Inorg. Chem. **2009**, *48*, 4580−4591

Inorganic Chemistry

Article

Effect of Hydrogen Atoms on the Structures of Trinuclear Metal Carbonyl Clusters: Trinuclear Manganese Carbonyl Hydrides

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Received December 18, 2008

The structures of the trinuclear manganese carbonyl hydrides $H_3Mn_3(CO)_n$ ($n = 12, 11, 10, 9$) have been investigated by density functional theory (DFT). Optimization of $H_3Mn_3(CO)_{12}$ gives the experimentally known structure in which all carbonyl groups are terminal and each edge of a central Mn_3 equilateral triangle is bridged by a single hydrogen atom. This structure establishes the canonical distance 3.11 Å for the Mn−Mn single bond satisfying the 18-electron rule. The central triangular $(\mu\text{-H})_3Mn_3$ unit is retained in the lowest energy structure of $H_3Mn_3(CO)_{11}$, which may thus be derived from the $H_3Mn_3(CO)_{12}$ structure by removal of a carbonyl group with concurrent conversion of one of the remaining carbonyl groups into a semibridging carbonyl group to fill the resulting hole. The potential energy surface of $H_3Mn_3(CO)_{10}$ is relatively complicated with six singlet and five triplet structures. One of the lower energy $H_3Mn_3(CO)_{10}$ structures has one of the hydrogen atoms bridging the entire Mn_3 triangle and the other two hydrogen atoms bridging Mn−Mn edges. This $H_3Mn_3(CO)_{10}$ structure achieves the favored 18-electron configuration with a very short Mn≡Mn triple bond of 2.36 Å. The other low energy $H_3Mn_3(CO)_{10}$ structure retains the $(\mu\text{-H})_3Mn_3$ core of $H_3Mn_3(CO)_{12}$ but has a unique six-electron donor η^2-μ_3 carbonyl group bridging the entire Mn_3 triangle similar to the unique carbonyl group in the known compound $Cp_3Nb_3(CO)_6(\eta^2\text{-}\mu_3\text{-CO})$. For $H_3Mn_3(CO)_9$ a structure with a central $(\mu_3\text{-H})_2Mn_3$ trigonal bipyramid lies >20 kcal/mol below any of the other structures. Triplet structures were found for the unsaturated $H_3Mn_3(CO)_n$ ($n = 11, 10, 9$) systems but at significantly higher energies than the lowest lying singlet structures.

1. Introduction

A classical synthesis of organotransition metal carbonyl derivatives uses thermal reactions of metal carbonyls with unsaturated organic molecules. An early example of such a reaction is the synthesis of butadieneiron tricarbonyl, $(\eta^4\text{-}C_4H_6)Fe(CO)_3$ by heating $Fe(CO)_5$ with butadiene in a sealed vessel.[1] However, the applications of such synthetic methods are limited by the temperatures required for carbonyl displacement from the simple mononuclear carbonyl. For iron carbonyl chemistry this difficulty can be circumvented by using a polynuclear iron carbonyl, namely $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$, as the starting material rather than $Fe(CO)_5$. This allows the carbonyl replacement reactions to proceed at lower temperatures than such reactions using $Fe(CO)_5$ as the starting material. Examples of early work in this area include reactions of $Fe_3(CO)_{12}$ with diolefins[2] and alkynes[3] to give a variety of organoiron carbonyl derivatives. A similar principle was later applied to the synthesis of organomanganese carbonyls. In this case the key reactive trinuclear manganese derivative is the hydride $H_3Mn_3(CO)_{12}$, which has been shown to react with a variety of unsaturated organometallic compounds under relatively mild conditions to give olefinic manganese carbonyl derivatives.[4]

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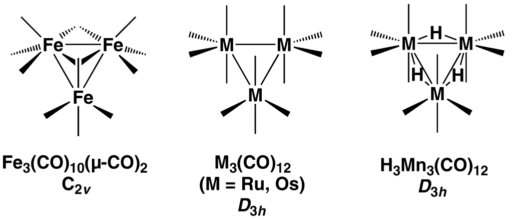

Figure 1. Comparison of the known $Fe_3(CO)_{10}(\mu\text{-}CO)_2$, $M_3(CO)_{12}$ (M = Ru, Os), and $H_3Mn_3(CO)_{12}$ structures. Carbonyl groups are omitted for clarity.

The synthesis of $H_3Mn_3(CO)_{12}$, which thus is a key starting material for the synthesis of organomanganese carbonyls, is reminiscent of that of the isoelectronic $Fe_3(CO)_{12}$ in that a simpler metal carbonyl derivative, namely, $Mn_2(CO)_{10}$ for manganese, is treated with a base followed by acidification.[5,6] However, $H_3Mn_3(CO)_{12}$ and $Fe_3(CO)_{12}$ have very different structures (Figure 1). Thus $Fe_3(CO)_{12}$ has a C_{2v} structure with one of the edges of the isosceles Fe_3 triangle bridged by two carbonyl groups. The remaining ten carbonyl groups in $Fe_3(CO)_{12}$ are all terminal carbonyl groups. However, the structure of $H_3Mn_3(CO)_{12}$ is found by X-ray diffraction to be an equilateral triangle with each of the edges bridged by a single hydrogen atom.[7] All 12 carbonyl groups in $H_3Mn_3(CO)_{12}$ are terminal carbonyl groups. This experimentally determined structure of $H_3Mn_3(CO)_{12}$ is consistent with earlier density functional theory (DFT) research[8] on binuclear manganese carbonyl hydrides, $H_2Mn_2(CO)_n$, which in almost all cases were found to favor structures with only bridging hydrogen atoms and only terminal carbonyl groups. This D_{3h} structure of $H_3Mn_3(CO)_{12}$ is closely related to the structures of the trinuclear carbonyls of the heavier congeners of iron, namely, $M_3(CO)_{12}$ (M = Ru,[9] Os[10,11]), which, unlike $Fe_3(CO)_{12}$, have exclusively terminal carbonyl groups (Figure 1).

Previous research has examined structures of the unsaturated homoleptic trinuclear carbonyls $M_3(CO)_n$ (M = Fe,[12] Ru,[13] Os;[14] $n = 11, 10, 9$) using DFT methods. Significant differences were found in the lowest energy structures for each of the Group 8 metals. In the work reported in this paper we use analogous DFT methods to investigate the effects of substituting an isoelectronic, but sterically different, HMn unit for the iron atoms in the trinuclear carbonyl derivatives. Significant differences were found since the tendency for the hydrogen atoms to occupy bridging positions in these metal carbonyl hydride structures leaves mainly terminal positions for the carbonyl groups.

2. Theoretical Methods

Electron correlation effects were considered by using DFT methods, which have evolved as a practical and effective computational tool, especially for organometallic compounds.[15−23] Two DFT methods were used in this study. The first method uses the popular B3LYP functional, which incorporates the three-parameter Becke functional (B3) with the Lee−Yang−Parr (LYP) generalized gradient correlation functional.[24,25] The other DFT method is the BP86 method, which combines Becke's 1988 exchange functional (B) with Perdew's 1986 gradient corrected correlation functional (P86).[26,27] It has been noted elsewhere that the BP86 method may be more reliable than B3LYP for the types of organometallic systems considered in this paper.[28−30] Previous research[31] has shown that these two functionals work quite well for related manganese carbonyl derivatives of the type $Mn_2(CO)_n$ ($n = 10, 9, 8, 7$), where comparison with experimental work is feasible for $Mn_2(CO)_{10}$.

All computations were performed using double-ζ plus polarization (DZP) basis sets. For carbon 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 $\alpha_d(C) = 0.75$, and $\alpha_d(O) = 0.85$ to the Huzinaga−Dunning standard contracted DZ sets.[32,33] For hydrogen, a set of p polarization functions is used with $\alpha_p(H) = 0.75$. The loosely contracted DZP basis set for manganese is the Wachters primitive set[34] augmented by two sets of p functions and a set of d functions, contracted following Hood, Pitzer, and Schaefer,[35] designated (14s11p6d/10s8p3d). For the trinuclear manganese carbonyl hydride derivatives $H_3Mn_3(CO)_{12}$, $H_3Mn_3(CO)_{11}$, $H_3Mn_3(CO)_{10}$, and $H_3Mn_3(CO)_9$, there are 522, 492, 462, and 432 contracted Gaussian basis functions, respectively.

The geometries of all structures were fully optimized using the DZP B3LYP and DZP BP86 methods. The vibrational frequencies were determined with the same computational methods by evaluating analytically the second derivatives of the energy with respect to the nuclear coordinates. The corresponding infrared intensities were also evaluated analytically. All of the computations were

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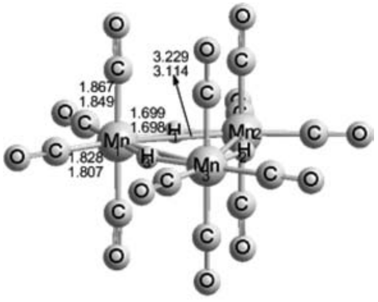

312-1

Figure 2. Structure of $H_3Mn_3(CO)_{12}$.

Table 1. Bond Distances (in Å), Total Energies (E in Hartree), and Relative Energies (ΔE in kcal/mol) for $H_3Mn_3(CO)_{12}$

	312−1 (D_{3h})		
	B3LYP	BP86	expt[7]
Mn−Mn	3.229	3.114	3.111
Mn−H	1.699	1.698	1.720
Mn−C(ax)	1.867	1.849	1.854
C−O(ax)	1.152	1.167	1.139
Mn−C(eq)	1.828	1.807	1.789
C−O(eq)	1.156	1.171	1.152
Mn−H−Mn	143.8	132.9	131
C(eq)−Mn-C(ax)	90.4	89.8	90.6
C(eq)−Mn-C(eq)	94.9	92.8	93.1
$-E$	4815.29642	4815.97585	
imaginary frequencies	none	none	

carried out with the Gaussian 03 program,[36] in which the fine grid option (75 radial shells, 302 angular points) is the default for evaluating integrals numerically, while the tight (10^{-8} hartree) designation is the default for the self-consistent field (SCF) 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 the DFT computations.[37] Thus all imaginary vibrational frequencies with a magnitude less than $100i$ cm^{-1} are considered questionable, and are given less weight in the analysis.[37−39] Therefore, we do not always follow such low imaginary vibrational frequencies. All of the predicted triplet structures are found to have negligible spin contamination, that is, $S(S+1)$ in all cases was between 2.00 and 2.15 as compared with the ideal value of 2.

Structures are designated by **ab-c** where **a** is the number of manganese atoms (or, equivalent the number of hydrogen atoms, **b** is the number of carbonyl groups, and **c** orders the structures in terms of their relative energies. Triplet structures are indicated by a **T** after this designation. Thus the lowest lying singlet structure of $H_3Mn_3(CO)_{12}$ is designated as **312−1**.

3. Results

3.1. $H_3Mn_3(CO)_{12}$. A single structure **312−1**, of D_{3h} symmetry, was found for $H_3Mn_3(CO)_{12}$ (Figure 2 and Table 1). This structure is very close to the structure determined by X-ray diffraction.[7] The manganese atoms form an equilateral triangle with each Mn−Mn edge bridged by a hydrogen atom. Each manganese atom bears four terminal carbonyl groups. The Mn−Mn bond distances in **312−1** are 3.229 Å (B3LYP) or 3.114 Å (BP86) as compared with the experimental value[7] of 3.111 Å. In this case the BP86 method obviously gives much closer agreement with experiment than the B3LYP method. For the purposes of this research, we take 3.11 Å as the canonical Mn−Mn single bond distance.

3.2. $H_3Mn_3(CO)_{11}$. Four singlet structures (Figure 3 and Table 2) and three triplet structures (Figure 4 and Table 3) were found for $H_3Mn_3(CO)_{11}$. The global minimum $H_3Mn_3(CO)_{11}$ structure, namely **311−1**, lies ~11 kcal/mol below any other of the $H_3Mn_3(CO)_{11}$ structures, indicating that it is a particularly favorable structure. Structure **311−1** has hydrogen atoms bridging each edge of an Mn_3 triangle and thus can be derived from the $H_3Mn_3(CO)_{12}$ structure **312−1** by removal of one of the terminal carbonyl groups. One of the remaining carbonyl groups in **311−1** becomes a semibridging carbonyl group with Mn−C distances of 1.857 Å and 2.651 Å (B3LYP) or 1.814 Å and 2.187 Å (BP86) and a lower ν(CO) frequency (BP86) at 1827 cm^{-1}. The Mn−Mn distance in **311−1** bridged by this carbonyl group is shortened to ~2.80 Å whereas the other two Mn−Mn distances remain at 3.0 to 3.1 Å.

The singlet structure **311−2** for $H_3Mn_3(CO)_{11}$ lies 11.6 kcal/mol (B3LYP) or 19.6 kcal/mol (BP86) above **311−1** (Figure 3 and Table 2). One of the Mn−Mn distances in **311−2** is relatively long at ~3.6 Å, whereas the other two Mn═Mn distances are relatively short at ~2.7 Å. One of the hydrogen atoms in **311−2** bridges all three manganese atoms whereas the other two hydrogen atoms bridge the ~2.7 Å Mn−Mn edges. All of the carbonyl groups in **311−2** are terminal carbonyl groups.

The relatively unsymmetrical singlet structure **311−3** for $H_3Mn_3(CO)_{11}$ lies 14.3 kcal/mol (B3LYP) or 9.4 kcal/mol (BP86) above **311−1** (Figure 3 and Table 2). One of the edges in the Mn_3 triangle is bridged by a carbonyl group, a second Mn−Mn edge is bridged by a single hydrogen atom, and the third edge is bridged by the remaining two hydrogen atoms. The doubly bridged Mn−Mn edge at 2.569 Å (B3LYP) or 2.512 Å (BP86) is much shorter than the other two Mn−Mn edges at 3.047 Å and 3.005 Å (B3LYP) or 2.953 Å and 2.882 Å (BP86). The singly carbonyl bridged edge in **311−3** is shorter than the singly hydrogen bridged edge using either method. The bridging carbonyl group in **311−3**, as expected, exhibits a relatively low ν(CO) frequency at 1854 cm^{-1} compared with the terminal metal carbonyls.

The remaining singlet $H_3Mn_3(CO)_{11}$ structure **311−4** at 15.7 kcal/mol (B3LYP) or 24.0 kcal/mol (BP86) above **311−1** (Figure 3 and Table 2) is similar to **311−1** in that each edge of the Mn_3 triangle is bridged by a hydrogen atom and all carbonyl groups are terminal carbonyl groups. Structure **311−4** for $H_3Mn_3(CO)_{11}$ is obviously derived from structure **312−1** for $H_3Mn_3(CO)_{12}$ by removal of one of the equatorial carbonyl groups (i. e., a carbonyl group coplanar with the Mn_3 triangle) with relatively little rearrangement of the carbonyl ligands (in contrast to **311−1**).

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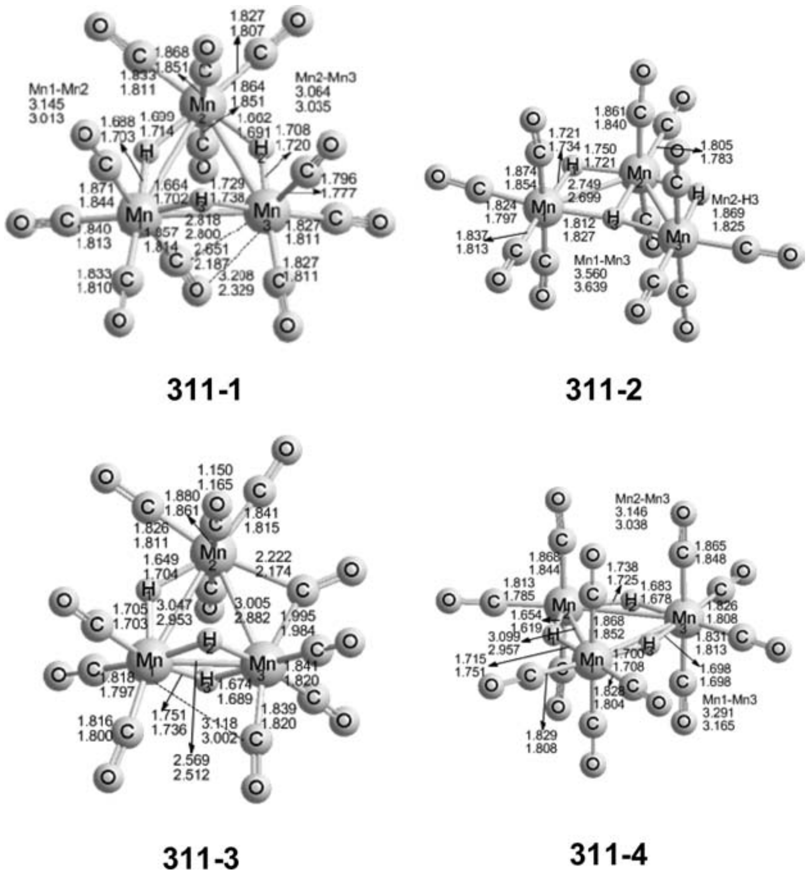


311-1 **311-2**

311-3 **311-4**

Figure 3. Four optimized singlet structures of $H_3Mn_3(CO)_{11}$.

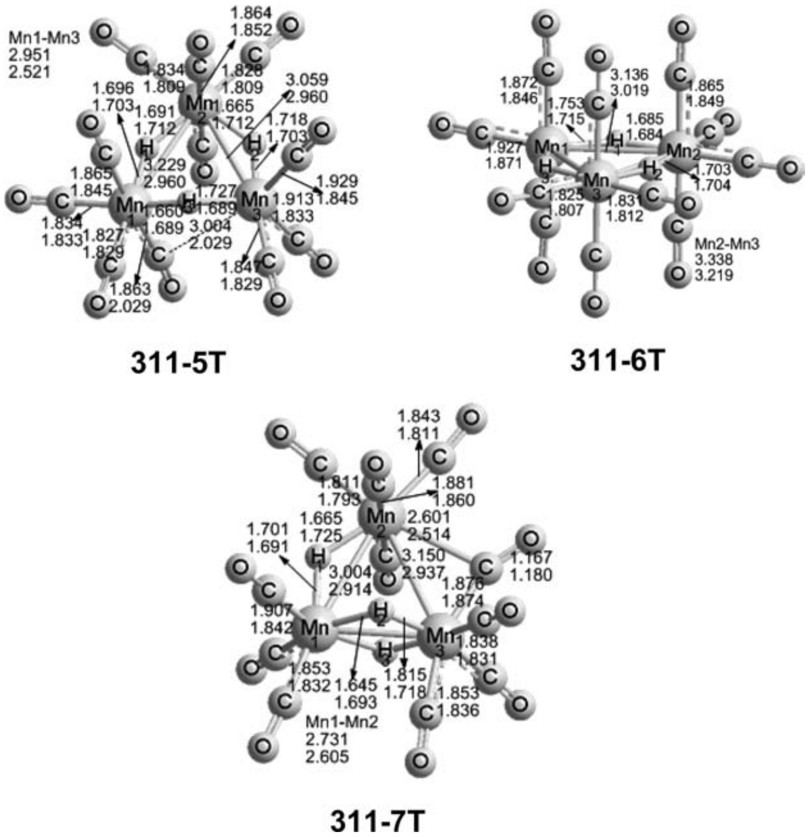
Table 2. Bond Distances (in Å), Total Energies (*E* in Hartree), and Relative Energies (Δ*E* in Kcal/mol) for the Optimized Singlet $H_3Mn_3(CO)_{11}$ Structures

	311−1 (C_1)		**311−2** (C_{2v})		**311−3** (C_s)		**311−4** (C_s)	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
Mn1−Mn2	3.145	3.013	2.749	2.699	3.047	2.953	3.099	2.957
Mn2−Mn3	3.064	3.035	2.749	2.699	3.005	2.882	3.146	3.038
Mn1−Mn3	2.818	2.800	3.560	3.639	2.569	2.512	3.291	3.165
Mn1−H1	1.688	1.703	1.721	1.734	1.705	1.703	1.715	1.751
Mn2−H1	1.699	1.714	1.750	1.721	1.649	1.704	1.654	1.619
Mn2−H2	1.662	1.691	1.750	1.721			1.738	1.725
Mn3−H2	1.708	1.720	1.721	1.734	1.674	1.689	1.683	1.678
Mn3−H3	1.729	1.738	1.812	1.827	1.674	1.689	1.698	1.698
Mn1−H3	1.664	1.702	1.812	1.827	1.751	1.736	1.700	1.708
Mn−C(bridge)	1.857/2.651	1.814/2.187			1.995/2.222	1.984/2.174		
Mn1−H1−Mn2	136.4	123.8	104.7	102.7	131.6	120.2	133.8	122.6
Mn2−H2−Mn3	130.9	125.7	104.7	102.7			133.8	126.5
Mn1−H3−Mn3	112.3	108.9	166.7	169.4	97.1	94.7	151.1	136.6
Mn−H3−Mn2			96.6	95.3				
−*E*	4701.92068	4702.59977	4701.90224	4702.56861	4701.89784	4702.58478	4701.89565	4702.56154
Δ*E*	0.0	0.0	11.6	19.6	14.3	9.4	15.7	24.0
imaginary frequencies	none	none	none	none	none	none	none	none

Three triplet $H_3Mn_3(CO)_{11}$ structures were found (Figure 4 and Table 3) at energies significantly above the singlet structures (Figure 3 and Table 2). Only **311−7T** among these structures has any imaginary vibrational frequencies, namely 23*i* (B3LYP) or 21*i* (BP86).

The two lowest lying triplet $H_3Mn_3(CO)_{11}$ structures, at 12.1 kcal/mol (B3LYP) or 18.9 kcal/mol (BP86) for **311−5T** and 13.3 kcal/mol (B3LYP) or 28.2 kcal/mol (BP86) for **311−6T** above the global minimum **311−1**, have hydrogen atoms bridging each edge of the Mn_3 triangle. One of the carbonyl groups in **311−5T**, as optimized by the BP86 method, is symmetrically edge-bridging with Mn−C distances of 2.029 Å and a relatively low ν(CO) frequency of 1851 cm^{-1}. The highest lying triplet $H_3Mn_3(CO)_{11}$ structure, namely, **311−7T** at the relatively high energy of 36.6 kcal/mol (B3LYP) or 37.2 kcal/mol (BP86), has two hydrogens bridging one Mn−Mn edge, one hydrogen bridging a second Mn−Mn edge, and a semibridging carbonyl group bridging the third Mn−Mn edge.

3.3. $H_3Mn_3(CO)_{10}$. Six singlet and five triplet structures were found for $H_3Mn_3(CO)_{10}$ within 30 kcal/mol of the global minimum (Figures 5 and 6 and Tables 4, 5, and



311-5T **311-6T**

311-7T

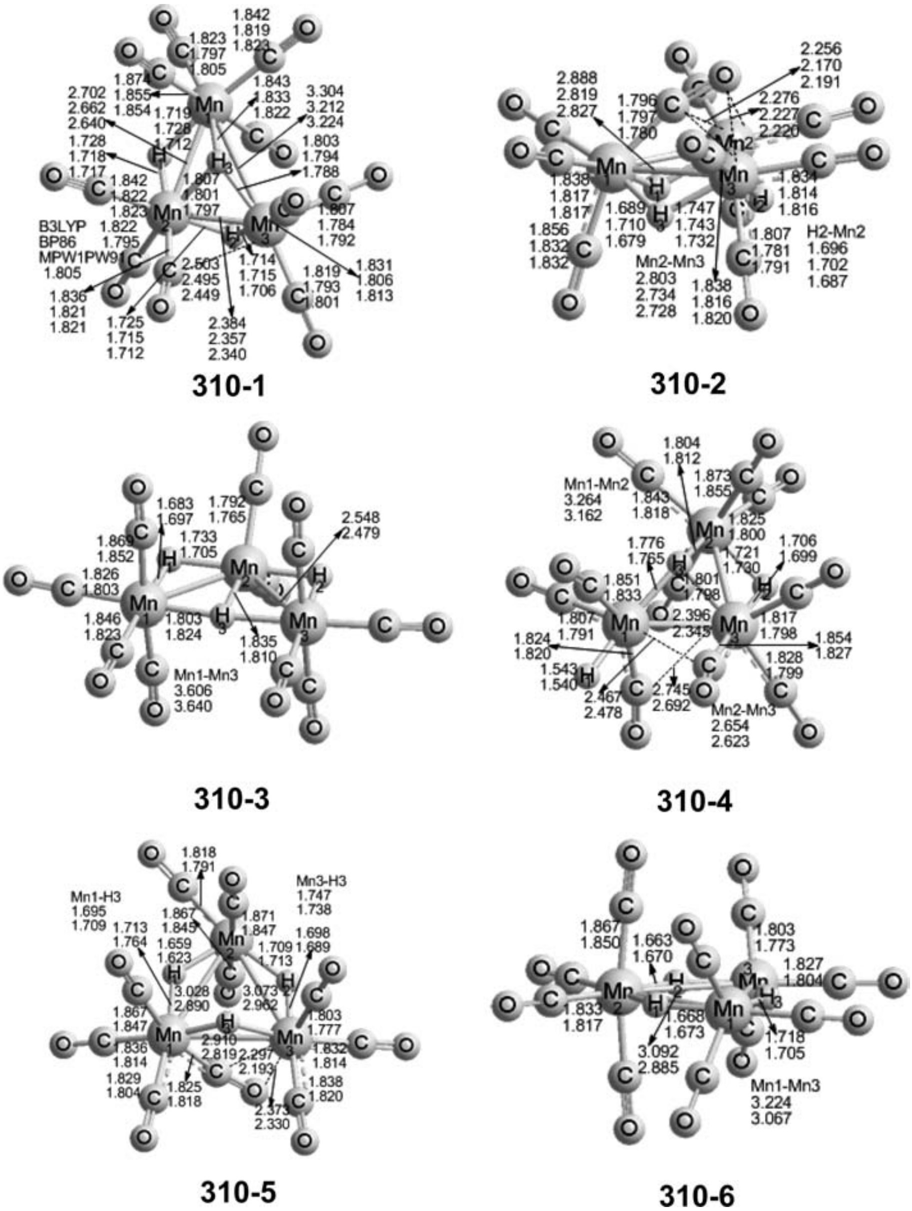
Figure 4. Three optimized triplet structures of $H_3Mn_3(CO)_{11}$.

Table 3. Bond Distances (in Å), Total Energies (E in Hartree), and Relative Energies (ΔE in Kcal/mol relative to **311-1**) for the Optimized Triplet $H_3Mn_3(CO)_{11}$ Structures

	311−5T ($^3A'$,C_1)		**311−6T** ($^3B_2$,C_{2v})		**311−7T** ($^3A''$,C_s)	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
Mn1−Mn2	3.229	2.960	3.136	3.019	3.004	2.914
Mn2−Mn3	3.059	2.960	3.136	3.019	3.150	2.937
Mn1−Mn3	2.951	2.521	3.338	3.219	2.731	2.605
Mn1−H1	1.696	1.703	1.685	1.684	1.701	1.691
Mn2−H1	1.691	1.712	1.753	1.715	1.665	1.725
Mn2−H2	1.665	1.712	1.753	1.715		
Mn3−H2	1.718	1.703	1.685	1.684	1.645	1.693
Mn3−H3	1.727	1.689	1.703	1.704	1.645	1.693
Mn1−H3	1.660	1.689	1.703	1.704	1.815	1.718
Mn−C(bridge)	1.863/3.004	2.029/2.029			2.601/1.876	2.514/1.874
Mn1−H1−Mn2	144.8	120.2	131.6	125.3	126.4	117.1
Mn2−H2−Mn3	129.4	120.2	131.6	125.3		
Mn1−H3−Mn3	121.1	96.5	157.2	141.8	104.2	99.6
$-E$	4701.90133	4702.56960	4701.89940	4702.55473	4701.86239	4702.54054
ΔE	12.1	18.9	13.3	28.2	36.6	37.2
imaginary frequencies	none	none	none	none	23i	21i

6). In the lowest energy B3LYP structure **310−1** of $H_3Mn_3(CO)_{10}$, which has no imaginary vibrational frequencies, one of the hydrogen atoms is a μ_3-H group bridging all three metal atoms whereas the remaining two hydrogen atoms bridge edges of the Mn_3 triangle. All of the carbonyl groups are terminal carbonyl groups. The Mn_3 triangle in **310−1** is very asymmetrical with the unbridged edge at 3.304 Å (B3LYP) or 3.212 Å (BP86) and the two bridged edges much shorter at 2.384 Å and 2.702 Å (B3LYP) or 2.357 Å and 2.662 Å (BP86). The short Mn≡Mn edge at 2.37 ± 0.02 Å are consistent with a formal triple bond, which, when combined with the longer Mn−Mn single bonds at the other two edges, gives each manganese atom in **310−1** the favored 18-electron configuration.

The lowest energy BP86 structure of $H_3Mn_3(CO)_{10}$ is **310−2** (Figure 5 and Table 5) at 2.7 kcal/mol above (B3LYP) or −3.7 kcal/mol below (BP86) **310−1** with no imaginary vibrational frequencies. To clarify this inconsistent energy order for structures **310−1** and **310−2** predicted by B3LYP and BP86, we have studied these specific structures using a third functional (MPW1PW91), which has proven to be useful for DFT studies on other transition metal compounds.[40] The MPW1PW91 result on $H_3Mn_3(CO)_{10}$ (Tables 4 and 5) shows that the energy difference between structures **310−1** and **310−2** by the MPW1PW91 method



310-1 **310-2** **310-3** **310-4** **310-5** **310-6**

Figure 5. Six optimized singlet structures of $H_3Mn_3(CO)_{10}$.

is only 0.5 kcal/mol. Thus, we can conclude that these two structures are essentially degenerate in energy. In structure **310−2** each manganese atom has three terminal carbonyl groups. The tenth carbonyl group in **310−2** is bonded to all three manganese atoms using a Mn−Mn σ-bond for one manganese atom and the orthogonal π-components of the C≡O triple bond for bonding to the other manganese atoms. This η^2-μ_3-CO bonding mode of the unique carbonyl group in **310−2** is supported by the two relatively short Mn−O distances of 2.276 Å (B3LYP) or 2.227 Å (BP86) in **310−2**. This unique carbonyl group in **310−2** is thus a formal six-electron donor similar to the η^2-μ_3-CO in the known compound[41] $(\eta^5\text{-}C_5H_5)_3Nb_3(CO)_6(\eta^2\text{-}\mu_3\text{-}CO)$ and exhibits a very low ν(CO) frequency at 1616 cm^{-1}.

The singlet structure **310−3** of $H_3Mn_3(CO)_{10}$ (Figure 5 and Table 4) lies 3.4 kcal/mol (B3LYP) or 7.0 kcal/mol (BP86) above **310−1** with no imaginary vibrational frequencies by B3LYP) and only very small vibrational frequencies by BP86. One of the Mn···Mn distances in this structure is very long at 3.606 Å (B3LYP) or 3.640 Å (BP86), which is clearly outside the range of a direct interaction. However, the other Mn−Mn distances are relatively short at 2.548 Å (B3LYP) or 2.479 Å (BP86). All of the carbonyl groups in **310−3** are terminal carbonyl groups. One of the hydrogen atoms in **310−3** bridges all three manganese atoms with typical Mn−H distances around 1.7 Å. The remaining two hydrogen atoms in **310−3** bridge the shorter ~2.5 Å Mn−Mn edges.

The singlet structure **310−4** of $H_3Mn_3(CO)_{10}$ lies 17.6 kcal/mol (B3LYP) or 12.9 kcal/mol (BP86) above **310−1** without any imaginary frequencies (Figure 5 and Table 4). One of the hydrogen atoms in **310−4** bridges all three metal

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(40) Zhao, S.; Wang, W.; Li, Z.; Liu, Z. P.; Fan, K.; Xie, Y.; Schaefer, H. F. *J. Chem. Phys.* **2006**, *124*, 184102.

(41) Herrmann, W. A.; Biersack, H.; Ziegler, M. L.; Weidenhammer, K.; Siegel, R.; Rehder, D. *J. Am. Chem. Soc.* **1981**, *103*, 1692.

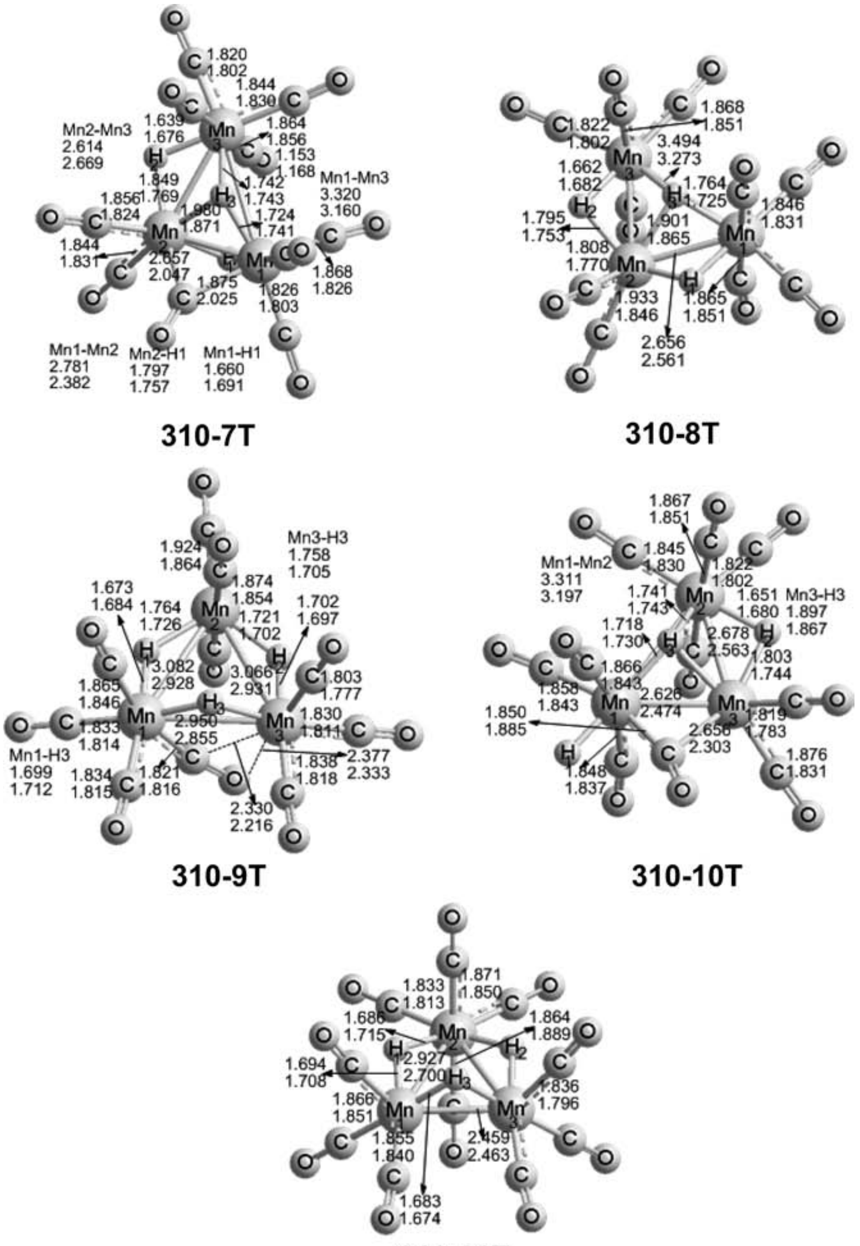


Figure 6. Five optimized triplet structures of $H_3Mn_3(CO)_{10}$.

atoms whereas the remaining two hydrogen atoms bridge edges of a very unsymmetrical Mn_3 triangle with edge lengths of 2.396 Å, 2.654 Å, and 3.264 Å (B3LYP) or 2.345 Å, 2.623 Å, and 3.162 Å (BP86).

The singlet structure **310−5** of $H_3Mn_3(CO)_{10}$ lies at 18.6 kcal/mol (B3LYP) or 19.2 kcal/mol (BP86) above **310−1** (Figure 5 and Tables 5) with no imaginary vibrational frequencies. The most distinctive structural feature of **310−5** is an unusual η^2-μ-CO carbonyl group bridging one of the edges of the Mn_3 triangle and functioning as a four-electron donor with one of the π orbitals of CO donating to one Mn atom and the lone pair of the CO carbon donating to the other Mn atom, as indicated by a relatively short Mn−O distance of 2.373 Å (B3LYP) or 2.330 Å (BP86) to this carbonyl group, as well as a relatively low ν(CO) frequency of 1826 cm^{-1} for this carbonyl group. Each of the three edges of the Mn_3triangle in **310−5** is bridged by a hydrogen atom.

The other singlet $H_3Mn_3(CO)_{10}$ structure within 30 kcal/mol of the global minimum is **310−6** at 19.0 kcal/mol (B3LYP) or 20.0 kcal/mol (BP86) above **310−1** (Figure 5 and Table 4). This structure has hydrogen atoms bridging each edge of the Mn_3 triangle and all terminal carbonyl groups and thus can be derived from $H_3Mn_3(CO)_{12}$ (**312−1** in Figure 2 and Table 1) by removal of two carbonyl groups. However, the $H_3Mn_3(CO)_{10}$ structure **310−6** is clearly a transition state, since it has a large imaginary vibrational frequency above 100*i* by either method.

Five triplet structures were found for $H_3Mn_3(CO)_{10}$ (Figure 6 and Table 6), none of which exhibited any imaginary vibrational frequencies. The lowest lying of these triplet

Table 4. Bond Distances (in Å), Total Energies (*E* in Hartree), and Relative Energies (Δ*E* in kcal/mol) for the Optimized Singlet $H_3Mn_3(CO)_{10}$ Structures with One Hydrogen Bridging All Three Manganese Atoms

	310−1(C_1)			**310−3** (C_{2v})		**310−4** (C_1)	
	B3LYP	BP86	MPW1PW91	B3LYP	BP86	B3LYP	BP86
Mn1−Mn2	2.702	2.662	2.640	2.548	2.479	3.264	3.162
Mn2−Mn3	2.384	2.357	2.340	2.548	2.479	2.654	2.623
Mn1−Mn3	3.304	3.212	3.224	3.606	3.640	2.396	2.345
Mn1−H1	1.719	1.728	1.712	1.683	1.697	1.543	1.540
Mn2−H1	1.728	1.718	1.717	1.733	1.705		
Mn2−H2	1.725	1.715	1.712	1.733	1.705	1.721	1.730
Mn3−H2	1.714	1.715	1.706	1.683	1.697	1.706	1.699
Mn3−H3	1.803	1.794	1.788	1.803	1.824	1.801	1.798
Mn1−H3	1.843	1.833	1.822	1.803	1.824	1.776	1.765
Mn2−H3	1.807	1.801	1.797	1.835	1.810	1.804	1.812
Mn−C(bridge)	1.836/2.503	1.821/2.495	1.821/2.448			1.854/2.467 1.824/2.745	1.827/2.478 1.820/2.692
Mn1−H1−Mn2	103.3	101.2	100.7	96.5	93.5		
Mn2−H2−Mn3	87.9	86.9	86.4	96.5	93.5	101.5	99.8
Mn3−H3−Mn1	129.9	124.7	126.6	177.8	172.0	84.1	82.3
Mn1−H3−Mn2	95.5	94.2	93.7	88.9	86.0	131.5	124.2
Mn2−H3−Mn3	82.7	81.9	815.5	88.9	86.0	94.8	93.2
−*E*	4588.55002	4589.21613	4588.37486	4588.54456	4589.20503	4588.52205	4589.19562
Δ*E*	0.0	0.0	0.0	3.4	7.0	17.6	12.9
imaginary frequencies	none	none	none	none	38*i*, 18*i*	none	none

Table 5. Bond Distances (in Å), Total Energies (*E* in Hartree), and Relative Energies (Δ*E* in kcal/mol) for the Other Optimized Singlet $H_3Mn_3(CO)_{10}$ Structures

	310−2 (C_s)			**310−5** (C_1)		**310−6** (C_{2v})	
	B3LYP	BP86	MPW1PW91	B3LYP	BP86	B3LYP	BP86
Mn1−Mn2	2.888	2.819	2.827	3.028	2.890	3.092	2.855
Mn2−Mn3	2.803	2.734	2.728	3.037	2.962	3.092	2.855
Mn1−Mn3	2.888	2.819	2.827	2.910	2.819	3.224	3.067
Mn1−H1	1.689	1.710	1.679	1.713	1.764	1.668	1.673
Mn2−H1	1.747	1.743	1.732	1.659	1.623	1.663	1.670
Mn2−H2	1.696	1.702	1.687	1.709	1.698	1.663	1.670
Mn3−H2	1.696	1.702	1.687	1.698	1.689	1.668	1.673
Mn3−H3	1.747	1.743	1.732	1.747	1.738	1.718	1.705
Mn1−H3	1.689	1.71	1.679	1.695	1.709	1.718	1.705
Mn−C(bridge)	1.796/2.256	1.797/2.170	1.780/2.191	1.825/2.297	1.818/2.193		
Mn1−H1−Mn2	114.4	109.4	111.9	128.8	117.1	136.3	117.3
Mn2−H2−Mn3	111.4	106.9	107.9	129.3	121.1	136.3	117.3
Mn3−H3−Mn1	114.4	109.4	111.9	115.4	109.8	140.1	128.1
−*E*	4588.54568	4589.22150	4588.37407	4588.52032	4589.18549	4588.51979	4589.18430
Δ*E*	2.7	−3.7	0.5	18.6	19.2	19.0	20.0
imaginary frequency	none	none	none	none	none	155*i*, 56*i* 23*i*, 12*i*	149*i*, 60i 37*i*

structures, namely **310−7T**, lies 6.7 kcal/mol (B3LYP) or 12.6 kcal/mol (BP86) above the global minimum **310−1**. Structure **310−7T** has one hydrogen atom bridging all three manganese atoms and the remaining two hydrogen atoms bridging edges of the Mn_3 triangle. One of the carbonyl groups in **310−7T** is edge-bridging and exhibits a relatively low ν(CO) frequency at 1889 cm^{-1}.

A hydrogen atom bridging three manganese atoms is also found in the triplet $H_3Mn_3(CO)_{10}$ structures **310−8T**, **310−10T**, and **310−11T** with the remaining two hydrogen atoms bridging edges of the Mn_3 triangle (Figure 6). Structure **310−9T** at 17.1 kcal/mol (B3LYP) or 24.5 kcal/mol (BP86) is clearly different from the other triplet structures in Figure 6, since all three hydrogen atoms each bridge only two manganese atoms. More strikingly, one of the carbonyl groups in **310−9T** bridges one of the Mn−Mn edges with a short Mn−O distance of 2.377 Å (B3LYP) or 2.333 Å (BP86), indicating a four-electron donor carbonyl group. This carbonyl group exhibits a relatively low ν(CO) frequency at 1828 cm^{-1} (Supporting Information) as is typical for such four-electron donor carbonyl groups.

3.4. $H_3Mn_3(CO)_9$. The $H_3Mn_3(CO)_9$ system is particularly interesting since its global minimum **39−1** (Figure 7 and Table 7) was found to be ~20 kcal/mol below that of any of the other $H_3Mn_3(CO)_9$ structures in this work, thereby suggesting the special stability of this structure. In the singlet structure **39−1** two of the three hydrogen atoms bridge the Mn_3 triangle leading to a H_2Mn_3 trigonal bipyramid. The third hydrogen bridges one of the Mn−Mn edges. One of the nine carbonyl groups in **39−1** is semibridging with Mn−C distances of 1.850 Å and 2.433 Å (B3LYP) or 1.845 Å and 2.405 Å (BP86). Two of the Mn−Mn distances in **39−1** are rather short (2.389 Å and 2.413 Å by B3LYP or 2.369 Å and 2.380 Å by BP86) whereas the third Mn−Mn distance is significantly longer at 2.936 Å (B3LYP) or 2.887 Å (BP86).

The singlet structure **39−2** for $H_3Mn_3(CO)_9$ lies 26.8 kcal/mol (B3LYP) or 22.7 kcal/mol (BP86) above **39−1** with no imaginary vibrational frequencies. Structure **39−2** is related to **310−2** with an Mn−Mn distance of 3.015 Å (B3LYP) or 2.743 Å (BP86) and a six-electron donor η^2-μ_3-CO group exhibiting a very low ν(CO) frequency of

Table 6. Bond Distances (in Å), Total Energies (*E* in Hartree), and Relative Energies (Δ*E* in Kcal/mol) for the Optimized Triplet $H_3Mn_3(CO)_{10}$ Structures

	310−7T (C_1)		**310−8T** (C_s)		**310−10T** (C_1)	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
Mn1−Mn2	2.781	2.382	2.656	2.561	3.311	3.197
Mn2−Mn3	2.614	2.669	2.656	2.561	2.678	2.563
Mn1−Mn3	3.320	3.160	3.494	3.273	2.626	2.474
Mn1−H1	1.660	1.691	1.662	1.682	1.546	1.541
Mn2−H1	1.797	1.757	1.795	1.753		
Mn2−H2	1.849	1.769	1.795	1.753	1.651	1.680
Mn3−H2	1.639	1.676	1.662	1.682	1.803	1.744
Mn3−H3	1.742	1.743	1.764	1.725	1.897	1.867
Mn1−H3	1.724	1.741	1.764	1.725	1.718	1.730
Mn2−H3	1.980	1.871	1.901	1.865	1.741	1.743
Mn−C(bridge)	2.657/1.875	2.047/2.025			1.850/2.656	1.885/2.303
Mn1−H1−Mn2	98.2	87.4	100.3	96.4		
Mn2−H2−Mn3	105.6	101.6	100.3	96.4	101.6	96.9
Mn3−H3−Mn1	146.6	130.2	164.1	143.2	93.1	86.8
Mn1−H3−Mn2	89.5	82.5	92.8	90.9	146.3	134.0
Mn2−H3−Mn3	96.5	95.1	92.8	90.9	94.7	90.4
−*E*	4588.53941	4589.19608	4588.53819	4589.19182	4588.51904	4589.17883
Δ*E*	6.7	12.6	7.4	15.3	19.4	23.4

	310−9T (C_1)		**310−11T** (C_s)	
	B3LYP	BP86	B3LYP	BP86
Mn1−Mn2	3.082	2.928	2.927	2.700
Mn2−Mn3	3.066	2.931	2.927	2.700
Mn1−Mn3	2.950	2.855	2.459	2.463
Mn1−H1	1.673	1.684	1.694	1.708
Mn2−H1	1.764	1.726	1.686	1.715
Mn2−H2	1.721	1.702	1.686	1.715
Mn3−H2	1.702	1.697	1.694	1.708
Mn3−H3	1.758	1.705	1.683	1.674
Mn1−H3	1.699	1.712	1.683	1.674
Mn−C(bridge)	1.821/2.330	1.816/2.216	—	—
Mn1−H1−Mn2	127.4	118.3	120.0	104.1
Mn2−H2−Mn3	127.2	119.1	120.0	104.1
Mn3−H3−Mn1	117.2	111.1	93.9	94.7
−*E*	4588.52272	4589.17707	4588.50548	4589.18398
Δ*E*	17.1	24.5	27.9	20.2

1630 cm^{-1}. In fact, structure **39−2** can be derived from **310−2** by removal of one of the carbonyl groups coplanar with the Mn_3 unit.

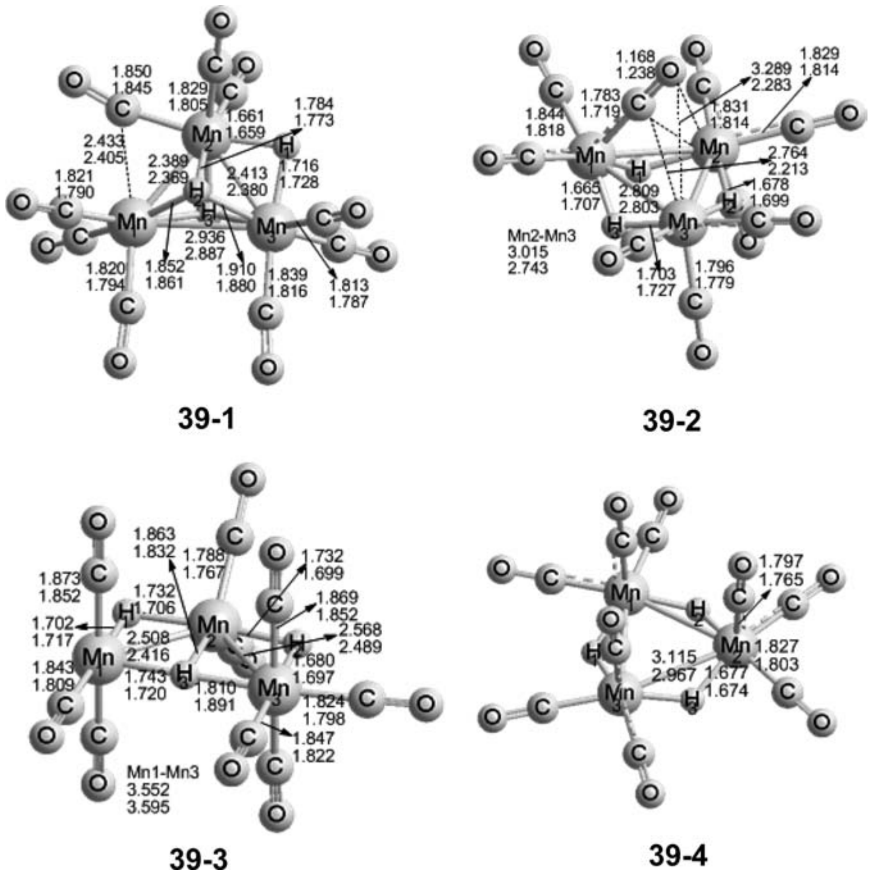
A much higher energy singlet structure **39−3** was also found for $H_3Mn_3(CO)_9$ in which one of the hydrogen atoms bridges all three manganese atoms and the remaining two hydrogen atoms bridge Mn−Mn edges (Figure 7 and Table 7). In **39−3**, which lies 30.2 kcal/mol (B3LYP) or 38.9 kcal/mol (BP86) above **39−1**, one of the Mn···Mn distances is relatively long at 3.552 Å (B3LYP) or 3.595 Å (BP86) so that this structure is closely related to **310−3** (Figure 5 and Table 4). In fact, structure **39−3** can be derived from **310−3** by removal of one of the carbonyl groups coplanar with the Mn_3 unit.

Structure **39−4** (Figure 7 and Table 8) were found for $H_3Mn_3(CO)_9$ at energies comparable to that of **39−3**. This structure (with C_{3v} symmetry) can be regarded as removing three axial carbonyls from structure **312−1**. It has a regular Mn_3 triangle, with three H-bridged Mn−Mn edges of 3.115 Å (B3LYP) or 2.967 Å (BP86). All nine CO groups are in the arrangements of the terminal carbonyl groups.

Two triplet structures (Figure 8 and Table 9) were found for $H_3Mn_3(CO)_9$ within 45 kcal/mol of the lowest energy structure **39−1**. The lowest energy of these triplet $H_3Mn_3(CO)_9$ structures, namely **39−5T** at 32.1 kcal/mol (B3LYP) or 34.8 kcal/mol (BP86), has a six-electron donor η^2-μ_3-CO group bridging all three manganese atoms with Mn−O distances of 2.252 Å (B3LYP) or 2.223 Å (BP86). This η^2-μ_3-CO group exhibits a very low ν(CO) frequency at 1562 cm^{-1} (Supporting Information). The edges of the Mn_3 triangle in **39−5T** are each bridged by a single hydrogen atom.

The other triplet structure of $H_3Mn_3(CO)_9$, namely, **39−6T** at 43.3 kcal/mol (B3LYP) or 41.6 kcal/mol (BP86) above **39−1**, has each edge of the Mn_3 triangle bridged by a single hydrogen atom. Structure **39−6T** has one symmetrical bridging carbonyl group with Mn−C distances of 2.011 Å (B3LYP) or 1.998 Å (BP86), which exhibits a relatively low ν(CO) frequency at 1855 cm^{-1} The remaining eight carbonyl groups in **39−6T** are terminal carbonyl groups. The Mn−Mn distances in **39−6T** are shorter than those in **39−5T** (Table 9) reflecting the effect of having a normal two-electron donor bridging carbonyl group in **39−6T** but a six-electron donor η^2-μ_3-CO bridging carbonyl group in **39−5T**.

3.5. Dissociation Energies. The dissociation energies for successive removal of carbonyls from $H_3Mn_3(CO)_{12}$ to give $H_3Mn_3(CO)_9$ based on the lowest energy structures are listed in Table 10. These carbonyl dissociation energies are predicted to be somewhat lower than the known carbonyl



39-1 **39-2**

39-3 **39-4**

Figure 7. Four optimized singlet structures of $H_3Mn_3(CO)_9$.

Table 7. Bond Distances (in Å), Total Energies (*E* in Hartree), and Relative Energies (Δ*E* in Kcal/mol) for the Optimized Singlet $H_3Mn_3(CO)_9$ Structures with at Least One Hydrogen Bridging All Three Manganese Atoms

	39−1 (C_s)		**39−3** (C_s)	
	B3LYP	BP86	B3LYP	BP86
Mn1−Mn2	2.389	2.369	2.508	2.416
Mn2−Mn3	2.413	2.380	2.568	2.489
Mn1−Mn3	2.936	2.887	3.552	3.595
Mn−H1	1.661/1.716	1.659/1.728	1.702/1.732	1.717/1.706
Mn−H2	1.852/1.784/1.910	1.861/1.773/1.880	1.732/1.680	1.699/1.697
Mn−H3	1.852/1.784/1.910	1.861/1.773/1.880	1.750/1.863/1.810	1.720/1.830/1.910
Mn−C(bridge)	2.433/1.850	2.405/1.845		
Mn1−H1−Mn2			93.8	89.8
Mn2−H1−Mn3	91.2	89.2		
Mn1−H2−Mn2	82.1	81.3		
Mn2−H2−Mn3	81.5	81.3	97.6	94.3
Mn3−H2−Mn1	102.6	101.0		
Mn1−H3−Mn2	82.1	81.3	88.0	85.6
Mn2−H3−Mn3	81.5	81.3	88.7	83.9
Mn3−H3−Mn1	102.6	101.0	176.7	169.5
Mn−C−O(bridge)	126.3/167.6	126.1/167.4		
−*E*	4475.18874	4475.84851	4475.14068	4475.78650
Δ*E*	0.0	0.0	30.2	38.9
imaginary frequency	none	none	none	29*i*, 14*i*

dissociation energies[42] of 37 kcal/mol for $Cr(CO)_6$ and 41 kcal/mol for $Fe(CO)_5$.

Another property of interest for the trinuclear $H_3Mn_3(CO)_n$ derivatives is their dissociation into smaller fragments. In this connection the energies of alternative pathways for the dissociation of the known[5−7] $H_3Mn_3(CO)_{12}$ into the lowest energy $H_2Mn(CO)_x$ + $HMn(CO)_y$ fragments ($x + y = 12$) fragments are listed in Table 11 using data for the $H_2Mn(CO)_x$ and $HMn(CO)_y$ fragments calculated in previous work using the same methods. The dissociation of the stable $H_3Mn_3(CO)_{12}$ into the stable $HMn(CO)_5$ and the reactive $H_2Mn_2(CO)_7$ fragment is predicted to be the lowest energy dissociation pathway requiring only ∼12 kcal/mol of energy. This relatively low dissociation energy of $H_3Mn_3(CO)_{12}$ into $HMn(CO)_5$ + $H_2Mn_2(CO)_7$ may relate to the use of $H_3Mn_3(CO)_{12}$ for the synthesis of olefinic manganese carbonyls.[4] Also the relatively low dissociation energy of $H_3Mn_3(CO)_{12}$ into mononuclear and binuclear fragments may make it difficult to find reaction conditions for the decarbonylation of $H_3Mn_3(CO)_{12}$ to give $H_3Mn_3(CO)_{11}$ or more

Table 8. Bond Distances (in Å), Total Energies (E in Hartree), and Relative Energies (ΔE in Kcal/mol) for the Optimized Singlet $H_3Mn_3(CO)_9$ Structures

	39−2 (C_s)		**39−4** (C_{3v})	
	B3LYP	BP86	B3LYP	BP86
Mn1−Mn2	2.809	2.803	3.115	2.967
Mn2−Mn3	3.015	2.743	3.115	2.967
Mn1−Mn3	2.809	2.803	3.115	2.967
Mn1−H1	1.665	1.707	1.677	1.674
Mn2−H1	1.703	1.727	1.677	1.674
Mn2−H2	1.678	1.699	1.677	1.674
Mn3−H2	1.678	1.699	1.677	1.674
Mn3−H3	1.703	1.727	1.677	1.674
Mn1−H3	1.665	1.707	1.677	1.674
Mn−C(bridge)	2.764	2.213		
Mn1−H1−Mn2	113	109.4	136.4	124.7
Mn2−H2−Mn3	127.9	107.6	136.4	124.7
Mn3−H3−Mn1	113	113.1	136.4	124.7
−E	4475.14606	4475.81241	4475.13756	4475.78970
ΔE	26.8	22.7	32.1	36.9
imaginary frequency	none	none	none	none

Table 9. Bond Distances (in Å), Total Energies (E in Hartree), and Relative Energies (ΔE in Kcal/mol) for the Optimized Triplet $H_3Mn_3(CO)_9$ Structures

	39−5T (C_s)		**39−6T** (C_s)	
	B3LYP	BP86	B3LYP	BP86
Mn1−Mn2	2.875	2.797	2.950	2.845
Mn2−Mn3	2.796	2.726	2.950	2.845
Mn1−Mn3	2.875	2.797	2.304	2.294
Mn1−H1	1.698	1.709	1.641	1.642
Mn2−H1	1.721	1.722	1.734	1.728
Mn2−H2	1.695	1.700	1.734	1.728
Mn3−H2	1.695	1.700	1.641	1.642
Mn3−H3	1.721	1.722	1.684	1.696
Mn1−H3	1.698	1.709	1.684	1.696
Mn−C(bridge)	1.855/2.304	1.819/2.200	2.011	1.998
Mn1−H1−Mn2	114.5	109.2	121.9	115.1
Mn2−H2−Mn3	111.1	106.6	121.9	115.1
Mn3−H3−Mn1	114.5	109.2	86.4	85.1
Mn−C−O(bridge)	153.4/72.2	157.4/74.7	145.0	144.9
−E	4475.13756	4475.79313	4475.11973	4475.78219
ΔE	32.1	34.8	43.3	41.6
imaginary frequencies	none	none	96i	none

highly unsaturated trinuclear derivatives without rupture of the Mn_3 triangle to give binuclear or mononuclear products.

Table 10. Dissociation Energies (kcal/mol) for the Successive Removal of Carbonyls from $H_3Mn_3(CO)_n$ Based on the Lowest Energy Structures of $H_mMn_m(CO)_n$

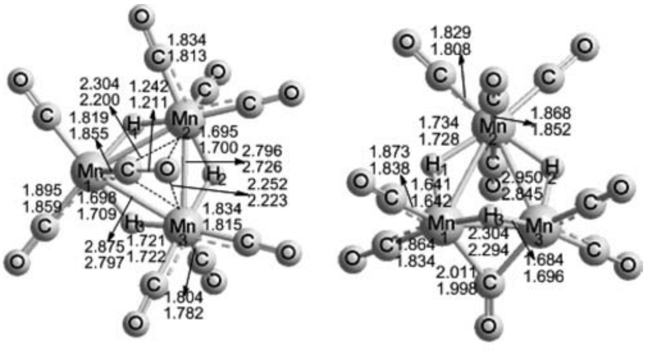
	B3LYP	BP86
$H_3Mn_3(CO)_{12} \rightarrow H_3Mn_3(CO)_{11} + CO$	29.5	30.6
$H_3Mn_3(CO)_{11} \rightarrow H_3Mn_3(CO)_{10} + CO$	26.4	35.4
$H_3Mn_3(CO)_{10} \rightarrow H_3Mn_3(CO)_9 + CO$	20.5	25.3

Table 11. Fragmentation Energies (kcal/mol) for Alternative Fragmentation Pathways of $H_3Mn_3(CO)_{12}$ Based on the Lowest Energy Structures

	B3LYP	BP86
$H_3Mn_3(CO)_{12} \rightarrow H_2Mn_2(CO)_7 + HMn(CO)_5$	11.8	12.3
$H_3Mn_3(CO)_{12} \rightarrow H_2Mn_2(CO)_8 + HMn(CO)_4$	31.2	34.1
$H_3Mn_3(CO)_{12} \rightarrow H_2Mn_2(CO)_9 + HMn(CO)_3$	59.4	62.6

4. Discussion

The only structure found for $H_3Mn_3(CO)_{12}$ is the known singlet structure[5−7] **312−1** (Figure 2) with all terminal carbonyl groups and each edge of the equilateral Mn_3 triangle bridged by a single hydrogen atom. This structure resembles the known structures of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ (Figure 1) except for the hydrogen bridges along each of the edges of the Mn_3 triangle in $H_3Mn_3(CO)_{12}$ (**312−1**). Furthermore, the tendency of hydrogen atoms to bridge metal−metal bonds is consistent with previous theoretical studies[8] on the binuclear manganese carbonyl hydrides $H_2Mn_2(CO)_n$ (n = 8, 7, 6), where all of the low energy structures were found to have doubly hydrogen-bridged manganese−manganese bonds.



39-5T **39-6T**

Figure 8. Two optimized triplet structures of $H_3Mn_3(CO)_9$.

The stability of the (μ-H)$_3$Mn$_3$ edge-bridged triangle structure unit found in the $H_3Mn_3(CO)_{12}$ structure **312−1** (Figure 2) is also indicated by the retention of this structural unit in the lowest energy structure of $H_3Mn_3(CO)_{11}$ (**311−1** in Figure 3). The unsaturated singlet structure **311−1** may be derived from the saturated $H_3Mn_3(CO)_{12}$ structure **312−1** (Figure 2) by loss of one of the carbonyl groups following by some reorientation of the carbonyl groups in the resulting $Mn(CO)_3$ unit and an adjacent $Mn(CO)_4$ unit to fill the hole left by the departing carbonyl group. During this reorientation process one of the originally terminal carbonyl groups in **312−1** in the $Mn(CO)_4$ unit becomes a semibridging carbonyl in **311−1**. Furthermore, in **311−1** one of the Mn−Mn distances at 2.80 Å is significantly shorter than the other two Mn−Mn distances in the 3.0 to 3.1 Å range.

The potential energy surface (PES) of $H_3Mn_3(CO)_{10}$ is the most complicated PES found in this study of $H_3Mn_3(CO)_n$ derivatives, with six singlet and five triplet stationary points (Figures 5 and 6). The global minimum of $H_3Mn_3(CO)_{10}$ depends upon the DFT method used. For the B3LYP method the lowest energy structure is the singlet **310−1** (Figure 5) with one hydrogen atom bridging the entire Mn_3 triangle and the remaining two hydrogen atoms bridging triangle edges. Similar μ_3 hydrogen atoms bridging metal triangles are found in (μ_3-H)$_4$Re$_4$(CO)$_{12}$, which has been shown by X-ray[43] and neutron[44] diffraction to have a hydrogen atom bridging each of the four faces of the Re_4 tetrahedron. Also in structure **310−1** one of the Mn≡Mn distances is very short at 2.36 Å suggesting a formal protonated triple bond to give the

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manganese atoms in $H_3Mn_3(CO)_{10}$ the favored 18-electron configuration.

The BP86 global minimum of $H_3Mn_3(CO)_{10}$ is a singlet structure **310−2** (Figure 5), which is very different from the presumably less reliable B3LYP global minimum **310−1**. In **310−2** the three hydrogen atoms bridge edges of the Mn_3 triangle just as they do in $H_3Mn_3(CO)_{12}$ (**312−1** in Figure 2), rather than having one of the three hydrogen atoms bridge the entire Mn_3 triangle as in **310−1**. Thus the $H_3Mn_3(CO)_{10}$ structure **310−2** may be derived from the $H_3Mn_3(CO)_{12}$ structure **312−1** by removal of two terminal carbonyl groups. However, such removal of two terminal carbonyl groups from **312−1** to give **310−2** leads to a major rearrangement of the remaining ten carbonyl groups so that one of the ten carbonyl groups becomes a formal six-electron donor η^2-μ_3-CO group similar to the unique carbonyl group in the known[41] triniobium compound $Cp_3Nb_3(CO)_6(\eta^2\text{-}\mu_3\text{-CO})$. Note that the Mn−Mn bonds in the Mn_3 triangle of **310−2** need only to be single bonds for each manganese atom to have the favored 18-electron configuration since the unsaturation in structure **310−2** of $H_3Mn_3(CO)_{10}$ is completely accommodated by the single six-electron donor carbonyl group. This is completely analogous to the situation in $Cp_3Nb_3(CO)_6(\eta^2\text{-}\mu_3\text{-CO})$. The three Mn−Mn bonds in the Mn_3 triangle of **310−2** fall in a relatively narrow range of 2.84 ± 0.05 Å (B3LYP) or 2.78 ± 0.05 Å (BP86) consistent with three formal single bonds.

The $H_3Mn_3(CO)_9$ potential energy surface is significantly simpler than the $H_3Mn_3(CO)_{10}$ energy surface since a single structure **39−1** (Figure 7) lies more than 20 kcal/mol below any of the other structures found in this work. This particularly stable singlet $H_3Mn_3(CO)_9$ structure has a central $(\mu_3\text{-H})_2Mn_3$ trigonal bipyramid obtained by axial hydrogen atoms bridging each side of an equatorial Mn_3 triangle. Despite its low energy, the $H_3Mn_3(CO)_9$ structure **39−1** has only C_s symmetry since one of the edges of the equatorial Mn_3 triangle is bridged by the third hydrogen atom, a second edge is bridged by an unsymmetrical bridging carbonyl group, and the third edge does not have any bridging groups.

Triplet structures were also investigated for the unsaturated $H_3Mn_3(CO)_n$ ($n = 11, 10, 9$) derivatives (Figures 4, 6, and 8). However, in all cases the triplet structures were found to be significantly higher in energy than isomeric singlet structures. For this reason the triplet structures are not considered in detail in this paper.

Acknowledgment. We are indebted to the 111 Project (B07012) and the National Natural Science Foundation (20873045) of China and the U.S. National Science Foundation (Grants CHE-0749868 and CHE-0716718) for support of this research.

Supporting Information Available: Tables S1 to S12: Harmonic vibrational frequencies and infrared intensities for $H_3Mn_3(CO)_n$ ($n = 12, 11, 10, 9$); Tables S13 to S37: Atomic coordinates of the optimized $H_3Mn_3(CO)_n$ ($n = 12, 11, 10, 9$) structures; Tables S38 to S40: The ν(CO) and ν(MnH) frequencies for the $H_3Mn_3(CO)_n$ ($n = 12, 11, 10, 9$) structures (BP86 method). Complete Gaussian 03 reference (ref 36). This material is available free of charge via the Internet at http://pubs.acs.org.

IC802413C