Heterobimetallic Chromium Manganese Carbonyl Nitrosyls: Comparison with Isoelectronic Homometallic Binuclear Chromium Carbonyl Nitrosyls and Manganese Carbonyls

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Abstract: The heterometallic chromium-manganese carbonyl nitrosyls CrMn(NO)(CO) n (n = 9, 8) have been investigated by density functional theory. The lowest energy CrMn(NO)(CO) 9 structures have unbridged staggered conformations with a ~2.99 Å Cr–Mn single bond similar to the experimental and lowest energy structures of the isoelectronic Mn 2(CO) 10 and Cr 2(NO)(CO) 8. A significantly higher energy CrMn(NO)(CO) 9 isomer has a nearly symmetrical bridging nitrosyl group and a very weakly semibridging carbonyl group. The two lowest energy structures of the unsaturated CrMn(NO)(CO) 8 have a five-electron donor bridging η 2-µ-CO nitrosyl group or a four-electron donor bridging η 2-µ-CO group, as well as a Cr–Mn single bond of length ~2.94 Å. The next higher energy CrMn(NO)(CO) 8 structure has exclusively terminal CO and NO ligands and a shorter Cr–Mn single bond of ~2.85 Å, suggesting an 18-electron configuration for the manganese atom and a 16-electron configuration for the chromium atom indicated by a vacant coordination site nearly perpendicular to the Cr–Mn bond.

Keywords: chromium; manganese; metal carbonyls; metal nitrosyls; metal–metal bonding; density functional theory

1. Introduction

The isoelectronic bimetallic molecules Mn 2(CO) 10 and Cr 2(NO)(CO) 8 have been known for some time [1]. Thus, Mn 2(CO) 10 can be synthesized by the reductive carboxylation of manganese(II) derivatives using sodium benzophenone ketyl [2] or triisobutylaluminum [3] as the reducing agent at elevated carbon monoxide pressure. In addition, an atmospheric pressure synthesis of Mn 2(CO) 10 is possible using the reductive carboxylation of the formerly (but not now) readily available (η 5-MeC 5H 4)Mn(CO) 3 with sodium metal in diglyme solution [4]. The isoelectronic Cr 2(NO)(CO) 8 can be synthesized by oxidation of the Cr(NO)(CO) 4 anion with [(C 6H 5) 3C][BF 4]− [5]. X-ray crystallography shows both Mn 2(CO) 10 and Cr 2(NO)(CO) 8 to have analogous unbridged structures with all of the CO and NO ligands in terminal positions and a formal metal–metal single bond joining two halves of the molecule (Figure 1) [5–8]. The metal atoms in Mn 2(CO) 10 and Cr 2(NO)(CO) 8, all have the favored 18-electron configuration.
Decarbonylation of Mn$_2$(CO)$_{10}$ and Cr$_2$(NO)$_2$(CO)$_8$ might be expected to give unsaturated structures requiring metal–metal multiple bonds, four-electron donor bridging η$^2$-μ-CO groups, and/or five-electron donor η$^2$-μ-NO groups to maintain the favored 18-electron configuration for all of the metal atoms. No such unsaturated Mn$_2$(CO)$_n$ or Cr$_2$(NO)$_2$(CO)$_{n-2}$ ($n < 10$) derivatives are known as stable species. Matrix isolation spectroscopic studies on photolysis products of the more extensively studied Mn$_2$(CO)$_{10}$ and Mn$_2$(CO)$_9$ systems, isoelectronic with the stable Mn$_2$(CO)$_{10}$ and Mn$_2$(CO)$_9$, respectively.

In view of the different types of low-energy structures predicted for isoelectronic unsaturated Mn$_2$(CO)$_n$ and Cr$_2$(NO)$_2$(CO)$_{n-2}$ derivatives, investigation of the intermediate isoelectronic heterobinuclear derivatives CrMn(NO)(CO)$_n$ is of interest. The saturated heterobinuclear CrMn(NO)(CO)$_9$ has not yet been reported, although the heterobinuclear metal carbonyl anion [CrMn(CO)$_3$L]$^-$ (L = CO, PR$_3$) is known [15–19]. However, CrMn(NO)(CO)$_9$ is potentially accessible from the metathesis of the known Cr(NO)(CO)$_4$ anion with the manganese carbonyl halides Mn(CO)$_5$X (X = Cl, Br, I) or the known Mn(CO)$_5$ anion with Cr(CO)$_3$(NO)X (X = Cl, Br, I). Analogous reactions have been used to synthesize the mixed metal carbonyl derivatives ReMn(CO)$_{10}$ and ReCo(CO)$_9$ [20]. This paper discusses theoretical studies on the CrMn(NO)(CO)$_9$ and CrMn(NO)(CO)$_8$ systems, isoelectronic with the stable Mn$_2$(CO)$_{10}$ and Mn$_2$(CO)$_9$, respectively.
2. Theoretical Methods

Electron correlation effects were considered using the density functional theory (DFT) methods. The first two DFT approaches employed herein were same as those in previous work on the Mn$_2$(CO)$_n$ system, i.e., the B3LYP and BP86 functionals [13]. The B3LYP functional is an HF/DFT hybrid method using Becke’s three-parameter functional (B3) [21] and the Lee-Yang-Parr generalized gradient correlation functional (LYP) [22], whereas the BP86 functional is a pure DFT method combining Becke’s 1988 exchange functional (B) [23] with Perdew’s 1986 gradient correlation functional (P86) [24]. In conjunction with the B3LYP and BP86 functionals, all-electron double zeta plus polarization (DZP) basis sets were used. For carbon, nitrogen, and oxygen atoms, the DZP basis sets begin with Dunning’s Wachters’ primitive set [27] augmented by two sets of p functions and one set of d functions = 0.85. The contraction scheme for the carbon, nitrogen, and oxygen basis sets is (9s5p1d). For chromium and manganese atoms, the DZP basis sets, designated as (14s11p6d/10s8p3d), use the Wachters’ primitive set [27] augmented by two sets of p functions and one set of d functions and contracted following Hood et al. [28]. For CrMn(NO)(CO)$_9$, there are 398 contracted Gaussian functions with the present DZP basis set.

In addition to the B3LYP and BP86 functionals, a newer generation functional, M06-L, was employed. The M06-L functional uses a meta-GGA functional proposed by Zhao and Truhlar [29], and has been reported to give better overall performance for organometallic compounds than previously used functionals [30,31]. The correlation-consistent polarized valence triple-c (cc-pVTZ) basis sets were used for the M06-L computations. The cc-pVTZ basis sets for carbon, nitrogen, and oxygen atoms are given by Dunning [32], while those for chromium and manganese atoms come from Balabanov and Peterson [33]. With the cc-pVTZ basis sets, the basis functions for CrMn(NO)(CO)$_n$ increase to 736.

Conceivable structures of CrMn(NO)(CO)$_n$ ($n = 9, 8$) were fully optimized at the B3LYP/DZP, BP86/DZP, and M06-L/cc-pVTZ levels of theory. Harmonic vibrational frequencies were also calculated at the same levels by evaluating analytically the second derivatives of the energy with respect to the nuclear coordinates. All of the B3LYP/DZP and BP86/DZP computations were carried out with the Gaussian 03 program [34] in which the fine grid (75, 302) was the default for evaluating the integrals numerically. All of the M06-L/cc-pVTZ computations were carried out utilizing the Gaussian 09 program [35] with an ultrafine grid (99, 590) for numerical integration. The three DFT methods generally predict similar results in the present work, so we discuss mainly the M06-L results in the text, except as otherwise indicated. The optimized geometries from the M06-L/cc-pVTZ computations are depicted in Figures 3 and 4 with all bond distances given in angstroms, while Table 1 lists their electronic states and energies. All of the B3LYP and BP86 results are listed in the Supplementary Materials.

![Figure 3](image-url)  
**Figure 3.** The three optimized CrMn(NO)(CO)$_9$ structures at the M06-L/cc-pVTZ level of theory.
Figure 4. The 12 optimized CrMn(NO)(CO)$_8$ structures at the M06-L/cc-pVTZ level of theory.

Table 1. Relative energies ($\Delta E$, in kcal/mol) and Cr–Mn distances (in Å) for the optimized CrMn(NO)(CO)$_n$ ($n = 9, 8$) structures at the M06-L/cc-pVTZ level of theory.

<table>
<thead>
<tr>
<th>Structure</th>
<th>State (Sym.)</th>
<th>$\Delta E$</th>
<th>Cr–Mn</th>
<th>Structure</th>
<th>State (Sym.)</th>
<th>$\Delta E$</th>
<th>Cr–Mn</th>
</tr>
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<tr>
<td>9-1S</td>
<td>$^1A_1$ ($C_{4v}$)</td>
<td>0.0</td>
<td>2.987</td>
<td>8-5S</td>
<td>$^1A'$ ($C_s$)</td>
<td>6.4</td>
<td>2.689</td>
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<tr>
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<td>$^1A'$ ($C_s$)</td>
<td>5.8</td>
<td>2.961</td>
<td>8-6S</td>
<td>$^1A'$ ($C_s$)</td>
<td>6.5</td>
<td>2.531</td>
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<td>$^1A'$ ($C_s$)</td>
<td>20.2</td>
<td>2.871</td>
<td>8-7S</td>
<td>$^1A$ ($C_1$)</td>
<td>7.4</td>
<td>2.879</td>
</tr>
<tr>
<td>8-1S</td>
<td>$^1A'$ ($C_s$)</td>
<td>0.0</td>
<td>2.937</td>
<td>8-9S</td>
<td>$^1A$ ($C_1$)</td>
<td>11.4</td>
<td>2.629</td>
</tr>
<tr>
<td>8-2S</td>
<td>$^1A'$ ($C_s$)</td>
<td>1.1</td>
<td>2.938</td>
<td>8-10S</td>
<td>$^1A'$ ($C_s$)</td>
<td>11.5</td>
<td>2.531</td>
</tr>
<tr>
<td>8-3S</td>
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<td>3.5</td>
<td>2.845</td>
<td>8-11S</td>
<td>$^1A'$ ($C_s$)</td>
<td>17.8</td>
<td>2.956</td>
</tr>
<tr>
<td>8-4S</td>
<td>$^1A'$ ($C_s$)</td>
<td>3.6</td>
<td>2.925</td>
<td>8-12S</td>
<td>$^1A'$ ($C_s$)</td>
<td>21.6</td>
<td>2.951</td>
</tr>
</tbody>
</table>
3. Results and Discussion

3.1. CrMn(NO)(CO)₉

Since it was discovered in 1954 [1], dimanganese decacarbonyl Mn₂(CO)₁₀ has been studied extensively [2-4,6-12,36-44]. The following three structures were studied for Mn₂(CO)₁₀ [13]:

1. The staggered (OC)₃Mn-Mn(OC)₅ structure with D₄ᵥ symmetry, which is the global minimum;
2. The eclipsed (OC)₅Mn-Mn(OC)₃ structure with D₄h symmetry, which is a transition state with a small imaginary vibrational frequency and somewhat higher energy;
3. The doubly bridged (OC)₃Mn(μ-CO)₂Mn(CO)₄ structure with D₂h symmetry, like the global minimum of Cr₂(CO)₁₀ [45], which is also a transition state and has much higher energy.

Replacing one MnCO unit in the above three Mn₂(CO)₁₀ structures by an isoelectronic CrNO unit gives seven possible CrMn(NO)(CO)₉ structures. Optimizing these seven starting structures gives only three CrMn(NO)(CO)₉ minima, i.e., 9-1S, 9-2S, and 9-3S (Figure 3 and Table 1).

The CrMn(NO)(CO)₉ structures 9-1S and 9-2S are very similar with staggered unbridged (OC)₅Mn-Cr(CO)₄(NO) conformations, corresponding to the staggered (OC)₅Mn-Mn(OC)₅ structure (Figure 3). They differ only in the positions of the nitrosyl group. The C₄ᵥ structure 9-1S with an axial NO group was found to be the lowest energy structure with all real vibrational frequencies. The Cr–Mn distance in 9-1S of 2.987 Å is similar to the metal–metal bond distances of the isoelectronic Mn₂(CO)₁₀ [13] and [Cr₂(CO)₁₀]²⁻ [45,46], suggesting a single bond thereby giving each metal atom the favored 18-electron configuration. The Cr–Mn distance of 2.961 Å in the C₄ᵥ CrMn(NO)(CO)₉ structure 9-2S, lying 5.8 kcal/mol in energy above 9-1S, and with an equatorial NO group is similar to that in 9-1S also suggesting a single bond.

We also optimized two eclipsed (OC)₅Mn-Cr(CO)₄(NO) structures, corresponding to the eclipsed (OC)₅Mn-Mn(OC)₅ structure. However, they both were found to be in transition states with small imaginary vibrational frequencies. The corresponding normal mode is related to the inner rotation around the Cr–Mn bond and leads to the corresponding staggered structures, i.e., 9-1S or 9-2S.

The third CrMn(NO)(CO)₉ structure, namely the C₅ structure 9-3S lying 20.2 kcal/mol above the global minimum 9-1S, has one bridging nitrosyl and one semibridging carbonyl, similar to the doubly bridged (OC)₅Mn(μ-CO)₂Mn(CO)₄ structure [13] and the global minimum of Cr₂(CO)₁₀ [45]. The nitrosyl bridge in 9-3S is nearly symmetrical with a Cr–N distance of 2.059 Å and an Mn–N distance of 1.905 Å. However, the CO bridge in 9-3S is actually a very weak semibridge bonded mainly to the chromium atom with a Cr–C distance of 1.928 Å with a long Mn–C distance of 2.658 Å. The Cr–Mn distance of 2.871 Å in 9-3S is shorter than the Cr–Mn bonds in 9-1S and 9-2S, but still can be interpreted as a formal single bond, which, however, is shortened by the NO and CO bridges. Structure 9-3S has all real vibrational frequencies with both B3LYP and BP86 methods, indicating a genuine minimum. However, the M06-L method predicts a tiny imaginary frequency of 2i cm⁻¹ for 9-3S, which may be an artifact arising from numerical integration errors.

3.2. CrMn(NO)(CO)₈

We have found 12 stationary points for the CrMn(NO)(CO)₈ stoichiometry, corresponding to the three kinds of previously studied [13] structures for Mn₂(CO)₁₀, namely (a) the singly bridged (OC)₄Mn(η²-μ-CO)Mn(CO)₄ structures, (b) the unbridged (OC)₅Mn-Mn(OC)₄ structures, and (c) the triply bridged (OC)₅Mn(μ-CO)₂Mn(CO)₃ structures (Figure 4 and Table 1) [13]. The C₅ singly nitrosyl-bridged structure (OC)₅Mn(μ-NO)Cr(CO)₄ 8-1S has the lowest energy and all real harmonic vibrational frequencies, suggesting it to be the global minimum of CrMn(NO)(CO)₈. In 8-1S, the short Mn–O distance of 2.104 Å to the bridging NO group suggests a five-electron donor bridging η²-μ-NO group. The Cr–Mn distance in 8-1S of 2.937 Å, which is similar to that in 9-1S, corresponds to the single bond required by the 18-electron rule if the bridging NO group is a five-electron donor.
Similar to 8-1S, the CrMn(NO)(CO)₈ structures 8-2S, 8-4S, and 8-7S also have singly bridged architectures, but with their NO groups as a terminal ligand bonded to the chromium atom with a carbonyl group bridging the Cr–Mn bond (Figure 4). Structures 8-2S, 8-4S, and 8-7S, lying 1.1, 3.6, and 7.4 kcal/mol, respectively, in energy above 8-1S (Table 1) are all genuine minima with all real harmonic vibrational frequencies. The Cr–Mn distances in 8-2S, 8-4S, and 8-7S of 2.88 to 2.94 Å, correspond to single bonds. The Mn–O distances to the bridging CO group in 8-2S, 8-4S, and 8-7S of 2.20 to 2.23 Å indicate four-electron donor µ-η²-CO bridging carbonyl groups thereby giving the favored 18-electron configuration to all metal atoms. The four CrMn(NO)(CO)₈ structures 8-1S, 8-2S, 8-4S, and 8-7S with a five-electron donor bridging η²-µ-NO group or a four-electron donor bridging η²-µ-CO group are related to the lowest energy Mn₂(μ-CO)₆ structure which has a four-electron donor CO group and an Mn–Mn distance of ~2.9 Å [13].

The two C₅ unbridged CrMn(NO)(CO)₈ structures 8-3S and 8-8S, lie 3.5 and 8.2 kcal/mol, respectively, above 8-1S (Figure 4 and Table 1). The Cr–Mn distances in 8-3S and 8-8S of 2.85 to 2.88 Å are similar to that in 8-1S, suggesting formal single bonds thereby giving each structure an 18-electron configuration for one metal atom and a 16-electron configuration for the other metal atom. The 16-electron configuration is indicated by a vacant coordination site nearly perpendicular to the Cr–Mn bond. In 8-3S the chromium atom has the vacant coordination site and the 16-electron configuration. However, in 8-8S the manganese atom has the vacant coordination site and thus the 16-electron configuration. Structures 8-3S and 8-8S can be derived from the lowest-energy CrMn(NO)(CO)₈ structure 9-1S by removing an equatorial carbonyl group. Structures 8-3S and 8-8S are genuine minima with all real harmonic vibrational frequencies with both the B3LYP and M06-L methods. However, the BP86 method computes a very small imaginary frequency of 9i cm⁻¹ for 8-3S or 3i cm⁻¹ for 8-8S. These very small imaginary frequencies might be considered as arising from numerical integration errors.

We originally guessed Cr=Mn double bonds in 8-3S and 8-8S since there were no vacant coordination sites at the chromium and/or manganese atoms based on the B3LYP and BP86 minima (see Figure S2 in the Supplementary Materials). However, the M06-L results clearly display a vacant coordination site at the chromium atom (in 8-3S) or the manganese atom (in 8-8S), so the Cr–Mn single bonds assigned above should be more reasonable.

The C₅ unbridged CrMn(NO)(CO)₈ structure 8-5S, lying 6.4 kcal/mol above 8-1S, has a Cr=Mn distance of 2.689 Å, which is ~0.3 Å shorter than that in 8-1S (Figure 4 and Table 1). This is clearly consistent with the formal Cr=Mn double bond needed to give each metal atom the favored 18-electron configuration with a positive charge on the chromium atom and a negative charge on the manganese atom. The CrMn(NO)(CO)₈ structure 8-5S is related to the two lowest energy Cr₂(NO)₂(CO)₂ structures which have exclusively terminal ligands and Cr=Cr distances of ~2.7 Å [14].

The two C₅ triply bridged CrMn(NO)(CO)₈ structures 8-6S and 8-10S have one normal bridging nitrosyl or carbonyl groups and two semibridging carbonyl groups (Figure 4). Structures 8-6S and 8-10S lie 6.5 and 11.5 kcal/mol, respectively, above 8-1S (Table 1). The relatively short Cr=Mn distances ~2.53 Å in these triply bridged species can be interpreted as the formal double bonds required to give each metal atom the favored 18-electron configuration. These Cr=Mn double bond distances are shortened by the three bridging CO and NO groups.

The CrMn(NO)(CO)₈ structure 8-9S, lying 11.4 kcal/mol above 8-1S, has three weakly semibridging carbonyl groups (Figure 4 and Table 1). Two of these semibridging carbonyl groups have long Mn–C distances of 2.59 to 2.71 Å whereas the third has a long Cr–C distance of 2.69 Å as shown by dashed lines in Figure 4. This indicates that 8-9S has a stereochemistry between that of unbridged (OC)₄Mn-Cr(CO)₄(NO) and triply bridged (OC)₃Mn(µ-CO)₃Cr(NO)(CO)₃(NO).

The C₅ unbridged CrMn(NO)(CO)₈ structures 8-11S and 8-12S are high-energy structures, lying 17.8 and 21.6 kcal/mol, respectively, in energy above 8-1S (Figure 4 and Table 1). Both 8-11S and 8-12S structures have Cr–Mn distances of ~2.95 Å suggesting formal single bonds. Structures 8-11S and
8-12S can be derived from the lowest-energy CrMn(NO)(CO)$_n$ structure 9-2S by removing an axial carbonyl group.

3.3. The Cr–Mn Wiberg Bond Indices Given by Natural Bond Orbital Analysis

Wiberg bond indices (WBIs) for the chromium–manganese interactions in the optimized CrMn(NO)(CO)$_n$ ($n = 9, 8$) structures were determined using the Weinhold’s NBO analysis, and are shown in Table 2. For metal–metal bonds involving d-block transition metals, the WBI values are only 10 to 30% of the formal bond order in singlet structures. For example, a WBI of only 0.11 was found for the formal Fe–Fe single bond in triply CO-bridged Fe$_2$(CO)$_6$ structure [47]. The WBI values for the analogous formal Cr–Mn single bonds in the CrMn(NO)(CO)$_n$ ($n = 9, 8$) structures range from 0.11 to 0.15. The WBIs for the formal Cr=Mn double bonds in CrMn(NO)(CO)$_n$ structures 8-5S, 8-6S, 8-9S, and 8-10S range from 0.18 to 0.26, which are roughly twice of those for the Cr–Mn single bonds. Generally, the WBI values are consistent with the bond orders assigned based on the chromium–manganese distances.

Table 2. The Wiberg bond indices (WBIs) of the chromium–manganese bonds by natural bond orbital (NBO) analysis for the optimized low-lying CrMn(NO)(CO)$_n$ ($n = 9, 8$) structures.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Cr–Mn (Å)</th>
<th>Formal Bond Order</th>
<th>WBI (Cr–Mn)</th>
<th>Structure</th>
<th>Cr–Mn (Å)</th>
<th>Formal Bond Order</th>
<th>WBI (Cr–Mn)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9-1S</td>
<td>2.987</td>
<td>1</td>
<td>0.11</td>
<td>8-5S</td>
<td>2.689</td>
<td>2</td>
<td>0.18</td>
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<tr>
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<td>0.11</td>
<td>8-6S</td>
<td>2.531</td>
<td>2</td>
<td>0.22</td>
</tr>
<tr>
<td>9-3S</td>
<td>2.871</td>
<td>1</td>
<td>0.13</td>
<td>8-7S</td>
<td>2.879</td>
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<td>0.14</td>
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<tr>
<td>8-1S</td>
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<td>0.12</td>
<td>8-8S</td>
<td>2.876</td>
<td>1</td>
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</tr>
<tr>
<td>8-2S</td>
<td>2.938</td>
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<td>2.629</td>
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<td>0.22</td>
</tr>
<tr>
<td>8-3S</td>
<td>2.845</td>
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</tr>
<tr>
<td>8-4S</td>
<td>2.925</td>
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<td></td>
<td>0.14</td>
<td></td>
<td></td>
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<td>0.22</td>
</tr>
</tbody>
</table>

3.4. Vibrational Frequencies

The predicted ν(CO) and ν(NO) stretching frequencies for the lowest energy structures of CrMn(NO)(CO)$_n$ ($n = 9, 8$) are very useful in detecting such species in future experimental work. Table 3 summarizes our theoretical ν(CO) and ν(NO) frequencies for the CrMn(NO)(CO)$_n$ ($n = 9, 8$) structures using the B3LYP functional. Though these frequencies were also calculated using the B3LYP and M06-L methods, the BP86 method has been shown to give ν(CO) frequencies closer to the experimental values without using any scaling factors than the B3LYP method [48,49]. The M06-L method gives similar ν(CO) and ν(NO) frequencies for the CrMn(NO)(CO)$_n$ ($n = 9, 8$) structures to the B3LYP method (see Tables S2 and S3 in the Supplementary Materials).

The data in Table 3 indicate that genuine terminal ν(CO) frequencies fall in the range 1939 to 2082 cm$^{-1}$ similar to other metal carbonyl derivatives. If the terminal ν(CO) group is weakly bonded in a semibridging manner to the other transition metal atom, such as those in structures 9-3S, 8-6S, 8-9S, and 8-10S, then this ν(CO) frequency can be somewhat lower with the ν(CO) frequency of 1923 cm$^{-1}$ in 9-3S being the lowest such ν(CO) frequency among the CrMn(NO)(CO)$_n$ structures discussed in this work. The ν(CO) frequencies for bridging carbonyl groups are significantly lower than the ν(CO) frequencies for terminal carbonyl groups in otherwise similar structures as is generally found for metal carbonyl derivatives. Thus the ν(CO) frequency for the two-electron donor bridging carbonyl group in 8-10S is 1853 cm$^{-1}$. The ν(CO) frequencies for four-electron donor $\eta^2$-µ-CO carbonyl groups are even lower than those for two-electron donor carbonyl groups. Thus the ν(CO) frequencies for the four-electron donor $\eta^2$-µ-CO groups are in 8-2S, 8-4S, and 8-7S range from 1739 to 1756 cm$^{-1}$.

The terminal ν(NO) frequencies for the CrMn(NO)(CO)$_n$ ($n = 9, 8$) structures are predicted to occur at 1775 to 1810 cm$^{-1}$ (Table 3). The ν(NO) frequencies for three-electron donor bridging nitrosyls in the CrMn(NO)(CO)$_n$ structures are predicted to occur at 1595 to 1618 cm$^{-1}$. Similar to four-electron donor $\eta^2$-µ-CO carbonyl group, the five-electron donor $\eta^2$-µ-NO nitrosyl group in 8-1S is predicted to
Table 3. The ν(CO) and ν(NO) vibrational frequencies (in cm⁻¹) and infrared intensities (in km/mol, given in parentheses) of the CrMn(NO)(CO)₉ (n = 9, 8) complexes at the BP86/DZP level.

<table>
<thead>
<tr>
<th>Struct.</th>
<th>ν(CO) *</th>
<th>ν(NO) *</th>
</tr>
</thead>
<tbody>
<tr>
<td>9-1S</td>
<td>1966 (0), 1966 (0), 1983 (288), 1994 (0), 1999 (2182), 1999 (2182), 2002 (0), 2020 (819), 2082 (86)</td>
<td>1807 (984)</td>
</tr>
<tr>
<td>8-1S</td>
<td>1954 (517), 1970 (86), 1970 (346), 1984 (869), 1995 (2232), 1996 (393), 2027 (1122), 2073 (93)</td>
<td>1511 (397)</td>
</tr>
<tr>
<td>8-2S</td>
<td>1742 (406), 1964 (204), 1966 (39), 1987 (463), 1999 (2207), 2000 (609), 2024 (845), 2070 (189)</td>
<td>1803 (991)</td>
</tr>
<tr>
<td>8-3S</td>
<td>1951 (20), 1965 (91), 1978 (320), 1988 (1127), 1993 (1058), 2011 (1039), 2068 (145)</td>
<td>1792 (856)</td>
</tr>
<tr>
<td>8-4S</td>
<td>1739 (499), 1966 (2), 1971 (701), 1978 (700), 1990 (107), 1995 (2296), 2026 (1184), 2067 (44)</td>
<td>1801 (430)</td>
</tr>
<tr>
<td>8-6S</td>
<td>1942 (476), 1944 (228), 1966 (1020), 1975 (643), 1995 (1175), 2002 (566), 2013 (1844), 2063 (133)</td>
<td>1618 (415)</td>
</tr>
<tr>
<td>8-7S</td>
<td>1756 (402), 1960 (128), 1974 (621), 1978 (1193), 1987 (631), 1999 (734), 2019 (1427), 2064 (380)</td>
<td>1810 (673)</td>
</tr>
<tr>
<td>8-8S</td>
<td>1949 (11), 1960 (67), 1972 (260), 1977 (1830), 1981 (89), 1988 (2072), 2070 (785), 2063 (60)</td>
<td>1805 (1093)</td>
</tr>
<tr>
<td>8-9S</td>
<td>1925 (208), 1941 (620), 1959 (97), 1970 (1165), 1978 (566), 1992 (1192), 2012 (1718), 2056 (51)</td>
<td>1796 (753)</td>
</tr>
<tr>
<td>8-10S</td>
<td>1853 (230), 1950 (558), 1957 (879), 1977 (959), 1993 (545), 1995 (691), 2011 (1662), 2060 (273)</td>
<td>1775 (897)</td>
</tr>
<tr>
<td>8-11S</td>
<td>1939 (357), 1955 (17), 1979 (364), 1987 (1996), 1987 (1448), 1999 (0), 2004 (827), 2071 (133)</td>
<td>1799 (661)</td>
</tr>
<tr>
<td>8-12S</td>
<td>1941 (318), 1947 (933), 1969 (556), 1985 (2029), 1986 (106), 1989 (882), 2012 (712), 2063 (66)</td>
<td>1800 (579)</td>
</tr>
</tbody>
</table>

* ν in italic means semibridging CO groups; ν in bold means bridging CO or NO groups; ν in bold and underlined means four-electron CO or five-electron NO bridges.

3.5. Carbonyl Dissociation Energies

The bond dissociation energies for the loss of one carbonyl group from the CrMn(NO)(CO)₉ global minimum 9-1S is 25.7 kcal/mol (B3LYP), 35.0 kcal/mol (BP86), or 37.1 kcal/mol (M06-L). This carbonyl dissociation energy is in approximate agreement with the experimental [50] carbonyl dissociation energies of 27 kcal/mol for Ni(CO)₄ or 37 kcal/mol for Cr(CO)₆. However, it is significantly lower than the experimental carbonyl dissociation energy of 41 kcal/mol for Fe(CO)₅.

4. Conclusions

The lowest energy CrMn(NO)(CO)₉ structures 9-1S and 9-2S have staggered unbridged configurations with octahedral coordination of each metal atom counting the metal–metal bond. Related structures are found by X-ray crystallography for the homometallic analogues Cr₂(NO)₂(CO)₈ and Mn₂(CO)₁₀, which are also computed to be the lowest energy structures. In the lowest energy CrMn(NO)(CO)₉ and Cr₂(NO)₂(CO)₈ structures the nitrosyl groups are located in axial positions trans to the metal–metal bonds. The higher energy staggered unbridged CrMn(NO)(CO)₉ isomer 9-2S has the nitrosyl group bonded to the chromium atom in an equatorial position, i.e., cis to the Cr–Mn bond.

Both Mn₂(CO)₁₀ and Cr₂(NO)₂(CO)₈ have significantly higher energy doubly bridged isomers lying ~20 kcal/mol above the lowest energy isomers, namely the staggered unbridged structures. For the lowest energy doubly bridged Cr₂(NO)₂(CO)₈ structure, albeit a high-energy structure relative to the unbridged isomers, both bridging groups are nitrosyl groups suggesting preference for nitrosyl rather than carbonyl bridges in such nitrosyl carbonyl systems. In this connection, the lowest energy bridged CrMn(NO)(CO)₉ structure 9-3S has a nearly symmetrical nitrosyl bridge within ~0.1 Å but only a very weakly semibridging carbonyl group.

The lowest energy Mn₂(CO)₉ structure has a four-electron donor bridging η²-µ-CO group with an Mn–O bond as well as Mn–C bonds in addition to eight terminal carbonyl groups (Figure 2). The three lowest-energy CrMn(NO)(CO)₈ structures 8-1S, 8-2S, and 8-4S are of this general type. However, the lowest energy among these three CrMn(NO)(CO)₈ structures, namely 8-1S, the bridging group is a five-electron donor η²-µ-NO group with an Mn–O bond as well as two M–N (M = Mn, Cr) bonds. In the other two of these CrMn(NO)(CO)₈ structures, namely 8-2S and 8-4S, the bridging group is a four-electron donor η²-µ-CO group similar to that in the lowest energy Mn₂(CO)₉ structure.
Low-energy Cr$_2$(NO)$_2$(CO)$_7$ structures with bridging four-electron donor $\eta^2$-µ-CO groups or five-electron donor $\eta^1$-µ-NO groups were not found in the previous theoretical study [14]. Instead the only two Cr$_2$(NO)$_2$(CO)$_8$ structures having energies found within ~10 kcal/mol of the global minimum have exclusively terminal CO and NO groups and Cr−Cr distances of ~2.8 Å interpreted as the formal double bonds required to give each chromium atom the favored 18-electron configuration. The CrMn(NO)(CO)$_9$ structure 8-SS is of this type with similar Cr=Mn distance of 2.7 Å. A related Mn$_2$(CO)$_9$ structure with exclusively terminal carbonyl groups and an Mn=Mn distance of ~2.74 Å is found to lie ~6 kcal/mol in energy above the Mn$_2$(CO)$_9$(η$^2$-µ-CO) lowest energy isomer [13].

**Supplementary Materials:** The following are available online at http://www.mdpi.com/2304-6740/7/10/127/s1.

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