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Binuclear Iron Carbonyl Nitrosyls: Bridging Nitrosyls versus Bridging Carbonyls

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The iron carbonyl nitrosyls $Fe_2(NO)_2(CO)_n$ ($n = 7, 6, 5, 4, 3$) have been studied by density functional theory (DFT) using the B3LYP and BP86 methods, for comparison of their predicted structures with those of isoelectronic cobalt carbonyl derivatives. The lowest energy structures for $Fe_2(NO)_2(CO)_7$ and $Fe_2(NO)_2(CO)_6$ have two NO bridges, and the lowest energy structure for $Fe_2(NO)_2(CO)_5$ has a single NO bridge with metal−metal distances (BP86) of 3.161, 2.598, and 2.426 Å, respectively, corresponding to the formal metal−metal bond orders of zero, one, and two, respectively, required for the favored 18-electron configuration for the iron atoms. The heptacarbonyl $Fe_2(NO)_2(CO)_7$ is thermodynamically unstable with respect to CO loss to give $Fe_2(NO)_2(CO)_6$. The favored structures for the more highly unsaturated $Fe_2(NO)_2(CO)_4$ and $Fe_2(NO)_2(CO)_3$ also have bridging NO groups but avoid iron−iron bond orders higher than two by formal donation of five electrons from bridging NO groups with relatively short Fe−O distances. The lowest energy structures of the unsaturated $Fe_2(NO)_2(CO)_n$ derivatives ($n = 5, 4, 3$) are significantly different from the isoelectronic cobalt carbonyls $Co_2(CO)_{n+2}$ owing to the tendency for $Fe_2(NO)_2(CO)_n$ to form structures with bridging NO groups and metal−metal formal bond orders no higher than two.

1. Introduction

A number of metal–carbonyl nitrosyls are known to be isoelectronic with homoleptic metal–carbonyl derivatives.[1] The most extensive such isoelectronic series is $Co(NO)(CO)_3 \rightarrow Fe(NO)_2(CO)_2 \rightarrow Mn(NO)_3CO \rightarrow Cr(NO)_4$, all isoelectronic with $Ni(CO)_4$. Similar series of stable mononuclear metal–carbonyl nitrosyls isoelectronic with $Fe(CO)_5$ and $Cr(CO)_6$ are less extensive, owing to the fact that the $CO \leftrightarrow NO^+$ isoelectronic analogy requires electron-poor oxophilic early transition metals such as vanadium and titanium to retain the favored 18-electron configuration. However, the range and stabilities of nitrosyl derivatives of such early transition metals are very limited owing to low energy decomposition pathways for many possible metal nitrosyl structures through metal–oxygen bond formation, with metal oxides and dinitrogen as the ultimate energy sinks. The instability of early transition metal nitrosyl derivatives is especially apparent with the instability[2] of the 18-electron vanadium nitrosyl $V(NO)(CO)_5$ under ambient conditions contrasted with the stability of the isoelectronic $Cr(CO)_6$ even toward steam distillation in air.

The stable binuclear homoleptic first row transition metal–carbonyls are $Mn_2(CO)_{10}$, $Fe_2(CO)_9$, and $Co_2(CO)_8$, all of which are commercial products and important starting materials for synthetic transition metal organometallic chemistry. Among the corresponding isoelectronic binuclear metal–carbonyl nitrosyls, only $Cr_2(NO)_2(CO)_8$, isoelectronic with $Mn_2(CO)_{10}$, is a stable well-characterized compound, prepared by the oxidation of the $Cr(NO)(CO)_4^-$ anion with the triphenylmethyl cation.[3] The manganese derivative $Mn_2(NO)_2(CO)_7$, isoelectronic with $Fe_2(CO)_9$, was claimed by the original discoverers of $Mn(NO)(CO)_4$ in a 1961 paper[4] as its air-sensitive red crystalline photolysis product on the basis of its ν(CO) and ν(NO) frequencies, by analogy to the well-known photolysis of $Fe(CO)_5$ to give $Fe_2(CO)_9$. However, no further work has been done on this substance in the intervening 45 years. Furthermore,

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a recent density functional theory (DFT) study[5] suggests that the ν(CO) and ν(NO) frequencies reported for the alleged $Mn_2(NO)_2(CO)_7$ are more likely to correspond to $Mn_2(NO)_2(CO)_5$ with a formal Mn≡Mn triple bond and a structure analogous to that[6,7] of $(\eta^5\text{-}C_5H_5)_2V_2(CO)_5$, obtained from the photolysis[8] of $(\eta^5\text{-}C_5H_5)V(CO)_4$.

This leaves $Fe_2(NO)_2(CO)_6$ as a possible isoelectronic nitrosyl analogue of a stable homoleptic first row transition metal–carbonyl, namely, $Co_2(CO)_8$. However, all efforts to date to synthesize $Fe_2(NO)_2(CO)_6$ have apparently been unsuccessful even though the stable tetrahedral anion $Fe(NO)(CO)_3^-$, readily available[9] from nitrite ion and $Fe(CO)_5$, is an obvious starting material. Thus efforts to oxidize $Fe(NO)(CO)_3^-$ to $Fe_2(NO)_2(CO)_6$ using conditions similar to the successful oxidation of $Cr(NO)(CO)_4^-$ to $Cr_2(NO)_2(CO)_8$ have been uniformly unsuccessful.[3] This failure to synthesize $Fe_2(NO)_2(CO)_6$ by methods succeeding for the synthesis of $Cr_2(NO)_2(CO)_8$ may relate to the properties of the corresponding isoelectronic homoleptic metal–carbonyl derivatives. Thus the chemical reactivity of $Co_2(CO)_8$ is much greater than that of $Mn_2(CO)_{10}$, suggesting the need for much more delicate methods to synthesize the nitrosyl analogue $Fe_2(NO)_2(CO)_6$ compared with methods for the synthesis of $Cr_2(NO)_2(CO)_8$.

Iron is sufficiently electron-rich that the possibility of one-electron versus three-electron donor NO groups[1] must be considered for the structures of its nitrosyls. Normally, in metal–carbonyl nitrosyls, the NO ligands are considered to be the nitrosonium cation, NO^+, isostructural and isoelectronic with a neutral CO group. 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 sum of the two ∠MNO angles and the single ∠MNM angle (Σ(μ-NO angles)) of approximately 360°. However, a terminal neutral NO group in late transition metal chemistry can sometimes function as a net one-electron donor corresponding to the nitroxyl anion NO^-. In this case, the M−N−O unit is bent rather than linear, with ∠MNO angles in the range of 120–140°. Analogously, one-electron donor bridging NO groups might be expected with a pyramidal configuration similar to NH_3, as recognized by Σ(μ-NO) angles appreciably less than 360°. The NO groups of various types are depicted in Figure 1.

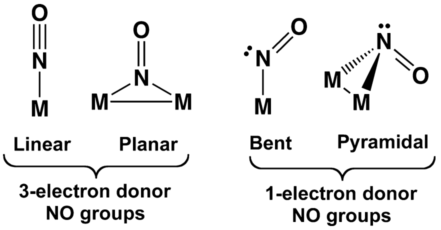

Figure 1. Terminal and bridging (neutral) NO groups acting as donors of one or three electrons to a metal atom M.

The research reported in this paper uses density functional theory (DFT) to examine the series of binuclear iron carbonyl nitrosyls $Fe_2(NO)_2(CO)_n$ ($n = 7, 6, 5, 4, 3$). This covers the range of compounds where a combination of the 18-electron rule and exclusively three-electron donor NO groups requires iron−iron formal bond orders ranging from zero in $Fe_2(NO)_2(CO)_7$ to four in $Fe_2(NO)_2(CO)_3$. However, the apparent iron−iron bond order can be increased if one or both of the NO groups function as formal one-electron donors (Figure 1) rather than three-electron donors, which typically can be recognized by structural features (see Figure 1) or, less reliably, ν(NO) frequencies. Similarly, the apparent iron−iron bond order is decreased if one or both iron atoms have fewer than the favored 18-electrons. The iron carbonyl nitrosyls studied in this paper are the isoelectronic analogues of the homoleptic binuclear cobalt carbonyls $Co_2(CO)_n$ ($n = 9, 8, 7, 6, 5$).

2. Theoretical Methods

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 $\alpha_d(C) = 0.75$, $\alpha_d(N) = 0.80$, and $\alpha_d(O) = 0.85$ to the Huzinaga–Dunning standard contracted DZ sets.[10,11] For Fe, 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.[12,13] For the binuclear iron carbonyl nitrosyls $Fe_2(NO)_2(CO)_7$, $Fe_2(NO)_2(CO)_6$, $Fe_2(NO)_2(CO)_5$, $Fe_2(NO)_2(CO)_4$, and $Fe_2(NO)_2(CO)_3$, there are 368, 338, 308, 278, and 248 contracted Gaussian basis functions, respectively.

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.[14–21] Two DFT methods were used in this study. The first functional is the hybrid B3LYP method, which incorporates Becke's three-parameter functional (B3)[22] with the Lee, Yang, and Parr (LYP) correlation functional.[23] The second approach is the BP86 method, which marries Becke's 1988 exchange functional (B)[24] with Perdew's 1986 correlation functional.[25]

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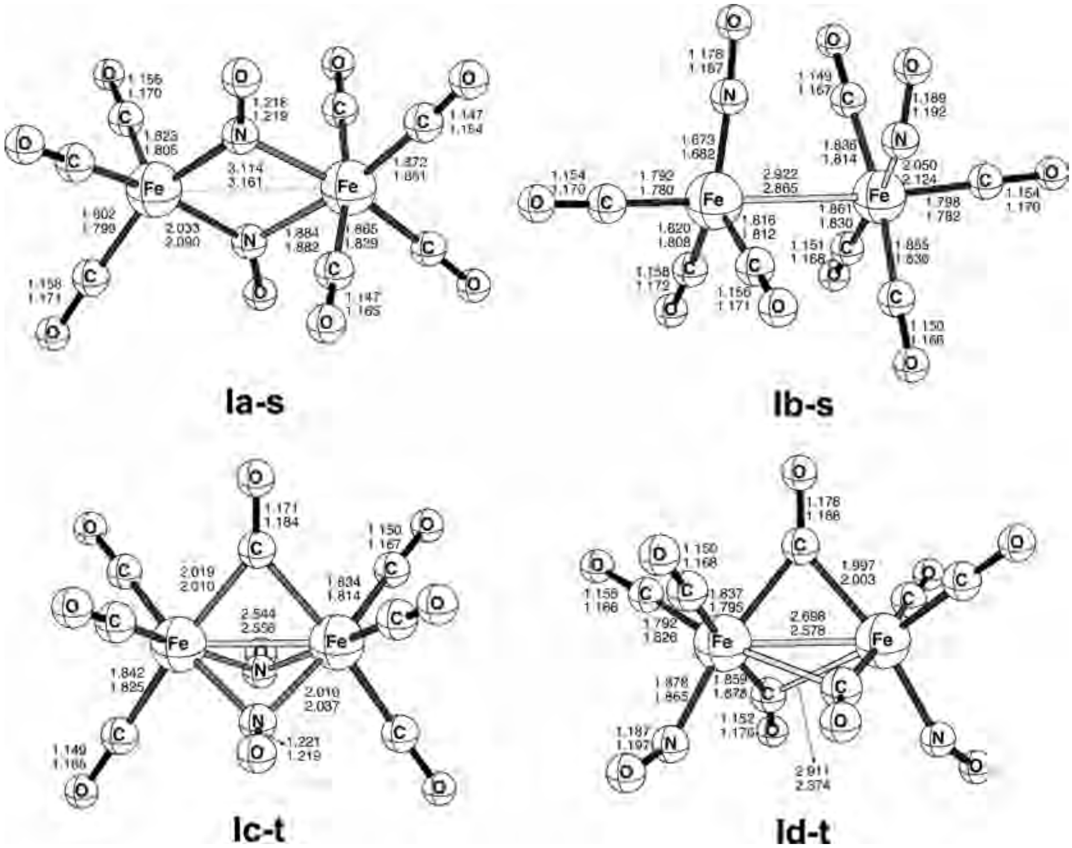

Figure 2. Singlet and triplet structures of $Fe_2(NO)_2(CO)_7$.

The geometries of all structures considered 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 predicted ν(CO) and ν(NO) frequencies discussed in this paper were obtained using the BP86 method, which has been shown to be more reliable than the B3LYP method for such information. Complete vibrational frequency data by both the BP86 and B3LYP methods are given in the Supporting Information. All of the computations were carried out with the Gaussian 03 program[26] in which the fine grid (75, 302) is the default for evaluating integrals numerically,[27] 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.[27] Thus, an imaginary vibrational frequency of magnitude less than $50i$ 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 $50i$ cm^{-1} in search of other minima.[28]

The optimized geometries from these computations are depicted in Figures 2–6 with all bond distances given in angstroms for both B3LYP (upper numbers) and BP86 (lower numbers).

3. Results

3.1. Molecular Structures. 3.1.1. $Fe_2(NO)_2(CO)_7$. Four energetically low-lying structures were found for $Fe_2(NO)_2(CO)_7$. They all have real vibrational frequencies, confirming that they are genuine minima on the energy surface. The global minimum structure **Ia-s** of $Fe_2(NO)_2(CO)_7$ (Figure 2 and Table 1) is a singlet ($S = 0$) electronic state with C_s symmetry and two bridging NO groups. The coplanar nature of the central $Fe_2(NO)_2$ unit indicates that

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Table 1. Bond Distances (in Å), Total Energies (E in hartree), and Relative Energies (ΔE in kcal/mol) for the Different $Fe_2(NO)_2(CO)_7$ Structures

	Ia-s (C_s)		**Ib-s** (C_1)		**Ic-t** (C_{2v})		**Id-t** (C_2)	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
Fe−Fe	3.114	3.161	2.922	2.865	2.544	2.556	2.698	2.578
Fe−C(bridge)	—	—	—	—	2.019	2.010	1.997	2.003
Fe−N(bridge)	1.884 2.033	1.882 2.090	—	—	2.010	2.037	—	—
Fe−N(terminal)	—	—	1.673 2.050	1.682 2.124	—	—	1.878	1.865
∠Fe−N−O	133.9	134.1	172.4 121.4	173.6 120.1	131.5	132.6	132.8	140.4
−energy	3580.96162	3581.50315	3580.94580	3581.49509	3580.94149	3581.48562	3580.93054	3581.47184
ΔE	0.0	0.0	9.9	5.1	12.6	11.0	19.5	19.6
imaginary frequencies	none	none	none	none	none	none	none	none

Table 2. Infrared ν(CO) and ν(NO) Frequencies Predicted for the $Fe_2(NO)_2(CO)_7$ Structures Using the BP86 Method (Calculated Infrared Intensities are Given in Parentheses in km/mol)

structure	ν(NO) frequencies	ν(CO) frequencies, cm^{-1}
Ia-s	1555(625), 1583(0)	1981(526), 1982(395), 2010(722), 2011(1460), 2021(20), 2027(1706), 2073(177)
Ib-s	1657(473), 1801(665)	1965(261), 1978(127), 1996(647), 2003(1246), 2007(610), 2023 (1490), 2067 (166)
Ic-t	1552(611), 1579(225)	1883(365), 1999(0), 2004(1267), 2010(16), 2016(1278), 2038(1853), 2070(1)
Id-t	1685(936), 1701(648)	1859(337), 1935(675), 1941(434), 2005(34), 2008(1410), 2025(1285), 2062(270)

the bridging NO groups are each three-electron donors. The predicted ν(NO) frequencies for these bridging NO groups are rather low at 1555 and 1583 cm^{-1} (Table 2) in accord with their bridging character. The long Fe···Fe bond distance of 3.114 Å (B3LYP) or 3.161 Å (BP86) in the planar $Fe_2(NO)_2$ core of **Ia-s** suggests no significant iron−iron interaction, in accord with the 18-electron rule and both NO groups being three-electron donors.

An attempt to optimize a singlet $Fe_2(NO)_2(CO)_7$ structure with bridging CO groups led instead to the unbridged structure **Ib-s** with two terminal NO groups, one linear (>170°) and one bent (~120°), indicating the presence of one three-electron donor and one one-electron donor NO group. Structure **Ib-s** lies 9.9 kcal/mol (B3LYP) or 5.1 kcal/mol (BP86) above the global minimum **Ia-s**. The Fe−Fe bond distance of 2.922 Å (B3LYP) or 2.865 Å (BP86) in **Ib-s** corresponds to the unbridged single bond required to give the 18-electron configuration with one three-electron donor and one one-electron donor NO group.

The triplet ($S = 1$) structures of $Fe_2(NO)_2(CO)_7$ were found to be significantly higher in energy than the singlet structures. Thus the triplet structure **Ic-t** with one CO bridge and two NO bridges lies 12.6 kcal/mol (B3LYP) or 11.0 kcal/mol (BP86) above **Ia-s**. Both of the NO bridges are nonplanar with $\Sigma(\mu\text{-NO})$ angles = 341.5° (B3LYP) or 342.9° (BP86), suggesting that they are one-electron rather than three-electron donors. The ν(NO) frequencies for these bridging NO groups are 1552 and 1579 cm^{-1} (Table 2), which are very close to the ν(NO) frequencies predicted for the bridging NO groups in **Ia-s**. This suggests that the bridging ν(NO) frequencies and N−O distances are insensitive to whether the NO groups are three-electron or one-electron donors. The triply bridging structure **Ic-t** of triplet $Fe_2(NO)_2(CO)_7$ (Figure 2) is very similar to that of singlet $Fe_2(CO)_9$, in which two of the three bridging CO groups in $Fe_2(CO)_9$ are replaced by one-electron donor bridging NO groups. The Fe−Fe distance in **Ic-t** of 2.544 Å (B3LYP) or 2.556 Å (BP86) is very close to the experimental distance[29] of 2.523 Å for $Fe_2(CO)_9$ and corresponds to the triply bridged single bond required to give each iron atom the 17-electron configurations consistent with the triplet state.

The triplet $Fe_2(NO)_2(CO)_4(\mu\text{-CO})_3$ structure with three symmetrical CO bridges collapses to a structure **Id-t** with C_2 symmetry, in which one CO bridge is retained and the remaining two CO bridges twist into semibridging groups (Figure 2). The two NO groups in **Id-t** are bent, indicating one-electron donors, and exhibit ν(NO) frequencies at 1685 and 1701 cm^{-1} (Table 2), which are relatively low for terminal NO groups but consistent with their bent nature implying a lower nitrogen−oxygen bond order. The Fe−Fe bond distances in **Id-t** of 2.698 Å (B3LYP) or 2.578 Å (BP86) are typical for the bridged formal Fe−Fe single bonds required to give both iron atoms the 17-electron configurations for a triplet structure.

3.1.2. $Fe_2(NO)_2(CO)_6$.

Three possible structures of $Fe_2(NO)_2(CO)_6$, namely, CO-bridged, NO-bridged, and unbridged structures, were used as starting points for optimizations of both singlet and triplet structures. Three singlet stationary points are predicted by the optimization procedure (Figure 3 and Table 3).

The singlet C_{2v} structure **IIa-s** with two bridging NO groups (Figure 3) is the global minimum of $Fe_2(NO)_2(CO)_6$ with no imaginary vibrational frequencies. The $\Sigma(\mu\text{-NO})$ angles of 358.7° (B3LYP) or 358.8° (BP86) indicate near planarity of the $Fe_2(\mu\text{-NO})$ units and three-electron donor bridging nitrosyl groups. The infrared ν(NO) frequencies for these bridging nitrosyl groups are 1624 and 1646 cm^{-1} (Table 4).

The C_{2v} structure **IIb-s**with two bridging CO groups lies 20.6 kcal/mol (B3LYP) or 2.3 kcal/mol (BP86) higher in energy than structure **IIa-s** and has only a very small imaginary vibrational

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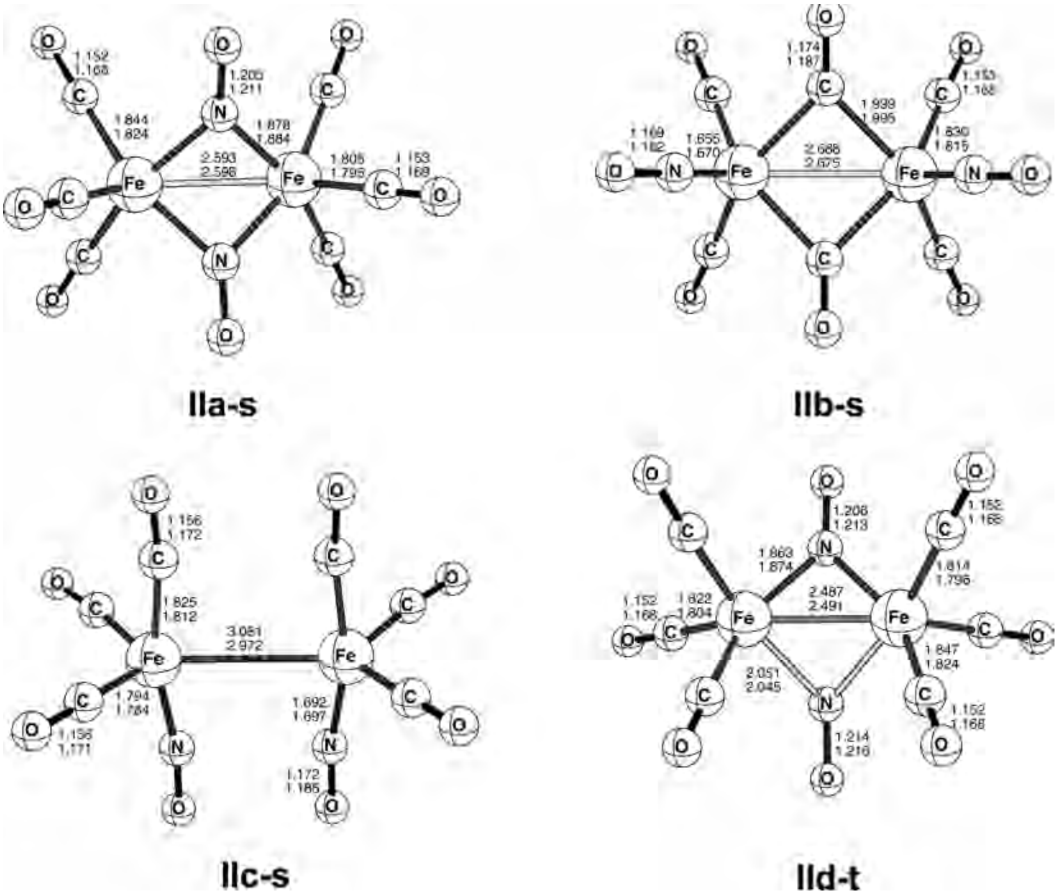


Figure 3. Singlet and triplet structures of $Fe_2(NO)_2(CO)_6$.

Table 3. The Bond Distances (in Å), Total Energies (E in hartree), and Relative Energies (ΔE in kcal/mol) for the Different $Fe_2(NO)_2(CO)_6$ Structures

	IIa-s (C_{2v})		**IIb-s** (C_{2v})		**IIc-s** (C_{2v})		**IId-t** (C_s)	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
Fe−Fe	2.593	2.598	2.688	2.675	3.081	2.972	2.487	2.491
Fe−C(bridge)	—	—	1.999	1.995	—	—	—	—
Fe−N(bridge)	1.878	1.884	—	—	—	—	1.863	1.874
Fe−N(terminal)	—	—	1.655	1.670	1.692	1.697	—	—
Fe−N−O	135.7	135.9	170.9	170.0	169.7	170.4	137.2	137.7
−energy	3467.64474	3468.17940	3467.61196	3468.17575	3467.58417	3468.13289	3467.61046	3468.13750
ΔE	0.0	0.0	20.6	2.3	38.0	29.2	21.5	26.3
imaginary frequencies	none	none	$22i$	none	$47i,38i,26i$	$44i,32i,31i$	$27i$	none

Table 4. Infrared ν(CO) and ν(NO) Frequencies Predicted for the $Fe_2(NO)_2(CO)_6$ Structures Using the BP86 Method (Infrared Intensities are Given in Parentheses in km/mol)

structure	ν(NO) frequencies	ν(CO) frequencies, cm^{-1}
IIa-s	1624(604), 1646(180)	1992(17), 1995(0), 2000(1544), 2003(1179), 2061(42), 2027(1771)
IIb-s	1830(934), 1836(585)	1864(726), 1887(913), 1989(0), 1999(1256), 2011(816), 2050(46)
IIc-s	1774(34), 1843(1131)	1964(2), 1982(0), 1988(1841), 1995(583), 2019(1643), 2053(187)
IId-t	1554(365), 1627(388)	1986(22), 1992(1), 1997(1299), 2000(1283), 2022(1845), 2057(80)

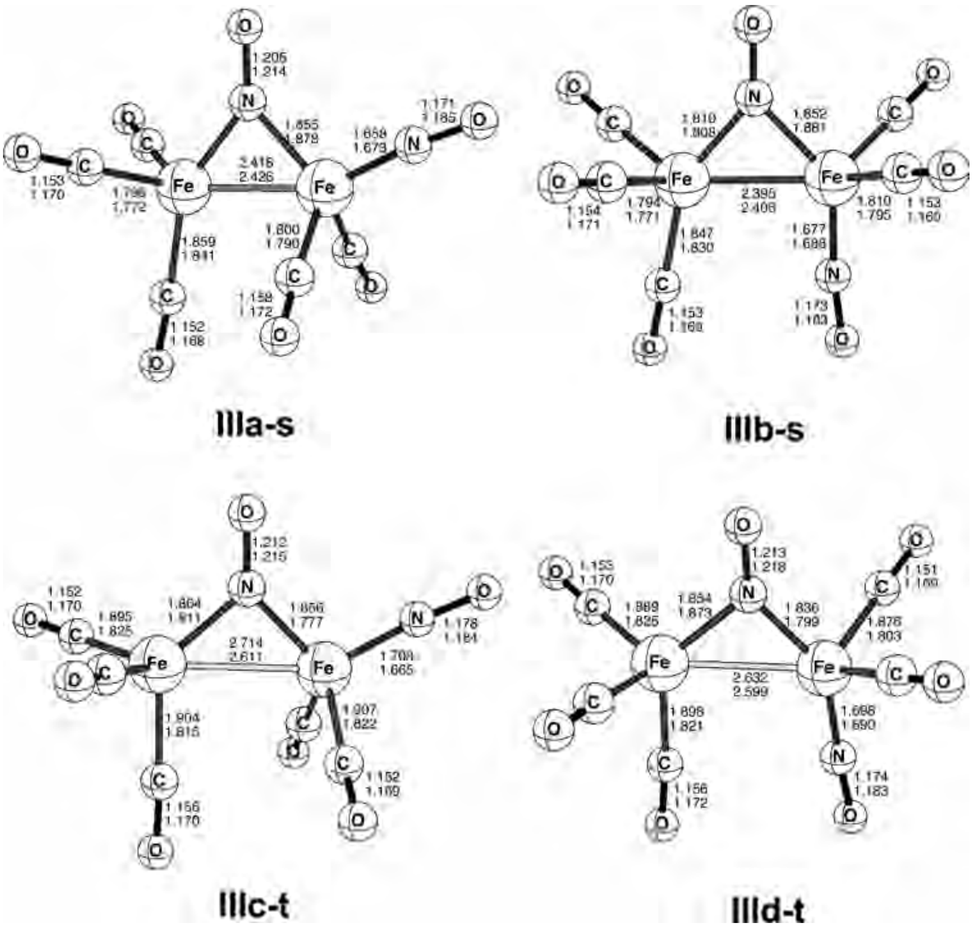
frequency ($22i$ cm^{-1}) by B3LYP. The terminal NO groups and bridging CO groups in **IIb-s** exhibit stretching frequencies in similar regions in the 1830–1887 cm^{-1}range.

The energy of the singlet C_{2v} unbridged structure **IIc-s** is higher than that of either structure **IIa-s** or structure **IIb-s**, by 38.0 kcal/mol (B3LYP) or 29.2 kcal/mol (BP86) above structure **IIa-s**. Furthermore, **IIc-s** has three imaginary frequencies, namely, $47i$, $38i$, and $26i$ (B3LYP) or $44i$, $32i$, and $31i$ (BP86) cm^{-1}. Following the highest imaginary frequency of **IIc-s** leads to **IIa-s** with two bridging NO groups. The terminal NO groups in **IIc-s** exhibit ν(NO) frequencies at 1774 and 1843 cm^{-1} in a typical region for terminal NO groups.

The C_s triplet structure **IId-t** with two bridging NO groups lies 21.5 kcal/mol (B3LYP) or 26.3 kcal/mol (BP86) above the analogous singlet structure **IIa-s**. The $\Sigma(\mu\text{-NO})$ angles of 358.1° (B3LYP) or 358.7° (BP86) for one of the NO groups and 336.2° (B3LYP) or 341.0° (BP86) for the other NO group suggests one three-electron donor NO group and one one-electron donor NO group, respectively.

Attempts to optimize an unbridged triplet $Fe_2(NO)_2(CO)_6$ leads to splitting into $Fe(NO)(CO)_3$ radicals.

The iron−iron distances in all four structures of $Fe_2(NO)_2(CO)_6$ can be interpreted to imply the Fe−Fe single bonds required to give both iron atoms the favored 18-electron



IIIa-s IIIb-s

IIIc-t IIId-t

Figure 4. Singlet and triplet structures of $Fe_2(NO)_2(CO)_5$.

Table 5. The Bond Distances (in Å), Total Energies (E in hartree), and Relative Energies (ΔE in kcal/mol) for $Fe_2(NO)_2(CO)_5$ Isomers

	IIIa-s (C_s)		**IIIb-s** (C_s)		**IIIc-t** (C_s)		**IIId-t** (C_s)	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
Fe−Fe	2.418	2.426	2.395	2.406	2.714	2.611	2.632	2.599
Fe−N(bridge)	1.855	1.878	1.810	1.808	1.864	1.911	1.854	1.836
			1.852	1.881	1.856	1.777	1.873	1.799
Fe−N(terminal)	1.658	1.673	1.677	1.688	1.708	1.665	1.698	1.690
Fe−N−O	174.0	171.7	173.7	173.5	173.5	174.8	177.9	176.7
	137.6	136.6	138.2	137.0	137.0	145.5	141.9	145.4
−energy	3354.26351	3354.80807	3354.26875	3354.80793	3354.26217	3354.78538	3354.26188	3354.78360
ΔE	0.0	0.0	−3.3	0.1	0.8	14.2	1.0	15.4
imaginary frequencies	12i	25i	none	none	none	14i	13i	18i

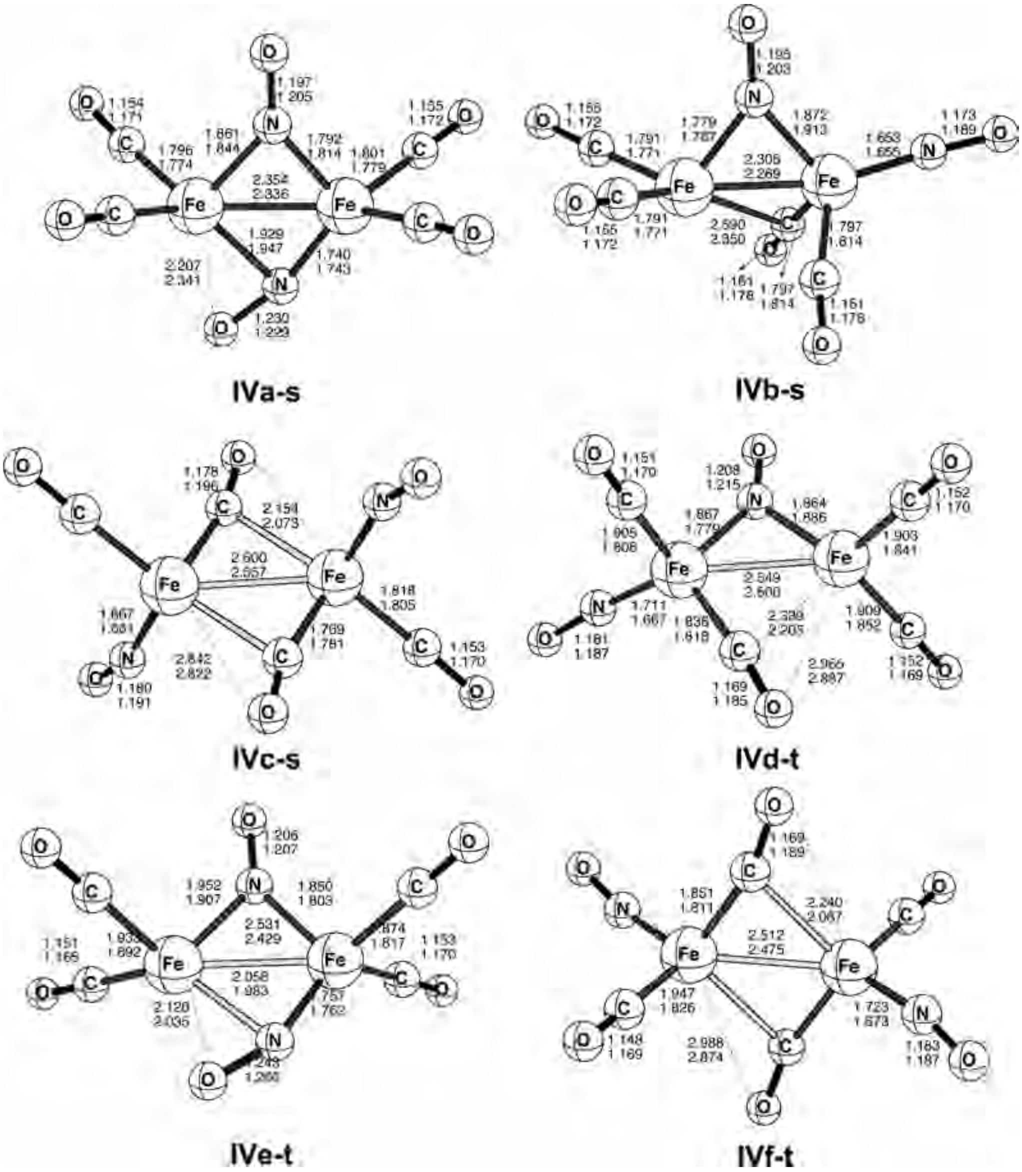
Table 6. Infrared ν(CO) and ν(NO) Frequencies Predicted for the $Fe_2(NO)_2(CO)_5$ Structures Using the BP86 Method (Infrared Intensities are Given in Parentheses in km/mol)

structure	ν(NO) frequencies	ν(CO) frequencies, cm^{-1}
IIIa-s	1641(491), 1831(1230)	1970(274), 1983(190), 1988(1195), 2004(1275), 2050(459)
IIIb-s	1644(480), 1814(602)	1980(345), 1986(757), 1993(1175), 2017(1702), 2047(9)
IIIc-t	1596(427), 1819(552)	1966(805), 1973(651), 1993(975), 1999(1766), 2038(122)
IIId-t	1609(417), 1836(1179)	1966(483), 1972(296), 1986(1226), 1989(1349), 2035(386)

configurations in the singlets and 17-electron configurations in the triplet **IId-t**. Thus the dibridged Fe−Fe bonds in **IIa-s**, **IIb-s**, and **IId-t** fall in the range of 2.48−2.68 Å. However, the unbridged Fe−Fe bond in **IIc-s** is significantly longer, namely, 3.081 Å (B3LYP) or 2.972 Å (BP86), in accord with the previously observed effect of bridging CO (and presumably bridging NO) groups in shortening metal−metal bonds of a given order by 0.1−0.4 Å.

3.1.3. $Fe_2(NO)_2(CO)_5$.

Optimizations have been carried out on singlet and triplet $Fe_2(NO)_2(CO)_5$ structures in which the CO or NO groups are either bridging or terminal. Four energetically low-lying $Fe_2(NO)_2(CO)_5$ structures were found, all with C_s symmetry (Figure 4 and Tables 5 and 6). Furthermore, all four structures have one bridging NO group and one terminal NO group. The Fe_2NO unit in the bridging NO group in all four $Fe_2(NO)_2(CO)_5$ structures is coplanar, consistent with a three-electron donor NO group. Similarly, the terminal NO groups are linear, also indicating three-electron donor groups. The ν(NO) frequencies of the bridging NO groups (Table 6) fall in the range of 1596−1641 cm^{-1},



IVa-s **IVb-s**

IVc-s **IVd-t**

IVe-t **IVf-t**

Figure 5. Singlet and triplet structures of $Fe_2(NO)_2(CO)_4$.

and those of the terminal NO groups fall in the range of 1814−1836 cm^{-1}.

The two singlet structures **IIIa-s** and **IIIb-s** for $Fe_2(NO)_2(CO)_5$ are very close in energy (Table 5) being within 3.3 kcal/mol (B3LYP) or 0.1 kcal/mol (BP86) of each other. This is not surprising since structures **IIIa-s** and **IIIb-s** have the same iron coordination environments and differ only in the placement of the terminal NO group relative to the bridging NO group.

The triplet structures found for $Fe_2(NO)_2(CO)_5$ have significantly higher energies than the corresponding singlet structures with the BP86 method. Thus the triplet structure **IIIc-t** is higher in energy by 14.2 kcal/mol (BP86) relative to the analogous singlet structure **IIIa-s**. The energy of the other triplet structure (**IIId-t**) is close to the triplet **IIIc-t**, at only 0.2 kcal/mol (B3LYP) or 1.2 kcal/mol (BP86) above **IIIc-t.**

The iron−iron bond distances of 2.418 Å (B3LYP) or 2.426 Å (BP86) in **IIIa-s** and 2.395 Å (B3LYP) or 2.406 Å (BP86) in **IIIb-s** are consistent with the Fe═Fe double bonds required to give both metal atoms the favored 18-electron configurations in these singlet structures, assuming the CO and NO groups to be the usual two- and three-electron donors, respectively. The iron−iron distances in the triplet structures are 2.611 Å (BP86) for **IIIc-t** and 2.599 Å (BP86) for **IIId-t**, which are longer than those in the corresponding singlet structures. These suggest the Fe−Fe single bonds required to give each metal atom a 17-electron configuration leading to triplet binuclear structures.

3.1.4. $Fe_2(NO)_2(CO)_4$. Three possible structures of $Fe_2(NO)_2(CO)_4$, namely, CO-bridged, NO-bridged, and unbridged structures, were used as starting points for optimizing both singlet and triplet structures. The unbridged singlet and triplet starting structures collapse to the structures **IVb-s** and **IVd-t**, respectively, with one CO bridge and one NO bridge upon optimization. A total of six stationary points were found for $Fe_2(NO)_2(CO)_4$ after optimization, indicating a rather complicated potential energy surface (Figure 5 and Tables 7−9).

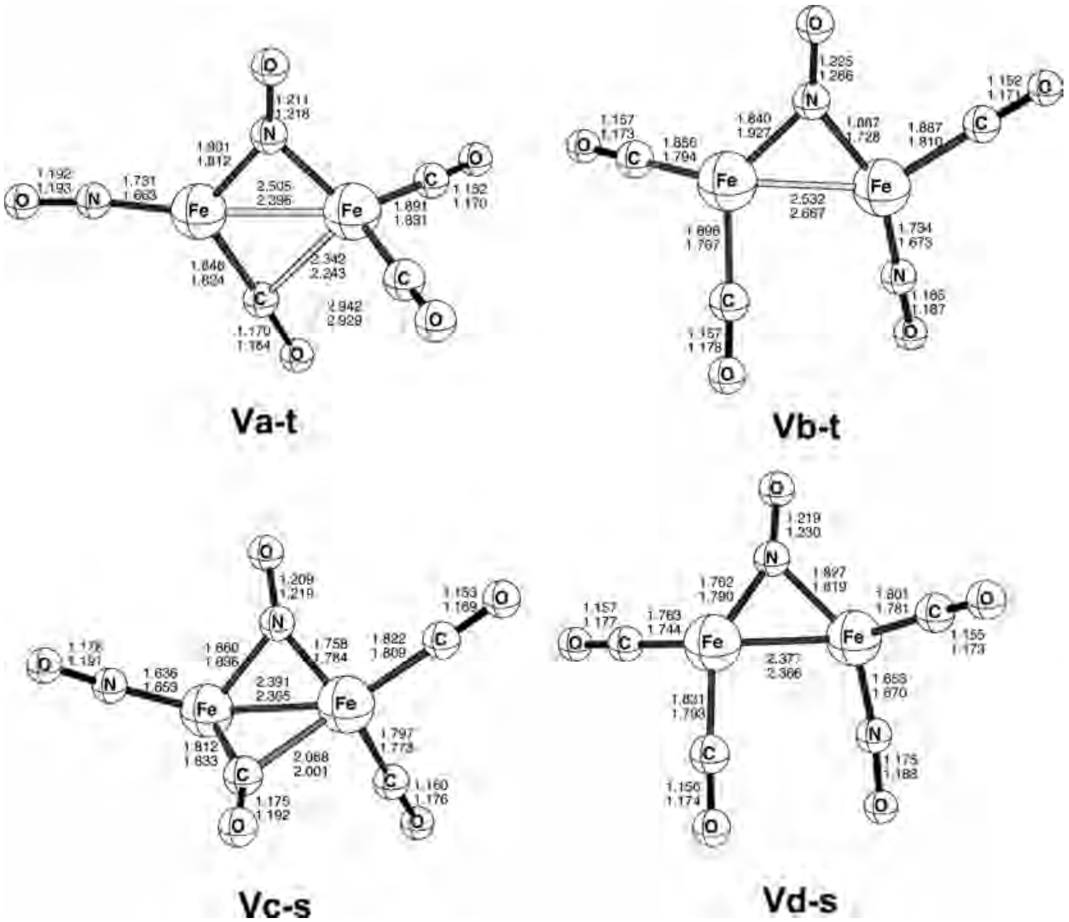


Figure 6. Singlet and triplet structures of $Fe_2(NO)_2(CO)_3$.

Table 7. Bond Distances (in Å), Total Energies (*E* in hartree), and Relative Energies (Δ*E* in kcal/mol) for the Singlet $Fe_2(NO)_2(CO)_4$ Structures

	IVa-s (C_s)		**IVb-s** (C_s)		**IVc-s** (C_i)	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
Fe−Fe	2.354	2.366	2.305	2.269	2.600	2.557
Fe−C(bridge)	—	—	2.597/1.797	2.350/1.814	2.154/1.769	2.073/1.781
Fe−N(bridge)	1.861/1.792 1.929/1.740	1.844/1.814 1.947/1.743	1.779/1.872	1.787/1.913	—	—
Fe−N(terminal)	—	—	1.653	1.655	1.667/1.818	1.681/1.805
Fe−N−O	165.23	170.47	176.01	175.62	151.96	153.30
−energy	3240.90151	3241.42902	3240.88611	3241.42801	3240.85615	3241.40447
Δ*E*	0.0	0.0	9.7	0.6	28.5	15.4
imaginary frequencies	none	none	44*i*	41*i*	17*i*	19*i*

Table 8. Bond Distances (in Å), Total Energies (*E* in hartree), and Relative Energies (Δ*E* in kcal/mol) for the Triplet $Fe_2(NO)_2(CO)_4$ Structures

	IVd-t (C_1)		**IVe-t** (C_1)		**IVf-t** (C_i)	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
Fe−Fe	2.549	2.500	2.531	2.429	2.512	2.475
Fe−C(bridge)	1.836/2.339	1.818/2.205	—	—	1.851/2.240	1.811/2.067
Fe−N(bridge)	1.867/1.864	1.779/1.886	1.952/1.850 2.058/1.757	1.907/1.803 1.983/1.762	—	—
Fe−N(terminal)	1.711	1.667	—	—	1.723	1.673
Fe−N−O	173.86	173.49	158.15	143.72	170.23	167.87
−energy	3240.90429	3241.41028	3240.89860	3241.39858	3240.88497	3241.40746
Δ*E*	1.7	11.8	1.8	19.1	10.4	13.5
imaginary frequencies	none	none	8*i*	none	19*i*	none

The global minimum **IVa-s** for $Fe_2(NO)_2(CO)_4$ has two bridging NO groups and no imaginary vibrational frequencies. One of the bridging NO groups is a five-electron donor as indicated by a relatively short Fe−O distance of 2.207 Å (B3LYP) or 2.341 Å (BP86). This NO group exhibits a low bridging ν(NO) frequency at 1553 cm^{-1} (BP86). A similar formal five-electron donor η^2-μ-NO group has previously been reported[30] in $[(\eta^5\text{-}C_5H_5)Mo(NO)(\mu\text{-}\eta^1{:}\eta^2\text{-}NO)(\mu\text{-}CHCMe_3)][(\eta^5\text{-}C_5H_5)Mo({=}CHCMe_3)]$ and is predicted[5] to be present in an energetically accessible isomer of $Mn_2(NO)_2$-

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(30) Legzdins, P.; Rettig, S. J.; Veltheer, J. E.; Batchelor, R. J.; Einstein, F. W. B. *Organometallics* **1993**, *12*, 3575.

Table 9. Infrared ν(CO) and ν(NO) Frequencies Predicted for the $Fe_2(NO)_2(CO)_4$ Structures Using the BP86 Method (Infrared Intensities are Given in Parentheses in km/mol)

structure	ν(NO) frequencies	ν(CO) frequencies, cm^{-1}
IVa-s	1553(478), 1680(365)	1973(72), 1982(1510), 2003(1763), 2032(51)
IVb-s	1688(564), 1830(1218)	1932(628), 1956(756), 1976(911), 2025(618)
IVc-s	1767(0), 1766(1889)	1836(836), 1856(0), 1991(2003), 2014(0)
IVd-t	1626(470), 1820(1109)	1895(437), 1966(996), 1994(1663), 2023(241)
IVe-t	1355(333), 1661(367)	1975(228), 1981(1451), 1997(1946), 2028(67)
IVf-t	1796(2240), 1802(0)	1854(977), 1874(0), 1984(2179), 2010(0)

$(CO)_5$. The second bridging NO group in **IVa-s** is a normal three-electron donor and exhibits a more conventional bridging ν(NO) frequency at 1680 cm^{-1}. The Fe═Fe bond distance of 2.354 Å (B3LYP) or 2.336 Å (BP86) can be interpreted as the double bond needed to give both iron atoms in **IVa-s** the favored 18-electron configuration. Note that this Fe═Fe double bond distance is 0.2−0.3 Å shorter than the Fe−Fe single bond distances in the doubly bridged singlet isomers **IIa-s** and **IIb-s** of $Fe_2(NO)_2(CO)_6$ (Figure 3 and Table 3).

The second singlet $Fe_2(NO)_2(CO)_4$ structure **IVb-s** lies 9.7 kcal/mol (B3LYP) or 0.6 kcal/mol (BP86) above the global minimum **IVa-s**. Thus the BP86 method suggests that structure **IVb-s** is nearly energetically degenerate to **IVa-s** after considering the reliability of DFT methods. One of the NO groups in **IVb-s** is a three-electron donor bridging NO group exhibiting a ν(NO) frequency of 1688 cm^{-1} (BP86). The second NO group is a linear terminal NO group, indicating a three-electron donor, and exhibits a typical terminal ν(NO) frequency at 1830 cm^{-1} (BP86). The Fe═Fe distance of 2.305 Å (B3LYP) or 2.269 Å (BP86) in **IVb-s** is within 0.07 Å of that in **IVa-s**, suggesting a double bond. This gives one of the two iron atoms in **IVb-s** only a 16-electron configuration. The "left" iron atom in structure **IVb-s** in Figure 5 has an apparent vacant coordination site *trans* to the bridging NO group, and thus is probably the iron atom having the 16-electron configuration.

The remaining singlet stationary point for $Fe_2(NO)_2(CO)_4$ is the C_i structure **IVc-s** (Figure 5) with two bridging CO groups and with bent terminal NO groups (152.0° by B3LYP or 153.3° by BP86) exhibiting ν(NO) frequencies at 1766 and 1767 cm^{-1}. The relatively long Fe$\cdots$O distances of ~2.8 Å to the bridging CO groups in **IVc-s** and the typical bridging ν(CO) frequencies at 1836 and 1856 cm^{-1} suggest that these CO groups are two-electron donors. The Fe−Fe distance of 2.600 Å (B3LYP) or 2.557 Å (BP86) in **IVc-s** is consistent with a single bond, which gives the iron atoms only 14-electron configurations if the bent NO groups are considered one-electron donors. The unusual features of **IVc-s** are consistent with its energy lying appreciably above the global minimum **IVa-s** at 28.5 kcal/mol (B3LYP) or 15.4 kcal/mol (BP86).

The energies of the triplet structures (Table 8) of $Fe_2(NO)_2(CO)_4$ are all higher than those of the corresponding singlet structures. The lowest lying of the three triplet structures is **IVd-t**, which lies 1.7 kcal/mol (B3LYP) or 11.8 kcal/mol (BP86) above the singlet global minimum **IVa-s**. Structure **IVd-t** has one bridging NO group exhibiting a bridging ν(NO) frequency at 1626 cm^{-1} and a semibridging CO group exhibiting a ν(CO) frequency at 1895 cm^{-1}. The remaining NO group in **IVd-t** is a linear terminal NO group exhibiting a normal ν(NO) frequency at 1820 cm^{-1}. The Fe═Fe distance of 2.549 Å (B3LYP) or 2.500 Å (BP86) needs to be interpreted as a double bond to give both iron atoms the 17-electron configurations required for triplet spin multiplicity.

The next triplet structure of $Fe_2(NO)_2(CO)_4$, namely, **IVe-t** (Figure 5 and Table 8) lying 1.8 kcal/mol (B3LYP) or 19.1 kcal/mol (BP86) above the singlet global minimum **IVa-s**, has two bridging NO groups. One of these NO groups has a very short Fe−O distance of 2.120 Å (B3LYP) or 2.035 Å (BP86), suggesting a five-electron donor. This NO group exhibits an abnormally low ν(NO) frequency of 1355 cm^{-1} (Table 9), implying a very low N−O bond order. The other NO group in **IVe-t** is a typical three-electron donor bridging NO group and exhibits a normal bridging ν(NO) frequency at 1661 cm^{-1}. The Fe−Fe distance of 2.531 Å (B3LYP) or 2.429 Å (BP86) can be interpreted as the single bond needed to give both iron atoms 17-electron configurations corresponding to the triplet spin multiplicity.

The remaining triplet structure of $Fe_2(NO)_2(CO)_4$, namely, **IVf-t** (Figure 5 and Table 8) lying 10.4 kcal/mol (B3LYP) or 13.5 kcal/mol (BP86) above **IVa-s**, has two slightly unsymmetrical bridging CO groups and two nearly linear (170.2° by B3LYP or 167.9° by BP86) terminal NO groups. The bridging CO groups in **IVf-t** exhibit typical bridging ν(CO) frequencies at 1854 and 1874 cm^{-1}. Similarly, the linear terminal CO groups in **IVf-t** display conventional terminal ν(NO) frequencies at 1796 and 1802 cm^{-1}. The Fe═Fe distance of 2.512 Å (B3LYP) or 2.475 Å (BP86) can be interpreted as the double bond needed to give both iron atoms the 17-electron configurations corresponding to triplet spin multiplicity.

3.1.5. $Fe_2(NO)_2(CO)_3$.

Four low-lying structures (two singlets and two triplets) were found for the highly unsaturated $Fe_2(NO)_2(CO)_3$ (Figure 6 and Tables 10 and 11). Unlike the less unsaturated $Fe_2(NO)_2(CO)_n$ (n = 7, 6, 5, 4) derivatives, the triplet isomers **Va-t** and **Vb-t** were found to have much lower energies by B3LYP or slightly lower energies by BP86 than the singlet isomers **Vc-s** and **Vd-s** (Table 10). The two DFT methods disagree on the relative energies of the two triplet isomers. Thus the B3LYP method predicts **Va-t** to lie below **Vb-t** by 9.7 kcal/mol, whereas the BP86 method predicts **Vb-t** to lie below **Va-t**, albeit by only 1.0 kcal/mol.

All four structures for $Fe_2(NO)_2(CO)_3$ (Figure 6) have a single bridging NO group and a single linear NO group. The bridging ν(NO) frequencies for the $Fe_2(NO)_2(CO)_3$ structures **Va-t**, **Vc-s**, and **Vd-s** fall in the narrow range of 1574−1610

Table 10. The Bond Distances (in Å), Total Energies (E in hartree), and Relative Energies (ΔE in kcal/mol) for $Fe_2(NO)_2(CO)_3$ Isomers

	Va-t (C_s)		**Vb-t** (C_1)		**Vc-s** (C_1)		**Vd-s** (C_1)	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
Fe−Fe	2.505	2.396	2.532	2.667	2.391	2.365	2.377	2.366
Fe−N(bridge)	1.901	1.812	1.840	1.927	1.758	1.784	1.762	1.790
			1.887	1.728	1.860	1.836	1.827	1.819
Fe−N(terminal)	1.731	1.663	1.734	1.673	1.636	1.653	1.653	1.670
Fe−N−O	172.5	174.6	177.3	172.9	161.6	163.3	171.4	169.3
−energy	3127.53701	3128.01723	3127.52154	3128.01874	3127.48000	3128.01568	3127.47398	3127.99589
ΔE	0.0	1.0	9.7	0.0	35.8	1.9	39.6	14.3
imaginary frequencies	none	none	none	none	none	none	none	none

Table 11. Infrared ν(CO) and ν(NO) Frequencies (cm^{-1}) Predicted for the $Fe_2(NO)_2(CO)_3$ Structures Using the BP86 Method (Infrared Intensities are Given in Parentheses in km/mol)

structure	ν(NO) frequencies	ν(CO) frequencies
Va-t	1610(512), 1810(1182)	1899(566), 1969(1069), 2016(766)
Vb-t	1425(324), 1819(874)	1955(527), 1987(1445), 2018(453)
Vc-s	1608(416), 1801(1201)	1864(747), 1963(780), 2013(937)
Vd-s	1574(524), 1807(748)	1953(640), 1978(1464), 2006(299)

Table 12. Energies (kcal/mol) for Carbonyl Dissociation of $Fe_2(NO)_2(CO)_n$ Structures

	B3LYP	BP86
$Fe_2(NO)_2(CO)_7$ (**Ia-s**) → $Fe_2(NO)_2(CO)_6$ (**IIa-s**) + CO	−11.3	−5.8
$Fe_2(NO)_2(CO)_6$ (**IIa-s**) → $Fe_2(NO)_2(CO)_5$ (**IIIa-s**) + CO	29.1	24.1
$Fe_2(NO)_2(CO)_5$ (**IIIa-s**) → $Fe_2(NO)_2(CO)_4$ (**IVa-s**) + CO	17.0	28.9
$Fe_2(NO)_2(CO)_4$ (**IVa-s**) → $Fe_2(NO)_2(CO)_3$ (**Va-s**) + CO	54.4	50.5

cm^{-1} (Table 11), which is expected to be typical for a bridging NO group. However, the bridging ν(NO) frequency for **Vb-t** is abnormally low at 1425 cm^{-1}, but its Fe···O distance appears too long for this to be a five-electron donor bridging NO group. In accord with the anomalous ν(NO) frequency of the bridging NO group in **Vb-t**, its N−O distance is somewhat longer (typically 0.05 Å) than the bridging N−O distances in the other $Fe_2(NO)_2(CO)_3$ derivatives. This may indicate appreciable contribution from a formal NO^{3-} resonance structure for this NO ligand, which would be derived from the triple deprotonation of hydroxylamine, NH_2OH. The second NO group in each of the $Fe_2(NO)_2(CO)_3$ structures is a linear terminal NO group, which exhibits ν(NO) frequencies in the narrow range of 1801−1819 cm^{-1}, typical for linear terminal NO groups.

Since all of the NO groups appear to be three-electron donors and all of the CO groups to be two-electron donors in each of the four structures found for $Fe_2(NO)_2(CO)_3$ (Figure 6), an iron−iron quadruple bond is required to give the favored metal 18-electron configurations for the singlet structures. Furthermore, an iron−iron triple bond is required to give the 17-electron configurations required for the triplet structures. However, the iron−iron distances in the range of 2.37–2.67 Å appear to be too long for such high formal bond orders, indicating coordinative unsaturation for all four of the $Fe_2(NO)_2(CO)_3$ structures found in this work.

3.2. Dissociation Energies. Table 12 lists the energies for removal of one CO group from the $Fe_2(NO)_2(CO)_n$ (n = 7, 6, 5, 4) derivatives based on the lowest energy structures. For comparison, the reported[31] CO dissociation energies are 37 ± 2, 41 ± 2, and 25 ± 2 kcal/mol for $Cr(CO)_6$, $Fe(CO)_5$, and $Ni(CO)_4$, respectively.

The dissociation of a carbonyl group from $Fe_2(NO)_2(CO)_7$ is seen to be an exothermic process, suggesting that the gain in energy by forming an Fe−Fe bond in going from $Fe_2(NO)_2(CO)_7$ to $Fe_2(NO)_2(CO)_6$ more than compensates for the energy required to break an Fe−CO bond. The thermodynamic instability of $Fe_2(NO)_2(CO)_7$ relates to the fact that the isoelectronic cobalt carbonyl derivative, namely, $Co_2(CO)_9$, can only be observed at high CO pressures[32] and decomposes spontaneously to $Co_2(CO)_8$ when the CO pressure is released.

The next two CO dissociation steps, namely, from $Fe_2(NO)_2(CO)_6$ to $Fe_2(NO)_2(CO)_5$ and from $Fe_2(NO)_2(CO)_5$ to $Fe_2(NO)_2(CO)_4$, have typical dissociation energies, comparable to that for the dissociation of one CO group from $Ni(CO)_4$.[31] The further dissociation of CO from $Fe_2(NO)_2(CO)_4$ to give $Fe_2(NO)_2(CO)_3$ at more than 50 kcal/mol is seen to be a relatively high energy process. The relatively high energy for this CO dissociation process is not surprising in view of the fact that all of the structures found for $Fe_2(NO)_2(CO)_3$ are coordinately unsaturated and thus relatively unfavorable.

4. Discussion

A general observation in this work is that $Fe_2(NO)_2(CO)_n$ structures with bridging NO groups are more stable than corresponding structures with bridging CO groups. This is especially true for the derivatives $Fe_2(NO)_2(CO)_5$ and $Fe_2(NO)_2(CO)_3$ with odd numbers of CO groups, for which all of the observed structures (Figures 4 and 6) have one symmetrical or nearly symmetrical bridging NO group. Also for $Fe_2(NO)_2(CO)_7$, the lowest lying structure with two bridging NO groups (**Ia-s** in Figure 2) lies nearly 20 kcal/mol below a structure with three bridging CO groups (**Id-t** in Figure 2). For $Fe_2(NO)_2(CO)_6$, the structure with two bridging NO groups (**IIa-s** in Figure 3) lies below a related structure with two bridging CO groups (**IIb-s** in Figure 3) using either DFT method.

Our previous DFT studies on the binuclear manganese carbonyl nitrosyls[5] $Mn_2(NO)_2(CO)_n$ (n = 7, 6, 5, 4) also indicated a clear energetic preference for structures with bridging NO groups relative to structures with bridging CO groups. However, a similar DFT study of the binuclear chromium carbonyl nitrosyls[33] $Cr_2(NO)_2(CO)_n$ (n = 8, 7, 6, 5) did not indicate a similar energetic preference of bridging NO groups over bridging CO groups. We suggest that the energetic preference for bridging NO groups over bridging CO groups is a feature of the relatively electron-rich later transition metals.

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Table 13. Bond Distances (in Å) and Formal Metal−Metal Bond Orders for the Lowest Energy Iron Carbonyl Nitrosyl and Their Isoelectronic Cobalt Carbonyl Structures (BP86 Results)

	symmetry	number of bridges	M−M distance	M−C/N(b) distances	C/N−O(b) distances	bond order
$Fe_2(NO)_2(CO)_7$ (**Ia-s**)	C_s	2(NO)	3.161	2.090/1.882	1.219	0
$Co_2(CO)_9$ (exptl)[32]	—	1(CO)	—	—	—	0
$Fe_2(NO)_2(CO)_6$ (**IIa-s**)	C_{2v}	2(NO)	2.598	1.884	1.211	1
$Co_2(CO)_8$ (2 μ-CO groups)	C_{2v}	2(CO)	2.550	1.957	1.188	1
$Co_2(CO)_8$ (unbridged)	D_{3d}	none	2.692	—	—	1
$Co_2(CO)_8$ (unbridged)	D_{2d}	none	2.629	—	—	1
$Fe_2(NO)_2(CO)_5$ (**IIIa-s**)	C_s	1(NO)	2.426	1.772/1.878	1.214	2
$Co_2(CO)_7$	C_{2v}	none	2.490	—	—	2
$Co_2(CO)_7$	C_s	1(CO)	2.423	1.932	1.187	2
$Fe_2(NO)_2(CO)_4$ (**IVa-s**)	C_s	2(NO)	2.336	1.844/1.814	1.205	2
$Co_2(CO)_6$	C_{2v}	2(CO)	2.254	1.913/1.952	1.179	3
$Fe_2(NO)_2(CO)_3$ (**Vb-t**)	C_1	1(NO)	2.667	1.927/1.728	1.266	2
$Co_2(CO)_5$	C_{2v}	1(CO)	2.173	1.898	1.186	4

Table 13 compares the lowest energy structures of isoelectronic $Fe_2(NO)_2(CO)_n$ and $Co_2(CO)_{n+2}$derivatives based on information from an earlier DFT study using the same methods.[34] The following observations can be made concerning the isoelectronic pairs:

(1) $Co_2(CO)_9$ versus $Fe_2(NO)_2(CO)_7$. The 18-electron rule suggests no Co···Co bond in $Co_2(CO)_9$, which was not included in the previous DFT study on binuclear cobalt carbonyls.[34] However, Whyman[32] has shown that $Co_2(CO)_8$ reacts with CO at elevated pressures to give $Co_2(CO)_9$, suggested by its infrared ν(CO) frequencies to consist of two $Co(CO)_4$ units linked by a bridging CO group. This species is only stable at high CO pressures and reverts to $Co_2(CO)_8$ upon release of the CO pressure. The lowest energy structure of the isoelectronic $Fe_2(NO)_2(CO)_7$ (**Ia-s** in Figure 2) has two bridging NO groups in contrast to the one bridging CO group in the suggested (but not proven) structure[32] of $Co_2(CO)_9$.

(2) $Co_2(CO)_8$ versus $Fe_2(NO)_2(CO)_6$. One doubly CO-bridged and two unbridged structures for $Co_2(CO)_8$ are found within 2 kcal/mol (B3LYP) or 6 kcal/mol (BP86) of each other.[34] However, for $Fe_2(NO)_2(CO)_6$, the doubly NO-bridged isomer **IIa-s** is of significantly lower energy than either the doubly CO-bridged isomer **IIb-s** or the unbridged isomer **IIc-s** (Figure 3and Table 3). This finding shows how bridging NO groups can contribute to the stability of binuclear iron carbonyl nitrosyl isomers.

(3) $Co_2(CO)_7$ versus $Fe_2(NO)_2(CO)_5$. The lowest energy structure for $Co_2(CO)_7$ is an unbridged $(OC)_4Co{=}Co(CO)_3$ structure.[34] No corresponding structure is found for the isoelectronic $Fe_2(NO)_2(CO)_5$. A singly CO-bridged $Co_2(CO)_7$ structure is predicted to lie 11.6 kcal/mol (B3LYP) or 4.2 kcal/mol (BP86) above this global minimum. This singly CO-bridged structure for $Co_2(CO)_7$ is closely related to the singly NO-bridged $Fe_2(NO)_2(CO)_5$ global minimum **IIIa-s** (Figure 3). In the singly bridged structures for both $Co_2(CO)_7$ and $Fe_2(NO)_2(CO)_5$ (**IIIa-s**), the metal−metal distances of 2.42 Å correspond to the M═M double bonds required to give both metal atoms the favored 18-electron rare gas electronic configuration.

(4) $Co_2(CO)_6$ versus $Fe_2(NO)_2(CO)_4$. The global minima for both $Co_2(CO)_6$ and $Fe_2(NO)_2(CO)_4$ are doubly bridged structures. In $Co_2(CO)_6$, this structure has a short enough Co≡Co distance (2.235 Å by BP86) to correspond to the triple bond required to give both metal atoms the favored 18-electrons. In the isoelectronic $Fe_2(NO)_2(CO)_4$ (**IVa-s** in Figure 5), one of the bridging NO groups is a five-electron donor, as indicated by its relatively short Fe−O bond (2.207 Å by B3LYP or 2.336 Å by BP86). Therefore, only an Fe═Fe double bond is needed to give both iron atoms the favored 18-electron configuration as indicated by the longer Fe═Fe distance of 2.336 Å in $Fe_2(NO)_2(CO)_4$ (**IVa-s**).

(5) $Co_2(CO)_5$ versus $Fe_2(NO)_2(CO)_3$. For $Co_2(CO)_5$, the global minimum is a singly CO-bridged structure with a very short quadruply bonded Co−Co distance of 2.173 Å, consistent with the quadruple bond required to give the cobalt atoms the favored 18-electron configuration. For $Fe_2(NO)_2(CO)_3$, the low energy triplet structure (a global minimum by BP86) has a single NO bridge but a much longer Fe═Fe distance of 2.667 Å, suggesting a bond order no higher than two, which corresponds to a 16-electron configuration for both metal atoms.

So far none of the $Fe_2(NO)_2(CO)_n$ (n = 7, 6, 5, 4, 3) derivatives discussed in this paper have been synthesized as stable molecules. A possible route to the saturated $Fe_2(NO)_2(CO)_6$ would be the oxidation of the readily available $Fe(CO)_3NO^-$ anion.[9] However, an attempted oxidation of $Fe(CO)_3NO^-$ with $C_7H_7^+BF_4^-$ led instead to decomposition.[3] Obviously, conditions need to be found to carry out this oxidation under much milder conditions, possibly electrochemically at low temperatures.

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Supporting Information Available: Complete tables of harmonic vibrational frequencies for $Fe_2(NO)_2(CO)_n$ (n = 7, 6, 5, 4, 3) isomers (Tables S1−S22). This material is available free of charge via the Internet at http://pubs.acs.org.

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