text{-}NO)_2(NO)_2$ structure found in this work, namely the *cis* doubly bridged structure **IVa** (Figure 5), has an Mn–Mn distance of 2.507 Å (B3LYP) or 2.513 Å (BP86), which is very similar to that in the $Cp_2Mn_2(NO)_2(CO)_2$ structures **Ia** and **Id** with two nitrosyl bridges (Table 1 and Figure 2). This suggests that the Mn–Mn bond in **IVa** is a formal single bond. In order for both manganese atoms to have the favored 18-electron configuration, one of the terminal nitrosyl groups needs to be the usual formal three-electron donor, but the other terminal nitrosyl group only a one-electron donor. Both of the terminal nitrosyl groups in **IVa** are predicted to be bent with an Mn–N–O angle of 146.0° (B3LYP) or 143.2° (BP86). This bent geometry of the terminal nitrosyl groups in **IVa** is consistent with a resonance hybrid of two structures. One of these structures has the terminal nitrosyl group on the "left" manganese atom as a one-electron donor and the terminal nitrosyl group on the "right" manganese atom as a three-electron donor. The other structure reverses the role of the two terminal nitrosyl groups.

3.1.5 $Cp_3Mn_2(NO)_3$ and $Cp_2Mn_2(NO)_3(NO_2)$

Because of the connection with experimental work,[7,8,15,16] the structures of the two $Cp_2Mn_2(\mu\text{-}NO)_2(NO)X$ (X = NO_2 and $\eta^1\text{-}C_5H_5$) compounds were optimized (Figure 6 and Table 5). The optimized structure **Va** for $Cp_3Mn_2(NO)_3$, namely $(\eta^5\text{-}C_5H_5)_2Mn_2(\mu\text{-}NO)_2(NO)(\eta^1\text{-}C_5H_5)$, has C_s symmetry, with both manganese atoms and the terminal nitrosyl group in the mirror plane. The Mn–Mn bond length is 2.553 Å (B3LYP) or 2.524 Å (BP86), which is close to the experimental result of 2.520 Å determined by X-ray diffraction.[8] This Mn–Mn distance is also very close to that in the $Cp_2Mn_2(\mu\text{-}CO)_2(NO)_2$ structures with two bridging carbonyl groups (Figure 2), consistent with the single bond needed to give both manganese atoms the favored 18-electron configuration in $(\eta^5\text{-}C_5H_5)_2Mn_2(\mu\text{-}NO)_2(NO)(\eta^1\text{-}C_5H_5)$. The two pairs of optimized bridging Mn–N bond lengths are 1.988 Å (B3LYP) or 1.959 Å (BP86), and 1.740 Å (B3LYP) or 1.759 Å (BP86), respectively. These calculated results agree fairly well with



**$(\eta^5\text{-}C_5H_5)_2Mn_2(NO)_3(\eta^1\text{-}C_5H_5)$
Va**

**$(\eta^5\text{-}C_5H_5)_2Mn_2(NO)_3(NO_2)$
VIa**

Figure 6. The optimized structures of the $Cp_2Mn_2(NO)_3X$ (X = $\eta^1\text{-}C_5H_5$ and NO_2) derivatives.

Table 5. Bond lengths [Å] and total energies *E* [Hartree] for the optimized $Cp_2Mn_2(NO)_3X$ (X = η^1-C_5H_5 and NO_2) structures.

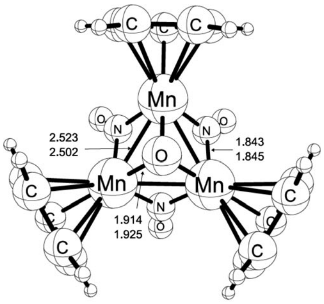
	$Cp_2Mn_2(NO)_3(\eta^1\text{-}C_5H_5)$ (**Va**, $^1A'$)			$Cp_2Mn_2(NO)_3(NO_2)$ (**VIa**, C_s $^1A'$)	
	B3LYP	BP86	Exp.[8]	B3LYP	BP86
Mn–Mn	2.553	2.524	2.520(1)	2.541	2.519
$Mn–N_{bridge}$	1.988, 1.740	1.959, 1.759	1.944(3), 1.752(3)	1.864	1.859
$Mn–N_{terminal}$	1.649	1.666	1.656(5)	1.660	1.668
Mn–C	2.149	2.146	2.161(6)	–	–
$N–O_{bridge}$	1.212	1.228	1.223(4)		
$N–O_{terminal}$	1.183	1.200	1.194(5)		
E	–3272.61239	–3273.11187	–	–3284.26829	–3284.79328
Imaginary frequencies	none	none	–	none	none

the experimental measurements, 1.944(3) Å and 1.752(3) Å and indicate highly unsymmetrical bonding of the bridging nitrosyl groups to the pair of manganese atoms. The Mn–N bond length to the terminal nitrosyl group in **Va** is 1.649 Å (B3LYP) or 1.666 Å (BP86), also in agreement with the experimental result of 1.656(5) Å. The other geometrical parameters predicted by DFT are similarly in good agreement with the experimental data obtained by X-ray diffraction (Table 5). In general, however, the agreement between predicted and experimental bond lengths for **Va** and related compounds is somewhat closer using the BP86 method rather than the B3LYP method.

For $Cp_3Mn_2(NO)_3(NO_2)$ the predicted Mn–Mn bond length in the optimized structure **VIa** is 2.541 Å (B3LYP) or 2.519 Å (BP86) (Figure 6 and Table 5), which corresponds to the expected single bond as in **Va**. The Mn–N distance to the terminal NO group is 1.660 Å (B3LYP) or 1.668 Å (BP86). The average Mn–N bond length to the bridging NO groups is 1.864 Å (B3LYP) or 1.859 Å (BP86), which, as expected, is significantly longer than that to the terminal nitrosyl group. The Mn–N distance to the nitro (NO_2) ligand is still longer at 2.017 Å (B3LYP) or 2.012 Å (BP86).

3.1.6 $Cp_3Mn_3(NO)_4$

The optimized $Cp_3Mn_3(NO)_4$ structure **VIIa** (Figure 7 and Table 6) has C_{3v} symmetry, with one μ_3-NO group located on the C_3 axis bridging three identical manganese atoms, three η^5-C_5H_5 rings, and three NO groups bridging the edges of the Mn_3 triangle (Figure 7 and Table 6). Three imaginary frequencies, namely one a_2 mode and a degenerate e mode of 27*i*, 20*i*, and 20*i* cm^{-1} (B3LYP) or 33*i*, 25*i*, and 25*i* cm^{-1} (BP86), respectively, were found in the original optimization of $Cp_3Mn_3(NO)_4$ by using the standard (75, 302) fine integration grid. Repeating the calculation by using the ultrafine integration grid (99, 590) predicts all real vibrational frequencies for $Cp_3Mn_3(NO)_4$.



$Cp_3Mn_3(\mu\text{-}NO)_3(\mu_3\text{-}NO)$
VIIa

Figure 7. Optimized structure **VIIa** of $Cp_3Mn_3(NO)_4$. The nitrogen atom in the μ_3-NO group is hidden behind the corresponding oxygen atom in order to show the threefold symmetry of this structure.

The Mn–Mn bond lengths in $Cp_3Mn_3(NO)_4$ (**VIIa** in Figure 7) are predicted to be 2.523 Å (B3LYP) or 2.502 Å (BP86). This value is very close to the experimental Mn–Mn distance of 2.506 Å for $Cp_3Mn_3(NO)_4$ by X-ray crystallography[12] as well as the Mn–Mn distances in $Cp_2Mn_2(\mu\text{-}NO)_2(CO)_2$ (**Ia** or **Id** in Figure 2) and $Cp_2Mn_2(NO)_3X$ (X = η^1-C_5H_5 or NO_2) containing Mn–Mn single bonds. Again the BP86 method gives closer agreement with experiment than the B3LYP method. A formal Mn–Mn single bond in $Cp_3Mn_3(NO)_4$ gives all three manganese atoms the favored 18-electron configuration. The distances of 1.914 Å (B3LYP) or 1.925 Å (BP86) between the manganese atoms and the nitrogen atom of the μ_3-NO nitrosyl group bridging the Mn_3 triangle are significantly longer than the distances

Table 6. Bond lengths [Å] and total energies *E* [Hartree] for the optimized $Cp_3Mn_3(NO)_4$ structure **VIIa**.

	VIIa (C_{3v}, $^1A_1$)		
	B3LYP	BP86	Exp.[12]
Mn–Mn	2.523	2.502	2.506
Mn-(μ_3-NO)	1.914	1.925	1.929
Mn-(μ-NO)	1.833	1.845	1.848
μ_3-N–O	1.245	1.258	1.247
μ-N–O	1.214	1.230	1.212
E	–4553.69858	–4554.43837	–
Imaginary frequencies	27*i*, 20*i*, 20*i* (none, when using ultrafine grid)	33*i*, 25*i*, 25*i*	–

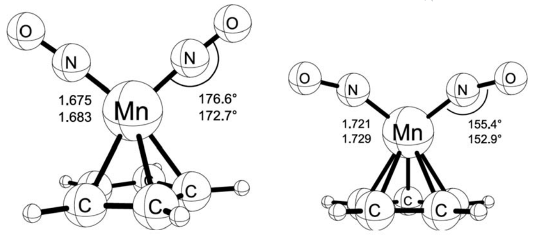
of 1.844 Å (B3LYP) or 1.845 Å (BP86) between the manganese atoms and the nitrogen atoms of the edge bridging nitrosyl groups.

The geometry of $Cp_3Mn_3(\mu\text{-}NO)(\mu_3\text{-}NO)$ (**VIIa** in Figure 7) with formal Mn–Mn single bonds in the Mn_3 triangle and particularly the three formal Mn–N single bonds to the μ_3-NO group suggest an analogy of **VIIa** to amine *N*-oxides, such as Me_3NO. However, the N–O distance in **VIIa** of 1.245 Å (B3LYP) or 1.258 Å (BP86) is appreciably shorter than the N–O distance of 1.388 Å in trimethylamine *N*-oxide determined by X-ray crystallography.[40]

3.1.7 Mononuclear Derivatives

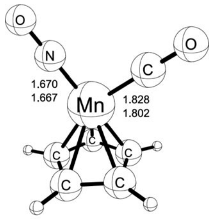
The mononuclear derivatives $CpMn(NO)_2$, CpMn(NO)(CO), and $CpMn(CO)_2$ were investigated by the same DFT methods as the dinuclear derivatives, in order to obtain thermodynamic information on interconversions of the (cyclopentadienyl)nitrosylmanganese derivatives discussed in this paper. For $CpMn(NO)_2$ both singlet and triplet structures were optimized in this work (Figure 8 and Table 7). The singlet structure **VIIIa** is predicted to be the global minimum of $CpMn(NO)_2$ with the triplet structure **VIIIb** lying 7.5 kcal/mol (B3LYP) or 10.4 kcal/mol (BP86) above **VIIIa**. The Mn–N bond lengths of the singlet structure **VIIIa** are 1.675 Å (B3LYP) or 1.683 Å (BP86), and the Mn–N–O angles are nearly linear at 176.6° (B3LYP) or 172.7° (BP86), in agreement with the nitrosyl groups being three-electron donors as required to give singlet $CpMn(NO)_2$, the favored 18-electron configuration. For the triplet structure **VIIIb** the Mn–N bond lengths are significantly longer at 1.721 Å (B3LYP) or 1.879 Å (BP86). Furthermore, the MnNO angles are bent in **VIIIb** at 155.4° (B3LYP) or 152.9° (BP86) in agreement with the pair of NO groups being only four-electron donors (i.e., $1{+}3 \longleftrightarrow 3{+}1$ electron-donor partitioning) rather than six-electron donors. This gives the manganese atom in **VIIIb** the 16-electron configuration required for triplet spin multiciplicity.

The dinuclear $Cp_2Mn_2(NO)_2(CO)_2$ structures (Figure 2) can be obtained by linking two CpMn(NO)(CO) free radical doublets by an Mn–Mn bond with concurrent reorganization of two of the carbonyl and/or nitrosyl groups to bridging positions across the Mn–Mn bond. The geometry of such a CpMn(NO)(CO) fragment was optimized by the B3LYP and BP86 methods (Figure 9 and Table 8). The predicted Mn–NO bond length in the optimized CpMn(NO)(CO) structure **IXa** is 1.670 Å (B3LYP) or 1.667 Å (BP86), and the predicted Mn–CO bond length is 1.828 Å (B3LYP) or 1.802 Å (BP86). The Mn–N–O and Mn–C–O angles are both essentially linear (Table 8).



VIIIa (singlet) **VIIIb (triplet)**

Figure 8. Optimized singlet and triplet structures for $CpMn(NO)_2$.



IXa

Figure 9. The optimized structure of CpMn(NO)(CO).

Table 8. Bond lengths [Å] and total energies *E* [Hartree] for the doublet CpMn(NO)(CO).

	IXa B3LYP ($^2A'$)	BP86 (^2A)
Mn–N	1.670	1.667
Mn–C	1.828	1.802
MnNO angle	179.3	178.1
MnCO angle	179.3	178.0
E	–1587.92658	–1588.14763
Imaginary frequencies	9*i* (none, when using ultrafine grid)	none

A previous study[41] led to an optimization of the $CpMn(CO)_2$ fragment in order to determine some of the thermodynamics of dissociation of dinuclear $Cp_2Mn_2(CO)_n$ derivatives. We also needed the energy of the $CpMn(CO)_2$ fragment to elucidate the thermodynamics of the unsymmetrical dissociation of $Cp_2Mn_2(NO)_2(CO)_2$ into $CpMn(NO)_2$ + $CpMn(CO)_2$. We therefore optimized both singlet and triplet structures of the $CpMn(CO)_2$ fragment

Table 7. Bond lengths [Å], total energies *E* [Hartree], relative energies Δ*E* [kcal/mol], and numbers of imaginary vibrational frequencies for different $CpMn(NO)_2$ structures.

	VIIIa (C_s $^1A'$)		**VIIIb** (C_1 ^3A)	
	B3LYP	BP86	B3LYP	BP86
Mn–N	1.675	1.683	1.721	1.729
Mn–N–O angle	176.6°	172.7°	155.4°	152.9°
E	–1604.51074	–1604.76118	–1604.49878	–1604.74456
Δ*E*	0.0	0.0	7.5	10.4
Imaginary frequencies	9*i*	none	none	none

Table 9. Bond lengths [Å], total energies E [Hartree] and relative energies ΔE [kcal/mol] for different $CpMn(CO)_2$ structures.

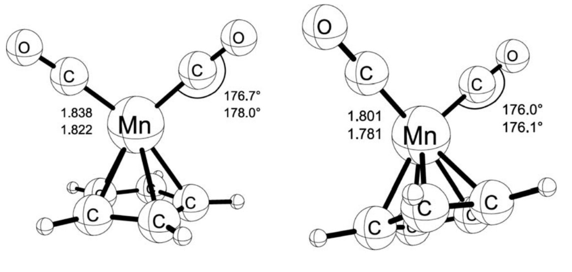
	Xa (C_s $^3A''$)		**Xb** (C_s $^1A'$)	
	B3LYP	BP86	B3LYP	BP86
Mn–C	1.838	1.822	1.801	1.781
MnCO	176.7	178.0	176.0	176.1
E	–1571.31225	–1571.50945	–1571.30004	–1571.50772
ΔE	0.0	0.0	7.7	1.1
Imaginary frequency	$21i$	$21i$	none	none

(Figure 10 and Table 9) using exactly the same methods as those used for the other compounds discussed in this paper. The triplet structure **Xa** (Figure 10) was found to be the global minimum for $CpMn(CO)_2$ with a geometry essentially identical to that found previously[41] (Figure 10). The singlet structure **Xb** of $CpMn(CO)_2$ is predicted to lie 7.7 kcal/mol (B3LYP) or 1.1 kcal/mol (BP86) above the singlet structure **Xa**. The Mn–C–O angles for both the singlet and triplet structures of $CpMn(CO)_2$ are essentially linear.

3.2 Thermodynamics of Reactions of (Cyclopentadienyl)-nitrosylmanganese Derivatives

The dissociation energies, including the zero-point energy (ZPEs) and basis-set superposition error (BSSE) corrections, are presented in Table 10. The BSSEs were calculated by using the Boys–Bernardi counterpoise procedure.[42]

The carbonyl dissociation energies of $Cp_2Mn_2(NO)_2(CO)_2$ and $Cp_2Mn_2(NO)_2(CO)$ (Table 10) are predicted to be only slightly lower than those of the simple binary carbonylmetal compounds as exemplified by the reported[43] experimental carbonyl dissociation energies of 37 kcal/mol for $Cr(CO)_6$ and 41 kcal/mol for $Fe(CO)_5$. Furthermore, both the symmetrical dissociation of $Cp_2Mn_2(NO)_2(CO)_2$ into two CpMn(NO)(CO) fragments and the unsymmetrical dissociation into $CpMn(NO)_2$ and $CpMn(CO)_2$ require significant amounts of energy. The symmetrical dissociation of $Cp_2Mn_2(NO)_2(CO)_2$ requires significantly less energy than the unsymmetrical dissociation (Table 10). These energetics are consistent with $Cp_2Mn_2(NO)_2(CO)_2$ being a molecule sufficiently stable for isolation.[9]



Xa
(triplet)

Xb
(singlet)

Figure 10. Optimized singlet and triplet structures for $CpMn(CO)_2$.

One characteristic of the chemistry of (cyclopentadienyl)-nitrosylmanganese compounds is the formation of $Cp_3Mn_3(NO)_4$ from the photolysis[9] of $Cp_2Mn_2(NO)_2(CO)_2$. Such a photolysis is likely to lead initially to successive carbonyl loss generating $Cp_2Mn_2(NO)_2$. The formation of $Cp_3Mn_3(NO)_4$ from $Cp_2Mn_2(NO)_2$ + $CpMn(NO)_2$ is predicted to be highly exothermic (Table 10) indicating that $Cp_3Mn_3(NO)_4$ is a "thermodynamic sink" in the (cyclopentadienyl)nitrosylmanganese system.

Simple electron counting suggests that $CpMn(NO)_2$, with the favored 18-electron configuration for the central manganese atom, should be a stable monomeric molecule like $CpCo(CO)_2$. However, our DFT studies suggest that $CpMn(NO)_2$ is thermodynamically unfavorable with respect to dimerization to $Cp_2Mn_2(NO)_4$ (Table 10), a feature not encountered in the isoelectronic carbonyl(cyclopentadienyl)cobalt chemistry.[5,6]

3.3 Infrared Spectra

Table 11 lists the predicted ν(CO) and ν(NO) frequencies for the carbonyl(cyclopentadienyl)nitrosylmanganese derivatives studied in this work by using the BP86 functional. The ν(CO) frequencies of the terminal carbonyl groups are predicted to fall in the range 1900–1975 cm^{-1}, whereas those of bridging carbonyl groups, as expected, are predicted to lie significantly lower, in the range 1790–

Table 10. Energies predicted for some reactions of (cyclopentadienyl)nitrosylmanganese derivatives including the ZPE and BSSE corrections.

Reaction	B3LYP	BP86
$Cp_2Mn_2(CO)_2(NO)_2$ (**Ia**) → $Cp_2Mn_2(NO)_2CO$ (**IIa**) + CO	29.5	40.4
$Cp_2Mn_2(NO)_2CO$ (**IIa**) → $Cp_2Mn_2(NO)_2$ (**IIIa**) + CO	25.3	37.5
$Cp_2Mn_2(CO)_2(NO)_2$ (**Ia**) → 2 CpMn(NO)(CO) (**IXa**)	14.3	38.7
$Cp_2Mn_2(CO)_2(NO)_2$ (**Ia**) → $CpMn(CO)_2$ (**Xa**) + $CpMn(NO)_2$ (**VIIIa**)	37.9	57.0
$Cp_2Mn_2(NO)_2$ (**IIIa**) + $CpMn(NO)_2$ (**VIIIa**) → $Cp_3Mn_3(NO)_4$ (**VIIa**)	–30.5	–64.8
2 $CpMn(NO)_2$ (**VIIIa**) → $Cp_2Mn_2(NO)_4$ (**IVb**)	–18.3	–14.8
CpMn(NO)(CO) (**Xa**) → CpMn(NO) + CO	45.8	60.2
2 CpMn(NO) → $Cp_2Mn_2(NO)_2$ (**IIIa**)	–53.0	–81.9

1850 cm^{-1}. For $Cp_2Mn_2(NO)_2(CO)_2$, the only compound listed in Table 11 that has been synthesized, the agreement between the predicted and experimental ν(CO) frequencies is good, within ca. 20 cm^{-1}.

Table 11. ν(NO) and ν(CO) frequencies [cm^{-1}] of carbonyl(cyclopentadienyl)nitrosylmanganese derivatives (BP86 method). Frequencies assigned to bridging CO or NO groups are given in *italics*. The infrared intensities [km/mol] (in parentheses) are also given.

Structure	ν(NO)	ν(CO)
$Cp_2Mn_2(NO)_2(CO)_2$ exp.	*1509*, 1707	*1781*, 1956
$Cp_2Mn_2(NO)_2(CO)_2$ (**Ia**)	*1565*(755), *1592*(5)	1929(463), 1971(1234)
$Cp_2Mn_2(NO)_2(CO)_2$ (**Ib**)	1769(260), 1784(633)	*1792*(871), *1842*(482)
$Cp_2Mn_2(NO)_2(CO)_2$ (**Ic**)	1763(0), 1767(1287)	*1795*(864), *1835*(0)
$Cp_2Mn_2(NO)_2(CO)_2$ (**Id**)	*1567*(751), *1594*(0)	1922(1611), 1943(0)
$Cp_2Mn_2(NO)_2(CO)_2$ (**Ie**)	*1575*(431), 1775(634)	*1810*(417), 1962(831)
$Cp_2Mn_2(NO)_2(CO)_2$ (**If**)	*1582*(423), 1767(673)	*1811*(499), 1940(635)
$Cp_2Mn_2(NO)_2(CO)$ (**IIa**)	*1580*(683), *1613*(294)	1827(475)
$Cp_2Mn_2(NO)_2(CO)$ (**IIb**)	1708(202), 1786(633)	*1724*(667)
CpMn(NO)(CO) (**IXa**)	1781(766)	1960(748)
$CpMn(CO)_2$ (**Xa**)	–	1908(916), 1957(745)
$CpMn(CO)_2$ (**Xb**)	–	1898(1324), 1971(677)

The predicted ν(NO) frequencies (Table 11) follow a similar pattern with terminal ν(NO) frequencies in the range 1700–1790 cm^{-1} and bridging ν(NO) frequencies significantly lower at 1500–1590 cm^{-1}. Here, the agreement between predicted and experimental ν(NO) frequencies in $Cp_2Mn_2(NO)_2(CO)_2$ is not as good as that for the ν(CO) frequencies. Thus, the predicted terminal and bridging ν(NO) frequencies for the $Cp_2Mn_2(NO)_2(CO)_2$ structure **Ie** lie ca. 70 cm^{-1} above the experimental values for $Cp_2Mn_2(NO)_2(CO)_2$. A similar discrepancy between the ν(NO) frequencies predicted by the same DFT method and the experimental ν(NO) frequencies was noted previously for $Mn(NO)(CO)_4$[44] and $Cr_2(NO)_2(CO)_8$[45], where the predicted ν(NO) frequencies were found to lie 59 and 65 cm^{-1}, respectively, above the experimental ν(NO) frequencies.

The chemistry of carbonyl(cyclopentadienyl)nitrosylmanganese compounds typically leads readily to the complete loss of carbonyl groups to give some (cyclopentadienyl)nitrosylmanganese derivatives with interesting structures. The ν(NO) frequencies of some of these carbonyl-free (cyclopentadienyl)nitrosylmanganese derivatives are reported in Table 12. In cases where comparison between predicted and experimental ν(NO) frequencies is possible, the predicted ν(NO) frequencies are again seen typically to be ca. 70 cm^{-1} above the experimental frequencies, particularly for bridging nitrosyl groups.

A carbonyl-free (cyclopentadienyl)nitrosylmanganese compound of particular interest is $CpMn(NO)_2$. Despite the fact that the manganese atom in $CpMn(NO)_2$ has the favored 18-electron configuration, monomeric $CpMn(NO)_2$ is predicted to be thermodynamically unstable with respect to dimerization to $Cp_2Mn_2(NO)_4$ (Table 10). In this connection, the photolysis of $CpMn(NO)(CO)_2^+$ with aqueous nitrite was reported as long ago as 1967 to give a black solid with elemental analyses,[13] including a direct oxygen analysis, in good agreement with the formula $[CpMn(NO)_2]_n$. Furthermore, the infrared ν(NO) frequencies (Table 12) reported for this black product (1525 and 1760 cm^{-1}) are in good agreement with those predicted for isomer **IVb** of $Cp_2Mn_2(NO)_4$ (1551 and 1760 cm^{-1}). However, subsequent work on the reactions of $CpMn(NO)(CO)_2^+$ with nucleophiles[16] suggest that this black product almost certainly is $Cp_2Mn_2(NO)_3(NO_2)$ (**VIa** in Figure 6). The ν(NO) frequencies of $Cp_2Mn_2(NO)_3(NO_2)$ at 1589 and 1799 cm^{-1} predicted by BP86 and found experimentally at 1532 and 1754 cm^{-1} (Table 12) also support reformulation of the reported[13] $[CpMn(NO)_2]_n$ as $Cp_2Mn_2(NO)_3(NO_2)$ (**VIa**). In this case, the ν(NO) frequencies alone are obviously not sufficient to identify the product even when accompanied by this DFT study.

Table 12. ν(NO) and ν(CO) frequencies [cm^{-1}] of carbonyl-free (cyclopentadienyl)nitrosylmanganese derivatives (BP86 method). Frequencies assigned to bridging NO groups are given in *italics*. The infrared intensities [km/mol] (in parentheses) are also given.

Structure	ν(NO)
$Cp_2Mn_2(NO)_2$ (**IIIa**)	*1539*(754), *1574*(9)
$Cp_2Mn_2(NO)_2$ (**IIIb**)	*1522*(669), *1560*(0)
$Cp_2Mn_2(NO)_2$ (**IIIc**)	1722(1179), 1741(0)
$Cp_2Mn_2(NO)_4$ (**IVa**)	*1549*(756), *1578*(194), 1633(354), 1685(748)
$Cp_2Mn_2(NO)_4$ (**IVb**)	*1551*(552), *1581*(0), 1760(1447), 1778(0)
$Cp_2Mn_2(NO)_3(\eta^1\text{-}C_5H_5)$ (**Va**)	*1565*(664), *1597*(15), 1760(712)
$Cp_2Mn_2(NO)_3(\eta^1\text{-}C_5H_5)$ exp.	*1525*, 1745
$Cp_2Mn_2(NO)_3(NO_2)$ (**VIa**)	1471(118), *1589*(768), *1621*(4), 1799(739)
$Cp_2Mn_2(NO)_3(NO_2)$ exp.	*1532*, 1754
"$CpMn(NO)_2$" exp.	1387, *1525*, 1760
$Cp_3Mn_3(NO)_4$ (**VIIa**)	*1422*(328), *1548*(700), *1595*(537)
$Cp_3Mn_3(NO)_4$ exp.	*1313* (μ_3-NO), *1475* (μ-NO), *1520* (μ-NO)
$CpMn(NO)_2$ (**VIIIa**)	1755(902), 1813(603)
$CpMn(NO)_2$ (**VIIIb**)	1665(1019), 1713(362)

4. Summary

Some features of the $Cp_2Mn_2(NO)_2(CO)_n$ (n = 2, 1, 0) systems are predicted to resemble those of the isoelectronic $Cp_2Fe_2(CO)_{n+2}$ systems, whereas other features are distinctly different. Six structures are found for $Cp_2Mn_2(NO)_2(CO)_2$ with various combinations of terminal and bridging carbonyl and nitrosyl groups within ca. 3 kcal/mol of each other, indicating a highly fluxional system analogous to the isoelectronic $Cp_2Fe_2(CO)_4$. For $Cp_2Mn_2(NO)_2(CO)$ a triplet-state triply bridged structure is predicted to be the global minimum just as it is for the isoelectronic $Cp_2Fe_2(CO)_3$. For $Cp_2Mn_2(NO)_2$ a doubly bridged triplet structure is predicted to lie ca. 30 kcal/mol below the corresponding singlet structure, unlike the isoelectronic $Cp_2Fe_2(CO)_2$, where the singlet structure is of lower energy.

The monomer $CpMn(NO)_2$ with a favorable 18-electron configuration for the manganese atom, is predicted to be unstable towards dimerization to give $Cp_2Mn_2(\mu\text{-}NO)_2(NO)_2$, for which two structures are found with similar energies. One $Cp_2Mn_2(\mu\text{-}NO)_2(NO)_2$ structure has an essentially non-bonding Mn···Mn distance of ca. 3.1 Å and linear terminal MnNO units, whereas the other $Cp_2Mn_2(\mu\text{-}NO)_2$-

$(NO)_2$ structure has a single-bond Mn–Mn distance of ca. 2.5 Å and bent terminal MnNO units.

The structures predicted for $Cp_2Mn(\mu\text{-}NO)_2(NO)X$ (X = NO_2 and $\eta^1\text{-}C_5H_5$) and $Cp_3Mn_3(\mu\text{-}NO)_3(\mu_3\text{-}NO)$ are close to the experimentally known structures. In $Cp_2Mn(\mu\text{-}NO)_2(NO)(\eta^1\text{-}Cp)$ derivatives, the $Mn_2(\mu\text{-}NO)_2$ unit is unsymmetrical with significantly different (by ca. 0.2 Å) Mn–N bond lengths to each side. However, in $Cp_2Mn_2(NO)_2(CO)_n$ (n = 2, 1, 0) and $Cp_2Mn_2(\mu\text{-}NO)_2(NO)_2$ the $Mn_2(\mu\text{-}NO)_2$ units are symmetrical with essentially the same Mn–N bond lengths to both manganese atoms.

Supporting Information (see footnote on the first page of this article): Tables S1–S10: Theoretical harmonic vibrational frequencies for $Cp_2Mn_2(NO)_2(CO)_2$ (6 structures),$Cp_2Mn_2(NO)_2(CO)$ (2 structures), $Cp_2Mn_2(NO)_2$ (3 structures), $Cp_2Mn_2(NO)_4$ (2 structures), $Cp_2Mn_2(NO)_3(\eta^1\text{-}C_5H_5)$ (1 structure), $Cp_2Mn_2(NO)_3(NO_2)$ (1 structure), $Cp_3Mn_3(NO)_4$ (1 structure), $CpMn(NO)_2$ (2 structures), $CpMn(NO)(CO)$ (1 structure), and $CpMn(CO)_2$ (2 structures) using the BP86 method; Tables S11–S31: $Cp_2Mn_2(NO)_2(CO)_2$ (6 structures), $Cp_2Mn_2(NO)_2(CO)$ (2 structures), $Cp_2Mn_2(NO)_2$ (3 structures),$Cp_2Mn_2(NO)_4$ (2 structures), $Cp_2Mn_2(NO)_3(\eta^1\text{-}C_5H_5)$ (1 structure), $Cp_2Mn_2(NO)_3(NO_2)$ (1 structure), $Cp_3Mn_3(NO)_4$ (1 structure), $CpMn(NO)_2$ (2 structures), $CpMn(NO)(CO)$ (1 structure), and $CpMn(CO)_2$ (2 structures) using the B3LYP method.

Acknowledgments

We are grateful to the U. S. National Science Foundation (Grants CHE-0451445 and CHE-0716718) for support of this work. B. Y. thanks the China Scholarship Council for financial support (CSC Grant No. 20063142) and the National Natural Science Foundation of China (Grant No. 10604022).

---

[1] T. J. Kealy, P. L. Pauson, *Nature* **1961**, *168*, 1039.
[2] S. A. Miller, J. A. Tebboth, J. F. Tremaine, *J. Chem. Soc.* **1952**, 632.
[3] E. O. Fischer, S. Vigoureux, *Chem. Ber.* **1958**, *91*, 2205.
[4] E. O. Fischer, R. Jira, *Z. Naturforsch. Teil B* **1954**, *9*, 618.
[5] T. S. Piper, F. A. Cotton, G. Wilkinson, *J. Inorg. Nucl. Chem.* **1955**, *1*, 165.
[6] E. O. Fischer, R. Jira, *Z. Naturforsch. Teil B* **1955**, *10*, 355.
[7] T. S. Piper, G. Wilkinson, *J. Inorg. Nucl. Chem.* **1956**, *2*, 38.
[8] J. L. Calderon, S. Fontana, E. Frauendorfer, V. W. Day, B. R. Stults, *Inorg. Chim. Acta* **1976**, *17*, L31.
[9] R. B. King, M. B. Bisnette, *Inorg. Chem.* **1964**, *3*, 791.
[10] R. B. King, *Inorg. Chem.* **1966**, *5*, 2227.
[11] R. C. Elder, F. A. Cotton, R. A. Schunn, *J. Am. Chem. Soc.* **1967**, *89*, 3645.
[12] R. C. Elder, *Inorg. Chem.* **1974**, *13*, 1037.
[13] R. B. King, *Inorg. Chem.* **1967**, *6*, 30.
[14] J. L. Calderon, F. A. Cotton, B. G. DeBoer, N. Martinez, *J. Chem. Soc., Chem. Commun.* **1971**, 1476.
[15] J. Müller, S. Schmitt, *Z. Anorg. Allg. Chem.* **1976**, *426*, 77.
[16] B. W. Hames, B. W. S. Kolthammer, P. Legzdins, *Inorg. Chem.* **1981**, *20*, 650.
[17] A. W. Ehlers, G. Frenking, *J. Am. Chem. Soc.* **1994**, *116*, 1514.
[18] B. Delly, M. Wrinn, H. P. Lüthi, *J. Chem. Phys.* **1994**, *100*, 5785.
[19] J. Li, G. Schreckenbach, T. Ziegler, *J. Am. Chem. Soc.* **1995**, *117*, 486.
[20] V. Jonas, W. Thiel, *J. Chem. Phys.* **1995**, *102*, 8474.
[21] T. A. Barckholtz, B. E. Bursten, *J. Am. Chem. Soc.* **1998**, *120*, 1926.
[22] S. Niu, M. B. Hall, *Chem. Rev.* **2000**, *100*, 353.
[23] P. Macchi, A. Sironi, *Coord. Chem. Rev.* **2003**, *238*, 383.
[24] J.-L. Carreon, J. N. Harvey, *Phys. Chem. Chem. Phys.* **2006**, *8*, 93.
[25] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.
[26] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.
[27] A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098.
[28] J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822.
[29] T. H. Dunning, *J. Chem. Phys.* **1970**, *53*, 2823.
[30] S. Huzinaga, *J. Chem. Phys.* **1965**, *42*, 1293.
[31] A. J. H. Wachters, *J. Chem. Phys.* **1970**, *52*, 1033.
[32] D. M. Hood, R. M. Pitzer, H. F. Schaefer, *J. Chem. Phys.* **1979**, *71*, 705.
[33] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03*, Revision D.01, Gaussian, Inc., Wallingford, CT, **2004**.
[34] M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, *Gaussian 94*, Revision E.2, Gaussian, Inc., Pittsburgh, PA, **1995**.
[35] B. N. Papas, H. F. Schaefer, *J. Mol. Struct.* **2006**, *768*, 175.
[36] Y. Xie, H. F. Schaefer, R. B. King, *J. Am. Chem. Soc.* **2000**, *122*, 8746.
[37] J. V. Caspar, T. J. Meyer, *J. Am. Chem. Soc.* **1980**, *102*, 7794.
[38] R. H. Hooker, K. A. Mahmoud, A. J. Rest, *J. Chem. Soc., Chem. Commun.* **1983**, 1022.
[39] A. F. Hepp, J. P. Blaha, C. Lewis, M. S. Wrighton, *Organometallics* **1984**, *3*, 174.
[40] A. Caron, G. J. Palenik, E. Goldish, J. Donohue, *Acta Crystallogr.* **1964**, *17*, 102.
[41] X. Zhang, Q.-S. Li, Y. Xie, R. B. King, H. F. Schaefer, *Organometallics* **2008**, *27*, 61.
[42] S. F. Boys, F. Bernardi, *Mol. Phys.* **1970**, *19*, 553.
[43] L. S. Sunderlin, D. Wang, R. R. Squires, *J. Am. Chem. Soc.* **1993**, *115*, 12060.
[44] H. Wang, Y. Xie, R. B. King, H. F. Schaefer, *Inorg. Chem.* **2006**, *45*, 10849.
[45] H. Wang, Y. Xie, J. D. Zhang, R. B. King, H. F. Schaefer, *Inorg. Chem.* **2007**, *46*, 1836.

Received: July 1, 2009
Published Online: July 31, 2009