

# Unsaturated Binuclear Cyclopentadienylmanganese Carbonyl Derivatives Related to Cymantrene

Xiuhui Zhang,<sup>†</sup> Qian-Shu Li,<sup>\*,†,‡</sup> Yaoming Xie,<sup>§</sup> R. Bruce King,<sup>\*,§</sup> and Henry F. Schaefer III<sup>§</sup>

School of Chemical Engineering and the Environment, Beijing Institute of Technology, Beijing 100081, People's Republic of China, Center for Computational Quantum Chemistry, South China Normal University, Guangzhou 510631, People's Republic of China, Department of Chemistry and Center for Computational Chemistry, University of Georgia, Athens, Georgia 30602

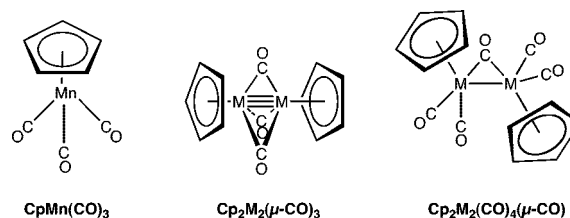
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The cyclopentadienylmanganese carbonyls  $\text{Cp}_2\text{Mn}_2(\text{CO})_n$  ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ;  $n = 5, 4, 3, 2$ ) have been studied by density functional theory using the B3LYP and BP86 functionals. The pentacarbonyl  $\text{Cp}_2\text{Mn}_2(\text{CO})_5$  is predicted to have a monobridged  $\text{Cp}_2\text{Mn}_2(\text{CO})_4(\mu\text{-CO})$  structure with an Mn–Mn distance of 2.804 Å (BP86), suggesting the single bond required for the 18-electron configuration. Its predicted infrared  $\nu(\text{CO})$  frequencies agree very well with the transient  $\nu(\text{CO})$  frequencies assigned to  $\text{Cp}_2\text{Mn}_2(\text{CO})_4(\mu\text{-CO})$  in the laser photolysis of  $\text{CpMn}(\text{CO})_3$  in hydrocarbon media. The tetracarbonyl  $\text{Cp}_2\text{Mn}_2(\text{CO})_4$  has an Mn=Mn distance of 2.509 Å (BP86), indicative of an Mn=Mn double bond, but is thermodynamically unstable with respect to disproportionation into  $\text{Cp}_2\text{Mn}_2(\text{CO})_5 + \text{Cp}_2\text{Mn}_2(\text{CO})_3$ . The tricarbonyl  $\text{Cp}_2\text{Mn}_2(\text{CO})_3$  has three bridging CO groups with an Mn≡Mn distance of 2.167 Å (BP86), suggesting an Mn≡Mn triple bond similar to the experimentally known structure of the stable  $(\eta^5\text{-Me}_5\text{C}_5)_2\text{Mn}_2(\text{CO})_3$ . A triplet structure for  $\text{Cp}_2\text{Mn}_2(\text{CO})_2$  with an Mn≡Mn triple bond (2.202 Å, BP86) is energetically preferred over a singlet structure with an Mn–Mn quadruple bond (2.067 Å, BP86).

## 1. Introduction

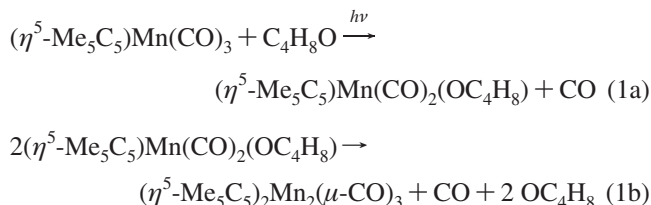
The chemistry of cyclopentadienylmanganese carbonyls dates back to 1954 shortly after the discovery of ferrocene with the synthesis of the mononuclear derivative  $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$  (Figure 1),<sup>1,2</sup> commonly known as cymantrene. This compound, with the favored 18-electron noble gas configuration for the manganese atom, is the most stable and least chemically reactive of the simple mononuclear and binuclear first-row transition metal cyclopentadienylmetal carbonyls. This chemical characteristic allows extensive organic chemistry to be done on the cyclopentadienyl (Cp) ring of cymantrene without disturbing the  $\text{Mn}(\text{CO})_3$  unit.<sup>3</sup> Thus the Cp ring in cymantrene may be considered to be an aromatic system analogous to benzene and thus susceptible to electrophilic substitution reactions to give a variety of substituted cyclopentadienylmanganese carbonyl derivatives.<sup>4</sup> Also, methylcymantrene,  $(\eta^5\text{-MeC}_5\text{H}_4)\text{Mn}(\text{CO})_3$ , is stable enough to have been used for a while as a lead-free antiknock derivative in gasoline and related fuels<sup>5</sup> until environmental considerations caused any metal-containing gasoline additives to be phased out of use.

The first binuclear cyclopentadienylmanganese carbonyl derivatives were prepared more than 30 years after the discovery of  $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$ . Thus in 1983 Herrmann, Serrano, and



**Figure 1.** Structures of  $\text{CpMn}(\text{CO})_3$ ,  $\text{Cp}_2\text{M}_2(\mu\text{-CO})_3$  ( $\text{M} = \text{Mn}, \text{Re}$ ), and  $\text{Cp}_2\text{Re}_2(\text{CO})_5$ .

Weichmann<sup>6</sup> synthesized  $(\eta^5\text{-Me}_5\text{C}_5)_2\text{Mn}_2(\mu\text{-CO})_3$  (middle of Figure 1) by the photolysis of  $(\eta^5\text{-Me}_5\text{C}_5)\text{Mn}(\text{CO})_3$  in tetrahydrofuran followed by spontaneous decomposition of the intermediate  $(\eta^5\text{-Me}_5\text{C}_5)\text{Mn}(\text{CO})_2(\text{OC}_4\text{H}_8)$  according to the following equations:



In this series of reactions no evidence has been found to date for the possible intermediate  $(\eta^5\text{-Me}_5\text{C}_5)_2\text{Mn}_2(\text{CO})_4$  in eq 1b. Determination of the structure of  $(\eta^5\text{-Me}_5\text{C}_5)_2\text{Mn}_2(\mu\text{-CO})_3$  by X-ray diffraction<sup>7</sup> indicates three bridging CO groups and a short manganese–manganese distance of 2.17 Å, suggesting the Mn≡Mn triple bond required to give both manganese atoms the favored 18-electron configuration (middle of Figure 1 with Me groups on the Cp rings).

No other stable binuclear pentamethylcyclopentadienyl- or cyclopentadienylmanganese carbonyl derivatives are known.

\* Corresponding author. E-mail: rbking@chem.uga.edu; qqli@senu.edu.cn.

<sup>†</sup> Beijing Institute of Technology.

<sup>‡</sup> South China Normal University.

<sup>§</sup> University of Georgia.

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However,  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mn}_2(\text{CO})_4(\mu\text{-CO})$  has been detected as a transient intermediate from the flash photolysis of  $\text{CpMn}(\text{CO})_3$  in heptane solution.<sup>8</sup> The lifetime of  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mn}_2(\text{CO})_4(\mu\text{-CO})$  is estimated to be approximately 0.1 s at room temperature.

Stable compounds of the three types  $(\eta^5\text{-Me}_5\text{C}_5)_2\text{Re}_2(\text{CO})_5$  (ref 9),  $(\eta^5\text{-Me}_5\text{C}_5)_2\text{Re}_2(\text{CO})_4$  (ref 10), and  $(\eta^5\text{-Me}_5\text{C}_5)_2\text{Re}_2(\text{CO})_3$  (ref 11) are known for rhenium, the congener of manganese in the third transition series. The structures of  $(\eta^5\text{-Me}_5\text{C}_5)_2\text{Re}_2(\text{CO})_n$  ( $n = 5, 4$ , and  $3$ ) have four terminal CO groups and one bridging CO group ( $n = 5$ ), two terminal CO groups and two semibridging CO groups ( $n = 4$ ), and three bridging CO groups ( $n = 3$ ), respectively. Experimental studies on similar compounds of the intermediate second-row element technetium are limited so only the mononuclear derivative  $\text{CpTc}(\text{CO})_3$  is known for technetium. Other related unsaturated binuclear metal–carbonyl derivatives include the stable triplet<sup>12</sup>  $(\eta^5\text{-Me}_5\text{C}_5)_2\text{Fe}_2(\mu\text{-CO})_3$  and the manganese carbonyls  $\text{Mn}_2(\text{CO})_n$  ( $n = 9, 8$ ) observed in low-temperature matrices.<sup>13</sup>

This paper examines possible structures for the binuclear cyclopentadienylmanganese carbonyls  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mn}_2(\text{CO})_n$  ( $n = 5, 4, 3, 2$ ) using density functional theory (DFT) methods with the objective of interpreting existing experimental information as well as predicting new structures.

## 2. Theoretical Methods

Electron correlation effects were considered by employing density functional theory (DFT) methods, which have evolved as a practical and effective computational tool, especially for organometallic compounds.<sup>14–22</sup> Thus two DFT methods were used in this study. The first functional is the 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.<sup>23,24</sup> 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).<sup>25,26</sup> It has been noted elsewhere that the BP86 method may be somewhat more reliable

**Table 1.** Total energies ( $E$ , in hartree), Relative Energies ( $\Delta E$ , in kcal/mol), Number of Imaginary Vibrational Frequencies ( $N_{\text{img}}$ ), and Mn–Mn distances (Å) for the Two Singlet Stationary Points of  $\text{Cp}_2\text{Mn}_2(\text{CO})_5$

		5S-1 ( $C_2$ )	5S-2 ( $C_1$ )
B3LYP	$E$	−3256.02894	−3256.01873
	$\Delta E$	0.0	6.4
	$N_{\text{img}}$	0	0
	Mn–Mn	2.858	2.917
BP86	$E$	−3256.48058	−3256.46883
	$\Delta E$	0.0	7.4
	$N_{\text{img}}$	0	0
	Mn–Mn	2.804	2.846

than B3LYP for the type of organometallic systems considered in this paper.<sup>27–29</sup> In the present study, the B3LYP and BP86 methods agree with each other fairly well in predicting the structural characteristics of the  $\text{Cp}_2\text{Mn}_2(\text{CO})_n$  derivatives of interest. Although both the B3LYP and BP86 results are shown in the figures and tables, unless specifically noted, only the BP86 results (geometries, energies, and vibrational frequencies) are discussed in the text.

All computations were performed using the double- $\zeta$  plus polarization (DZP) basis sets. The DZP basis sets used for carbon and oxygen add one set of pure spherical harmonic d functions with orbital exponents  $\alpha_d(\text{C}) = 0.75$  and  $\alpha_d(\text{O}) = 0.85$  to the standard Huzinaga–Dunning contracted DZ sets<sup>30,31</sup> and are designated (9s5p1d/4s2p1d). For hydrogen, a set of p polarization functions  $\alpha_p(\text{H}) = 0.75$  is added to the Huzinaga–Dunning DZ set. The loosely contracted DZP basis set for manganese is the Wachters primitive set<sup>32</sup> augmented by two sets of p functions and a set of d functions, contracted following Hood, Pitzer, and Schaefer,<sup>33</sup> designated (14s11p6d/10s8p3d).

The geometries of all structures were fully optimized using the DZP B3LYP and DZP BP86 methods. The vibrational frequencies were determined 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 carried out with the Gaussian 03 program,<sup>34</sup> exercising the fine grid option (75 radial shells, 302 angular points) for evaluating integrals numerically,<sup>35</sup> while the tight ( $10^{-8}$  hartree) designation is the default for the self-consistent-field (SCF) convergence.

## 3. Results

**3.1.  $\text{Cp}_2\text{Mn}_2(\text{CO})_5$ .** Two energetically low-lying structures were found for  $\text{Cp}_2\text{Mn}_2(\text{CO})_5$  (Figure 1 and Table 1). The global minimum of  $\text{Cp}_2\text{Mn}_2(\text{CO})_5$ , **5S-1**, is a  $C_2$  *trans* structure with one normal bridging and two semibridging CO groups. The normal bridging CO group in **5S-1** exhibits a  $\nu(\text{CO})$  frequency at  $1777\text{ cm}^{-1}$ , in the typical region for bridging CO groups (Table 2). The Mn–Mn distance in **5S-1** is predicted to be 2.804 Å, which is consistent with the single bond required to give 18-electron configurations to both manganese atoms. The equivalent Mn–C distances to the bridging carbonyl are 1.982 Å. For the two semibridging carbonyls, the Mn–C distances are 2.955 and 1.790 Å, and the Mn–C–O bond angles are close to  $180^\circ$ . For the terminal carbonyl, the Mn–C distance is 1.773 Å.

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**Table 2.**  $\nu(\text{CO})$  Vibrational Frequencies ( $\text{cm}^{-1}$ ) Predicted for the Two Isomers of  $\text{Cp}_2\text{Mn}_2(\text{CO})_5$  (infrared intensities in parentheses are in  $\text{km/mol}$ ; bridging  $\nu(\text{CO})$  frequencies are in bold type)

	B3LYP	BP86
<b>5S-1</b> ( $C_2$ )	<b>1860(426)</b> , 1990(43), 2013(1229), 2032(1726), 2057(22)	<b>1777(353)</b> , 1906(27), 1927(1020), 1949(1431), 1973(21)
<b>5S-2</b> ( $C_1$ )	<b>1855(452)</b> , 1987(379), 2024(639), 2034(690), 2076(1339)	<b>1769(377)</b> , 1892(355), 1940(546), 1950(511), 1992(1099)

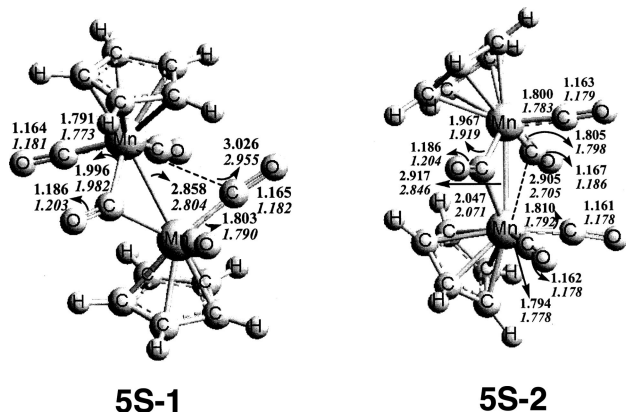
**Table 3.** Total Energies ( $E$ , in hartree), Relative Energies ( $\Delta E$ , in kcal/mol), Spin Contamination ( $\langle S^2 \rangle$ ), Number of Imaginary Vibrational Frequencies ( $N_{\text{img}}$ ), and Mn–Mn Distances ( $\text{\AA}$ ) for the Four Stationary Points of  $\text{Cp}_2\text{Mn}_2(\text{CO})_4$  (two singlets and two triplets)

		4S-1 ( $C_1$ )	4S-2 ( $C_2$ )	4T-1 ( $C_{2h}$ )	4T-2 ( $C_s$ )
B3LYP	$E$	-3142.64589	-3142.64266	-3142.65101	-3142.65030
	$\Delta E$	0.0	2.0	-3.2	-2.8
	$\langle S^2 \rangle$	0	0	2.23	2.23
	$N_{\text{img}}$	0	0	0	1 (12i)
	Mn–Mn	2.526	2.518	2.469	2.476
BP86	$E$	-3143.08574	-3143.07962	-3143.08408	-3143.08343
	$\Delta E$	0.0	3.8	1.0	1.4
	$\langle S^2 \rangle$	0	0	2.06	2.06
	$N_{\text{img}}$	0	0	1 (16i)	1 (21i)
	Mn–Mn	2.509	2.505	2.457	2.461

A second isomer of  $\text{Cp}_2\text{Mn}_2(\text{CO})_5$ , namely, a *cis*  $C_1$  isomer, **5S-2**, is predicted to lie 7.4 kcal/mol above the global minimum **5S-1**. This isomer has one semibridging carbonyl and one bridging carbonyl. The bridging carbonyl exhibits a  $\nu(\text{CO})$  frequency at  $1769 \text{ cm}^{-1}$ . The Mn–C distances for the bridging carbonyl are 1.919 and 2.071  $\text{\AA}$ , and those for the semibridging carbonyl are 2.705 and 1.798  $\text{\AA}$ . The Mn–Mn distance is 2.846  $\text{\AA}$ , which is about 0.04  $\text{\AA}$  longer than that of **5S-1**.

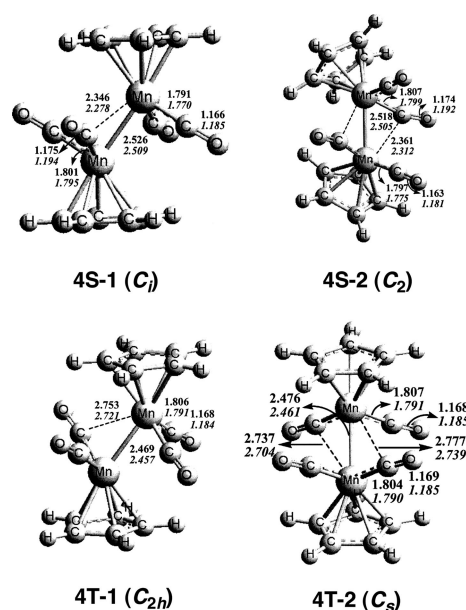
Table 2 summarizes the theoretical  $\nu(\text{CO})$  frequencies for the two  $\text{Cp}_2\text{Mn}_2(\text{CO})_5$  isomers. The calculated  $\nu(\text{CO})$  frequencies of 1777, 1906, 1927, 1949, and  $1973 \text{ cm}^{-1}$  for the global minimum **5S-1** of  $\text{Cp}_2\text{Mn}_2(\text{CO})_5$  are seen to be very close to the experimental infrared frequencies of 1777, 1907, 1934, 1955, and  $1993 \text{ cm}^{-1}$  of the transient species observed in the flash photolysis of  $\text{CpMn}(\text{CO})_3$  in hydrocarbon solution.<sup>8</sup> This species has been suggested to be a  $\text{Cp}_2\text{Mn}_2(\text{CO})_4(\mu\text{-CO})$  isomer of  $\text{Cp}_2\text{Mn}_2(\text{CO})_5$ , presumably with a structure very similar to **5S-1**.

**3.2.  $\text{Cp}_2\text{Mn}_2(\text{CO})_4$ .** Four low-lying structures (two singlets and two triplets) were found for  $\text{Cp}_2\text{Mn}_2(\text{CO})_4$  (Figure 3 and Table 3). The global minimum can be either a singlet structure, **4S-1**, or a triplet structure, **4T-1**, depending on the methods (Table 3). The B3LYP method predicts the triplet structure **4T-1** to lie below the singlet structure **4S-1** by about 3.2 kcal/mol, whereas the BP86 method predicts the singlet isomer **4S-1** to lie below **4T-1** by about 1.0 kcal/mol.

**Figure 2.** The two structures found for  $\text{Cp}_2\text{Mn}_2(\text{CO})_5$ . Distances in Figures 2 to 7 are given in  $\text{\AA}$ . The upper numbers were obtained from B3LYP, while the lower numbers were obtained from BP86. The data in the other figures have the same arrangement.

The lowest lying singlet isomer of  $\text{Cp}_2\text{Mn}_2(\text{CO})_4$  (**4S-1** in Figure 3) exhibits a  $C_1$  *trans* structure with two semibridging CO groups and two terminal CO groups. The Mn–C distances to the two semibridging carbonyls are 1.795 and 2.278  $\text{\AA}$ , and the Mn–C–O bond angles are close to  $180^\circ$ . The Mn–C distances to the two terminal carbonyls are 1.770  $\text{\AA}$ . The two semibridging CO groups exhibit  $\nu(\text{CO})$  frequencies at 1846 and  $1856 \text{ cm}^{-1}$ , while the two terminal CO groups exhibit  $\nu(\text{CO})$  frequencies at 1919 and  $1937 \text{ cm}^{-1}$  (Table 4). The Mn–Mn distance is 2.509  $\text{\AA}$ , in accord with the Mn=Mn double bond required to give each manganese atom an 18-electron configuration. A structure closely related to **4S-1** is found for the known<sup>10</sup> rhenium analogue  $\eta^5\text{-(Me}_5\text{C}_5)_2\text{Re}_2(\text{CO})_4$ .

Another stable singlet  $\text{Cp}_2\text{Mn}_2(\text{CO})_4$  isomer, **4S-2** (Figure 3 and Table 3), has a  $C_2$  *cis* geometry, which is predicted to lie 3.8 kcal/mol above structure **4S-1**. This isomer (**4S-2**) has two semibridging carbonyls. The Mn–C distances to the two semibridging carbonyls are 1.799 and 2.312  $\text{\AA}$ , while those to the terminal carbonyls are 1.775  $\text{\AA}$ . The Mn=Mn distance is 2.505  $\text{\AA}$ , which is very close to that of **4S-1** and also corresponds to the double bond required to give both metal atoms 18-electron configurations.

**Figure 3.** The four isomers of  $\text{Cp}_2\text{Mn}_2(\text{CO})_4$ .



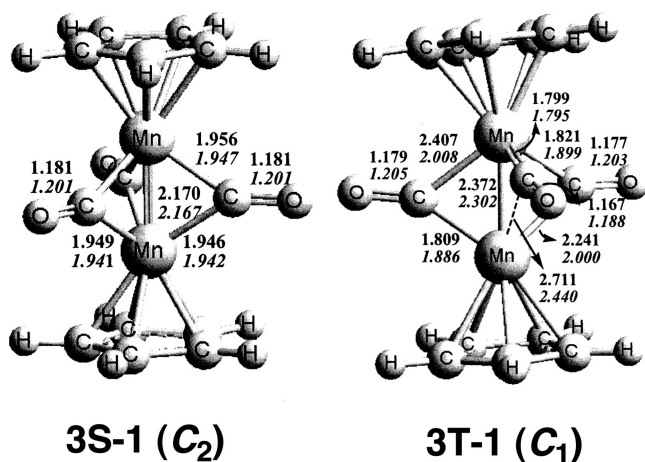
**Table 4.**  $\nu(\text{CO})$  Vibrational Frequencies ( $\text{cm}^{-1}$ ) Predicted for the Four Lowest Energy Stationary Points of  $\text{Cp}_2\text{Mn}_2(\text{CO})_4$  (infrared intensities in parentheses are in  $\text{km/mol}$ ; bridging  $\nu(\text{CO})$  frequencies are shown in bold type)

	B3LYP	BP86
<b>4S-1</b> ( $C_i$ )	1939(0), 1956(1240), 2014(1626), 2031(0)	1846(0), 1856(839), 1919(1410), 1937(0)
<b>4S-2</b> ( $C_2$ )	1947(29), 1964(1265), 2019(225), 2057(1491)	1859(29), 1869(856), 1929(275), 1965(1203)
<b>4T-1</b> ( $C_{2h}$ )	1965(1651), 1969(0), 1986(1538), 2036(0)	1891(0), 1907(1291), 1912(1122), 1956(0)
<b>4T-2</b> ( $C_s$ )	1964(1628), 1968(1), 1985(1537), 2036(0)	1890(2), 1906(1285), 1911(1110), 1955(0)

The triplet stationary point **4T-1** (Table 3 and Figure 3) has  $C_{2h}$  symmetry. It can be considered a minimum since it has all real vibrational frequencies by B3LYP and a negligibly small imaginary vibrational frequency of  $16i \text{ cm}^{-1}$  by BP86. All four CO groups in **4T-1** are semibridging, with Mn–C distances of 1.791 and 2.721 Å. The  $C_s$  isomer **4T-2** has a similar geometry (except for the orientation of the Cp rings) and similar energy to **4T-1** (Table 3). Structure **4T-2** has a very small imaginary vibrational frequency of  $21i \text{ cm}^{-1}$ . There is relatively little spin contamination for **4T-1** and **4T-2**, i.e.,  $\langle S^2 \rangle = 2.06$ . The Mn–Mn distance in **4T-1** is 2.457 Å, which is shorter than that in **4S-1** by  $\sim 0.04$  Å.

**3.3.  $\text{Cp}_2\text{Mn}_2(\text{CO})_3$ .** Two energetically low-lying structures were found for  $\text{Cp}_2\text{Mn}_2(\text{CO})_3$  (Figure 4 and Table 5). The global minimum **3S-1** is a singlet with three symmetrical bridging CO groups. The structure of **3S-1** is very close to the  $(\eta^5\text{-Me}_5\text{C}_5)_2\text{Mn}_2(\text{CO})_3$  structure reported experimentally.<sup>6,7</sup> This  $\text{Cp}_2\text{Mn}_2(\mu\text{-CO})_3$  isomer **3S-1** is predicted to exhibit strong infrared-active bridging  $\nu(\text{CO})$  frequencies at 1814 and 1815  $\text{cm}^{-1}$  (Table 6) as compared with the experimental observation of a very strong  $\nu(\text{CO})$  frequency at 1785  $\text{cm}^{-1}$  in hexane solution for  $(\eta^5\text{-Me}_5\text{C}_5)_2\text{Mn}_2(\text{CO})_3$ .<sup>6</sup> The shift of the  $\nu(\text{CO})$  band in  $(\eta^5\text{-Me}_5\text{C}_5)_2\text{Mn}_2(\text{CO})_3$  to 30  $\text{cm}^{-1}$  below that predicted for the corresponding isomer of  $\text{Cp}_2\text{Mn}_2(\text{CO})_3$  can arise from the electron-releasing properties of the methyl substituents in the  $\eta^5\text{-Me}_5\text{C}_5$  ligand as compared with the  $\eta^5\text{-C}_5\text{H}_5$  ligand. An infrared-inactive  $\nu(\text{CO})$  frequency of **3S-1** is also predicted to appear at 1849  $\text{cm}^{-1}$  in **3S-1**. The infrared inactivity of this  $\nu(\text{CO})$  frequency may relate to the fact that the symmetry of **3S-1** increases from the actual  $C_2$  point group to  $D_{3h}$  if the cyclopentadienyl rings are approximated by circles rather than the actual pentagons.

The Mn≡Mn distance in **3S-1** is predicted to be 2.167 Å, consistent with the formal triple bond required to give each



**Figure 4.** Singlet and triplet structures of  $\text{Cp}_2\text{Mn}_2(\text{CO})_3$ .

**Table 5.** Total Energies ( $E$ , in hartree), Relative Energies ( $\Delta E$ , in kcal/mol), Number of Imaginary Vibrational Frequencies ( $N_{\text{img}}$ ), and Mn–Mn Distances (Å) for the Two Isomers of  $\text{Cp}_2\text{Mn}_2(\text{CO})_3$

		<b>3S-1</b> ( $C_2$ )	<b>3T-1</b> ( $C_1$ )
B3LYP	$E$	−3029.29136	−3029.27611
	$\Delta E$	0.0	9.6
	$N_{\text{img}}$	0	0
BP86	$E$	−3029.73388	−3029.69810
	$\Delta E$	0.0	22.5
	$N_{\text{img}}$	0	0
	Mn–Mn	2.170	2.372
	Mn–Mn	2.167	2.302

**Table 6.**  $\nu(\text{CO})$  Vibrational Frequencies ( $\text{cm}^{-1}$ ) Predicted for the Two Structures of  $\text{Cp}_2\text{Mn}_2(\text{CO})_3$  (infrared intensities in parentheses are in  $\text{km/mol}$ ; bridging  $\nu(\text{CO})$  frequencies are in bold type)

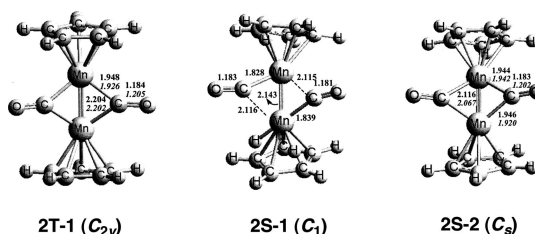
	B3LYP	BP86
<b>3S-1</b> ( $C_2$ )	<b>1909(1102), 1910(1120),</b> <b>1943(0)</b>	<b>1814(876), 1815(893),</b> <b>1849(0)</b>
<b>3T-1</b> ( $C_1$ )	<b>1918(1160), 1938(620),</b> 2011(479)	<b>1786(907), 1805(291),</b> 1899(477)

manganese atom the favored 18-electron configuration and in agreement with the 2.17 Å Mn≡Mn distance found by X-ray crystallography<sup>7</sup> for  $(\eta^5\text{-Me}_5\text{C}_5)_2\text{Mn}_2(\mu\text{-CO})_3$ . For the bridging carbonyls in **3S-1**, the Mn–C distances fall in the narrow range 1.941 to 1.947 Å.

The triplet isomer **3T-1** of  $\text{Cp}_2\text{Mn}_2(\text{CO})_3$  is a  $C_1$  structure with one semibridging and two normal bridging carbonyl groups lying 22.5 kcal/mol (BP86) or 9.6 kcal/mol (B3LYP) above **3S-1** (Figure 4 and Table 5). The suggested degree of spin contamination of **3T-1** is very small, i.e.,  $\langle S^2 \rangle = 2.04$ . The Mn–C distances to one of the bridging CO groups are 1.886 and 2.008 Å, and those to the other bridging CO group are 1.899 and 2.000 Å. The Mn–C distances to the semibridging CO group are 1.795 and 2.440 Å. The Mn–C–O bond angle is close to 180°, confirming the semibridging character of this CO group. The  $\nu(\text{CO})$  frequencies at 1786 and 1805  $\text{cm}^{-1}$  can be assigned to the normal bridging CO groups, whereas the  $\nu(\text{CO})$  frequency at 1899  $\text{cm}^{-1}$  can be assigned to the semibridging CO group (Table 6). The Mn–Mn distance of 2.302 Å in **3T-1**, which is longer than that in **3S-1** by 0.14 Å (BP86), corresponds to the Mn=Mn double bond required to give 17-electron configurations to both manganese atoms in **3T-1**.

**3.4.  $\text{Cp}_2\text{Mn}_2(\text{CO})_2$ .** Three low-lying structures (one triplet and two singlets) were found for  $\text{Cp}_2\text{Mn}_2(\text{CO})_2$  (Figure 5 and Table 7). In all three of these  $\text{Cp}_2\text{Mn}_2(\text{CO})_2$  structures both CO groups are fairly symmetrical bridging CO groups, as indicated by their infrared  $\nu(\text{CO})$  frequencies in the range 1790–1826  $\text{cm}^{-1}$  (Table 8).

The global minimum **2T-1** is predicted to be a  $C_{2v}$  triplet with two bridging CO groups. These bridging CO groups are predicted to exhibit  $\nu(\text{CO})$  frequencies at 1790 and 1805  $\text{cm}^{-1}$  (Table 8). There is a relatively small degree of spin contamination, i.e.,  $\langle S^2 \rangle = 2.04$ . Structure **2T-1** has a very small imaginary



**Figure 5.** The three  $\text{Cp}_2\text{Mn}_2(\text{CO})_2$  isomers.

**Table 7.** Total Energies ( $E$ , in hartree), Relative Energies ( $\Delta E$ , in kcal/mol), Number of Imaginary Vibrational Frequencies ( $N_{\text{img}}$ ), and Mn–Mn Distances (Å) for the Three Stationary Points of  $\text{Cp}_2\text{Mn}_2(\text{CO})_2$ 

		2T-1 ( $C_{2v}$ )	2S-1 ( $C_1$ )	2S-2 ( $C_s$ )
B3LYP	$E$	−2915.88881	−2915.85826	−2915.85741
	$\Delta E$	0.0	19.2	19.7
	$N_{\text{img}}$	2 (17i, 14i)	0	1 (132i)
	Mn–Mn	2.204	2.143	2.116
BP86	$E$	−2916.29983	(same as 2S-2)	−2916.29454
	$\Delta E$	0.0		3.3
	$N_{\text{img}}$	1 (19i)		1 (23i)
	Mn–Mn	2.202		2.067

**Table 8.**  $\nu(\text{CO})$  Vibrational Frequencies ( $\text{cm}^{-1}$ ) Predicted for the Three Lowest Energy Isomers of  $\text{Cp}_2\text{Mn}_2(\text{CO})_2$  (infrared intensities in parentheses are in  $\text{km/mol}$ ).

	B3LYP	BP86
2T-1 ( $C_{2v}$ )	1881(1312), 1901(178)	1790(974), 1805(105)
2S-1 ( $C_1$ )	1912(1193), 1929(318)	1805(1002), 1826(197)
2S-2 ( $C_s$ )	1897(1291), 1918(260)	1805(1002), 1825(195)

**Table 9.** Dissociation Energies (kcal/mol) for the Successive Removal of Carbonyl Groups from the  $\text{Cp}_2\text{Mn}_2(\text{CO})_n$  Derivatives

	B3LYP/ DZP	BP86/ DZP
$\text{Cp}_2\text{Mn}_2(\text{CO})_5(5\text{S-1}) \rightarrow \text{Cp}_2\text{Mn}_2(\text{CO})_4(4\text{S-1}) + \text{CO}$	34.1	42.4
$\text{Cp}_2\text{Mn}_2(\text{CO})_4(4\text{S-1}) \rightarrow \text{Cp}_2\text{Mn}_2(\text{CO})_3(3\text{S-1}) + \text{CO}$	16.2	15.5
$\text{Cp}_2\text{Mn}_2(\text{CO})_3(3\text{S-1}) \rightarrow \text{Cp}_2\text{Mn}_2(\text{CO})_2(2\text{T-1}) + \text{CO}$	46.4	67.0

vibrational frequency of 19i, which becomes real when a finer (120, 974) integration grid is used, indicating that this small imaginary frequency arises from numerical integration error. The Mn–C distances for the two bridging carbonyls are 1.926 Å. The Mn≡Mn distance is 2.202 Å, in accord with the triple bond required to give each manganese atom a 17-electron configuration consistent with the triplet electronic state.

The two DFT methods disagree on the singlet structures of  $\text{Cp}_2\text{Mn}_2(\text{CO})_2$ . The isomer **2S-2** has a  $C_s$  structure with two bridging CO groups lying 3.3 kcal/mol (BP86) or 19.7 kcal/mol (B3LYP) above **2T-1** (Table 7). The Mn–C distances for the two bridging carbonyls in **2S-2** are 1.942 and 1.920 Å by BP86 and 1.944 and 1.946 Å by B3LYP. The Mn–Mn distance in **2S-2** is 2.116 (B3LYP) or 2.067 (BP86) Å, which is shorter than that in **2T-1** by  $\sim 0.1$  Å, suggesting the formal Mn–Mn quadruple bond required to give 18-electron configurations to both manganese atoms. With the BP86 method structure **2S-2** has a very small imaginary vibrational frequency of 23i  $\text{cm}^{-1}$ , which can be removed with a finer grid (120, 974), indicating that this small imaginary frequency arises from numerical integration error. However, **2S-2** has a significant imaginary vibrational frequency of 132i  $\text{cm}^{-1}$  by B3LYP. Following the corresponding normal mode, structure **2S-2** collapses to **2S-1**, which is a  $C_1$  structure lying 0.5 kcal/mol below **2S-2**. The Mn–C distances for one of the semibridging carbonyls are 1.828 and 2.116 Å, and for the other one are 1.839 and 2.115 Å. The Mn–Mn distance is 2.143 Å, which may still be a formal Mn–Mn quadruple bond. With BP86, structure **2S-1** is identical to **2S-2**.

**3.5. Dissociation and Disproportionation Reactions.** Table 9 shows the dissociation energies for the reactions  $\text{Cp}_2\text{Mn}_2(\text{CO})_n \rightarrow \text{Cp}_2\text{Mn}_2(\text{CO})_{n-1} + \text{CO}$ . The dissociation energy for the loss of one CO group from  $\text{Cp}_2\text{Mn}_2(\text{CO})_4$  to give  $\text{Cp}_2\text{Mn}_2(\text{CO})_3$  is seen to be small (15.5 kcal/mol) relative to that for the further dissociation of CO from  $\text{Cp}_2\text{Mn}_2(\text{CO})_3$  to give  $\text{Cp}_2\text{Mn}_2(\text{CO})_2$  (67.0 kcal/mol). This is in accord with the experimental observation of  $(\eta^5\text{-Me}_5\text{C}_5)_2\text{Mn}_2(\text{CO})_3$  rather than the tetracar-

**Table 10.** Disproportionation Energies (kcal/mol)

	B3LYP/ DZP	BP86/ DZP
$2\text{Cp}_2\text{Mn}_2(\text{CO})_4 \rightarrow \text{Cp}_2\text{Mn}_2(\text{CO})_5 + \text{Cp}_2\text{Mn}_2(\text{CO})_3$	−17.9	−27.0
$2\text{Cp}_2\text{Mn}_2(\text{CO})_3 \rightarrow \text{Cp}_2\text{Mn}_2(\text{CO})_2 + \text{Cp}_2\text{Mn}_2(\text{CO})_4$	30.1	51.6
$2\text{Cp}_2\text{Mn}_2(\text{CO})_2 \rightarrow \text{Cp}_2\text{Mn}_2(\text{CO}) + \text{Cp}_2\text{Mn}_2(\text{CO})_3$	−24.2	−4.1

**Table 11.** Total Energies ( $E$ , in hartree) for  $\text{CpMn}(\text{CO})_n$  ( $n = 3, 2, 1$ ) and Number of Imaginary Vibrational Frequencies ( $N_{\text{img}}$ ) for Each Structure

	CpMn(CO)	CpMn(CO) <sub>2</sub>	CpMn(CO) <sub>3</sub>	CO
single	( $C_s$ )	( $C_s$ )	( $C_s$ )	
B3LYP/ $E$	−1457.88391	−1571.30007	−1684.71391	−113.328656
DZP $N_{\text{img}}$	0	0	0	0
BP86/ $E$	−1458.07593	−1571.50774	−1684.93693	−113.32724
DZP $N_{\text{img}}$	0	0	0	0

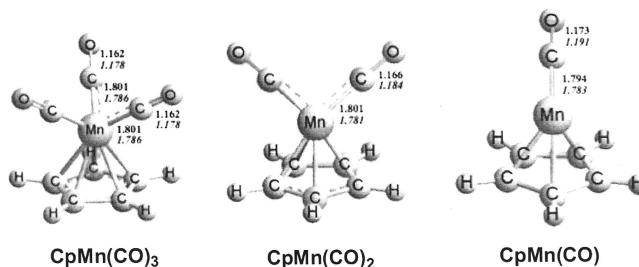
**Table 12.** Dissociation Energies of the Binuclear Cyclopentadienylmanganese Carbonyls into Mononuclear Fragments (kcal/mol)

	B3LYP/DZP	BP86/DZP
$\text{Cp}_2\text{Mn}_2(\text{CO})_5 \rightarrow \text{CpMn}(\text{CO})_3 + \text{CpMn}(\text{CO})_2$	9.4	22.5
$\text{Cp}_2\text{Mn}_2(\text{CO})_4 \rightarrow 2\text{CpMn}(\text{CO})_2$	28.7	44.1
$\text{Cp}_2\text{Mn}_2(\text{CO})_3 \rightarrow \text{CpMn}(\text{CO})_2 + \text{CpMn}(\text{CO})$	67.4	94.3
$\text{Cp}_2\text{Mn}_2(\text{CO})_2 \rightarrow 2\text{CpMn}(\text{CO})$	75.9	92.9

bonyl or dicarbonyl from the decomposition of  $(\eta^5\text{-Me}_5\text{C}_5)_2\text{Mn}(\text{CO})_2(\text{OC}_4\text{H}_8)$ .<sup>6</sup>

Table 10 lists the energies of the disproportionation reactions  $2\text{Cp}_2\text{Mn}_2(\text{CO})_n \rightarrow \text{Cp}_2\text{Mn}_2(\text{CO})_{n+1} + \text{Cp}_2\text{Mn}_2(\text{CO})_{n-1}$ . These data indicate that the experimentally observed  $\text{Cp}_2\text{Mn}_2(\text{CO})_3$  is stable with respect to such disproportionation, whereas  $\text{Cp}_2\text{Mn}_2(\text{CO})_4$  is unstable with respect to similar disproportionation. The exothermic disproportionation of  $\text{Cp}_2\text{Mn}_2(\text{CO})_4$  as well as its relatively low CO dissociation energy (Table 9) suggests such derivatives are unlikely to be stable molecules.

Also of interest is the dissociation of the  $\text{Cp}_2\text{Mn}_2(\text{CO})_n$  derivatives into mononuclear  $\text{CpMn}(\text{CO})_m$  fragments. In order to obtain such energetic data, the structures of the mononuclear  $\text{CpMn}(\text{CO})_m$  were optimized by the same DFT methods as used to study the binuclear derivatives (Figure 6

**Figure 6.** Optimized  $\text{CpMn}(\text{CO})_m$  ( $m = 3, 2, 1$ ) fragments used to calculate the dissociation energies of  $\text{Cp}_2\text{Mn}_2(\text{CO})_n$  listed in Table 12.

and Table 11). Using this information the dissociation energies of the binuclear metal–carbonyl derivatives into mononuclear fragments were obtained (Table 12). These data show that the global minima of all of the  $\text{Cp}_2\text{Mn}_2(\text{CO})_n$  derivatives are stable with respect to dissociation into mononuclear fragments. Also the dissociation energies of  $\text{Cp}_2\text{Mn}_2(\text{CO})_n$  increase monotonically with decreasing  $n$  in accord with the corresponding increase in formal metal–metal bond order.

#### 4. Discussion

The present theoretical studies predict a structure for  $\text{Cp}_2\text{Mn}_2(\text{CO})_5$  (**5S-1**) with a single symmetrical bridging carbonyl group, a *trans* arrangement of the cyclopentadienyl rings, and a Mn–Mn distance consistent with the single bond required to give each manganese atom the favored 18-electron rare gas electronic configuration analogous to the experimentally known rhenium analogue.<sup>9</sup> This species is produced as a transient intermediate in the laser flash photolysis of  $\text{CpMn}(\text{CO})_3$  in hydrocarbon media,<sup>8</sup> as indicated by the close agreement of the experimental  $\nu(\text{CO})$  frequencies with those predicted for **5S-1**.

Four structures (two singlet and two triplets) of very similar energies (within about 7 kcal/mol) are found for  $\text{Cp}_2\text{Mn}_2(\text{CO})_4$ . These structures, with two to four semibridging CO groups, are similar to the known<sup>36</sup> structure of stable  $\text{Cp}_2\text{Cr}_2(\text{CO})_4$  as well as that of  $(\eta^5\text{-Me}_5\text{C}_5)_2\text{Re}_2(\text{CO})_4$  (ref 10). However, the  $\text{Cp}_2\text{Mn}_2(\text{CO})_4$  requires only a metal–metal double bond for each metal atom to attain the favored 18-electron configuration, in contrast to the chromium compound, which requires a  $\text{Cr}=\text{Cr}$  triple bond. Thus the Mn=Mn distance in  $\text{Cp}_2\text{Mn}_2(\text{CO})_4$  is predicted to be 2.509 Å, in contrast to the shorter  $\text{Cr}=\text{Cr}$  distance<sup>36</sup> of 2.239 Å in  $\text{Cp}_2\text{Cr}_2(\text{CO})_4$ . The predicted exothermic disproportionation of  $\text{Cp}_2\text{Mn}_2(\text{CO})_4$  to  $\text{Cp}_2\text{Mn}_2(\text{CO})_5$  +  $\text{Cp}_2\text{Mn}_2(\text{CO})_3$  makes it unlikely that  $\text{Cp}_2\text{Mn}_2(\text{CO})_4$  will be synthesized as a stable compound.

Our DFT studies predict a triply bridged structure for  $\text{Cp}_2\text{Mn}_2(\text{CO})_3$  (**3S-1**) in accord with experiment. A related tribridged structure is known for  $\text{Cp}_2\text{Fe}_2(\text{CO})_3$ , which has been characterized by X-ray diffraction.<sup>12</sup> The Mn≡Mn triple bond distance of 2.167 Å in  $\text{Cp}_2\text{Mn}_2(\text{CO})_3$  is, as expected, shorter than the Fe=Fe double bond distance of 2.268 Å in  $\text{Cp}_2\text{Fe}_2(\text{CO})_3$  and essentially identical to the experimental 2.17 Å Mn≡Mn distance in  $(\eta^5\text{-Me}_5\text{C}_5)_2\text{Mn}_2(\text{CO})_3$ .

For  $\text{Cp}_2\text{Mn}_2(\text{CO})_2$  our studies predict that a doubly bridged triplet with an Mn≡Mn triple bond is of lower energy than the corresponding singlet with a shorter Mn–Mn quadruple bond, again suggesting unfavorable energetics in increasing the metal–metal bond order from three to four.

It is also interesting to compare the predicted structures for the binuclear cyclopentadienylmanganese carbonyls with isoelectronic binuclear chromium carbonyls.<sup>37</sup> Since the Cp ligand uses three orbitals for bonding to the manganese atom, the CpMn unit can be considered to be isoelectronic with a  $\text{Cr}(\text{CO})_3$  unit. However, a Cp ligand is less sterically demanding than three CO groups, so some differences between the two systems are expected.

In this connection the unknown  $\text{Cr}_2(\text{CO})_{11}$ , studied theoretically in our previous work,<sup>38</sup> may be considered to be an analogue of  $\text{Cp}_2\text{Mn}_2(\text{CO})_5$  discussed in this paper. However, there is an important difference in the stability of these compounds since  $\text{Cp}_2\text{Mn}_2(\text{CO})_5$  is thermodynamically stable with respect to dissociation into  $\text{CpMn}(\text{CO})_3$  +  $\text{CpMn}(\text{CO})_2$  fragments, whereas  $\text{Cr}_2(\text{CO})_{11}$  is thermodynamically unstable with respect to dissociation into  $\text{Cr}(\text{CO})_6$  +  $\text{Cr}(\text{CO})_5$  fragments,<sup>38</sup> therefore accounting for the fact that it has never been prepared. This may be a consequence of the greater steric requirements of three CO groups relative to a single Cp ring.

The lowest energy structure for  $\text{Cp}_2\text{Mn}_2(\text{CO})_4$  is a singlet with an Mn=Mn double bond and no bridging carbonyl groups. This is different from the predicted structure for the unknown  $\text{Cr}_2(\text{CO})_{10}$ , which has two bridging CO groups and a chromium–chromium distance rather long for a double bond.<sup>39</sup> A higher lying structure for  $\text{Cr}_2(\text{CO})_{10}$ , namely, a triplet with a  $\text{Cr}=\text{Cr}$  double bond analogous to the double bond in  $\text{O}_2$ , is also found and is related to the predicted singlet structure of  $\text{Cp}_2\text{Mn}_2(\text{CO})_4$  except for the spin multiplicity. This difference in the spin multiplicity may relate to a difference in the frontier orbital separation because of the lower symmetry of the  $\text{CpMn}(\text{CO})_2$  unit relative to the  $\text{Cr}(\text{CO})_5$  unit forming the dimer.

In contrast to the  $\text{Cp}_2\text{Mn}_2(\text{CO})_5/\text{Cr}_2(\text{CO})_{11}$  and  $\text{Cp}_2\text{Mn}_2(\text{CO})_4/\text{Cr}_2(\text{CO})_{11}$  isoelectronic pairs, the predicted  $\text{Cp}_2\text{Mn}_2(\text{CO})_3$  and  $\text{Cr}_2(\text{CO})_9$  structures<sup>40</sup> are quite analogous since both compounds form triply bridged structures with metal–metal distances corresponding to the triple bonds required to give the metal atoms the favored 18-electron configuration.

The predicted structure for  $\text{Cp}_2\text{Mn}_2(\text{CO})_2$  is a triplet with a Mn≡Mn triple bond. The analogous  $\text{Cr}_2(\text{CO})_8$  also appears to have a  $\text{Cr}=\text{Cr}$  triple bond rather than the quadruple bond required to give the chromium atoms the 18-electron configuration.<sup>41</sup> The next two higher lying structures of  $\text{Cr}_2(\text{CO})_8$  avoid a quadruple bond by having two four-electron donor bridging CO groups, leading to a  $\text{Cr}=\text{Cr}$  double bond consistent with the chromium–chromium distance. An analogous structure is not found for  $\text{Cp}_2\text{Mn}_2(\text{CO})_2$ .

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**Supporting Information Available:** Tables S1–S10: the theoretical harmonic vibrational frequencies for the  $\text{Cp}_2\text{Mn}_2(\text{CO})_n$  ( $n = 2$ –5) structures using the BP86 method; Tables S11–S20: the theoretical Cartesian coordinates for the  $\text{Cp}_2\text{Mn}_2(\text{CO})_n$  ( $n = 2$ –5) structures using the BP86 method; the complete Gaussian reference (ref 34) This material is available free of charge via the Internet at <http://pubs.acs.org>.

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