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Chromium Carbonyl Nitrosyls: Comparison with Isoelectronic Manganese Carbonyl Derivatives

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Density functional methods indicate that the global minimum for $Cr_2(NO)_2(CO)_8$ is a staggered D_{4d} structure in accord with experiment and analogous to the isoelectronic $Mn_2(CO)_{10}$. For the unsaturated $Cr_2(NO)_2(CO)_n$ derivatives the lowest energy structures are very different from the lowest energy structures for the isoelectronic $Mn_2(CO)_{n+2}$ derivatives. Thus the global minimum for $Cr_2(NO)_2(CO)_7$ is an unbridged structure with a $Cr(NO)(CO)_4$ fragment linked to a $Cr(NO)(CO)_3$ fragment through a $Cr=Cr$ double bond. For $Cr_2(NO)_2(CO)_6$ the global minimum is a structure with two bridging CO groups, whereas the global minimum for $Mn_2(CO)_8$ is an unbridged structure. For $Cr_2(NO)_2(CO)_5$ both NO groups are bridging NO groups with one of them having a short enough Cr–O distance to be considered a formal five-electron donor η^2-μ-NO group. Thus the isoelectronic substitution of NO for CO with a necessary adjustment in the central metal atom can lead to significant shifts in the relative energies of various structural types of metal carbonyl nitrosyls, particularly for unsaturated molecules. For the mononuclear $Cr(NO)_2(CO)_3$ the theoretical structure differs from that deduced from matrix isolation experiments. Moreover, the $\nu(CO)$ and $\nu(NO)$ vibrational frequencies predicted here for $Cr(NO)_2(CO)_3$ correspond more closely with the unassigned species labeled "$Cr(NO)(CO)_x$" in the experiments rather than the species claimed to be $Cr(NO)_2(CO)_3$.

1. Introduction

Two neutral chromium carbonyl nitrosyls have been prepared experimentally. Thus $Cr_2(NO)_2(CO)_8$ isoelectronic with $Mn_2(CO)_{10}$ was isolated as a stable orange crystalline solid from the oxidation of the anion $Cr(NO)(CO)_4^-$ with $[(C_6H_5)_3C]^+[BF_4]^-$ and shown by X-ray crystallography to be an unbridged dimer held together by only a Cr–Cr single bond.[1] In addition, the photolysis of $Cr(CO)_6$ with NO in low-temperature argon matrices has been suggested by infrared spectroscopy to give relatively unstable $Cr(NO)_2(CO)_3$ isoelectronic with $Mn(NO)(CO)_4$ and $Fe(CO)_5$ as an intermediate in the complete substitution of CO by NO to give the homoleptic derivative $Cr(NO)_4$.[2] No unsaturated binuclear chromium carbonyl nitrosyls of the type $Cr_2(NO)_2(CO)_n$ ($n = 7$, 6, and 5), required by the 18-electron rule to

have chromium−chromium multiple bonds, have yet been prepared. Such $Cr_2(NO)_2(CO)_n$ ($n = 7$, 6, and 5) derivatives are potentially accessible by the photochemical decarbonylation of the stable $Cr_2(NO)_2(CO)_8$, most likely in low-temperature matrices.

This research uses density functional theory (DFT) methods to examine the effect of unsaturation on the structure and bonding in the unsaturated chromium carbonyl nitrosyls $Cr_2(NO)_2(CO)_n$ ($n = 7$, 6, and 5) for comparison with the isoelectronic homoleptic manganese carbonyl derivatives $Mn_2(CO)_n$ ($n = 9$, 8, and 7) studied previously.[3] The mononuclear $Cr(NO)_2(CO)_3$, observed experimentally,[2] and the 17-electron complex $Cr(NO)(CO)_4$, potentially obtainable by the homolytic cleavage of the stable $Cr_2(CO)_8(NO)_2$, have also been studied.

2. Theoretical Methods

Electron correlation effects were included by employing density functional theory (DFT) methods, which have evolved as a practical and effective computational tool, especially for organometallic

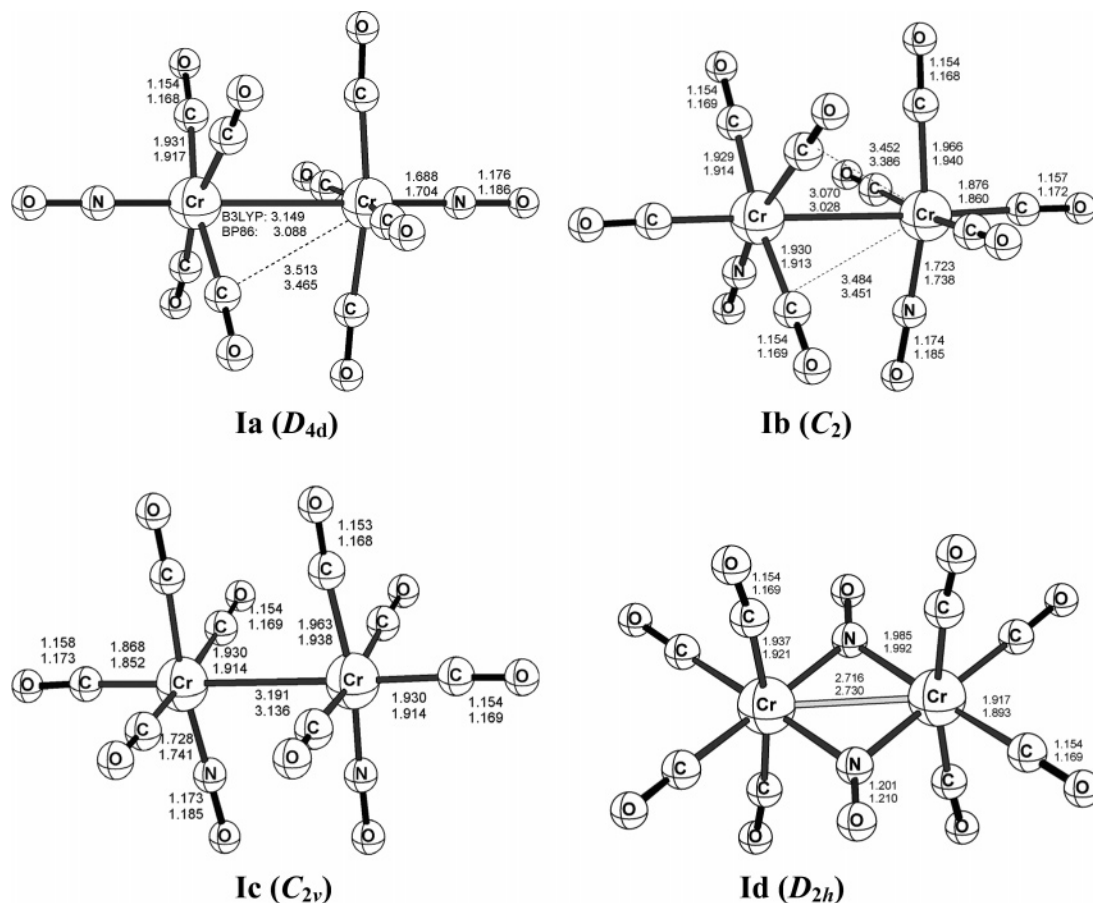* To whom correspondence should be addressed. E-mail: wanghyxx@yahoo.com, rbking@chem.uga.edu.
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Figure 1. Optimized geometries for $Cr_2(NO)_2(CO)_8$ isomers. All bond distances are in Å in all of the figures.

Table 1. Bond Distances (in Å), Total Energies (*E* in Hartree), and Relative Energies (Δ*E* in kcal/mol) for the $Cr_2(NO)_2(CO)_8$ Isomers

|	**Ia** (D_{4d})		**Ib** (C_2)		**Ic** (C_2)		**Id** (D_{2h})	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
Cr−Cr	3.149	3.088	3.070	3.028	3.191	3.136	2.716	2.730
Cr−N(bridge)							1.985	1.992
Cr−N(terminal)	1.688	1.704	1.723	1.738	1.728	1.741		
Cr−N−O	180.0	180.0	179.1	179.1	177.5	176.7	136.8	136.7
−Energy	3255.87669	3256.33961	3255.86179	3256.32339	3255.85747	3256.31871	3255.84487	3256.30761
Δ*E*	0.0	0.0	9.3	10.2	12.1	13.1	20.0	20.1
imaginary freq	none	none	none	none	18*i*	19*i*	none	none

compounds.[4−11] Thus two DFT methods were used in this study. The first functional is the hybrid B3LYP method, which is the hybrid HF/DFT method using the combination of the three-parameter Becke functional (B3) with the Lee−Yang−Parr (LYP) generalized gradient correlation functional.[12,13] The other DFT method used in the present paper is BP86, which combines Becke's 1988 exchange functional (B) with Perdew's 1986 gradient corrected correlation functional method (P86).[14,15] It has been noted

elsewhere that the BP86 method may be somewhat more reliable than B3LYP for the type of organometallic systems considered in this paper.[16−18]

For carbon, nitrogen, and oxygen, the double-ζ plus polarization (DZP) basis set used here (9s5p/4s2p) adds one set of pure spherical harmonic d functions with orbital exponents $\alpha_d(C) = 0.75$, $\alpha_d(N) = 0.80$, and $\alpha_d(O) = 0.85$ to the Huzinaga−Dunning standard contracted DZ sets.[19,20] For Cr, in our loosely contracted DZP basis set, the Wachters' primitive set is used but is augmented by two sets of p functions and one set of d functions, contracted following

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IIa-s (C_s) IIb-s (C_1)

IIc-s (C_{2v}) IId-t (C_1)

IIe-t-B3LYP(C_1) IIe-t-BP86(C_1)
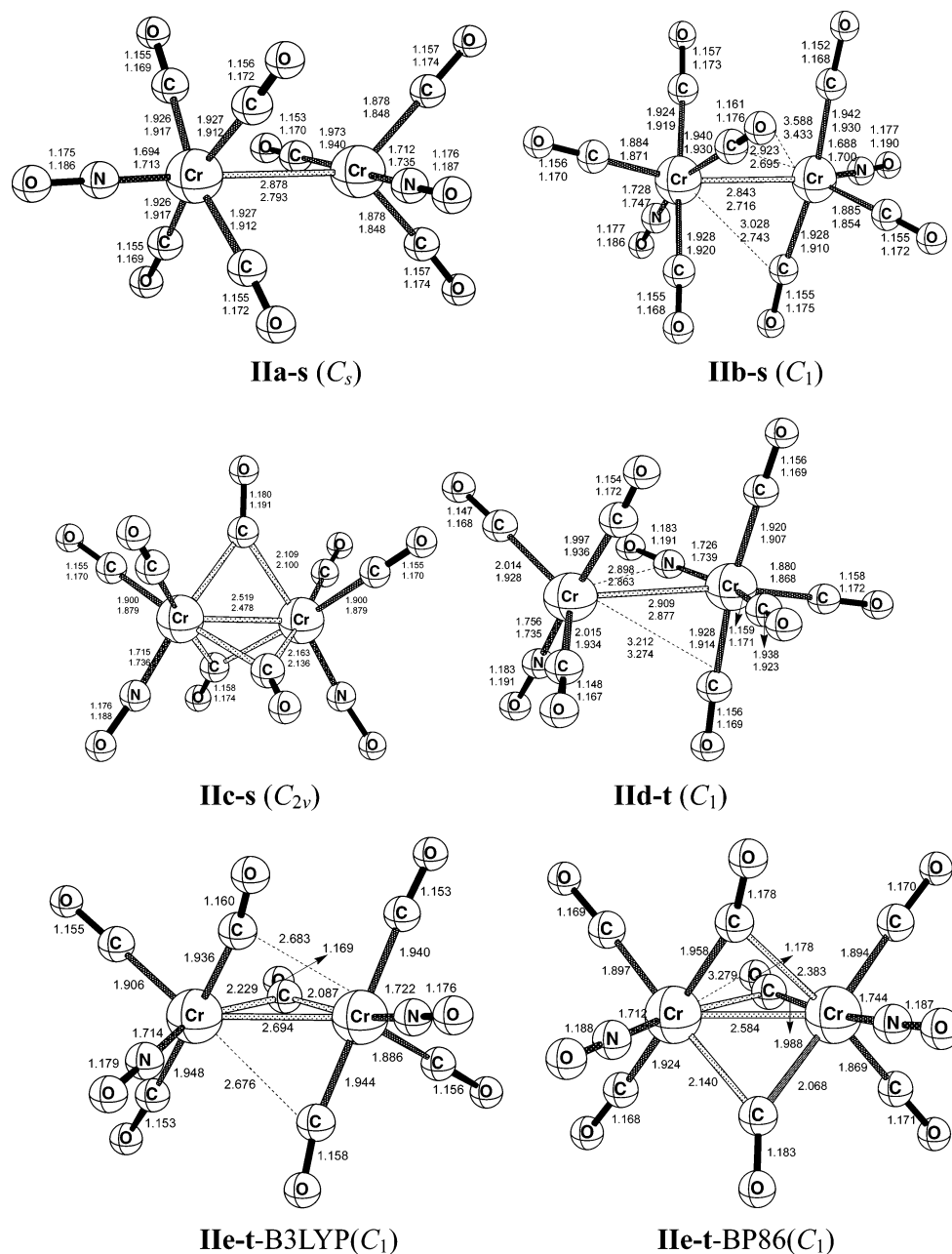
Figure 2. Optimized geometries for $Cr_2(NO)_2(CO)_7$ isomers.

Table 2. Bond Distances (in Å), Total Energies (E in Hartree), and Relative Energies (ΔE in kcal/mol) for the $Cr_2(NO)_2(CO)_7$ Singlet Isomers

	IIa-s (C_s)		IIb-s (C_1)		IIc-s (C_{2v})	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
Cr−Cr	2.878	2.793	2.843	2.716	2.519	2.478
Cr−C(bridge)					2.109	2.100
Cr−N(terminal)	1.694/1.712	1.713/1.735	1.728/1.688	1.747/1.700	1.715	1.736
Cr−N−O	179.5/175.6	178.1/173.0	177.9/175.6	174.9/176.0	175.5	173.7
−Energy	3142.48855	3142.94493	3142.48567	3142.94360	3142.45692	3142.92725
ΔE	0.0	0.0	1.8	0.8	19.8	11.1
imaginary freq	none	none	none	none	224i, 203i, 36i	219i, 145i, 36i

Hood et al., and designated (14s11p6d/10s8p3d).[21,22] For Cr(NO)-
(CO)$_4$, there are 199 contracted Gaussian basis functions. For the
binuclear chromium carbonyl nitrosyls $Cr_2(NO)_2(CO)_8$, $Cr_2(NO)_2$-
(CO)$_7$, $Cr_2(NO)_2(CO)_6$, and $Cr_2(NO)_2(CO)_5$, there are 398, 368, 338,
and 308 contracted Gaussian basis functions, respectively.

The geometries of all of the structures were fully optimized using
both the DZP B3LYP and DZP BP86 methods. The harmonic
vibrational frequencies were determined at the same levels by
evaluating analytically the second derivatives of the energy with

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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[23] 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 using all currently implemented DFT methods, low magnitude imaginary vibrational frequencies are suspect because of significant limitations in the numerical integration procedures used in standard DFT computations. Thus all imaginary vibrational frequencies with magnitudes less than $50i$ cm^{-1} are considered questionable and are not always pursued in the analysis.[24,25] That is, we do not always follow such low imaginary vibrational frequencies.

3. Results and Discussion

3.1. Molecular Structures. 3.1.1. $Cr_2(NO)_2(CO)_8$. Four different structures were studied for $Cr_2(NO)_2(CO)_8$ (Figure 1 and Table 1). The staggered D_{4d} unbridged structure **Ia** with the NO ligands in the axial positions is found, in agreement with experiment,[1] to be the global minimum. The Cr—Cr bond distance in **Ia** is computed to be 3.149 Å (B3LYP) or 3.088 Å (BP86), which is slightly longer than that found by X-ray crystallography (3.00–3.02 Å).[1] The C_2 staggered **Ib** structure of $Cr_2(NO)_2(CO)_8$ has a somewhat shorter Cr—Cr bond distance (3.070 Å by B3LYP or 3.028 Å by BP86) and an energy of 9.3 kcal/mol (B3LYP) or 10.2 kcal/mol (BP86) above the **Ia** global minimum. The C_{2v} structure **Ic** with NO ligands in equatorial positions lies 12.1 kcal/mol (B3LYP) or 13.1 kcal/mol (BP86) higher in energy than structure **Ia** with the NO ligands in axial positions and has only a small imaginary vibrational frequency ($18i$ cm^{-1} by B3LYP or $19i$ cm^{-1} by BP86). The **Id** (D_{2h}) structure has two bridging nitrosyls analogous to the two bridging carbonyls in the global minimum of neutral $Cr_2(CO)_{10}$ (ref 26) and lies substantially higher in energy above **Ia** by 20.0 kcal/mol (B3LYP) or 20.1 kcal/mol (BP86) (Table 1).

The Cr—Cr distances of **Ia**, **Ib**, and **Ic** fall in the range 3.03–3.19 Å. Thus these chromium–chromium distances in the three nonbridged isomers of $Cr_2(NO)_2(CO)_8$ may be interpreted to imply the Cr—Cr single bond required to give both Cr atoms the favored 18-electron configurations. However, the Cr—Cr bond in the bridged isomer **Id** is significantly shorter, namely 2.716 Å (B3LYP) or 2.730 Å (BP86), in accord with the previously observed effect of bridging NO groups in shortening metal–metal bonds.

3.1.2. $Cr_2(NO)_2(CO)_7$. Both singlet and the triplet structures were optimized for $Cr_2(NO)_2(CO)_7$, and these are labeled by "**s**" and "**t**," respectively, in their structural designations. The optimized structures are shown in Figure

Table 3. Bond Distances (in Å), Total Energies (*E* in Hartree), and Relative Energies (Δ*E* in kcal/mol Compared to **IIa-s** in Table 2) for the $Cr_2(NO)_2(CO)_7$ Triplet Isomers

	IId-t(C_1)		**IIe-t**(C_1)	
	B3LYP	BP86	B3LYP	BP86
Cr—Cr	2.909	2.877	2.694	2.584
Cr—C(bridge)			2.087/2.229	2.413/1.988
Cr—N(terminal)	1.756/1.726	1.735/1.739	1.714/1.722	1.712/1.744
Cr—N—O	178.1/177.9	178.5/178.3	178.7/177.6	180.0/175.0
−Energy	3142.47082	3142.91336	3142.46738	3142.93014
Δ*E*	11.1	19.8	13.3	9.3
imaginary freq	none	none	none	none

2, and the optimized structural parameters are presented in Tables 2 and 3 for the singlet and triplet isomers, respectively. For the singlet, the global minimum of $Cr_2(NO)_2(CO)_7$ (**IIa-s** in Figure 2 and Table 2) is a C_s unbridged structure. A second unbridged isomer **IIb-s** of $Cr_2(NO)_2(CO)_7$ with the NO ligands in different positions lies very slightly above **IIa-s** by 1.8 kcal/mol (B3LYP) or 0.8 kcal/mol (BP86). Both isomers exhibit only real harmonic vibrational frequencies. The Cr—Cr bond distances of 2.878 Å (B3LYP) or 2.793 Å (BP86) in **IIa-s** and 2.843 Å (B3LYP) or 2.716 Å (BP86) in **IIb-s** correspond to the double bonds required by the 18-electron rule, assuming the linear terminal NO groups to be three-electron donors. A singlet triply bridged structure with C_{2v} symmetry **IIc-s** is predicted to be a stationary point with rather higher energy at 19.8 kcal/mol (B3LYP) or 11.1 kcal/mol (BP86) above **IIa-s**. Structure **IIc-s** has three imaginary vibrational frequencies. Following the corresponding normal modes lead to the **IIa-s** global minimum.

Using the B3LYP method the triplet triply bridged $Cr_2(NO)_2(CO)_7$ structure collapses to a structure **IIe-t** without symmetry, in which one CO bridge is retained and the remaining two CO bridges twist into semibridging modes (Figure 2). However, in the BP86 method the three CO bridges are retained. Structure **IIe-t** lies 13.3 kcal/mol (B3LYP) or 9.3 kcal/mol (BP86) above the global minimum **IIa-s** in energy. The Cr—Cr bond distance is shortened by 0.184 Å (B3LYP) or 0.209 Å (BP86) compared to that in **IIa-s** owing to the CO bridge. The triplet unbridged $Cr_2(NO)_2(CO)_7$ structure **IId-t** is found to be a local minimum with real vibrational frequencies. The Cr—Cr bond distance is the longest, namely 2.909 Å (B3LYP) or 2.877 Å (BP86), found for any of the of $Cr_2(NO)_2(CO)_7$ isomers.

3.1.3. $Cr_2(NO)_2(CO)_6$. Three possible isomers of $Cr_2(NO)_2(CO)_6$, namely CO-bridged, NO-bridged, and unbridged structures, were used as starting points for optimization for both singlet and triplet structures. Four stationary singlet points are predicted by the optimization procedure (Figure 3 and Table 4). The C_2 structure **IIIa-s** with two bridging CO groups is the lowest in energy and has only a small imaginary vibrational frequency ($45i$ by B3LYP) or no imaginary vibrationary frequencies (BP86), showing this structure to be a genuine minimum. The energy of the C_{2v} structure **IIIb-s** with two bridging CO groups is extremely close to the global minimum **IIIa-s** at only 0.4 kcal/mol (B3LYP) or 0.02 kcal/mol (BP86) above **IIIa-s**, showing that these structures are essentially degenerate. The C_{2v} structure **IIIc-s** with two bridging NO groups lies 4.1 kcal/

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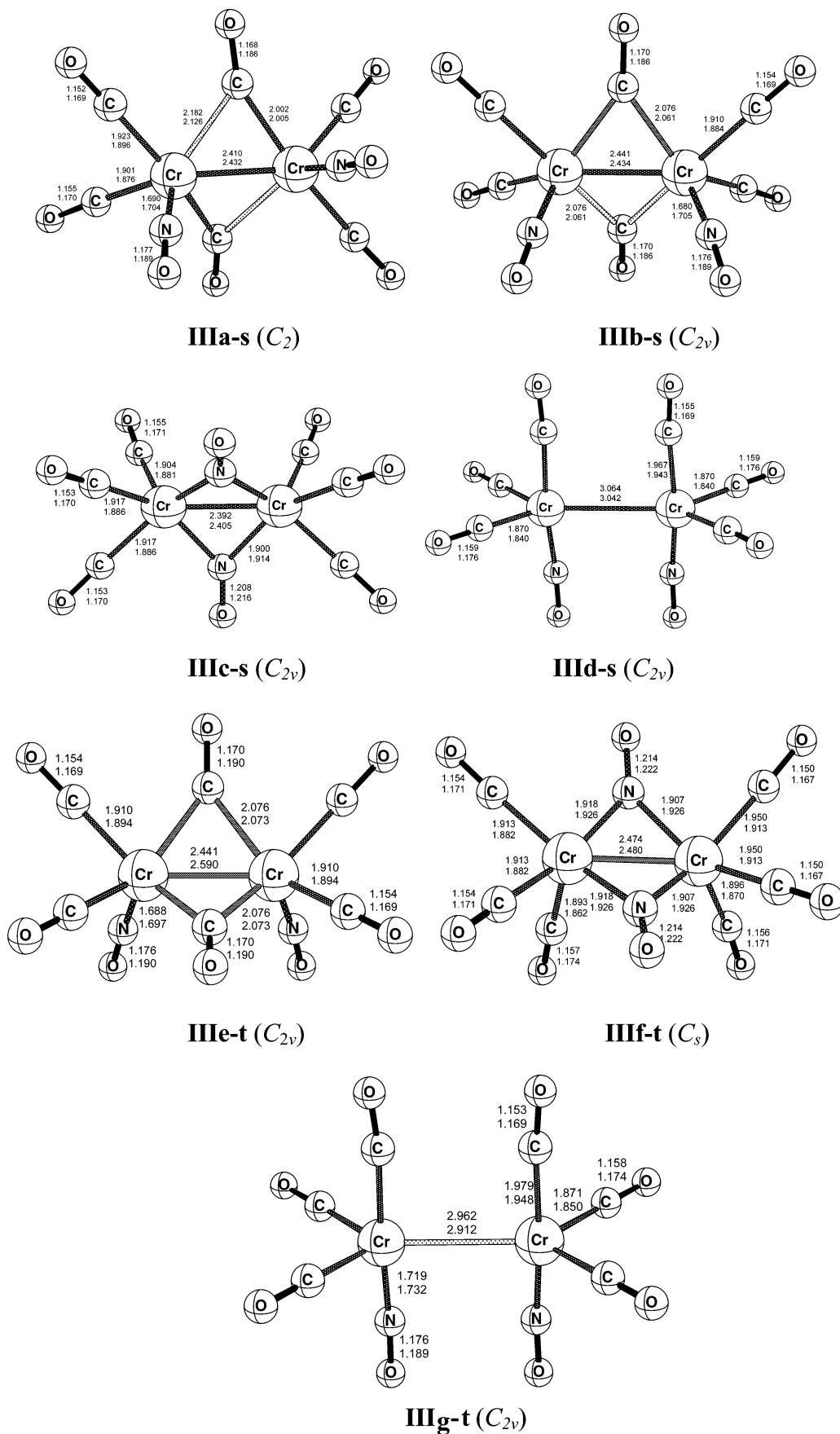
Figure 3. Optimized geometries for Cr$_2$(NO)$_2$(CO)$_6$ isomers.

Table 4. Bond Distances (in Å), Total Energies (*E* in Hartree), and Relative Energies (Δ*E* in kcal/mol) for $Cr_2(NO)_2(CO)_6$ Singlet Isomers

	IIIa-s (C_2)		IIIb-s (C_{2v})		IIIc-s (C_{2v})		IIId-s (C_{2v})	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
Cr–Cr	2.410	2.432	2.441	2.434	2.392	2.405	3.064	3.042
Cr–C(bridge)	2.002/2.182	2.005/2.126	2.076	2.061				
Cr–N(bridge)					1.900	1.914		
Cr–N(terminal)	1.690	1.704	1.680	1.705			1.716	1.732
Cr–N–O	176.1	176.9	176.4	177.3	141.0	141.1	174.9	173.9
–Energy	3029.10906	3029.57207	3029.10844	3029.57204	3029.10255	3029.56073	3029.08220	3029.52224
Δ*E*	0.0	0.0	0.4	<0.1	4.1	7.1	16.9	31.3
imaginary freq	45*i*	none	24*i*, 12*i*	10*i*	87*i*	35*i*	64*i*, 31*i*, 18*i*	98*i*, 34*i*, 33*i*

Table 5. Bond Distances (in Å), Total Energies (*E* in Hartree), and Relative Energies (Δ*E* in kcal/mol Compared to Structure IIIa-s) for $Cr_2(NO)_2(CO)_6$ Triplet Isomers

	IIIe-t (C_{2v})		IIIf-t (C_s)		IIIg-t (C_{2v})	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
Cr–Cr	2.441	2.590	2.474	2.480	2.962	2.912
Cr–C(bridge)	2.076	2.073				
Cr–N(terminal)	1.688	1.697			1.719	1.732
Cr–N(bridge)			1.918/1.907	1.926		
Cr–N–O	176.4	177.8	139.0/140.4	139.9/140.0	176.0	175.1
–Energy	3029.09781	3029.55558	3029.09768	3029.54837	3029.06578	3029.51522
Δ*E*	7.1	10.3	7.1	14.9	27.2	35.7
imaginary freq	none	none	22*i*	8*i*	115*i*, 25*i*, 14*i*	75*i*, 28*i*, 22*i*, 21*i*

mol (B3LYP) or 7.1 kcal/mol (BP86) higher in energy than structure **IIIa-s** with two bridging CO groups and has only one small imaginary vibrational frequency (87*i* cm⁻¹ by B3LYP or 35*i* cm⁻¹ by BP86). The energy of the C_{2v} unbridged structure **IIId-s** is higher than that of the structure **IIIa-s** at 16.9 kcal/mol (B3LYP) or 31.3 kcal/mol (BP86). Furthermore, **IIId-s** has three imaginary frequencies, namely 64*i*, 31*i*, and 18*i* (B3LYP) or 98*i*, 34*i*, and 33*i* (BP86) cm⁻¹. Following the highest imaginary frequency of **IIId-s** leads to **IIIa-s** with two bridging CO groups.

The chromium–chromium bond distances (2.39–2.45 Å) in the singlet doubly bridged structures of $Cr_2(NO)_2(CO)_6$, namely **IIIa-s**, **IIIb-s**, and **IIIc-s** (Figure 3 and Table 4), are much shorter than any of those in the $Cr_2(NO)_2(CO)_8$ and $Cr_2(NO)_2(CO)_7$ structures (Figures 1 and 2), suggesting a higher bond order consistent with the Cr≡Cr triple bonds required to give the metal atoms the 18-electron configurations in $Cr_2(NO)_2(CO)_6$. However, the chromium–chromium bond distance in the singlet unbridged $Cr_2(NO)_2(CO)_6$ structure **IIId-s** is 3.064 Å (B3LYP) or 3.042 Å (BP86), which is more consistent with a Cr–Cr single bond and 16-electron configurations for the chromium atoms.

All three triplet structures found for $Cr_2(NO)_2(CO)_6$ have significantly higher energies than the corresponding singlet structures (Table 5). The C_{2v} structure **IIIe-t** with two bridging CO groups is the lowest energetically of the triplet isomers. It is a genuine minimum with all real vibrational frequencies. However, its energy is higher than that of the singlet C_{2v} structure **IIIb-s** by 7.1 kcal/mol (B3LYP) or 10.3 kcal/mol (BP86). The C_s triplet structure **IIIf-t** with two bridging NO groups is higher in energy by 3.0 kcal/mol (B3LYP) or 7.7 kcal/mol (BP86) relative to the analogous singlet structure **IIIc-s**. The triplet unbridged structure **IIIg-t** is not a genuine minimum, since it exhibits relatively larger imaginary frequencies, e.g., 115*i* cm⁻¹ by B3LYP. The chromium–chromium distances in the triplet structure are 2.590 Å (BP86) for **IIIe-t** and 2.480 Å (BP86) for **IIIf-t**,

which are longer than these in the corresponding singlet structures. These suggest the Cr=Cr double bonds required to give each metal atom a 17-electron configuration leading to triplet binuclear structures.

3.1.4. $Cr_2(NO)_2(CO)_5$. Optimizations have been carried out on singlet and triplet $Cr_2(NO)_2(CO)_5$ structures in which the CO or NO groups are either bridging or terminal. The results (Figure 4) are strongly dependent on the method used (B3LYP or BP86). Using the B3LYP method, the singlet structure **IVa-s** for $Cr_2(NO)_2(CO)_5$ has the lowest energy. However, the BP86 method predicts a lower energy for **IVb-s**, which lies 2.9 kcal/mol below **IVa-s**. These structures thus appear to be nearly energetically degenerate after considering the reliability of DFT methods. Structure **IVa-s** has two bridging NO groups, whereas structure **IVb-s** has one bridging CO group. The chromium–chromium distance in **IVa-s** is 2.583 Å (B3LYP) or 2.572 Å (BP86) and about 0.352 Å (B3LYP) or 0.236 Å (BP86) shorter than that in **IVb-s**, suggesting significantly stronger metal–metal bonding in **IVa-s** relative to **IVb-s**. The unbridged structure **IVc-s** for $Cr_2(NO)_2(CO)_5$ lies 12.4 kcal/mol (B3LYP) or 8.9 kcal/mol (BP86) above structure **IVa-s** in energy. Both structures **IVa-s** and **IVb-s** are genuine minima with all real vibrational frequencies. Structure **IVc-s** has a tiny imaginary vibrational frequency (5*i* cm⁻¹ by B3LYP), which might be considered a consequence of numerical integration errors. The chromium–chromium bond distance in structure **IVc-s** is shorter than that in the structure **IVa-s**, namely 2.388 Å (B3LYP) or 2.324 Å (BP86), suggesting a chromium–chromium bond order of at least three.

The energies of the triplet structures of $Cr_2(NO)_2(CO)_5$ are all higher than those of the corresponding singlet structures. Triplet structures **IVd-t** and **IVf-t** are similar to the structures **IVa-s** and **IVc-s** with two NO bridges and with one NO semibridge and one CO semibridge, respectively. The chromium–chromium distances in the triplet structures are longer than those for the singlet structures.

IVa-s (C_s)

IVb-s (C_1)

IVc-s (C_1)

IVd-t (C_1)

IVe-t-B3LYP(C_1)

IVe-t-BP86(C_1)

IVf-t (C_1)
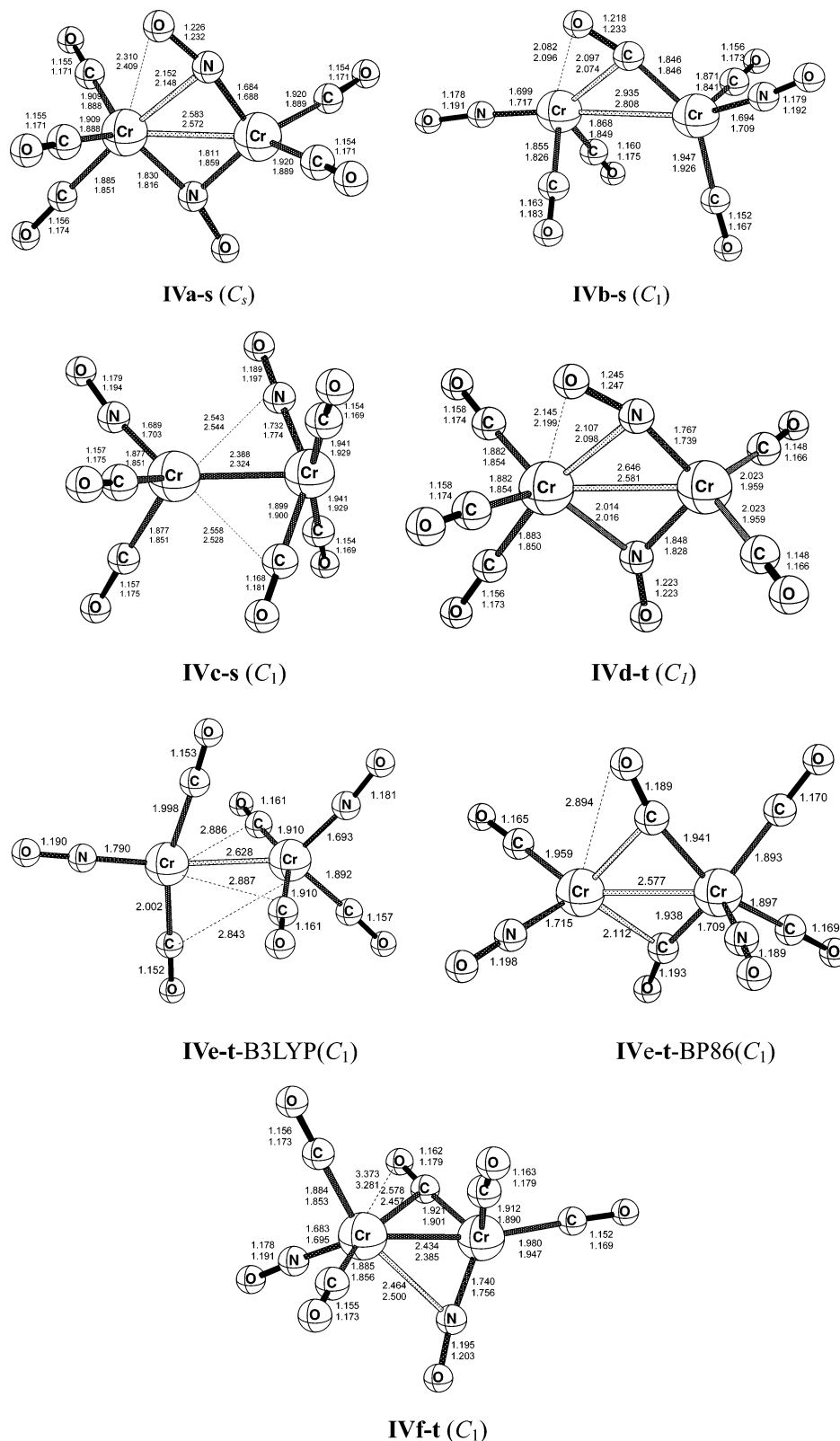
Figure 4. Optimized geometries for $Cr_2(NO)_2(CO)_5$ isomers.

For example, the chromium−chromium distance in **IVd-t** is 2.646 Å (B3LYP) or 2.581 Å (BP86), which is 0.063 Å (B3LYP) or 0.009 Å (BP86) longer than in the corresponding singlet structure **IVa-s**. The structures of $Cr_2(NO)_2(CO)_5$ found with CO bridge(s) and terminal NO groups are different in the B3LYP and BP86 methods (**IVe-t**). In the

B3LYP method, the CO bridge is lost upon optimization, whereas in the BP86 method, two CO bridges remain after optimization. A formal four-electron donor bridging CO group or a formal five-electron donor bridging NO group to the pair of metal atoms is found in all of the $Cr_2(NO)_2(CO)_5$ isomers except **IVc** and **IVe** (B3LYP) as indicated by Cr−O
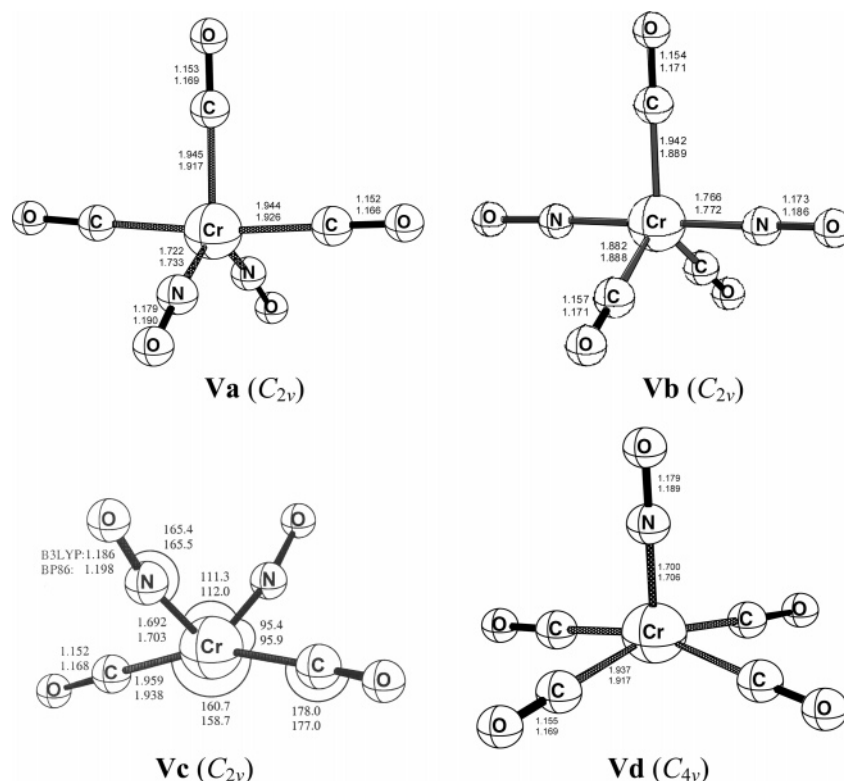
Figure 5. Optimized geometries for $Cr(NO)_2(CO)_3$, $Cr(NO)_2(CO)_2$, and $Cr(NO)(CO)_4$.

Table 6. Bond Distances (in Å), Total Energies (E in Hartree), and Relative Energies (ΔE in kcal/mol) for $Cr_2(NO)_2(CO)_5$ Singlet Isomers

	IVa-s (C_s)		IVb-s (C_1)		IVc-s (C_1)	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
Cr–Cr	2.583	2.572	2.935	2.808	2.388	2.324
Cr–C(bridge)			1.846/2.097	1.846/2.074		
Cr–N(bridge)	1.684/2.152	1.688/2.148			1.732	1.774
	1.811/1.830	1.859/1.816				
Cr–N(terminal)			1.694/1.699	1.709/1.717	1.689	1.703
Cr–N–O	165.0/163.7	162.5/169,8	174.1/175.4	173.6/172.2	179.8/171.3	180.0/170.3
–Energy	2915.74785	2916.18661	2915.74362	2916.19125	2915.72807	2916.17247
ΔE	0.0	0.0	2.7	−2.9	12.4	8.9
imaginary freq	none	none	none	none	5i	none

distances in the range 2.0–2.4 Å. Such isomers of $Cr_2(NO)_2$-$(CO)_5$ need only a Cr≡Cr triple bond to give each metal atom the favored 18-electron rare gas configuration.

3.1.5. $Cr(NO)_2(CO)_3$ and $Cr(NO)(CO)_4$. The mononuclear chromium carbonyl nitrosyl $Cr(NO)_2(CO)_3$, which is isoelectronic with the stable $Mn(NO)(CO)_4$ and $Fe(CO)_5$, has been prepared in frozen gas matrices.[2] A trigonal bipyramidal structure with both NO groups in axial positions has been suggested for $Cr(NO)_2(CO)_3$ on the basis of the observation of one infrared active $\nu(CO)$ frequency and one infrared active $\nu(NO)$ frequency in the low-temperature matrix infrared spectra.

We have investigated structures for $Cr(NO)_2(CO)_3$ with two equatorial NO groups (**Va**) and with two axial NO groups (**Vb**) using the DFT methods (Figure 5 and Table 8). The structure **Vb** with the two NO groups in axial positions suggested for the experimentally observed species in low-temperature matrices[2] is found to be higher in energy by 21.1 kcal/mol (B3LYP) or 17.8 kcal/mol (BP86) than the structure **Va** with both NO groups in equatorial posi-

tions. The Cr–N bond distance in structure **Vb** is longer by 0.044 Å (B3LYP) or 0.039 Å (BP86) than that in structure **Va**. The BP86 method predicts structure **Vb** to be a genuine minimum without any imaginary vibrational frequencies. However, the B3LYP method predicts one large imaginary vibrational frequency of 209i cm^{-1} in structure **Vb**. Following the normal mode corresponding to this imaginary vibrational frequency leads to structure **Va**. All of these observations indicate that the structure **Va** for $Cr(NO)_2(CO)_3$ with two equatorial NO groups is preferred over structure **Vb** with two axial NO groups. An analogous situation was previously[27] found for $Mn(NO)(CO)_4$, isoelectronic with $Cr(NO)_2(CO)_3$, where the isomer with an equatorial NO group rather than an axial NO group is the one both observed experimentally and predicted from DFT calculations.

Loss of a carbonyl group from $Cr(NO)_2(CO)_3$ is expected

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Table 7. Bond Distances (in Å), Total Energies (E in Hartree), and Relative Energies (ΔE in kcal/mol) for $Cr_2(NO)_2(CO)_5$ Triplet Isomers

	IVd-t (C_s)		IVe-t (C_1)		IVf-t (C_1)	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
Cr−Cr	2.646	2.581	2.628	2.577	2.434	2.385
Cr−C(bridge)				2.134/1.941/2.112/1.938	2.578/1.921	2.457/1.901
Cr−N(bridge)	2.107/1.767	2.098/1.739			2.464/1.740	2.500/1.756
	2.014/1.848	2.016/1.828				
Cr−N(terminal)			1.790/1.693	1.715/1.709	1.683	1.695
Cr−N−O	160.4/134.7	161.6/136.7	179.5/172.0	178.0/176.3	174.7/172.1	174.9/172.2
−Energy	2915.74622	2916.17236	2915.73644	2916.17697	2915.73132	2916.17103
ΔE	1.0	8.9	7.2	6.0	10.4	9.8
imaginary freq	none	none	none	none	none	none

Table 8. Bond Distances (in Å), Total Energies (E in Hartree), and Relative Energies (ΔE in kcal/mol) for the $Cr(NO)_2(CO)_3$ Isomers

	$Cr(NO)_2(CO)_3$ (Va) C_{2v}		$Cr(NO)_2(CO)_3$ (Vb) C_{2v}	
	B3LYP	BP86	B3LYP	BP86
M−N	1.722	1.733	1.766	1.772
N−O	1.179	1.190	1.173	1.186
M−C(eq/ax)	1.944/1.945	1.926/1.917	1.942/1.882	1.889/1.888
C−O(eq/ax)	1.152/1.153	1.166/1.169	1.154/1.157	1.171/1.171
M−N/C−O(ax)	180.0	180.0	180.0	180.0
M−C/N−O(eq)	180.0/174.0	180.0/175.3	178.6/177.5	180.0/180.0
N/C−M−C	119.3/87.0	119.9/84.9	127.9/85.8	120.2/89.9
−Energy	1644.53091	1644.78000	1644.49734	1644.75164
ΔE	0.0	0.0	21.1	17.8
imaginary freq	none	none	209i	none

Table 9. Bond Distances (in Å), Total Energies (E in Hartree), and Relative Energies (ΔE in kcal/mol) for $Cr(NO)_2(CO)_2$ and $Cr(NO)(CO)_4$

	$Cr(NO)_2(CO)_2$ (Vc) C_{2v}		$Cr(NO)(CO)_4$ (Vd) C_{4v}	
	B3LYP	BP86	B3LYP	BP86
M−N	1.692	1.703	1.700	1.706
N−O	1.186	1.198	1.179	1.189
M−C	1.959	1.938	1.937	1.917
C−O	1.152	1.168	1.155	1.169
M−N/C−O	180.0	180.0	180.0	180.0
M−C/N−O	178.0/165.4	177.0/165.5	178.8	179.3
N/C−M−N/C	111.3/160.7	112.0/258.7	100.1	100.3
−Energy	1531.14633	1531.38695	1627.91962	1628.14632
imaginary freq	none	none	none	none

to give a 16-electron four-coordinate complex $Cr(NO)_2(CO)_2$. If the NO groups are considered formally as NO^+, the complex $Cr(NO)_2(CO)_2$ is a d^8 Cr(−II) complex. Our DFT studies predict a flattened tetrahedral (**Vc** in Figure 5) rather than square planar structure for $Cr(NO)_2(CO)_2$ similar to that found experimentally[28] in the isoelectronic d^8 Ru(0) complex $Ru(CO)_2(PBu^t_2Me)_2$. The C−Cr−C and N−Cr−N angles are predicted to be 160.7° (B3LYP) or 158.7° (BP86) and 111.3° (B3LYP) or 112.0° (BP86), respectively, as compared with the reported corresponding angles of 165.6° (P−Ru−P) and 133.3° (C−Ru−C), respectively, in $Ru(CO)_2(PBu^t_2Me)_2$.

Homolytic cleavage of the Cr−Cr single bond in the global minimum for $Cr_2(NO)_2(CO)_8$ might be expected to give a metal-based free radical •$Cr(NO)(CO)_4$. We predict a square pyramidal structure **Vd** for •$Cr(NO)(CO)_4$ with the NO group in the apical position (Figure 5) corresponding to half of the global minimum structure **Ia** (Figure 1) for $Cr_2(NO)_2(CO)_8$. The dissociation of $Cr_2(NO)_2(CO)_8$ into two •$Cr(NO)(CO)_4$ fragments is predicted to be endothermic by 18.9 kcal/mol (B3LYP) or 24.3 kcal/mol (BP86).

3.2. Vibrational Frequencies. The harmonic vibrational frequencies and their infrared intensities for all of the structures have been predicted with the B3LYP and BP86 methods. Complete reports of the vibrational frequencies and their infrared intensities are given in the Supporting Information.

The relatively strong $\nu(CO)$ and $\nu(NO)$ frequencies are useful for experimentally characterizing metal carbonyl nitrosyls. In this connection Table 10 lists the infrared $\nu(CO)$ and $\nu(NO)$ frequencies for the binuclear chromium carbonyl nitrosyls $Cr_2(NO)_2(CO)_n$ ($n = 8$, 7, 6, and 5) obtained with the BP86 method that generally gives $\nu(CO)$

and $\nu(NO)$ frequencies closer to the experimental values than does the B3LYP method. These frequencies follow the expected pattern. Thus terminal $\nu(CO)$ frequencies fall in the range 2072−1905 cm^{-1} and shift slightly downward as the number of CO groups decreases. This is in accord with the greater metal electron density per CO group for back-bonding reducing the carbon-oxygen bond order. Bridging $\nu(CO)$ frequencies and terminal $\nu(NO)$ frequencies fall in the range 1640−1861 cm^{-1} with the bridging $\nu(CO)$ frequencies typically at the upper end of this range and the terminal $\nu(NO)$ frequencies at the lower end of this range. The predicted infrared $\nu(CO)$ frequencies of 2010m and 2000s cm^{-1} and $\nu(NO)$ frequency of 1804s for the D_{4d} global minimum **Ia** of $Cr_2(NO)_2(CO)_8$ (Figure 1) using the BP86 method (Table 10) compare with the $\nu(CO)$ frequencies of 2023 and 1987 cm^{-1} and the $\nu(NO)$ frequency of 1739 cm^{-1} found experimentally for $Cr_2(NO)_2(CO)_8$ in n-hexane solution.[1]

Still lower $\nu(NO)$ frequencies, typically in the range 1501−1623 cm^{-1}, are found for bridging NO groups. The lowest $\nu(NO)$ frequency found in this work, namely 1501 cm^{-1}, arises from the unusual η^2-μ-NO formal five-electron donor bridging NO group in isomer **IVa** of $Cr_2(NO)_2(CO)_5$, in which the N≡O π-bond is involved in the bonding to one of the chromium atoms. Such π-bonding is expected to lower the effective nitrogen−oxygen bond order, thereby leading to an unusually low $\nu(NO)$ frequency. A similar formal five-electron donor η^2-μ-NO group has previously been reported[29] in $[(\eta^5-C_5H_5)Mo(NO)(\mu-\eta^1:\eta^2-NO)(\mu-CHC-Me_3)][(\eta^5-C_5H_5)Mo(=CHCMe_3)]$ and was predicted[27] to be present in an energetically accessible isomer of $Mn_2(NO)_2-(CO)_5$.

Table 11 compares the $\nu(CO)$ and $\nu(NO)$ frequencies for both isomers of $Cr(NO)_2(CO)_3$ (**Va** and **Vb** in Figure 5) with

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Table 10. Infrared ν(CO) and ν(NO) Frequencies Calculated for Binuclear Chromium Carbonyl Nitrosyls Using the BP86 Method[e]

compound	infrared ν(CO) and ν(NO) frequencies, cm^{-1} (BP86)
Cr$_2$(NO)$_2$(CO)$_8$ (**Ia**)	2072(0), 2010(585), 2003(0), 2000(2230),[d] 1979(0), 1964(0),[d] 1812(0),[c] 1804(1987)[c]
Cr$_2$(NO)$_2$(CO)$_8$ (**Ib**)	2064(172), 2014(1159), 1999(700), 1992(1926), 1978(873), 1973(34), 1966(205), 1964(607), 1815(1146),[c] 1784(173)[c]
Cr$_2$(NO)$_2$(CO)$_8$ (**Ic**)	2065(180), 2012(1417), 2006(612), 1994(2297), 1978(353), 1972(49), 1963(784), 1961(0), 1830(1372),[c] 1773(5)[c]
Cr$_2$(NO)$_2$(CO)$_8$ (**Id**)	2061(0), 2012(2435), 1987(1340), 1987(0), 1983(2434), 1981(466), 1980(0), 1951(0), 1623(0),[a] 1599(750)[a]
Cr$_2$(NO)$_2$(CO)$_7$ (**IIa-s**)	2049(194), 1998(1031), 1984(614), 1975(1200), 1964(1407), 1960(212), 1951(67), 1806(1082),[c] 1787(661)[c]
Cr$_2$(NO)$_2$(CO)$_7$ (**IIb-s**)	2048(236), 2004(1309), 1987(1221), 1973(856), 1955(276), 1943(800), 1936(233), 1797(1013),[c] 1790(536)[c]
Cr$_2$(NO)$_2$(CO)$_7$ (**IId-t**)	2047(225), 1994(1448), 1986(1394), 1979(1211), 1973(723), 1965(294), 1945(17), 1780(977),[c] 1755(344)[c]
Cr$_2$(NO)$_2$(CO)$_7$ (**IIe-t**)	2038(302), 1995(1731), 1982(1216), 1973(372), 1920(329),[b] 1906(471),[b] 1883(755),[b] 1800(1026),[c] 1790(661)[c]
Cr$_2$(NO)$_2$(CO)$_6$ (**IIIa-s**)	2034(185), 2002(2193), 1982(1281), 1979(58), 1861(689),[b] 1857(0),[b] 1803(1535),[c] 1776(138)[c]
Cr$_2$(NO)$_2$(CO)$_6$ (**IIIb-s**)	2033(203), 2002(2169), 1982(1325), 1979(0),[c] 1856(684), 1854(1),[b] 1804(1558),[b] 1775(107)[c]
Cr$_2$(NO)$_2$(CO)$_6$ (**IIIc-s**)	2034(29), 2000(2470), 1973(1561), 1973(1048), 1971(0), 1957(3), 1598(76),[a] 1594(680)[a]
Cr$_2$(NO)$_2$(CO)$_6$ (**IIId-s**)	2029(419), 1987(2045), 1976(481), 1953(18), 1945(1666), 1941(0), 1807(1328),[c] 1748(0)[c]
Cr$_2$(NO)$_2$(CO)$_6$ (**IIIe-t**)	2028(299), 1994(2047),1981(1483), 1976(0), 1841(369),[b] 1823(585),[b] 1797(1117),[c] 1784(287)[c]
Cr$_2$(NO)$_2$(CO)$_6$ (**IIIf-t**)	2029(57), 1981(892), 1973(1231), 1973(1231), 1971(387), 1944(312), 1564(50),[a] 1547(525)[a]
Cr$_2$(NO)$_2$(CO)$_6$ (**IIIg-t**)	2028(379), 1975(574), 1969(3502), 1951(162), 1948(1818), 1943(0), 1806(1307),[c] 1749(33)[c]
Cr$_2$(NO)$_2$(CO)$_5$ (**IVa-s**)	2026(61), 1994(1952), 1961(1913), 1958(434), 1952(222), 1570(237),[a] 1501(400)[a]
Cr$_2$(NO)$_2$(CO)$_5$ (**IVb-s**)	2022(699), 1972(770), 1958(439), 1905(621), 1788(385),[b] 1774(1985),[c] 1640(404)[c]
Cr$_2$(NO)$_2$(CO)$_5$ (**IVc-s**)	2030(177), 1983(1015), 1977(1844), 1942(277), 1910(390), 1777(1187),[c] 1724(265)[c]
Cr$_2$(NO)$_2$(CO)$_5$ (**IVd-t**)	2026(20), 1994(1854), 1980(1441), 1959(487), 1941(798), 1563(325),[a] 1470(237)[a]
Cr$_2$(NO)$_2$(CO)$_5$ (**IVe-t**)	2029(490), 2003(1622), 1982(637), 1850(431),[b] 1831(628),[b] 1794(990),[a] 1747(793)[a]
Cr$_2$(NO)$_2$(CO)$_5$ (**IVf-t**)	2015(363), 1978(1585), 1958(850), 1925(65), 1907(929),[b] 1789(780),[c] 1693(644)[a]

[a] Bridging ν(NO) frequency. [b] Bridging ν(CO) frequency. [c] Terminal ν(NO) frequency. [d] Doubly degenerate frequency. [e] Theoretical infrared intensities are given in parentheses in km/mol.

Table 11. Infrared ν(CO) and ν(NO) Frequencies for the Cr(NO)$_2$(CO)$_3$ Isomers, Cr(NO)$_2$(CO)$_2$, and Cr(NO)(CO)$_4$[c]

	infrared ν(CO) and ν(NO) frequencies, cm^{-1}	
	B3LYP	BP86
Cr(NO)$_2$(CO)$_3$ (**Va**)	2145(129), 2091(1598), 2083(622), 1851(903),[a] 1821(1541)[a]	2053(113), 1998(1426), 1985(540), 1797(749),[a] 1774(1191)[a]
Cr(NO)$_2$(CO)$_3$ (**Vb**)	2126(0), 2066(1560), 2054(1270), 1871(3), 1834(2090)[a]	2037(0), 1974(1260), 1973(1260), 1817(0), 1786(1550)
"Cr(NO)$_2$(CO)$_3$" (expt)[2]		2052s(CO), 1705s(NO)
"Cr(NO)(CO)$_x$" (expt)[2]		2002s(CO), 1758s(NO)
Cr(NO)$_2$(CO)$_2$ (**Vc**)	2130(108), 2077(1024), 1823(774)[a], 1786(1313)[a]	2030(114), 1975(1600), 1767(614),[a] 1738(998)[a]
Cr(NO)(CO)$_4$ (**Vd**)	2139(85), 2066(0), 2062(1791),[b] 1837(1122)[a]	2052(69), 1979(0), 1972(1558),[b] 1792(881)[a]

[a] ν(NO) frequency. [b] Doubly degenerate frequency corresponding to an e mode. [c] Calculated infrared intensities are given in parentheses in km/mol.

those found experimentally for Cr(NO)$_2$(CO)$_3$ in low-temperature matrices.[2] The ν(CO) and ν(NO) frequencies calculated by the BP86 method are found to be much closer to the experimental values than those calculated by the B3LYP method. More significantly, the calculated ν(CO) and ν(NO) frequencies for either isomer of Cr(NO)$_2$(CO)$_3$ (**Va** or **Vb**) are closer to the bands assigned to "Cr(NO)-

(CO)$_x$" than to "Cr(NO)$_2$(CO)$_3$" (Table 10) in the low-temperature matrix study.[2] The ν(CO) and ν(NO) frequencies of 2052 and 1705 cm^{-1} assigned in the matrix isolation experiments to Cr(NO)$_2$(CO)$_3$ do not correspond very closely to the ν(CO) and ν(NO) frequencies calculated for any of the compounds studied in this work. Significant progress has occurred in matrix isolation spectroscopy since 1978, and

Table 12. Bond Distances (in Å) and Formal Metal–Metal Bond Orders for the Lowest Energy Binuclear Chromium Carbonyl Nitrosyl and Their Isoelectronic Manganese Carbonyl Structures (BP86 Results)

	symmetry	no. of bridges	M–M distance	M–C/N(b) distances	C/N–O(b) distances	formal bond order
$Cr_2(NO)_2(CO)_8$ (**Ia**)	D_{4d}	0	3.088	1.917/1.704	1.168/1.187	1
$Mn_2(CO)_{10}$	D_{4d}	0	2.954	1.803	1.172	1
$Cr_2(NO)_2(CO)_7$ (**IIa-s**)	C_s	0	2.878	2.089/2.082	1.188	2
$Mn_2(CO)_9$	C_s	1	2.914	1.811/2.140	1.208	1
$Cr_2(NO)_2(CO)_6$ (**IIIa-s**)	C_2	2	2.452	2.005/2.126	1.186	3
$Mn_2(CO)_8$	D_{2d}	0	2.300	1.853	1.172	3
$Cr_2(NO)_2(CO)_5$ (**IVa-s**)	C_s	2	2.573	1.688/2.148	1.242/1.232	3
$Mn_2(CO)_7$	C_s	0	2.207			4

we encourage new experiments on the photochemical Cr-$(CO)_6$ + NO system to try to clarify the nature of this product.

3.3. Comparison of Binuclear Chromium Carbonyl Nitrosyls with Their Isoelectronic Manganese Carbonyl Derivatives. Table 12 compares the predicted structures of the isoelectronic binuclear chrominum carbonyl nitrosyls and manganese carbonyls[3] with respect to the number and types of CO and/or NO bridges, the metal–metal distances and implied formal bond orders, and the M–C/N and C/N–O distances to the CO and NO ligands. Only the global minima are compared.

3.3.1. $Cr_2(NO)_2(CO)_8$ versus $Mn_2(CO)_{10}$. The structures for $Cr_2(NO)_2(CO)_8$ without CO or NO bridges are energetically preferred over those with bridging NO groups. The global minimum structure for $Cr_2(NO)_2(CO)_8$ has D_{4d} symmetry, analogous to the calculated global minimum and experimental structure for $Mn_2(CO)_{10}$.

3.3.2. $Cr_2(NO)_2(CO)_7$ versus $Mn_2(CO)_9$. The global minimum structure for $Mn_2(CO)_9$ has a four-electron bridging CO group and an Mn–Mn single bond.[3] An analogous structure is not found for $Cr_2(NO)_2(CO)_7$. Instead the global minimum for $Cr_2(NO)_2(CO)_7$ (**IIa-s**) is an unbridged structure consisting of a $Cr(NO)(CO)_4$ fragment (similar to **Vd** in Figure 5) linked to a $Cr(NO)(CO)_3$ fragment through a 2.878 Å (B3LYP) or 2.793 Å (BP86) Cr=Cr double bond similar to the next higher energy structure for $Mn_2(CO)_9$ (**9–2** in ref 3) at 5.8 kcal/mol (B3LYP) or 7.2 kcal/mol (BP86) above the global minimum. A triplet $Cr_2(NO)_2(CO)_4(\mu\text{-}CO)_3$ structure (**IIe-t**-BP86 in Figure 2) is also found for $Cr_2(NO)_2(CO)_7$ analogous to an energetically accessible triplet structure $Mn_2(CO)_6(\mu\text{-}CO)_3$ for $Mn_2(CO)_9$ (**9–3** in ref 3).

3.3.3. $Cr_2(NO)_2(CO)_6$ versus $Mn_2(CO)_8$. The lowest energy predicted isomer for $Cr_2(NO)_2(CO)_6$ (**IIIa-s** in Figure 3) has two bridging CO groups and a Cr≡Cr distance suggesting a triple bond analogous to an isomer of $Mn_2(CO)_8$ (**8–5** in ref 3) at 15.2 kcal/mol (B3LYP) or 6.3 kcal/mol (BP86) above a global unbridged minimum, which corresponds to isomer **IIId-s** for $Cr_2(NO)_2(CO)_6$.

3.3.4. $Cr_2(NO)_2(CO)_5$ versus $Mn_2(CO)_7$. The lowest energy predicted isomer for $Cr_2(NO)_2(CO)_5$ (**IVa-s** in Figure 4) has a bridging formal five-electron donor $\eta^2\text{-}\mu\text{-}NO$ group as well as a second normal bridging NO group. By contrast the lowest energy predicted isomer for $Mn_2(CO)_7$ (**7–1** in ref 3) is an unbridged structure with an $Mn(CO)_4$ unit linked to an $Mn(CO)_3$ unit with a very short metal–metal distance (2.257 Å by B3LYP or 2.207 by BP86) suggesting an

Mn≡Mn triple bond (or possibly even a quadruple bond). A structure analogous to this $Mn_2(CO)_7$ global minimum is also found for $Cr_2(NO)_2(CO)_5$, namely **IVc-s** at 12.4 kcal/mol (B3LYP) or 8.9 kcal/mol (BP86) above the global minimum **IVa-s**.

4. Summary

Density functional methods indicate that the global minimum for $Cr_2(NO)_2(CO)_8$ is an unbridged D_{4d} structure in accord with experiment and analogous to the isoelectronic $Mn_2(CO)_{10}$. However, for the unsaturated $Cr_2(NO)_2(CO)_n$ derivatives the lowest energy structures are very different from the lowest energy structures for the isoelectronic $Mn_2(CO)_{n+2}$ derivatives. Thus the global minimum for $Cr_2(NO)_2(CO)_7$ is an unbridged structure with a $Cr(NO)(CO)_4$ fragment linked to a $Cr(NO)(CO)_3$ fragment through a Cr=Cr double bond. However, the global minimum for $Mn_2(CO)_9$ has a formal four-electron donor bridging $\eta^2\text{-}\mu\text{-}CO$ group not even found in any of the higher energy $Cr_2(NO)_2(CO)_7$ isomers within accessible range of the global minimum. For $Cr_2(NO)_2(CO)_6$ the global minimum is a structure with two bridging CO groups, whereas the global minimum for $Mn_2(CO)_8$ is an unbridged structure. However, both of these structures have metal–metal distances corresponding to the M≡M triple bonds required for the favored 18-electron configurations for the metal atoms. For $Cr_2(NO)_2(CO)_5$ both NO groups are bridging groups with one of them having a short enough Cr–O distance to be considered a formal five-electron donor $\eta^2\text{-}\mu\text{-}NO$ group. However, the lowest energy isomer predicted for $Mn_2(CO)_7$ has an unbridged structure with an $Mn(CO)_4$ unit linked to an $Mn(CO)_3$ unit. Thus the isoelectronic substitution of NO for CO with a necessary adjustment in the central metal atom can lead to significant shifts in the relative energies of various structural types of metal carbonyl nitrosyls, particularly for unsaturated molecules.

Supporting Information Available: Harmonic vibrational frequencies for $Cr(NO)_2(CO)_n$ ($n = 8, 7, 6, 5$) isomers (Tables S1–S22), $Cr(NO)_2(CO)_3$ isomers (Tables S23 and S24), $Cr(NO)_2(CO)_2$ (Table S25), and $Cr(NO)(CO)_4$ (Table S26). This material is available free of charge via the Internet at http://pubs.acs.org.

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