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Binuclear Cyclopentadienylmetal Nitrosyls of Iron, Cobalt, and Nickel: Comparison with Related Carbonyl Derivatives

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The binuclear cyclopentadienylmetal nitrosyls and carbonyls $Cp_2M_2(AO)_n$ (A = N, M = Fe, Co, Ni; A = C, M = Ni; n = 2, 1) are studied by density functional theory using the B3LYP and BP86 functionals. In general, structures with bridging AO ligands are energetically preferred over those with terminal AO ligands. Thus, the global minima for $Cp_2M_2(AO)_2$ are all found to have closely related axial dimetallocene structures with two symmetrically bridging AO ligands but variable planarity of the central $M(\mu\text{-}AO)_2M$ units. Similarly, the single AO ligands in the global minima for $Cp_2M_2(AO)$ are found to bridge symmetrically the pair of metal atoms. However, structures with terminal AO groups and a single bridging Cp ligand are also found at accessible energies for $CpM_2(NO)(\mu\text{-}Cp)$ (M = Fe and Co) and $CpNi_2(CO)(\mu\text{-}Cp)$. The metal–metal bond distances in $Cp_2M_2(AO)_n$ derivatives correlate reasonably well with the requirements of the 18-electron rule. In this connection, the unusual dimer $Cp_2Ni_2(\mu\text{-}NO)_2$ has a Ni–Ni bond distance suggestive of a single bond and geometry suggesting one one-electron donor bridging NO group and one three-electron donor bridging NO group. However, dissociation of $Cp_2Ni_2(\mu\text{-}NO)_2$ into the well-known stable monomer CpNiNO is highly favored energetically.

1. Introduction

Iron and cobalt are known to form stable binuclear cyclopentadienylmetal nitrosyls of the type $Cp_2M_2(NO)_2$ (Cp = η^5-cyclopentadienyl or substituted cyclopentadienyl; M = Fe[1] and Co[2]). In order for the metal atoms to attain the favored 18-electron configuration in these derivatives, the cobalt derivative requires a Co−Co single bond whereas the iron derivative requires an Fe═Fe double bond. On the other hand, nickel is known to form the very stable mononuclear cyclopentadienylnickel nitrosyl[3] CpNiNO, which also obeys the favored 18-electron rule.

These 18-electron configurations for dimeric $Cp_2M_2(NO)_2$ (M = Fe and Co) with metal−metal double and single bonds, respectively, and monomeric CpNiNO assume that the neutral NO ligands function as three-electron donors, whether terminal or bridging.[4,5] Alternatively and equivalently, the NO group may be considered as the nitrosonium cation, NO^+, isostructural and isoelectronic with a neutral CO group. In either case, the M−NO interactions for such three-electron donor NO groups are very similar to the M−CO interactions in analogous metal carbonyl derivatives.[4] Such three-electron donor neutral NO groups are linear when terminal, as recognized by an ∠MNO angle close to 180°. Analogously, neutral bridging μ-NO groups donating three electrons to the pair of metal atoms have structures with coplanar $N(O)M_2$ units similar to BF_3, as recognized by a dihedral ∠MMNO angle close to 180°. However, in some cases, particularly with late transition metal nitrosyls, a terminal neutral NO group can function as a net one-electron donor corresponding to the nitroxyl anion, NO^-. In this case, the M−NO angle is bent rather than linear with ∠MNO angles in the range 120−140°. Analogously, one-electron bridging μ-NO groups might be expected with a pyramidal $N(O)M_2$ configuration similar to NH_3, as recognized by dihedral angles around 120° or less. The NO groups of various types are depicted in Figure

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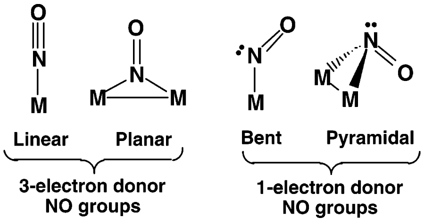

Figure 1. Terminal and bridging (neutral) NO groups acting as donors of one or three electrons to a metal atom M.

1. Also note that, since the NO ligand has an odd number of electrons, the binuclear mononitrosyls $Cp_2M_2(NO)$ necessarily are paramagnetic with at least one unpaired electron.

The electronic structures of the dimeric cyclopentadienylmetal nitrosyls $Cp_2M_2(NO)_2$ and related compounds have been examined by a number of workers. Thus, Pinhas and Hoffmann[6] found that the two metal atoms and the bridging carbonyls or nitrosyls in the structures of $Cp_2M_2(NO)_2$ and $Cp_2M_2(CO)_x(NO)_{2-x}$ are coplanar in nearly all cases. The differences in metal−metal bond lengths do not correlate well with electron count, leading to an apparent contradiction between the theory and the structural facts for this series of compounds. This is consistent with an earlier conclusion by Bernal, Korp, Reisner, and Herrmann[7] that the successive increase in bond order predicted by the 18-electron rule is not observed. In subsequent work,[8] the Fenske−Hall molecular orbital method was used to investigate the electronic structures of $Cp_2Fe_2(NO)_2$, $Cp_2Co_2(CO)_2$, $Cp_2Co_2(NO)_2$, and $Cp_2Ni_2(CO)_2$ with a view to discerning the similarities and differences among these four complexes in terms of metal−metal and metal−bridge interactions.

Experimental methods have also been used to investigate the electronic structures of two cobalt dimers containing bridging nitrosyl groups, namely $Cp_2Co_2(\mu\text{-}NO)_2$ and $Cp_2Co_2(\mu\text{-}NO)(\mu\text{-}CO)$. Thus, information obtained by vapor-phase UV photoelectron (PE) spectroscopy and electrochemical techniques[9] was incorporated into a unique bonding picture using discrete variational-Xα calculations. The UV PE spectrum of $Cp_2Co_2(\mu\text{-}NO)_2$ is consistent with a bent $Co_2(\mu\text{-}NO)_2$ core in the vapor phase, in contrast to the planar core observed in the solid state.[7] The theoretical calculations predict a direct Co−Co interaction for the bent geometry in contrast to the planar geometry for which no charge accumulation between the metal atoms is computed. On the other hand, $Cp_2Ni_2(CO)_2$ was found to adopt a planar geometry in the solid state, as shown by X-ray crystallography[10] and the appearance of only one ν(CO) frequency in its solid-state infrared spectrum. However, the solution-state infrared spectrum of $Cp_2Ni_2(CO)_2$ exhibits two ν(CO) frequencies, indicative of a bent geometry.[11,12] The valence PE ionizations of $Cp_2Fe_2(\mu\text{-}NO)_2$, $Cp^*_2Fe_2(\mu\text{-}NO)_2$, $Cp_2Ru_2(\mu\text{-}NO)_2$, and $Cp^*_2Co_2(\mu\text{-}CO)_2$ ($Cp = \eta^5\text{-}C_5H_5$ and $Cp^* = \eta^5\text{-}Me_5C_5$) were examined for comparison with several theoretical calculations of the electronic structure and bonding in these complexes.[13] Since as many metal−metal antibonding orbitals are occupied as metal−metal bonding orbitals, the formal metal−metal bond order was inferred to be zero. In addition, Raman and infrared spectral data on the vibrational modes of the CpM unit were collected and the fundamental frequencies were determined.[14]

Quelch and Hillier[15] used ab initio configuration interaction (CI) calculations on $Cp_2Co_2(\mu\text{-}NO)_2$ and $Cp_2Co_2(\mu\text{-}CO)_2$ to suggest quartet bonding schemes and interpret their PE spectra. Subsequent ab initio MO−SCF and multiconfiguration SCF calculations on the d^9-d^9 complex $Cp_2Co_2(\mu\text{-}NO)_2$ indicate that the ground state of this molecule might be a triplet separated by 280 cm^{-1} from the associated covalent singlet.[16] This conclusion is in agreement with the similarity of the metal−metal bond lengths observed for various d^8-d^8 and d^9-d^9 complexes. However, the ground-state electronic structure of $Cp_2Co_2(\mu\text{-}NO)_2$ has been a topic of some discussion since Berg and Anderson concluded that $Cp_2Co_2(\mu\text{-}NO)_2$ is a diamagnetic singlet in the solid state (5−280 K) and in C_6H_6 solution (303−327 K).[17]

Day and co-workers[18] showed by X-ray crystallography that the structure of $Cp_2Fe_2(\mu\text{-}NO)_2$ has symmetrically bridging NO groups and an iron−iron distance suggesting an Fe═Fe double bond. Subsequent workers[19] used ab initio SCF and CI calculations to interpret the UV PE spectrum and electronic structure of $Cp_2Fe_2(\mu\text{-}NO)_2$. Symmetry-adapted (ab initio) SCF calculations carried out on $Cp_2Fe_2(\mu\text{-}NO)_2$ with a planar $Fe_2(NO)_2$ core indicate a C_{2h} conformation with staggered C_5H_5 rings to be more stable by 60 kcal/mol than a C_{2v} conformation with eclipsed rings. This unexpected barrier for the rotation of the Cp ring is shown to arise from the space symmetry constraints acting on the NO π^* orbital combinations for the eclipsed conformation.[20] The intramolecular translocation of a nitrogen atom from a nitrosyl to a cyclopentadienyl ligand of $(C_5H_5)_2Fe_2NO^+$ was probed by neutralization reionization mass spectrometry (NRMS), in which the unimolecular loss of C_5H_5N is observed. This neutral C_5H_5N fragment was unequivocally characterized as pyridine by means of NRMS.[21] The electronic structure of $Cp_2Ni_2(\mu\text{-}CO)_2$ has been discussed on the

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Table 1. Bond Distances (in Å), Total Energies (E in Hartree) and Relative Energies (ΔE in kcal/mol) for $Cp_2Fe_2(NO)_2$ and $Cp_2Fe_2(NO)$

	$Cp_2Fe_2(\mu\text{-}NO)_2$ **Ia** (C_{2v})			$Cp_2Fe_2(NO)_2$ **Ib** (C_{2h})		$Cp_2Fe_2(\mu\text{-}NO)$ **IIa** (C_{2v})		$CpFe_2(NO)(\mu\text{-}Cp)$ **IIb** (C_s)	
	B3LYP	BP86	exptl[18]	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
Fe−Fe	2.349	2.339(2.326)	2.326	2.311	2.326	1.972	1.988	2.482	2.105
Fe−N	1.781	1.792(1.768)	1.768	1.611	1.622	1.819	1.814	1.727	1.617
N−O	1.219	1.231(1.254)	1.254	1.189	1.203	1.206	1.219	1.200	1.208
∠FeFeNO	179.3°	179.2°				180.0°	180.0°		
∠FeNO	138.7°	139.3°		167.4°	167.6°	147.2°	146.8°	179.1°	175.9°
−energy	3174.59421	3175.09015		3174.51285	3175.02418	3044.51455	3045.00037	3044.57307	3044.99219
ΔE	0	0		51.1	41.4	36.7	0	0	5.1
imaginary frequency	$17i$	$8i$		$63i$, $56i$	$60i$, $52i$	$311i$	none	$38i$	$81i$

basis of the He(I) and He(II) excited PE spectra and extended Hückel calculations.[22]

In previous papers,[23] we report systematic density functional theory (DFT) studies of the structures and harmonic vibrational frequencies of the binuclear cyclopentadienylmetal carbonyls $Cp_2Co_2(CO)_n$ (n = 3, 2, and 1) and $Cp_2Fe_2(CO)_n$ (n = 4, 3, 2, and 1). In this paper, we use related methods to study the analogous cyclopentadienylmetal nitrosyls $Cp_2M_2(NO)_n$ (M = Fe and Co; n = 2 and 1). In addition, we extend our DFT studies to the related nickel derivatives $Cp_2Ni_2(AO)_n$ (A = C and N; n = 2 and 1).

2. Theoretical Methods

For carbon and oxygen, the double-ς plus polarization (DZP) basis set used here (9s5p/4s2p) adds one set of pure spherical harmonic d functions with orbital exponents $\alpha_d(C) = 0.75$ and $\alpha_d(O) = 0.85$ to the Huzinaga−Dunning standard contracted DZ sets. For H, a set of p polarization functions $\alpha_p(H) = 0.75$ is added to the Huzinaga−Dunning DZ sets.[24,25] For Fe, Co, and Ni, our loosely contracted DZP basis set (14s11p6d/10s8p3d) uses the Wachters' primitive set augmented by two sets of p functions and one set of d functions contracted following Hood et al.[26,27] For the dinitrosyls $Cp_2Fe_2(NO)_2$, $Cp_2Co_2(NO)_2$, and $Cp_2Ni_2(NO)_2$, there are 358 contracted Gaussian functions. For the mononitrosyls $Cp_2Fe_2(NO)$, $Cp_2Co_2(NO)$, and $Cp_2Ni_2(NO)$, there are 328 contracted Gaussian functions.

Electron correlation effects were included by employing DFT which has been found to be a practical and effective computational tool, especially for organometallic compounds. 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)[28] with the Lee, Yang, and Parr (LYP) correlation functional.[29] The second approach is the BP86 method, which marries Becke's 1988 exchange functional (B)[30] with Perdew's 1986 correlation functional.[31]

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 are evaluated analytically as well. All of the computations were carried out with the Gaussian 94 program[32] 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.[33]

The optimized geometries from these computations are depicted in Figures 2−6 with all bond distances given in Ångstroms.

3. Results and Discussion

3.1. Molecular Structures. 3.1.1. $Cp_2Fe_2(NO)_2$ and $Cp_2Fe_2(NO)$. There are two types of stationary points for $Cp_2Fe_2(NO)_2$ (Figure 2 and Table 1), namely a C_{2v} dibridged structure, **Ia**, and a C_{2h} trans-unbridged structure, **Ib**. Structure **Ia** is found to be the global minimum with only a single very small imaginary vibrational frequency at $17i$ (B3LYP) or $8i$ cm^{-1} (BP86). The trans-unbridged structure, **Ib,** for $Cp_2Fe_2(NO)_2$ is found to have an energy higher than that of the bridged structure, **Ia**, by 51.1 (B3LYP) or 41.4 kcal/mol (BP86). Structure **Ib** has two small imaginary vibrational frequencies of $63i$ and $56i$ cm^{-1} (B3LYP) or $60i$ and $52i$ cm^{-1} (BP86) and thus is very close to the actual minimum.

In the dibridged structure, **Ia** (Figure 2), the $Fe(\mu\text{-}NO)_2Fe$ core is virtually coplanar and perpendicular to the planes of the cyclopentadienyl ligands. The 5-fold axes of the cyclopentadienyl groups are nearly collinear with the iron−iron bond and perpendicular to the vector joining the two bridging nitrosyl groups. The iron−iron bond distance is 2.349

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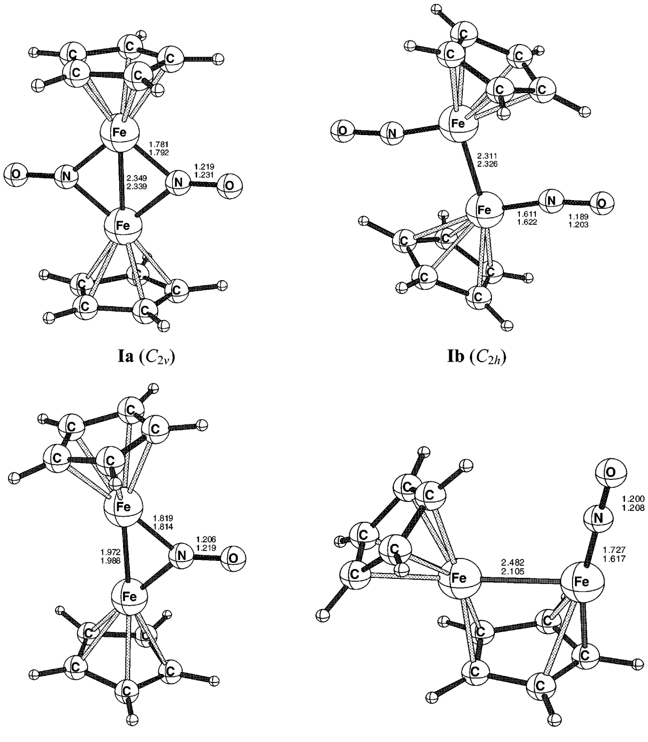
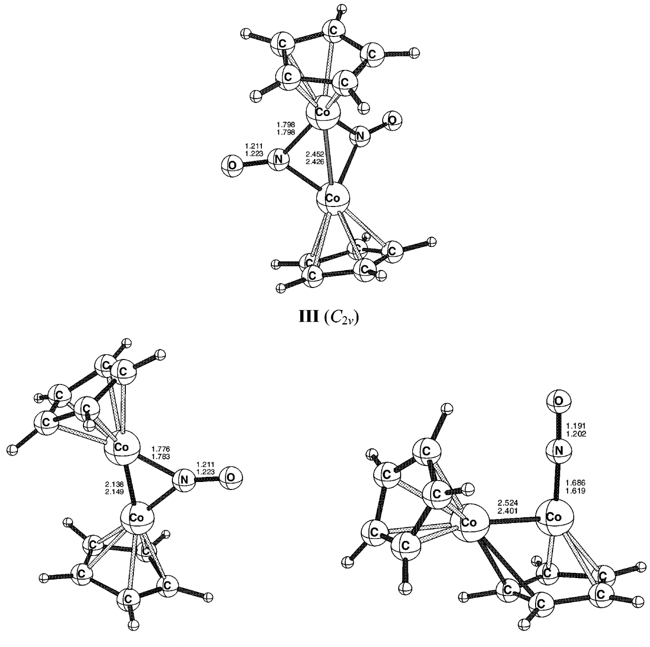


Ia (C_{2v}) **Ib** (C_{2h})

IIa (C_{2v}) **IIb** (C_s)

Figure 2. Optimized geometries for $Cp_2Fe_2(NO)_2$ and $Cp_2Fe_2(NO)$ isomers.



III (C_{2v})

IVa (C_{2v}) **IVb** (C_s)

Figure 3. Optimized geometries for $Cp_2Co_2(NO)_2$ and $Cp_2Co_2(NO)$ isomers.

(B3LYP) or 2.339 Å (BP86), which is close to the experimental value of 2.326 Å determined by X-ray crystallography[18] and consistent with the Fe═Fe double bond required to give each iron atom the favored 18-electron rare gas configuration.

Optimizations using the BP86 functional show the mononitrosyl $Cp_2Fe_2(\mu\text{-NO})$ (**IIa** in Figure 2) with a bridging NO ligand to be a genuine minimum with no imaginary frequencies. However, the corresponding optimized $Cp_2Fe_2(\mu\text{-NO})$ structure using the B3LYP method has a large imaginary frequency of 311*i* cm^{-1}. Following this imaginary frequency leads to the C_s structure $CpFe_2(NO)(\mu\text{-Cp})$ **(IIb)** with a terminal NO group and a bridging Cp group at 36.7 kcal/mol lower energy. With the BP86 functional, the structure $CpFe_2(NO)(\mu\text{-Cp})$ **(IIb)** lies 5.1 kcal/mol above the global minimum, **IIa**.

The iron−iron bond distance in $Cp_2Fe_2(\mu\text{-NO})$ (**IIa**) is predicted to be 1.972 (B3LYP) or 1.988 Å (BP86), which is shorter than the metal−metal bond distance in the structure **IIb** (2.482 Å by B3LYP or 2.105 Å by BP86). If the pentahapto-bonded cyclopentadienyl rings and bridging nitrosyl groups are regarded as five- and three-electron donors, respectively, each of the iron atoms in the $Cp_2Fe_2(\mu\text{-NO})$ structures can achieve a 18-electron configuration only by forming an iron−iron bond of order $3^1/_2$, possibly a $\sigma + 2\pi + {}^1/_2\delta$ seven-electron bond.

3.1.2. $Cp_2Co_2(NO)_2$ and $Cp_2Co_2(NO)$. The only structure optimized for $Cp_2Co_2(NO)_2$ was the singlet dibridged structure, **III** (Figure 3 and Table 2). An attempt to optimize an unbridged structure for $Cp_2Co_2(NO)_2$ instead led to the same dibridged structure **III**. Structure **III** has small imaginary vibrational frequencies of 20*i* and 13*i* (B3LYP) or 22*i* cm^{-1} (BP86) and is thus likely to be close to the actual minimum.

The cobalt−cobalt bond distance in $Cp_2Co_2(\mu\text{-NO})_2$ (**III**) is predicted to be 2.452 (B3LYP) or 2.426 Å (BP86). The BP86 distance is 0.054 Å longer than the experimental 2.372 Å determined by X-ray diffraction[7] and is consistent with the Co−Co single bond required to give each cobalt atom in $Cp_2Co_2(\mu\text{-NO})_2$ the favored 18-electron configuration assuming three-electron donor NO groups. The $Co_2(\mu\text{-NO})_2$ core in structure **III** is bent with dihedral angles of 127.9° (B3LYP) or 132.3° (BP86), along the Co−Co axis. The bond angles ∠CoNCo and ∠CoNO are 85.9° and 136.5° (B3LYP) or 84.9° and 137.2° (BP86), respectively, which are very close to the values of 81.1° and 139.4° determined by X-ray diffraction.[7] The bent $Co_2(\mu\text{-NO})_2$ core structure agrees with UV PE spectroscopic observations on this compound[9] but not with the structure determined by X-ray diffraction, which shows a planar $Co_2(\mu\text{-NO})_2$ core.[7]

For $Cp_2Co_2(NO)$ (Figure 3 and Table 2), we predict two types of stationary points. One is the doublet axial C_{2v} dimetallocene structure $Cp_2Co_2(\mu\text{-NO})$ (**IVa**) with a symmetrical bridging NO ligand. The other stationary point (**IVb**) is a doublet structure $CpCo_2(NO)(\mu\text{-Cp})$ but with a terminal NO group and a bridging Cp ligand.

The two methods B3LYP and BP86 disagree significantly in the predictions of the relative energies of isomers **IVa** and **IVb** of $Cp_2Co_2(NO)$. Thus, the predicted global minimum for $Cp_2Co_2(NO)$ using the BP86 method is the isomer $Cp_2Co_2(\mu\text{-NO})$ (**IVa**) rather than the isomer $CpCo_2(\mu\text{-Cp})(NO)$ (**IVb**) found using the B3LYP method. Furthermore, isomer **IVa** is lower in energy than isomer **IVb** by 10.1 kcal/mol using the BP86 method while higher in energy than structure **IVb** by 2.5 kcal/mol using the B3LYP method. The large imaginary vibrational frequency of 533*i* cm^{-1} for **IVa**

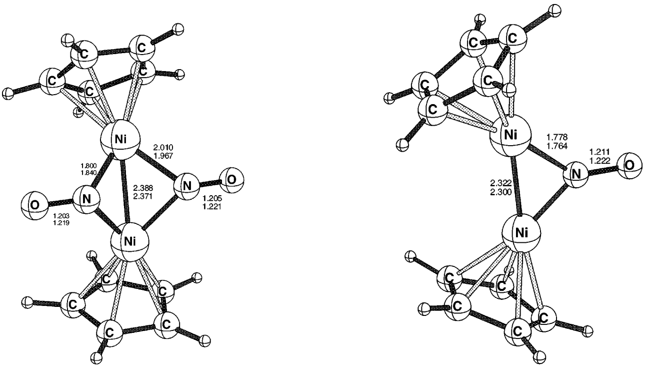
Table 2. Bond Distances (in Å), Total Energies (E in Hartree) and Relative Energies (ΔE in kcal/mol) for the $Cp_2Co_2(NO)_2$ and $Cp_2Co_2(NO)$ Isomers

	$Cp_2Co_2(\mu\text{-}NO)_2$ **III** (C_{2v})			$Cp_2Co_2(\mu\text{-}NO)$ **IVa** (C_{2v})		$CpCo_2(NO)(\mu\text{-}Cp)$ **IVb** (C_s)	
	B3LYP	BP86	exptl[7]	B3LYP	BP86	B3LYP	BP86
Co−Co	2.452	2.426	2.372	2.138	2.149	2.524	2.401
Co−N	1.798	1.798	1.824	1.776	1.783	1.686	1.619
N−O	1.211	1.223	1.187	1.211	1.223	1.191	1.202
∠CoCoNO	127.9°	132.3°		180.0°	180.0°		
∠CoNO	136.5°	137.2°		143.0°	142.9°	176.7°	176.8°
−energy	3412.70723	3413.22771		3282.69657	3283.18973	3282.70051	3283.17370
ΔE	−	−		0	0	−2.5	10.1
imaginary frequency	20i, 13i	22i		533i, 20i, 8i	11i	none	26i

by B3LYP shows that **IVa** is not an actual minimum. Following the mode corresponding to this vibrational frequency leads to structure **IVb**. However, the BP86 method shows **IVa** and **IVb** to be close to the corresponding real minima with very small imaginary frequencies of 11i (**IVa**) and 26i cm^{-1} (**IVb**).

The metal−metal bond in the NO-bridged structure $Cp_2Co_2(\mu\text{-}NO)$ (**IVa**) has a formal bond order of $2^1/_2$ if both cobalt atoms follow the 18-electron rule, and the bridging NO group is a three-electron donor, as suggested by the dihedral ∠CoCoNO angle of 180°. In this connection, the Co−Co distance of 2.138 (B3LYP) or 2.149 Å (BP86) in $Cp_2Co_2(\mu\text{-}NO)$ (**IVa**) is significantly shorter by 0.314 (B3LYP) or 0.277 Å (BP86) than that in $Cp_2Co_2(\mu\text{-}NO)_2$ (**III**) requiring only a Co−Co single bond. However, the Co−Co bond in the Cp-bridged structure $CpCo_2(\mu\text{-}Cp)(NO)$ (**IVb**) is longer than that in **IVa** by 0.072 Å (B3LYP), in contrast to the BP86 result. The Co−N distances to the symmetrical bridging NO groups in structure **III** are longer than the Co−N distance to the bridging NO group in structure **IVa** by 0.022 (B3LYP) or 0.015 Å (BP86), suggesting stronger metal−NO π-back-bonding to the μ-NO group in **IVa** relative to **III**. This is consistent with the fact that the cobalt electron density is shared between two NO groups in **III** whereas it is all available for a single NO group in **IVa**.

3.1.3. $Cp_2Ni_2(NO)_2$ and $Cp_2Ni_2(NO)$. In analogy to $Cp_2Fe_2(NO)_n$ and $Cp_2Co_2(NO)_n$ (n = 1 or 2) discussed above, we tried to optimize dibridged, monobridged, and unbridged isomers of $Cp_2Ni_2(NO)_2$ and $Cp_2Ni_2(NO)$. However, only one dibridged $Cp_2Ni_2(\mu\text{-}NO)_2$ isomer (**V**) and one monobridged $Cp_2Ni_2(\mu\text{-}NO)$ isomer (**VI**) were obtained (Figure 4 and Table 3). Both of these isomers were found to be stationary points with small imaginary vibrational frequencies (57i by B3LYP or 19i and 13i cm^{-1} by BP86 for $Cp_2Ni_2(\mu\text{-}NO)_2$ and 13i and 7i cm^{-1} by B3LYP or 13i and 4i cm^{-1} by BP86 for $Cp_2Ni_2(\mu\text{-}NO)$). The Ni−Ni bond distance in **V** is longer than that in **VI** by 0.066 (B3LYP) or 0.071 Å (BP86). The $Ni_2(\mu\text{-}NO)_2$ core in **V** is bent, with ∠NiNiNO dihedral angles of 117.9° (B3LYP) or 116.8° (BP86) along the Ni−Ni axis, just like the $Co_2(\mu\text{-}NO)_2$ butterfly core.



V (C_1) **VI** (C_{2v})

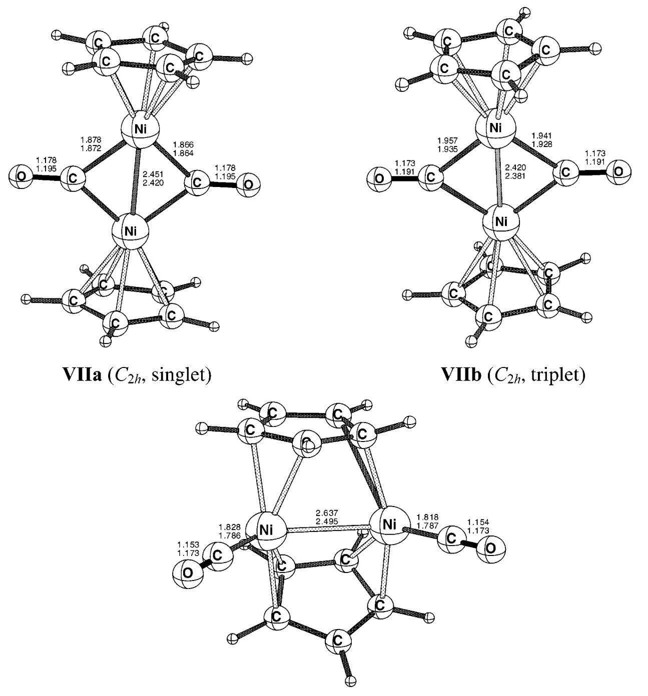
Figure 4. Optimized geometries for $Cp_2Ni_2(NO)_2$ and $Cp_2Ni_2(NO)$.

Table 3. Bond Distances (in Å), Total Energies (E in Hartree), and Relative Energies (ΔE in kcal/mol) for $Cp_2Ni_2(NO)_2$ and $Cp_2Ni_2(NO)$

	$Cp_2Ni_2(\mu\text{-}NO)_2$ **V** (C_1)		$Cp_2Ni_2(\mu\text{-}NO)$ **VI** (C_{2v})	
	B3LYP	BP86	B3LYP	BP86
Ni−Ni	2.388	2.371	2.322	2.300
Ni−N	2.010 1.800	1.967 1.840	1.778	1.764
N−O	1.205 1.203	1.221 1.219	1.211	1.222
∠NiNiNO	156.3°, 113.6°	143.1°, 119.6°	180.0°	180.0°
∠NiNO	135.9°	123.2°	139.2°	139.3°
−energy	3663.76596	3664.30645	3533.84742	3534.33732
imaginary frequencies	57i	19i, 13i	13i, 7i	13i, 4i

3.1.4. $Cp_2Ni_2(CO)_2$ and $Cp_2Ni_2(CO)$. Four structures were optimized for $Cp_2Ni_2(CO)_2$ and $Cp_2Ni_2(CO)$ (Figure 5 and Table 4), namely singlet and triplet dibridged structures, as well as unbridged structures. Two types of stationary points (singlet and triplet) were found for $Cp_2Ni_2(CO)_2$ (Figure 5) as was previously[23] found for $Cp_2Co_2(CO)_2$. Structures **VIIa** and **VIIb** for $Cp_2Ni_2(CO)_2$ are coaxial structures with two bridging CO ligands. The singlet isomer, **VIIa**, is lower in energy than the triplet isomer, **VIIb**, by 13.7 (B3LYP) or 21.0 kcal/mol (BP86). Both **VIIa** and **VIIb** have some imaginary frequencies (see Table 4), but these fall below 30i cm^{-1} so that structures **VIIa** and **VIIb** are likely to be identical or very close to the actual minima. The Ni−Ni bond distance is found to be 2.451 (B3LYP) or 2.420 Å (BP86) for the singlet isomer **VIIa** of $Cp_2Ni_2(\mu\text{-}CO)_2$, where the 18-electron rule requires a formal Ni−Ni single bond. The Ni−Ni bond distance in the triplet isomer **VIIb** is found to be shorter than that in the singlet structure **VIIb** by 0.031 (B3LYP) or 0.039 Å (BP86). The Ni−Ni bond distance in **VIIb** is close to the experimental value of 2.363 Å found by X-ray diffraction.[10] The unbridged coaxial structure for $Cp_2Ni_2(CO)_2$ is not stable but collapses to **VIIa** or **VIIb** upon optimization. The singlet perpendicular structure $\perp\text{-}Cp_2Ni_2(CO)_2$ also collapses to the dibridged isomer **VIIa**.

The other stationary point for $Cp_2Ni_2(CO)_2$ is a triplet

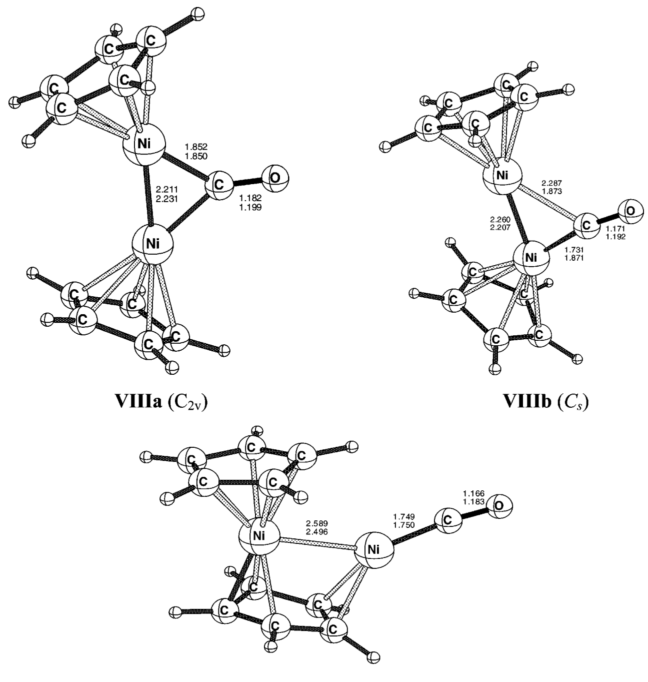


VIIa (C_{2h}, singlet)

VIIb (C_{2h}, triplet)

VIIc (C_1)

Figure 5. Optimized geometries for $Cp_2Ni_2(CO)_2$ isomers.



VIIIa (C_{2v})

VIIIb (C_s)

VIIIc (C_s)

Figure 6. Optimized geometries for $Cp_2Ni_2(CO)$ isomers.

perpendicular isomer $\perp$-$Cp_2Ni_2(CO)_2$ (**VIIc**) with two terminal CO ligands and with the Ni−Ni bond perpendicular to the axes of the Cp rings. This isomer lies much higher in energy than the singlet dibridged coaxial global minimum isomer of $Cp_2Ni_2(\mu\text{-}CO)_2$ (**VIIa**) by 29.5 (B3LYP) or 48.8 kcal/mol (BP86), similar to previous predictions[23] for $Cp_2Co_2(CO)_2$ isomers. The Ni−Ni distance in the perpendicular structure $\perp$-$Cp_2Ni_2(CO)_2$ (**IVc**), namely 2.637 Å by B3LYP or 2.495 Å by BP86, is found to be longer than that in the coaxial structure **VIIa** (2.451 Å by B3LYP or 2.420 Å by BP86).

The Ni−C distances to the bridging CO groups in $Cp_2Ni_2(\mu\text{-}CO)_2$ (**VIIa**) are 1.878 and 1.866 Å (B3LYP) or 1.872 and 1.864 Å (BP86), which are close to the experimental value of 1.859 Å determined by X-ray diffraction.[29] However, these Ni−C distances to the bridging CO groups in **VIIa** are longer than those to the terminal CO groups in **VIIc** by 0.008 (B3LYP) or 0.036 Å (BP86). The nickel−nickel distance in the perpendicular structure $\perp$-$Cp_2Ni_2(CO)_2$ (**VIIc**), required by the 18-electron rule to have a Ni−Ni single bond, is longer than the cobalt−cobalt distance[23] in the corresponding $\perp$-$Cp_2Co_2(CO)_2$, required by the 18-electron rule to have a Co=Co double bond, by 0.241 (B3LYP) or 0.068 Å (BP86).

Optimizations have been carried out on triplet and singlet $Cp_2Ni_2(CO)$ structures in which the single CO group is either bridging or terminal (Figure 6 and Table 5). The predicted global minimum for $Cp_2Ni_2(CO)$ using the B3LYP method is the triplet unsymmetrically bridged isomer $Cp_2Ni_2(\mu\text{-}CO)$ (**VIIIb**). However, the BP86 method predicts the symmetrically bridged singlet structure **VIIIa** to be 1.5 kcal/mol below the triplet structure **VIIIb.** A singlet $CpNi_2(CO)(\mu\text{-}Cp)$ isomer with a bridging Cp group and a terminal CO group (**VIIIc)** is found to be 22.0 (B3LYP) or 13.6 kcal/mol (BP86) above the global minimum.

3.2. Comparison of the Structures $Cp_2M_2(AO)_n$ (M = Fe, Co, Ni; A = C, N; n = 2, 1). Table 6 summarizes the computed metal−metal distances for the $Cp_2M_2(AO)_n$ (M = Fe, Co, Ni; A = C, N; n = 2, 1) derivatives studied in this and previous[23] work using the BP86 method, as well as the formal metal−metal bond orders assuming that the favored 18-electron metal configurations are approached as

Table 4. Bond Distances (in Å), Total Energies (E in Hartree), and Relative Energies (ΔE in kcal/mol) for the Isomers of $Cp_2Ni_2(CO)_2$

	$Cp_2Ni_2(\mu\text{-}CO)_2$ (C_{2h})					$\perp$-$Cp_2Ni_2(CO)_2$ (C_1)	
	^1A_g (**VIIa**)			^3A_u (**VIIb**)		^3A (**VIIc**)	
	B3LYP	BP86	exptl[10]	B3LYP	BP86	B3LYP	BP86
Ni−Ni	2.451	2.420	2.363	2.420	2.381	2.637	2.495
Ni−C	1.878	1.872	1.859	1.957	1.935	1.818	1.787
						1.828	1.786
C−O	1.178	1.195	1.163	1.173	1.191	1.154	1.173
						1.153	1.173
−energy	3630.60717	3631.10785	−	3630.58534	3631.07439	3630.56021	3631.03016
ΔE (kcal/mol)	0	0	−	13.7	21.0	29.5	48.8
imaginary frequencies	28i, 19i, 16i	30i, 21i, 18i	−	9i	9i	none	none

Table 5. Bond Distances (in Å), Total Energies (*E* in Hartree), and Relative Energies (Δ*E* in kcal/mol) for $Cp_2Ni_2(CO)$ Isomers

	$Cp_2Ni_2(CO)$					
	$^1A_1$ (**VIIIa**)		$^3A'$ (**VIIIb**)		$^1A'$ (**VIIIc**)	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
Ni−Ni	2.211	2.231	2.260	2.207	2.589	2.496
Ni−C	1.852	1.850	1.731	1.871	1.749	1.750
C−O	1.182	1.199	1.171	1.192	1.166	1.183
−energy	3517.21176	3517.69949	3517.22952	3517.697103	3517.19450	3517.67790
Δ*E*	11.1	0.0	0.0	1.5	22.0	13.6
imaginary frequency	none	none	4*i*	none	28*i*	34*i*

Table 6. Bond Distances (in Å) and Formal Metal−Metal Bond Orders for the Global Minimum $Cp_2M_2(AO)_{1,2}$ (M = Fe, Co, Ni; A = C, N) Structures (BP86 results)

	M	A	M−M	M−A	A−O	formal M−M bond order	dihedral angle, °
$Cp_2M_2(AO)_2$	Fe	N	2.339	1.792	1.231	2	180.0
	Fe	C	2.120	1.906	1.198	3	128.5
	Co	N	2.426	1.798	1.223	1	132.3
	Co	C	2.346	1.860	1.204	2	180.0
	Ni	N	2.371	1.904	1.200	0	116.8
	Ni	C	2.420	1.872	1.195	1	180.0
$Cp_2M_2(AO)$	Fe	N	1.988	1.814	1.216	$3^1/_2$	
	Fe	C	1.998	1.827 2.078	1.195	4	
	Co	N	2.149	1.783	1.223	$2^1/_2$	
	Co	C	2.050	1.904	1.192	3	
	Ni	N	2.300	1.764	1.222	$1^1/_2$	
	Ni	C	2.231	1.850	1.199	2	

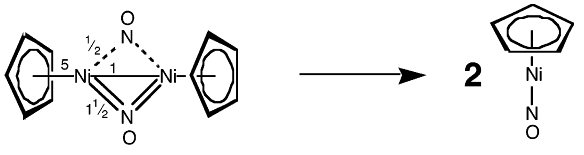
closely as possible and all of the NO groups are formal three-electron donors considered as neutral ligands.

In general, Table 6 considers the global minimum structures $Cp_2M_2(AO)_n$ ($n = 2$, 1). For the $Cp_2M_2(AO)_2$ derivatives, these structures have two bridging AO groups. For the $Cp_2M_2(AO)$ derivatives, the single AO group bridges the pair of metals. This bridging is symmetrical except for the global minimum of $Cp_2Fe_2(CO)$, where the bridging CO group is highly unsymmetrical with the two Fe−C distances differing by approximately 0.25 Å. Note that the binuclear mononitrosyls $Cp_2M_2(NO)$ (M = Fe, Co, Ni) are doublets with the formal half-integer metal−metal bond orders of $3^1/_2$, $2^1/_2$, and $1^1/_2$, respectively, arising from the odd electron of a single NO group.

The metal−metal distances in the structures of $Cp_2M_2(AO)_n$ (M = Fe, Co, Ni; A = C, N; $n = 2$, 1) are seen to correlate in most cases with the ligand types and the formal metal−metal bond orders. Thus, each unit increase in the formal metal−metal bond order is predicted to shorten the metal−metal bond distances by roughly 0.2 Å in accord with the known crystal structures of $Cp_2Fe_2(\mu\text{-}NO)_2$ (ref 18) and $Cp_2Co_2(\mu\text{-}NO)_2$ (ref 7).. For a given metal−metal bond order, the metal−metal bond distance is almost the same whether the AO ligand(s) is(are) CO or NO. Thus, the Fe═Fe distance in $Cp_2Fe_2(\mu\text{-}NO)_2$ (**Ia**) is 2.339 Å, which is very close to the Co═Co distance of 2.346 Å in $Cp_2Co_2(\mu\text{-}CO)_2$. Both of these structures require M═M double bonds to give both metal atoms the favored 18-electron rare gas configuration. This suggests that the NO groups in these complexes are the usual three-electron donors considered as neutral ligands and thereby bond to the metal atoms in ways completely analogous to CO ligands in metal carbonyls (see Figure 1 for the possibilities). This is consistent with the 179.3° (B3LYP) or 179.2° (BP86) ∠FeFeNO dihedral angles in $Cp_2Fe_2(\mu\text{-}NO)_2$ (**Ia**).

An exception may be the $Cp_2Ni_2(\mu\text{-}NO)_2$ dimer (**V** in Figure 3), since the 18-electron rule would predict a Ni⋯Ni bond order of zero assuming that both NO groups are the usual three-electron donors. However, the nickel−nickel distance in $Cp_2Ni_2(\mu\text{-}NO)_2$ (**V**) is 2.371 Å, suggesting a Ni−Ni single bond by comparison of this distance with the other metal−metal distances in Table 6. This is consistent with formulation of $Cp_2Ni_2(\mu\text{-}NO)_2$ (**V**) with one one-electron donor NO group and one three-electron donor NO group (Figure 7) in accord with the nonequivalence of the two μ-NO groups in **V**. Furthermore, one of these μ-NO groups is highly pyramidal with a ∠NiNiNO dihedral angle of 113.6° (B3LYP) or 119.6° (BP86), suggesting that it is a one-electron donor to the pair of nickel atoms. However, the other μ-NO group in **V** is much less pyramidal with a ∠NiNiNO dihedral angle of 156.3° (B3LYP) or 143.1° (BP86), suggesting that it could be a three-electron donor to the pair of nickel atoms. Calculations indicate that the dissociation of $Cp_2Ni_2(\mu\text{-}NO)_2$ into the long known[3] very stable monomer CpNiNO (Figure 7) is highly exothermic (45.2 kcal/mol by B3LYP or 19.8 kcal/mol by BP86). For this reason, we think that it is thermodynamically unlikely that $Cp_2Ni_2(\mu\text{-}NO)_2$ will be prepared; thus, any reactions which might give $Cp_2Ni_2(\mu\text{-}NO)_2$ would instead be expected to give 2 equiv of CpNiNO.

The geometries of the $M(\mu\text{-}AO)_2M$ cores in the $Cp_2M_2(AO)_2$ derivatives are of interest. For $Cp_2Fe_2(\mu\text{-}NO)_2$ (**Ia** in Figure 2), the planar $Fe(\mu\text{-}NO)_2Fe$ geometry is calculated to be the most stable, which is consistent with the crystal structure found by X-ray diffraction.[18] Similarly, a bent $Ni(\mu\text{-}CO)_2Ni$ geometry is calculated to be the most stable for $Cp_2Ni_2(\mu\text{-}CO)_2$ (**VIIa** in Figure 5) in accord with the experimental structure determined by X-ray diffraction.[10]



V

Figure 7. Dissociation of $Cp_2Ni_2(\mu\text{-}NO)_2$ (**V**) into 2 equiv of CpNiNO. The numbers around the "left" nickel atom in **V** indicate the number of electrons donated by each of these ligands to give the nickel atom the eight electrons required for it to attain the favored 18-electron configuration. The "top" NO group in **V** is the one-electron donor, and the "bottom" NO group in **V** is the three-electron donor.

Table 7. ν(NO) and ν(CO) Frequencies (in cm^{-1}) Predicted for the $Cp_2M_2(AO)_{2,1}$ (M = Fe, Co, Ni; A = C, N) Isomers[a]

		B3LYP	BP86	exptl[b]
$Cp_2Fe_2(\mu\text{-}NO)_2$	**Ia** (C_{2v})	1661(a$_1$,0)	1604(a$_1$,0)	1506[1]
		1607(b$_1$,1078)	**1566(b$_1$,811)**	
$Cp_2Fe_2(NO)_2$	**Ib** (C_{2h})	1830(a$_g$,0)	1769(a$_g$,0)	
		1797(b$_u$,1888)	**1751(b$_u$,1307)**	
$Cp_2Fe_2(\mu\text{-}NO)$	**IIa** (C_{2v})	**1703(a$_1$,619)**	**1647(a$_1$,497)**	
$Cp_2Fe_2(NO)$	**IIb** (C_s)	**1789(a′,538)**	**1756(a′,865)**	
$Cp_2Co_2(\mu\text{-}NO)_2$	**III** (C_{2v})	**1689(a$_1$,199)**	**1628(a$_1$,145)**	1610[2]
		1643(b$_1$,845)	**1588(b$_1$,685)**	1559[2]
$Cp_2Co_2(\mu\text{-}NO)$	**IVa** (C_{2v})	**1678(a$_1$,699)**	**1623(a$_1$,519)**	
$Cp_2Co_2(NO)$	**IVb** (C_s)	**1816(a′,1007)**	**1783(a′,743)**	
$Cp_2Ni_2(\mu\text{-}NO)_2$	**V** (C_1)	**1595(784)**	**1536(677)**	
		1696(452)	**1603(303)**	
$Cp_2Ni_2(\mu\text{-}NO)$	**VI** (C_{2v})	**1678(a$_1$,575)**	**1627(a$_1$,526)**	
$Cp_2Ni_2(\mu\text{-}CO)_2$	**VIIa** (C_{2h})	1963(a$_g$,0)	1870(a$_g$,0)	1896 (w)[11]
		1908(b$_u$,1082)	**1830(b$_u$,850)**	**1854 (s)**[11]
$Cp_2Ni_2(\mu\text{-}CO)_2$	**VIIb** (C_{2h})	1977(a$_g$,0)	1876(a$_g$,0)	
		1916(b$_u$,1218)	**1834(b$_u$,922)**	
$Cp_2Ni_2(CO)_2$	**VIIc** (C_{2h})	2078(a$_g$,0)	1966(a$_g$,0)	
		2044(b$_u$,2940)	**1953(b$_u$,2223)**	
$Cp_2Ni_2(\mu\text{-}CO)$	**VIIIa** (C_{2v})	**1931(a$_1$,824)**	**1847(a$_1$,643)**	
$Cp_2Ni_2(\mu\text{-}CO)$	**VIIIb** (C_s)	**2034(a′,1608)**	**1947(a′,1301)**	
$Cp_2Ni_2(CO)$	**VIIIc** (C_s)	**1971(a$_1$,750)**	**1861(a$_1$,562)**	

[a] Infrared intensities are given in parentheses in km/mol; infrared active frequencies are given in bold type. [a] Experimental data are measurements in saturated hydrocarbon solvents.

However, our calculations predict a bent Co(μ−NO)$_2$Co geometry (dihedral angle of 132.3°) for $Cp_2Co_2(\mu\text{-}NO)_2$ in agreement with the vapor phase structure determined experimentally by UV PE spectroscopy[9] but in disagreement with the solid-state structure determined by X-ray diffraction.[7] In this case, solid-state packing effects must lead to a structure different from that calculated for an isolated molecule, such as that found in the vapor phase.

3.2. Vibrational Frequencies. The harmonic vibrational frequencies and their infrared intensities for all of the structures have been calculated by the B3LYP and BP86 methods (Table 7). Complete reports of the vibrational frequencies and infrared intensities are given in the Supporting Information. These results have been used to determine whether a structure is a genuine minimum.

In general, the ν(NO) and ν(CO) frequencies predicted by the BP86 functional are found to be 60−100 cm^{-1} lower than those predicted by the B3LYP functional. Furthermore, the ν(NO) infrared frequencies computed with the BP86 functional are in reasonably close agreement with the experimental ν(NO) infrared frequencies in hydrocarbon solvents for $Cp_2Co_2(\mu\text{-}NO)_2$ and about 60 cm^{-1} too high for $Cp_2Fe_2(\mu\text{-}NO)_2$ (1566 vs 1506 cm^{-1}). In general, the ν(NO) frequencies in $(C_5H_5)_2M_2(NO)_n$ (n = 2, 1) are ~200 cm^{-1} lower than those of the corresponding ν(CO) frequencies of the analogous $(\eta^5\text{-}C_5H_5)_2M_2(CO)_n$.

The ν(CO) frequencies of typical symmetrical two-electron donor bridging CO groups in transition metal carbonyl chemistry are well known to occur 150−200 cm^{-1} below the ν(CO) frequencies of terminal CO groups in a given type of metal carbonyl derivative. This same trend is found for the nitrosyl $Cp_2M_2(NO)_n$ (M = Fe, Co, Ni; n = 2, 1) derivatives studied in this work, where the bridging ν(NO) frequencies fall in the range 1566−1661 cm^{-1} and the terminal ν(NO) frequencies fall in the range 1751−1830 cm^{-1} (BP86). Similar observations concerning bridging and terminal ν(CO) frequencies were made for the $Cp_2M_2(CO)_n$ (M = Fe, Co, Ni; n = 2, 1) derivatives.

4. Summary

The energetically preferred structures of the binuclear cyclopentadienylmetal nitrosyls and carbonyls $Cp_2M_2(AO)_n$ (A = N, M = Fe, Co, Ni; A = C, M = Ni; n = 2, 1) generally have bridging AO ligands rather than terminal AO ligands. Thus, the global minima for $Cp_2M_2(AO)_2$ are all found to have closely related axial dimetallocene structures with two symmetrically bridging AO ligands but variable planarity of the central M(μ-AO)$_2$M units. Similarly, the single AO ligands in the global minima for $Cp_2M_2(AO)$ are found to bridge the pair of metal atoms. However, structures with terminal AO groups and a single bridging Cp ligand are also found at accessible energies for $CpM_2(NO)(\mu\text{-}Cp)$ (M = Fe and Co) and $CpNi_2(CO)(\mu\text{-}Cp)$. The metal−metal bond distances in these $Cp_2M_2(AO)_n$ derivatives correlate reasonably well with the requirements of the 18-electron rule. In this connection, the dimer $Cp_2Ni_2(\mu\text{-}NO)_2$ is predicted by the 18-electron rule to have a Ni···Ni bond order of zero, assuming that both NO groups are three-electron donors. However, $Cp_2Ni_2(\mu\text{-}NO)_2$ instead has a Ni−Ni bond distance suggesting a single bond and geometry suggesting one one-electron donor bridging NO group and one three-electron donor bridging NO group. However, dissociation of $Cp_2Ni_2(\mu\text{-}NO)_2$ into the well-known stable monomer CpNiNO is highly favored energetically.

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Supporting Information Available: Tables S1−S15: harmonic vibrational frequencies for $Cp_2Fe_2(NO)_2$ (two isomers), $Cp_2Fe_2(NO)$ (one isomer), $Cp_2Co_2(NO)_2$ (two isomers), $Cp_2Co_2(NO)$ (one isomer), $Cp_2Ni_2(NO)_2$ (one isomer), $Cp_2Ni_2(NO)$ (one isomer), $Cp_2Ni_2(NO)_2$ (three isomers), and $Cp_2Ni_2(CO)$ (three isomers); Table S16: Cartesian coordinates for the 15 structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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