Unsaturation in Binuclear Benzene Manganese Carbonyls: Comparison with Isoelectronic Cyclopentadienyliron and Cyclobutadienecobalt Derivatives

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The binuclear benzenemanganese carbonyls $(\eta^6\text{-}C_6H_6)_2Mn_2(CO)_n$ (n = 4, 3, 2, 1) have been studied by density functional theory (DFT) using the B3LYP and BP86 methods. The singlet doubly bridged and unbridged isomers of the saturated $(\eta^6\text{-}C_6H_6)_2Mn_2(CO)_4$ are nearly degenerate, suggesting a highly fluxional system. The global minimum of $(\eta^6\text{-}C_6H_6)_2Mn_2(CO)_3$ is a triplet electronic state—a triply bridged isomer analogous to the known isoelectronic triplet $Cp_2Fe_2(\mu\text{-}CO)_3$. The doubly bridged singlet structure $(\eta^6\text{-}C_6H_6)_2Mn_2(CO)(\mu\text{-}CO)_2$ lies 9 kcal/mol (B3LYP) or 7 kcal/mol (BP86) above this global minimum. The global minimum of $(\eta^6\text{-}C_6H_6)_2Mn_2(CO)_2$ is a doubly bridged structure with a short manganese−manganese distance suggestive of a Mn≡Mn triple bond. Singlet and triplet structures are found for $(\eta^6\text{-}C_6H_6)_2Mn_2(CO)$ with a two-electron donor CO group and metal−metal distances suggesting a M−M quadruple bond for the singlet state and a M≡M triple bond for the triplet state.

1. Introduction

Benzene manganese carbonyl chemistry dates back to 1961 when Winkhaus, Pratt, and Wilkinson[1] synthesized the cation $(\eta^6\text{-}C_6H_6)Mn(CO)_3^+$ by the reaction of $Mn(CO)_5Br$ in boiling benzene with aluminum chloride as a strong Lewis acid catalyst. The scope of η^6-arene manganese carbonyl chemistry was originally found to be limited by the tendency of the benzene ring in $(\eta^6\text{-}C_6H_6)Mn(CO)_3^+$ to undergo addition reactions with nucleophiles to give η^5-cyclohexadienylmanganese derivatives.[2,3] Thus, reaction of $(\eta^6\text{-}C_6H_6)Mn(CO)_3^+$ with $LiAlH_4$ was found to give $(\eta^5\text{-}C_6H_7)Mn(CO)_3$ rather than a benzene manganese carbonyl derivative (Figure 1).

The scope of η^6-arene manganese carbonyl chemistry was extended significantly approximately 30 years later when Eyman and co-workers[4–6] found that use of hexamethylbenzene rather than unsubstituted benzene suppressed nucleophilic addition to give cyclohexadienylmanganese derivatives. Thus, a greater variety of manganese carbonyl derivatives with η^6-arene ligands could be prepared. Particularly important among these η^6-hexamethylbenzene manganese carbonyl derivatives is the dimer $(\eta^6\text{-}Me_6C_6)_2Mn_2(CO)_2(\mu\text{-}CO)_2$ (Figure 1), which is isoelectronic with $\eta^5\text{-}Cp_2Fe_2(CO)_2(\mu\text{-}CO)_2$, which has been known for more than 50 years[7] and is a very important synthon in cyclopentadienyliron carbonyl chemistry.

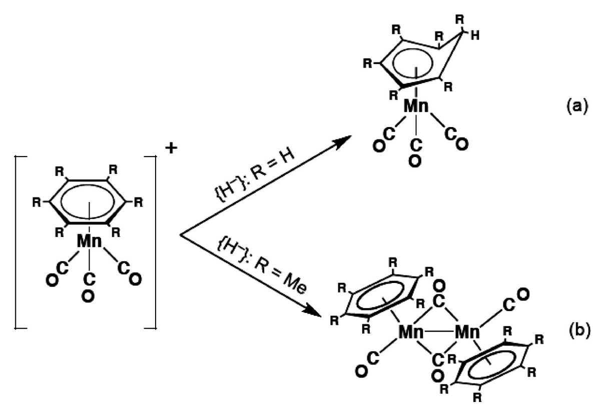

Figure 1. Alternative reduction pathways of $(\eta^6\text{-arene})Mn(CO)_3^+$ cations to give η^5-cyclohexadienyl derivatives (a: R = H) or binuclear $(\eta^6\text{-arene})_2Mn_2(CO)_4$ derivatives (b: R = Me).

An important aspect of the chemical reactivity of $\eta^5\text{-}Cp_2Fe_2(CO)_4$ is its decarbonylation to give unsaturated derivatives. Thus, a major product from the photolysis of $\eta^5\text{-}Cp_2Fe_2(CO)_4$ is the triply bridged triplet $\eta^5\text{-}Cp_2Fe_2(\mu\text{-}CO)_3$, which can be considered to have an Fe═Fe double bond of σ + 2/2 π-type analogous to the O═O double bond in O_2.[8] In addition, further decarbonylation of $\eta^5\text{-}Cp_2Fe_2(CO)_4$ in a low temperature matrix[9] appears to give a dicarbonyl $Cp_2Fe_2(CO)_2$. A related dicarbonyl $Cp_2Fe_2(CO)_2$ is a probable intermediate in the pyrolysis[10] of $\eta^5\text{-}Cp_2Fe_2(CO)_4$ at around 100 °C to give the very stable tetramer $\eta^5\text{-}Cp_4Fe_4(\mu_3\text{-}CO)_4$. Such unsaturated

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binuclear cyclopentadienyliron carbonyls have also been investigated recently by density functional theory.[11]

The availability of (η^6-$Me_6C_6)_2Mn_2(CO)_2(\mu$-$CO)_2$ provides access to analogous unsaturated binuclear η^6-hexamethylbenzene manganese carbonyl derivatives through various types of decarbonylation reactions. In order to probe such possibilities, we have investigated such compounds by DFT methods using methods analogous to previous work[11] on unsaturated binuclear cyclopentadienyliron carbonyl derivatives. Benzene rather than hexamethylbenzene manganese carbonyl derivatives were chosen for these DFT studies. This paper presents our results on (η^6-$C_6H_6)_2Mn_2(CO)_n$ ($n = 4, 3, 2, 1$) derivatives. The availability of these results combined with previous research on not only the cyclopentadienyliron derivatives η^5-$Cp_2Fe_2(CO)_n$ but also isoelectronic cyclobutadienecobalt derivatives[12] (η^4-$C_4H_4)_2$-$Co_2(CO)_n$ ($n = 4, 3, 2, 1$) provides an opportunity to examine the effect of ring size on the preferred types of unsaturated metal carbonyl derivatives in isoelectronic systems.

2. Theoretical Methods

Electron correlation effects were included by employing density functional theory (DFT) methods, which have evolved as a practical and effective computational tool, especially for organometallic compounds.[13–20] Two DFT methods were used in this study. The first functional is the hybrid B3LYP method, which incorporates Becke's three-parameter exchange functional (B3) with the Lee, Yang, and Parr (LYP) correlation functional.[21,22] The second approach is the BP86 method, which marries Becke's 1988 exchange functional (B) with Perdew's 1986 correlation functional.[23,24] It has been noted that the BP86 method may be somewhat more reliable than the B3LYP method for the type of organometallic systems considered in this paper.[25,26]

The geometries of all of the structures were fully optimized using both the DZP B3LYP and DZP BP86 methods. The harmonic vibrational frequencies were determined at the same levels by evaluating analytically the second derivatives of the energy with respect to the nuclear coordinates. The corresponding infrared intensities were evaluated analytically as well. All of the computations were carried out with the Gaussian 94 program in which the fine grid (75, 302) is the default for evaluating integrals numerically and the tight (10^{-8} hartree) designation is the default for the energy convergence.[27]

For carbon and oxygen, the double-ζ plus polarization (DZP) basis set used here 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 and is designated (9s5p1d/4s2p1d).[28,29] For H, a set of p polarization functions $\alpha_p(H) = 0.75$ is added to the Huzinaga−Dunning DZ sets. For Mn, in our loosely contracted DZP basis set, the Wachters' primitive set is used but augmented by two sets of p functions and one set of d functions. This basis is contracted following Hood et al. and designated (14s11p6d/10s8p3d).[30,31]

In the search for minima, low magnitude imaginary vibrational frequencies are suspect because the numerical integration procedures used in existing DFT methods have significant limitations.[32] Thus, an imaginary vibrational frequency of magnitude less than $100i$ cm^{-1} should imply that there is a minimum with energy very similar to that of the stationary point in question. In most cases, we do not follow the eigenvectors corresponding to imaginary frequencies less than $100i$ cm^{-1} in search of another minimum.[33]

The optimized geometries from these computations are depicted in Figures 2–5 with all bond distances given in angstroms.

3. Results

3.1. Molecular Structures. 3.1.1. ($C_6H_6)_2Mn_2(CO)_4$. Four possible isomers of $(C_6H_6)_2Mn_2(CO)_4$, namely doubly CO-bridged *cis* and *trans* isomers as well as unbridged *cis* and *trans* isomers, were used as starting points for optimizations with the B3LYP and BP86 methods. The optimized structures are shown in Figure 2, and the optimized structural parameters are presented in Tables 1 and 2 for the singlet- and triplet-state isomers, respectively.

Three stable singlet isomers of $(C_6H_6)_2Mn_2(CO)_4$ were obtained (Table 1), namely the C_{2h} *trans*-dibridged isomer **Ia-s**, the C_2 *cis*-dibridged isomer **Ib-s**, and the C_{2h} *trans*-unbridged isomer **Ic-s.** The relative energies of these three singlet isomers were within 5 kcal/mol, suggesting a highly fluxional system. In addition, two triplet isomers of $(C_6H_6)_2Mn_2(CO)_4$ were found, namely the C_s *trans*-dibridged isomer **Ia-t** and the C_1 *cis* doubly bridged isomer **Ib-t** (Table 2). These triplet isomers were significantly higher in energy than any of the singlet isomers of $(C_6H_6)_2Mn_2(CO)_4$. Thus, the lowest energy triplet isomer **Ia-t** was 18.0 kcal/mol (B3LYP) or 30.2 kcal/mol (BP86) above the global minimum singlet isomer **Ia-s**. The *trans* unbridged triplet isomer of $(C_6H_6)_2Mn_2(CO)_4$ **Ic-t** essentially dissociates to $(C_6H_6)Mn(CO)_2$ units upon optimization. The *cis* unbridged isomers of $(C_6H_6)_2Mn_2(CO)_4$ are not stationary points but collapse to the *cis*-dibridged stable isomers **Ib** upon optimization for both the singlet and triplet.

The *cis* doubly bridged isomer **Ib-s** and *trans*-unbridged isomer **Ic-s** have real vibrational frequencies, confirming that they are genuine minima on the respective potential energy surfaces. However, the *trans* doubly bridged isomer **Ia-s** is found to have two very small imaginary vibrational frequencies of $26i$ and $15i$ cm^{-1} (B3LYP) or $17i$ cm^{-1} (BP86), which may arise from integration error.

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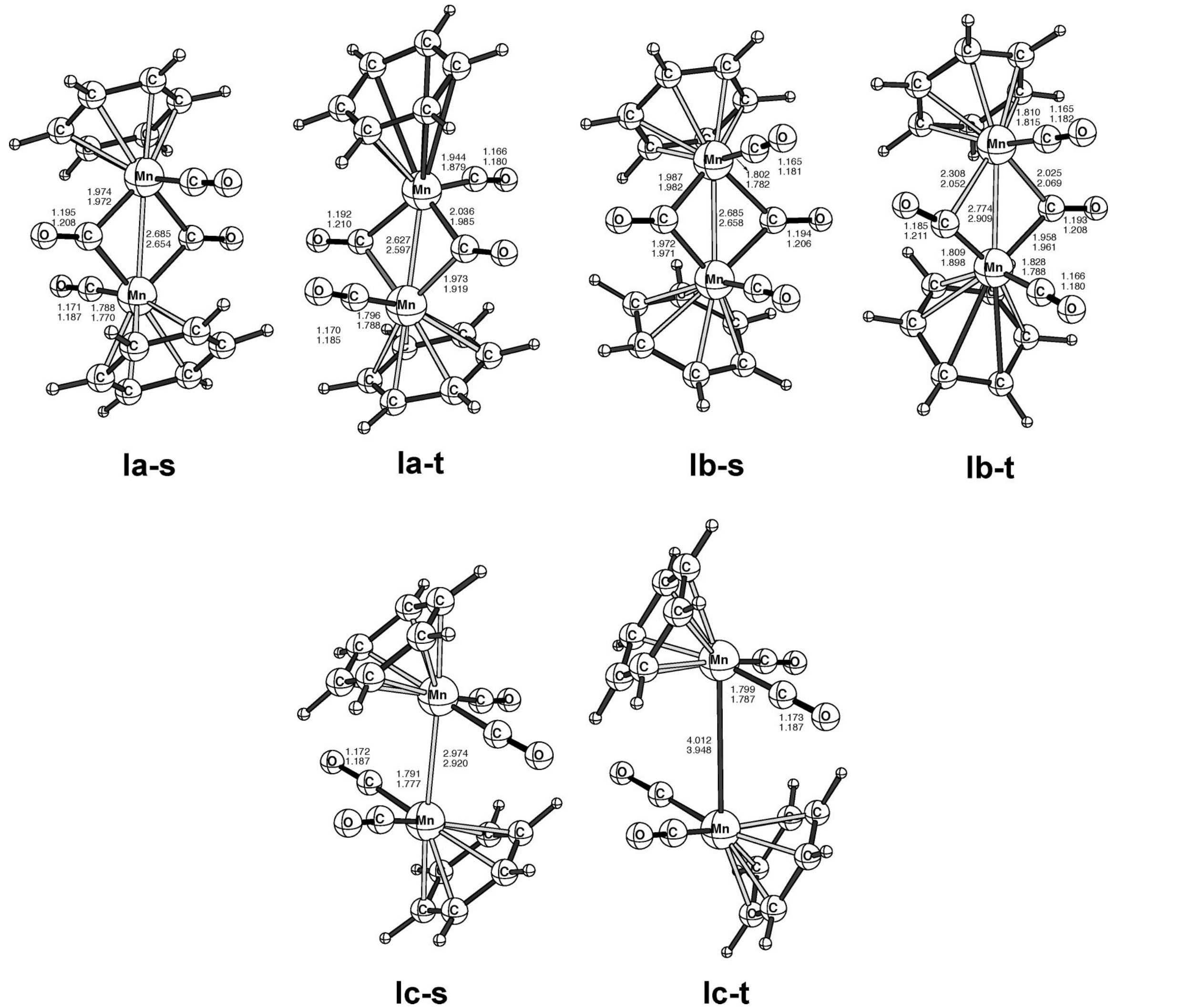

Figure 2. Optimized geometries for the $(C_6H_6)_2Mn_2(CO)_4$ stationary points (bond distances are in Å).

Table 1. Bond Distances (in Å), Total Energies (*E* in Hartree), and Relative Energies (Δ*E* in kcal/mol) for the Singlet $(C_6H_6)_2Mn_2(CO)_4$ Structures

	trans-$(C_6H_6)_2Mn_2(CO)_2(\mu\text{-}CO)_2$			*cis*-$(C_6H_6)_2Mn_2(CO)_2(\mu\text{-}CO)_2$		*trans*-$(C_6H_6)_2Mn_2(CO)_4$	
	Ia-s (C_{2h})			**Ib-s** (C_2)		**Ic-s** (C_{2h})	
	B3LYP	BP86	expt[6]	B3LYP	BP86	B3LYP	BP86
Mn−Mn	2.685	2.654	2.669	2.685	2.658	2.974	2.920
Mn−C (bridge)	1.974	1.972	1.963	1.972	1.971		
				1.987	1.982		
Mn−C (terminal)	1.788	1.770	1.770	1.802	1.782	1.791	1.777
C−O (bridge)	1.195	1.208	1.191	1.194	1.206		
C−O (terminal)	1.171	1.187	1.159	1.165	1.181	1.172	1.187
energy	3220.06140	3220.51044		3220.05884	3220.50629	3220.06182	3220.50260
Δ*E*	0.3	0.0		1.9	2.6	0.0	4.9
imag freq	26*i*, 15*i*	17*i*		none	none	none	none

The Mn−Mn distances predicted for the singlet doubly bridged isomers $(\eta^4\text{-}C_6H_6)_2Mn_2(CO)_2(\mu\text{-}CO)_2$, namely **Ia-s** and **Ib-s**, fall in the range 2.685−2.654 Å and are shorter than the 2.974 Å (B3LYP) and 2.920 Å(BP86) distance for the unbridged Mn−Mn single bond in **Ic-s**. The Mn−Mn distances in the *cis* doubly bridged triplet isomers **Ib-t** is 2.774 Å (B3LYP) and 2.909 Å(BP86), which is about 0.1 Å (B3LYP) or 0.2 Å (BP86) longer than the Mn−Mn distance in the corresponding dibridged singlet isomers **Ib-s**. However, the Mn−Mn distance in the trans-dibridged triplet isomer **Ia-t** is shorter than in the corresponding dibridged singlet isomers **Ia-s** by 0.06 Å.

X-ray diffraction[6] indicates the known hexamethylbenzene derivative $(\eta^6\text{-}Me_6C_6)_2Mn_2(CO)_4$ to have a *trans* doubly bridged structure very similar to structure **Ia-s** (Figure 2), predicted by DFT to be the global minimum for the benzene analogue $(\eta^6\text{-}C_6H_6)_2\text{-}Mn_2(CO)_4$. The experimental Mn−Mn distance[6] of 2.669 Å found for $(\eta^6\text{-}Me_6C_6)_2Mn_2(CO)_4$ is close to the Mn−Mn distance of 2.685 Å (B3LYP) or 2.654 Å (BP86) predicted for **Ia-s** (Table 1). In addition, the experimental Mn−C and C−O distances found in the X-ray structure of $(\eta^6\text{-}Me_6C_6)_2Mn_2(CO)_4$ are close to those predicted by DFT for **Ia-s**.

3.1.2. $(C_6H_6)_2Mn_2(CO)_3$. Isomers of $(C_6H_6)_2Mn_2(CO)_3$ having three, two, or one bridging CO groups have been studied (Figure 3 and Tables 3 and 4). The singly bridged isomer $(C_6H_6)_2Mn_2(CO)_2(\mu\text{-}CO)$ was found to collapse to the triply

Table 2. Bond Distances (in Å), Total Energies (*E* in Hartree), and Relative Energies (Δ*E* in kcal/mol) for the Triplet $(C_6H_6)_2Mn_2(CO)_4$ Structures

	trans-$(C_6H_6)_2Mn_2(CO)_2(\mu\text{-}CO)_2$		*cis*-$(C_6H_6)_2Mn_2(CO)_2(\mu\text{-}CO)_2$		*trans*-$(C_6H_6)_2Mn_2(CO)_4$	
	Ia-t (C_s)		**Ib-t** (C_1)		**Ic-t** (C_{2h})	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
Mn−Mn	2.627	2.597	2.774	2.909	4.012	3.948
Mn−C (bridge)	2.036	1.985	2.025	2.069		
	1.973	1.919	1.958	1.961		
			2.308	2.052		
			1.809	1.898		
Mn−C (terminal)	1.796	1.788	1.810	1.815	1.799	1.787
	1.944	1.879	1.828	1.788		
C−O (bridge)	1.192	1.210	1.193	1.208		
			1.185	1.211		
C−O (terminal)	1.170	1.185	1.165	1.182	1.173	1.187
	1.166	1.180	1.166	1.180		
energy	3220.03267	3220.46239	3220.02197	3220.45689	3220.05213	3220.46900
Δ*E*	18.0	30.2	24.7	33.6		
imag freq	86*i*, 21*i*	60*i*, 8*i*	none	none	4*i*	22*i*, 10*i*

Table 3. Bond Distances (in Å), Total Energies (*E* in Hartree), and Relative Energies (Δ*E* in kcal/mol) for the Singlet State $(C_6H_6)_2Mn_2(CO)_3$ Stationary Point Structures

	$(C_6H_6)_2Mn_2(CO)(\mu\text{-}CO)_2$		$(C_6H_6)_2Mn_2(\mu\text{-}CO)_3$	
	IIa-s (C_s)		**IIb-s** (C_2)	
	B3LYP	BP86	B3LYP	BP86
Mn−Mn	2.533	2.477	2.387	2.366
Mn−C (bridge)	1.979	1.987	1.974	1.965
	1.928	1.912	1.988	1.973
			1.926	1.926
Mn−C (terminal)	1.801	1.797		
C−O (bridge)	1.198	1.210	1.190 1.202	1.205 1.215
C−O (terminal)	1.169	1.183		
energy	3106.66999	3107.11024	3106.66121	3107.10899
Δ*E*	0.0	0.0	5.5	0.8
imag freq	31*i*, 5*i*	35*i*	3*i*	none

bridged isomer $(C_6H_6)_2Mn_2(\mu\text{-}CO)_3$ for both the singlet and triplet electronic states (**IIb** in Figure 3).

The lowest energy structure for $(C_6H_6)_2Mn_2(CO)_3$ found by BP86 (Tables 2 and 3) is the triplet-state triply bridged isomer $(C_6H_6)_2Mn_2(\mu\text{-}CO)_3$ (**IIb-t** in Figure 3), which has the D_{3h} symmetry for the central $Mn(\mu\text{-}CO)_3Mn$ core. This isomer is found to be a ground-state triplet and to have only very small imaginary vibrational frequencies, namely 34*i* and 22*i* cm^{-1}. For the singlet state, the energy of the triply bridged isomer $(C_6H_6)_2Mn_2(\mu\text{-}CO)_3$ (**IIb-s**) is very close to the energy of the doubly bridged isomer $(C_6H_6)_2Mn_2(CO)(\mu\text{-}CO)_2$ (**IIa-s**) by BP86. The triply bridged singlet isomer of $(C_6H_6)_2Mn_2(\mu\text{-}CO)_3$ (**IIb-s**) lies 7.7 kcal/mol (BP86) above the triply bridged triplet **IIb-t**, which appears to be the global minimum.

The Mn−Mn bond distance for the doubly bridged singlet state structure **IIa-s** is 2.533 Å (B3LYP) or 2.477 Å (BP86), which is significantly longer than that in the triply bridged singlet structure **IIb-s** (2.387 Å by B3LYP or 2.366 Å by BP86). These Mn═Mn bond distances are all consistent with the double bond required to give both metal atoms the favored 18-electron configuration. The predicted Mn═Mn distance in the triply bridged triplet **IIb-t** of 2.349 Å is also consistent with a double bond giving both metal atoms 18-electron configurations. In this case the Mn═Mn double bond is a $\sigma + 2/2\pi$ bond analogous to the Fe═Fe double bond in the known[8] triplet state $(\eta^5\text{-}Me_5C_5)_2Fe_2(\mu\text{-}CO)_3$ and the O═O bond in O_2. However, in the doubly bridged triplet **IIa-t** the Mn−Mn distance of 2.606 Å (B3LYP) or 2.570 Å (BP86) is consistent with the single bond, thereby giving each manganese atom a 17-electron configuration. Thus the triplets **IIa-t** and **IIb-t** are fundamentally different since in **IIa-t** the two unpaired electrons are in the 17-electron configurations of the two manganese atoms whereas in **IIb-t** the two unpaired electrons are in the $\sigma + 2/2\pi$ Mn═Mn double bond.

3.1.3. $(C_6H_6)_2Mn_2(CO)_2$. Six structures were optimized for $(C_6H_6)_2Mn_2(CO)_2$, namely singlet and triplet doubly bridged structures as well as *trans*-unbridged and *cis*-unbridged structures. However, there are only two types of stationary points for $(C_6H_6)_2Mn_2(CO)_2$ (Figure 4) for both the singlet and triplet structures, since the unbridged structures collapse to the singly bridged isomers $(C_6H_6)_2Mn_2(CO)(\mu\text{-}CO)$ (**IIIb-s** and **IIIb-t**).

The probable global minimum for $(C_6H_6)_2Mn_2(CO)_2$ is the singlet C_{2v} structure **IIIa-s** with two symmetrical bridging CO ligands and with insignificant imaginary vibrational frequencies of 26*i* and 23*i* cm^{-1} (B3LYP) or 26*i* cm^{-1} (BP86) almost certainly arising from integration errors. The theoretical manganese−manganese distance in **IIIa-s** is only 2.197 Å (B3LYP) or 2.156 Å (B3LYP) consistent with the Mn≡Mn triple bond required to give each manganese atom in **IIIa-s** the favored 18-electron rare gas configuration.

The energy of the triplet doubly bridged structure **IIIa-t** is higher than that of the corresponding singlet **IIIa-s** by 5.3 kcal/mol (B3LYP) or 1.5 kcal/mol (BP86). The Mn═Mn distance

Table 4. Bond Distances (in Å), Total Energies (*E* in Hartree), and Relative Energies (Δ*E* in kcal/mol) for the Triplet State $(C_6H_6)_2Mn_2(CO)_3$ Stationary Structures

	$(C_6H_6)_2Mn_2(CO)(\mu\text{-}CO)_2$		$(C_6H_6)_2Mn_2(\mu\text{-}CO)_3$	
	IIa-t (C_s)		**IIb-t** (D_{3h})	
	B3LYP	BP86	B3LYP	BP86
Mn−Mn	2.606	2.570	2.349	2.349
Mn−C (bridge)	1.992	1.982	1.964	1.960
Mn−C (terminal)	1.799	1.789		
C−O (bridge)	1.197	1.211	1.192	1.206
C−O (terminal)	1.168	1.183		
energy	3106.68566	3107.10949	3106.68413	3107.12131
Δ*E*	−9.8	0.5	−8.9	−6.9
imag freq	24*i*	25*i*	25*i*, 7*i*	34i, 22*i*

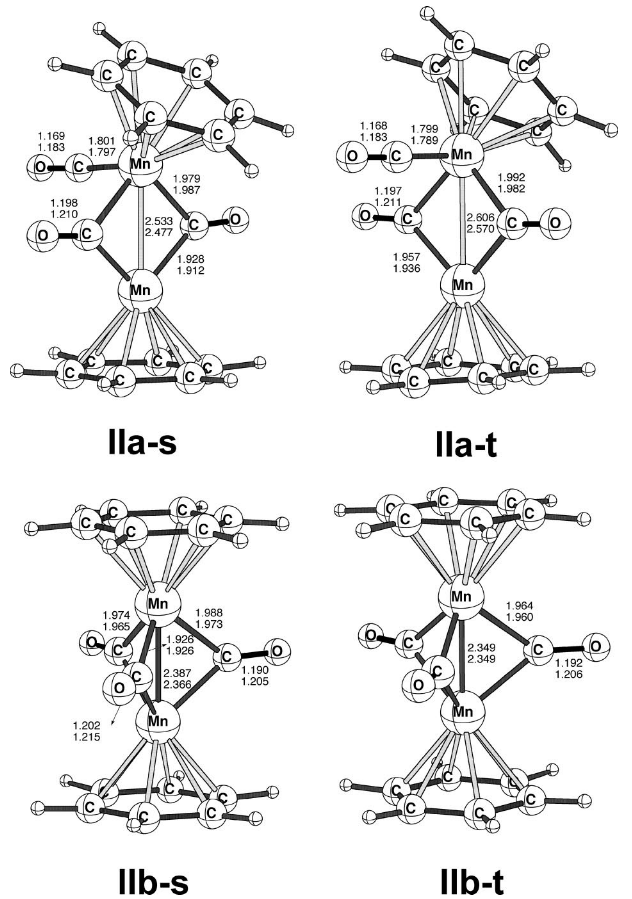

Figure 3. Optimized geometries for $(C_6H_6)_2Mn_2(CO)_3$ (bond distances are in Å).

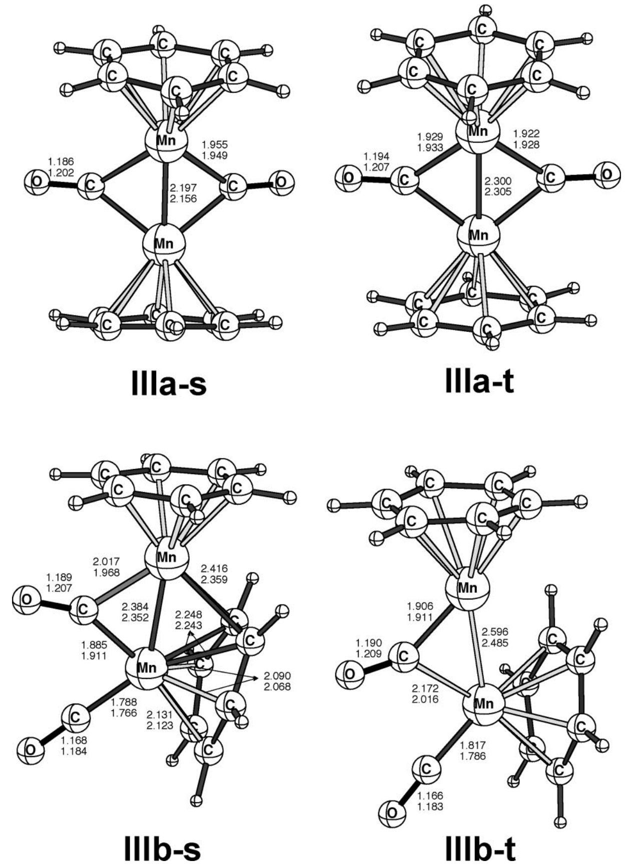

Figure 4. Optimized geometries for $(C_6H_6)_2Mn_2(CO)_2$ (bond distances are in Å).

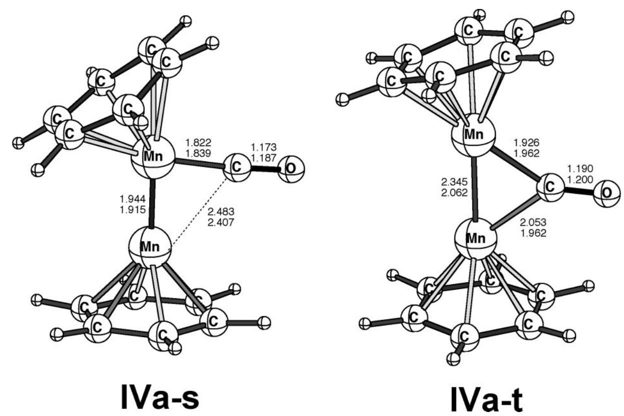

Figure 5. Optimized geometries for $(C_6H_6)_2Mn_2(CO)$ (bond distances are in Å).

in **IIIa-t** at 2.300 Å (B3LYP) or 2.305 Å (BP86) is ~0.1 Å (B3LYP) or ~0.15 Å (BP86) longer than the Mn≡Mn distance in **IIIa-s**, consistent with the double bond required to give the manganese atoms in **IIIa-t** the 17-electron configurations expected for a triplet.

The triplet $(C_6H_6)_2Mn_2(CO)_2$ isomer **IIIb-t** with only a single bridging CO group has a significant imaginary vibrational frequency at 100*i* (B3LYP). Following the corresponding normal mode converts the singly bridged triplet **IIIb-t** into the doubly bridged structure **IIIa-t**.

One of the benzene rings in the singlet $(C_6H_6)_2Mn_2(CO)_2$ isomer **IIIb-s** with only a single bridging CO group has an unusual η^6,η^2 bridging configuration between the two manganese atoms (Figure 4). The six η^6 Mn−C distances to one of the manganese atoms (the "lower" Mn atom in Figure 4) fall in the range 2.07−2.25 Å, whereas the two equivalent η^2 Mn−C distances to the other manganese atom (the "upper" Mn atom in Figure 4) are significantly longer (2.416 Å by B3LYP or 2.359 Å by BP86). This benzene ring may be regarded as semibridging. This isomer **(IIIb-s)** of $(C_6H_6)_2Mn_2(CO)_2$ lies ~15 kcal/mol above the global minimum **IIIa-s**.

3.1.4. $(C_6H_6)_2Mn_2(CO)$. Optimizations have been carried out on triplet and singlet state $(C_6H_6)_2Mn_2(CO)$ structures in which the single CO group is either bridging or terminal. The triplet unbridged structure of $(C_6H_6)_2Mn_2(CO)$ collapses to the C_s triplet structure **IVa-t**, which has a bridging CO group that is symmetrical (BP86 with Mn−C at 1.962 Å) or nearly symmetrical (B3LYP with Mn−C at 1.926 Å and 2.053 Å). However, the singlet state bridged structure of $(C_6H_6)_2Mn_2(CO)$ collapses to the C_s singlet structure **IVa-s** with a highly unsymmetrical bridging CO group at 1.822 and 2.483 Å (B3LYP) or 1.839 and 2.407 Å (BP86).

For $(C_6H_6)_2Mn_2(CO)$ the B3LYP and BP86 methods disagree on the relative energies of the triplet structure **IVa-t** and the singlet structure **IVa-s**, with **IVa-t** being lower than **IVa-s** by 16.2 kcal/mol using B3LYP but higher by 2.4 kcal/mol using BP86 (Table 7). The very short Mn−Mn distance of 1.944 Å (B3LYP) or 1.915 Å (BP86) in the singlet isomer **IVa-s** of $(C_6H_6)_2Mn_2(CO)$ is consistent with the quadruple bond required to give both metal atoms the favored 18-electron configuration. However, this Mn−Mn quadruple bond in **IVa-s** is obviously polarized because of the nonequivalence of the two manganese atoms arising from the highly unsymmetrical bridging carbonyl. The Mn≡Mn distance in the triplet state structure **IVa-t** is longer

Table 5. Bond Distances (in Å), Total Energies (*E* in Hartree), and Relative Energies (Δ*E* in kcal/mol) for the Singlet State $(C_6H_6)_2Mn_2(CO)_2$ Structures

	$(C_6H_6)_2Mn_2(\mu\text{-}CO)_2$		$(C_6H_6)(\mu\text{-}C_6H_6)Mn_2(CO)(\mu\text{-}CO)$	
	IIIa-s (C_{2v})		**IIIb-s** (C_s)	
	B3LYP	BP86	B3LYP	BP86
Mn−Mn	2.197	2.156	2.384	2.352
Mn−C (bridge)	1.955	1.949	1.885	1.911
			2.017	1.968
Mn−C (terminal)			1.788	1.766
C−O (bridge)	1.186	1.202	1.189	1.207
C−O (terminal)			1.168	1.184
energy	2993.30120	2993.73166	2993.27644	2993.70791
Δ*E*	0.0	0.0	15.5	15.0
imag freq	26*i*, 23*i*	26*i*	28*i*	31*i*

Table 6. Bond Distances (in Å), Total Energies (*E* in Hartree), and Relative Energies (Δ*E* in kcal/mol) for the Triplet State $(C_6H_6)_2Mn_2(CO)_2$ Structures

	$(C_6H_6)_2Mn_2(\mu\text{-}CO)_2$		$(C_6H_6)_2Mn_2(CO)(\mu\text{-}CO)$	
	IIIa-t (C_2)		**IIIb-t** (C_s)	
	B3LYP	BP86	B3LYP	BP86
Mn−Mn	2.300	2.305	2.596	2.485
Mn−C (bridge)	1.925	1.930	2.172 2.016	1.906 1.911
Mn−C (terminal)			1.817	1.786
C−O (bridge)	1.194	1.207		
C−O (terminal)			1.166	1.183
energy	2993.29270	2993.72946	2993.29140	2993.68795
Δ*E*	5.3	1.5	6.1	27.4
imag freq	none	none	32*i*, 26*i*	100*i*, 33*i*

Table 7. Bond Distances (in Å), Total Energies (*E* in Hartree), and Relative Energies (Δ*E* in kcal/mol) for the $(C_6H_6)_2Mn_2(CO)$ Structures

	$(C_6H_6)_2Mn_2(CO)$		$(C_6H_6)_2Mn_2(\mu\text{-}CO)$	
	IVa-s (C_s)		**IVa-t** (C_s)	
	B3LYP	BP86	B3LYP	BP86
Mn−Mn	1.944	1.915	2.345	2.062
Mn−C (bridge)			1.926	1.962
			2.053	1.962
Mn−C (terminal)	1.822	1.839		
C−O (bridge)			1.190	1.200
C−O (terminal)	1.173	1.187		
energy	2879.87314	2880.30975	2879.89895	2880.30587
Δ*E*	0.0	0.0	−16.2	2.4
imag freq	17*i*	18*i*	24*i*, 16*i*	28*i*, 17*i*

Table 8. Energies (kcal/mol) for Carbonyl Dissociation and Disproportionation of $(C_6H_6)_2Mn_2(CO)_n$ Derivatives

	B3LYP	BP86
$(C_6H_6)_2Mn_2(CO)_4$ (**Ia-s**) → $(C_6H_6)_2Mn_2(CO)_3$ (**IIb-t**) + CO	26.6	35.2
$(C_6H_6)_2Mn_2(CO)_3$ (**IIb-t**) → $(C_6H_6)_2Mn_2(CO)_2$ (**IIIa-s**) + CO	30.2	35.6
$(C_6H_6)_2Mn_2(CO)_2$ (**IIIa-s**) → $(C_6H_6)_2Mn_2(CO)$ (**IVa-s**) + CO	58.5	55.8
$2(C_6H_6)_2Mn_2(CO)_3$ (**IIb-t**) → $(C_6H_6)_2Mn_2(CO)_4$ (**Ia-s**) + $(C_6H_6)_2Mn_2(CO)_2$ (**IIIa-s**)	3.5	0.3
$2(C_6H_6)_2Mn_2(CO)_3$ (**IIa-s**) → $(C_6H_6)_2Mn_2(CO)_4$ (**Ia-s**) + $(C_6H_6)_2Mn_2(CO)_2$ (**IIIa-s**)	−14.2	−13.6
$2\ (C_6H_6)_2Mn_2(CO)_2$ (**IIIa-s**) → $(C_6H_6)_2Mn_2(CO)_3$ (**IIb-t**) + $(C_6H_6)_2Mn_2(CO)$ (**IVa-s**)	28.3	20.2

than that in the singlet **IVa-s** and consistent with the Mn≡Mn triple bond required to give each manganese a 17-electron configuration with spin $S = 1$.

3.2. Dissociation Energies. Table 8 reports the energies of the single carbonyl dissociation steps

$$(C_6H_6)_2Mn_2(CO)_n \rightarrow (C_6H_6)_2Mn_2(CO)_{n-1} + CO \quad (1)$$

In determining these dissociation energies, the fragments were allowed to relax.

The predicted dissociation energy of one CO group from $(C_6H_6)_2Mn_2(CO)_4$ (Table 8) is 26.6 kcal/mol (B3LYP) or 35.2 kcal/mol (BP86). Further dissociation of a CO group from $(C_6H_6)_2Mn_2(CO)_3$ to give $(C_6H_6)_2Mn_2(CO)_2$ requires a similar energy of 30.2 kcal/mol (B3LYP) or 35.6 kcal/mol (BP86). These CO dissociation energies are typical for metal carbonyls as indicated by the reported[34] CO dissociation energies of 37 ± 2, 41 ± 2, and 25 ± 2 kcal/mol for $Cr(CO)_6$, $Fe(CO)_5$, and $Ni(CO)_4$, respectively.

The next CO dissociation process, namely the $(C_6H_6)_2Mn_2(CO)_2$ dissociation process to $(C_6H_6)_2Mn_2(CO)$ + CO, requires the much higher energy of 58.5 kcal/mol (B3LYP) or 55.8 kcal/mol (BP86). Thus $(C_6H_6)_2Mn_2(CO)_2$ appears to be very stable with respect to extrusion of a carbonyl ligand. This suggests an energy barrier for a pair of manganese atoms to form a bond of formal order higher than three.

The energies of the disproportionation reaction $2(C_6H_6)_2Mn_2(CO)_n \rightarrow (C_6H_6)_2Mn_2(CO)_{n+1} + (C_6H_6)_2Mn_2(CO)_{n-1}$ (Table 8) indicate that $(C_6H_6)_2Mn_2(CO)_2$ is energetically stable with respect to such disproportionation. However, the analogous disproportionation energy of $(C_6H_6)_2Mn_2(CO)_3$ into $(C_6H_6)_2Mn_2(CO)_4$ and $(C_6H_6)_2Mn_2(CO)_2$ is small (only 0.3 kcal/mol by the BP86 method) even if the triplet state global minimum for $(C_6H_6)_2Mn_2(CO)_3$, namely **IIb-t**, is considered. Nevertheless, dissociation of a triplet state into two singlets is spin forbidden, so triplet $(C_6H_6)_2Mn_2(\mu\text{-}CO)_3$ (**IIb-t**) has some chance of being stable under ambient conditions. The disproportionation of the lowest energy singlet structure **IIa-s** of $(C_6H_6)_2Mn_2(CO)_3$ into the global minima of $(C_6H_6)_2Mn_2(CO)_4$ and $(C_6H_6)_2Mn_2(CO)_2$ is significantly exothermic at −14.2 kcal/mol (B3LYP) or −13.6 kcal/mol (BP86), suggesting that singlet isomers of $(C_6H_6)_2Mn_2(CO)_3$ is not stable thermodynamically.

3.3. Vibrational Frequencies. The harmonic vibrational frequencies and their infrared intensities for all of the $(C_6H_6)_2Mn_2(CO)_n$ structures have been evaluated by the B3LYP and BP86 methods. Complete reports of the vibrational frequencies and infrared intensities are given in the Supporting Information. These results have been used to determine if a structure is a genuine minimum. In general the vibrational frequencies determined by the BP86 functional have been found to be closer to experiment than those determined by the B3LYP functional.[35,36]

The predicted ν(CO) frequencies for the $(C_6H_6)_2Mn_2(CO)_n$ (n = 4, 3, 2, and 1) structures are of particular interest, since any future experimental work to detect such species is likely to rely on the relatively strong ν(CO) frequencies for initial product characterization. The predicted ν(CO) stretching frequencies are listed in Table 9 for all of the $(C_6H_6)_2Mn_2(CO)_n$ (n = 4, 3, 2, and 1) species investigated in this work. In general, the ν(CO) frequencies predicted by the BP86 functional are 60−100 cm^{-1} lower than those predicted by the B3LYP functional and significantly closer to the anticipated experimental values. For the known $(\eta^6\text{-}Me_6C_6)_2Mn_2(CO)_4$ isomer with a *trans* doubly bridged structure similar to **Ia-s** (Figure 2), the experimental ν(CO) frequencies are 1854 and 1692 cm^{-1} in tetrahydrofuran solution as compared with the 1900 and 1747 cm^{-1} values (BP86) or 1976 and 1795 cm^{-1} values (B3LYP) predicted for $(\eta^6\text{-}C_6H_6)_2Mn_2(CO)_2(\mu\text{-}CO)_2$ (**Ia-s**: Figure 2). The discrepancy of ∼+50 cm^{-1} between the ν(CO) frequencies for $(\eta^6\text{-}C_6H_6)_2Mn_2(CO)_2(\mu\text{-}CO)_2$ predicted by BP86 and those found

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Table 9. Metal Carbonyl ν(CO) Frequencies (in cm^{-1}) Predicted for the $(C_6H_6)_2Mn_2(CO)_n$ (n = 4, 3, 2, and 1) Isomers[a]

		B3LYP	BP86
$(C_6H_6)_2Mn_2(CO)_4$	**Ia-s** (C_{2h})	**1795^b (a_u, 1123)**	**1747^b (a_u, 852)**
		1833^b (a_g, 0)	1768^b (a_g, 0)
		1976 (b_u, 1565)	**1900 (b_u, 1252)**
		1983 (a_g, 0)	1906 (a_g, 0)
	Ib-s (C_2)	**1803^b (b, 123)**	**1756^b (b, 853)**
		1841^b (a, 2)	1777^b (a, 2)
		1995 (b, 101)	1918 (b, 96)
		2037 (a, 1640)	**1958 (a, 1345)**
	Ic-s (C_{2h})	1947 (b_g, 0)	1879 (b_g, 0)
		1961 (b_u, 1419)	**1910 (b_u, 1078)**
		1963 (a_u, 1419)	**1891 (a_u, 1136)**
		1994 (a_g, 0)	1923 (a_g, 0)
	Ia-t (C_s)	**1812^b (a″, 1080)**	**1735^b (a″, 819)**
		1799^b (a′, 47)	1752^b (a′, 6)
		1979 (a′, 1796)	**1905 (a′, 1399)**
		1995 (a′, 154)	1918 (a′, 0)
	Ib-t (C_1)	**1800^b (412)**	**1725^b (654)**
		1873^b (642)	1745^b (62)
		1990 (191)	**1911 (208)**
		2027 (1818)	**1950 (1347)**
$(C_6H_6)_2Mn_2(CO)_3$	**IIa-s** (C_s)	**1791^b (a″, 1113)**	**1743^b (a″, 857)**
		1822^b (a′, 20)	1762^b (a′, 11)
		1999 (a′, 827)	**1929 (a′, 664)**
	IIb-s (C_2)	**1789b (a, 1033)**	**1741^b (a, 782)**
		1806^b (b, 713)	**1762^b (b, 529)**
		1866^b (a, 213)	**1796^b (a, 117)**
	IIa-t (C_s)	**1793^b (a″, 1093)**	**1736^b (a″, 843)**
		1803^b (a′, 7)	1757^b (a′, 3)
		1999 (a′, 958)	**1928 (a′, 789)**
	IIb-t ($D_{3\ h}$)	**1828^b (e′, 1024)**	**1768^b (e′, 791)**
		1855^b (a_1′, 0)	1796^b (a_1′, 0)
$(C_6H_6)_2Mn_2(CO)_2$	**IIIa-s** (C_{2v})	**1881^b (a_1,257)**	**1812^b (a_1,257)**
		1871^b (b_1,1192)	**1793^b (b_1,876)**
	IIIb-s(C_s)	**1847^b (a′, 429)**	**1766^b (a′, 301)**
		2011 (a′, 1382)	**1933 (a′, 1077)**
	IIIa-t (C_2)	**1840^b (a, 59)**	**1773^b (a, 40)**
		1811^b (b, 1283)	**1757^b (b, 920)**
	IIIb-t (C_s)	**1835^b (a′, 376)**	**1742^b (a′, 304)**
		2003 (a′, 1652)	**1929 (a′, 1232)**
$(C_6H_6)_2Mn_2(CO)$	**IVa-s** (C_s)	**1964 (a′, 922)**	**1889 (a′, 723)**
	IVa-t (C_s)	**1839^b (a′, 767)**	**1814^b (a′, 642)**

[a] Infrared intensities are given in parentheses and are in km/mol; infrared *active* CO frequencies are given in bold type. The superscript “b” implies a bridging ν(CO) frequency.

experimentally for (η^6-$Me_6C_6)_2Mn_2(CO)_2(\mu$-$CO)_2$ may arise from the inductive effect of the six methyl substituents on each benzene ring, which would be expected to lower the ν(CO) frequencies significantly.

In transition-metal carbonyl chemistry the ν(CO) frequencies of typical symmetrical two-electron donor bridging CO groups are well-known[37] to occur 150−200 cm^{-1} below the ν(CO) frequencies of terminal CO groups in a given type of metal carbonyl derivative. This same trend is found for the $(C_6H_6)_2Mn_2(CO)_n$ (n = 4, 3, 2, and 1) derivatives studied in this work where the bridging ν(CO) frequencies fall in the range 1725−1812 cm^{-1} and the terminal ν(CO) frequencies fall in the range 1900−1950 cm^{-1} (BP86). Similar observations concerning bridging and terminal ν(CO) frequencies were made in previous work with $Cp_2Fe_2(CO)_n$ (n = 4, 3, 2, and 1)[11] and $(C_4H_4)_2Co_2(CO)_n$ (n = 3, 2, and 1)[12] derivatives.

4. Discussion

Table 10 compares the global minimum structures for $(C_4H_4)_2Co_2(CO)_n$, $Cp_2Fe_2(CO)_n$, and $(C_6H_6)_2Mn_2(CO)_n$ (n = 4, 3, 2, and 1) using the BP86 method. Table 10 also includes the formal metal−metal bond orders assuming that the favored 18-electron metal configurations are approached as closely as possible.

Similarly to $(C_4H_4)_2Co_2(CO)_n$ and $Cp_2Fe_2(CO)_n$, each additional bridging CO group for a $(C_6H_6)_2Mn_2(CO)_n$ (n = 4, 3, 2, and 1) derivative shortens the Mn−Mn bond distances by roughly 0.1 Å for a given bond order. Furthermore, each unit increase in the formal Mn−Mn bond order is predicted to shorten the Mn−Mn bond distances (BP86) by roughly 0.2 Å, in accord with the known crystal structures of $Cp_2Fe_2(CO)_n$ (n = 4 and 3). The Mn−Mn distances in the structures of $(C_6H_6)_2Mn_2(CO)_n$ (n = 4, 3, 2, and 1) are seen to correlate with the number of bridging CO groups and the formal Mn−Mn bond order required to give both manganese atoms the favored 18-electron configuration (Table 10).

It is instructive to compare the global minimum structures for analogous $(C_4H_4)_2Co_2(CO)_n$, $Cp_2Fe_2(CO)_n$,and $(C_6H_6)_2Mn_2(CO)_n$ (n = 4, 3, 2, and 1) derivatives as follows:

1. (η^n-$C_nH_n)_2M_2(CO)_4$: The singlet state *trans* doubly bridged derivatives (η^n-$C_nH_n)_2M_2(CO)_2(\mu$-$CO)_2$ analogous to structure **Ia-s** (Figure 2) for (η^6-$C_6H_6)_2Mn_2(CO)_2(\mu$-$CO)_2$ are predicted to be the global minima for all three metals. The corresponding permethylated derivatives (η^n-$Me_nC_n)_2M_2(CO)_2(\mu$-$CO)_2$ have been synthesized for all three metals.

2. (η^n-$C_nH_n)_2M_2(CO)_3$: In the case of the (η^n-$C_nH_n)_2M_2(CO)_3$ derivatives there is a major difference between the three metals. For Mn (n = 6) and Fe (n = 5), the global minimum is the triplet-state triply bridged structure (η^n-$C_nH_n)_2M_2(\mu$-$CO)_3$ analogous to structure **IIb-t** for (η^6-$C_6H_6)_2Mn(\mu$-$CO)_3$ (Figure 3). The permethylated iron derivative (η^5-$Me_5C_5)_2Fe_2(\mu$-$CO)_3$ has been characterized structurally.[8] However, for the cyclobutadienecobalt carbonyls the corresponding structure (η^4-$C_4H_4)_2Co_2(\mu$-

Table 10. Bond Distances (in Å) and Formal Metal−metal Bond Orders for the Global Minima of $(C_4H_4)_2Co_2(CO)_n$, $Cp_2Fe_2(CO)_n$, and $(C_6H_6)_2Mn_2(CO)_n$ (n = 4, 3, 2, and 1) Using the BP86 Method

	isomer	state	no. of bridging COs	M−M	M−C	C−O	formal M−M bond order
$(C_4H_4)_2Co_2(CO)_4$	**Ib-s**	^1A_g	2	2.499	1.929/1.766	1.195/1.175	1
$Cp_2Fe_2(CO)_4$	**Ia**	$^1A'$	2	2.540	1.922/1.745	1.201/1.180	1
$(C_6H_6)_2Mn_2(CO)_4$	**Ia-s**	^1A_g	2	2.654	1.972/1.770	1.208/1.187	1
$(C_4H_4)_2Co_2(CO)_3$	**IIa-s**	$^1A_1$	2	2.387	1.946/1.767	1.199/1.174	2
$Cp_2Fe_2(CO)_3$	**IIa**	$^3B_1$	3	2.264	1.920/1.922	1.198	2
$(C_6H_6)_2Mn_2(CO)_3$	**IIb-t**	$^3A'$	3	2.349	1.960	1.206	2
$(C_4H_4)_2Co_2(CO)_2$	**IIIa-s**	$^1A_1$	2	2.188	1.897	1.193	3
$Cp_2Fe_2(CO)_2$	**IIIa**	$^1A_1$	2	2.120	1.906	1.198	3
$(C_6H_6)_2Mn_2(CO)_2$	**IIIa-s**	$^1A_1$	2	2.156	1.949	1.202	3
$(C_4H_4)_2Co_2(CO)$	**IVb-t**	$^3A'$	1	2.220	1.872/1.946	1.198	3[a]
$Cp_2Fe_2(CO)$	**IVa**	$^1A_1$	1	1.998	1.827/2.076	1.196	4
$(C_6H_6)_2Mn_2(CO)$	**IVa-s**	$^1A'$	0	1.915	1.839/2.407	1.187	4

[a] Since the CO group in this isomer of $(C_4H_4)_2Co_2(CO)$ is a four-electron donor (see text), only a Co≡Co triple bond is required to give each metal atom the favored 18-electron configuration.

CO)$_3$ lies 5.3 kcal/mol (BP86) above a singlet doubly bridged global minimum $(\eta^4\text{-}C_4H_4)_2Co_2(CO)(\mu\text{-}CO)_2$.

3. $(\eta^n\text{-}C_nH_n)_2M_2(CO)_2$: The singlet doubly bridged derivatives $(\eta^n\text{-}C_nH_n)_2M_2(\mu\text{-}CO)_2$ analogous to structure **IIIa-s** (Figure 3) for $(\eta^6\text{-}C_6H_6)_2Mn_2(\mu\text{-}CO)_2$ are predicted to be the global minima for all three metals. The iron derivative $(\eta^5\text{-}C_5H_5)_2Fe_2(\mu\text{-}CO)_2$ is a probable intermediate in the pyrolysis[10] of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)_2$ to give $(\eta^5\text{-}C_5H_5)_4Fe_4(\mu_3\text{-}CO)_4$.

4. $(\eta^n\text{-}C_nH_n)_2M_2(CO)$: For Mn ($n$ = 6) and Fe (n = 5) the global minimum has a two-electron bridging or semibridging carbonyl group and a very short M≣M distance (1.9 to 2.0 Å) consistent with a quadruple bond. However, for Co (n = 4) the global minimum has a four-electron bridging carbonyl group and a longer Co≡Co distance (2.22 Å by BP86) consistent with a triple bond.

In summary the $(\eta^n\text{-}C_nH_n)_2M_2(CO)_n$ systems of all three metals (M = Mn, Fe, Co; n = 6, 5, 4, respectively) are analogous for $(\eta^n\text{-}C_nH_n)_2M_2(CO)_4$ with formal M−M single bonds and $(\eta^n\text{-}C_nH_n)_2M_2(CO)_2$ with formal M≡M triple bonds. The significant differences arise for $(\eta^n\text{-}C_nH_n)_2M_2(CO)_3$ where the 18-electron rule predicts a formal M=M double bond. In this case, the iron and manganese systems prefer the triplet structures $(\eta^n\text{-}C_nH_n)_2M_2(\mu\text{-}CO)_3$ with an M=M double bond similar to the O=O bond in dioxygen and all three carbonyl groups bridging the pair of metal atoms. However, the cobalt system prefers a singlet $(\eta^4\text{-}C_4H_4)_2Co_2(CO)(\mu\text{-}CO)_2$ structure with only two bridging carbonyl groups. This relative destabilization of triplet $(\eta^4\text{-}C_4H_4)_2Co_2(\mu\text{-}CO)_3$ may relate to a greater mismatch between the local C_3 symmetry of the triply CO bridging system and the local C_4 symmetry of the $\eta^4\text{-}C_4H_4$ ring as compared with the local C_n symmetries of the $\eta^5\text{-}C_5H_5$ and $\eta^6\text{-}C_6H_6$ rings in the iron and manganese complexes, respectively.

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Supporting Information Available: Complete tables of harmonic vibrational frequencies for $(C_6H_6)_2Mn_2(CO)_n$ (n = 4, 3, 2, 1) isomers (Tables S1−S15); complete Gaussian reference (ref 27). This material is available free of charge via the Internet at http://pubs.acs.org.

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