Inorg. Chem. **2003**, *42*, 5219–5230

Inorganic Chemistry
Article

Binuclear Homoleptic Manganese Carbonyls: $Mn_2(CO)_x$ ($x = 10, 9, 8, 7$)

Yaoming Xie,[†] Jee Hwan Jang,[‡] R. Bruce King,[†] and Henry F. Schaefer, III*,[†]

Center for Computational Quantum Chemistry and Department of Chemistry,
University of Georgia, Athens, Georgia 30602, and Computational Science Engineering Center,
Samsung Advanced Institute of Technology, P.O. Box 111, Suwan 440-600, Korea

Received April 3, 2003

The unsaturated homoleptic manganese carbonyls $Mn_2(CO)_n$ ($n = 7, 8, 9$) are characterized by their equilibrium geometries, thermochemistry, and vibrational frequencies using methods from density functional theory (DFT). The computed metal–metal distances for global minima range from 3.01 Å for the unbridged $Mn_2(CO)_{10}$ with a Mn–Mn single bond to 2.14 Å for a monobridged $Mn_2(CO)_7$ formulated with a metal–metal quadruple bond. The global minimum for $Mn_2(CO)_9$ has a four-electron bridging μ-η^2-CO group and a 2.96 Å Mn–Mn distance suggestive of the single bond required for 18-electron configurations for both metal atoms. This structure is closely related to an experimentally realized structure for the isolated and structurally characterized stable phosphine complex $[R_2PCH_2PR_2]_2Mn_2(CO)_4(\mu$-$\eta^2$-CO). An unbridged $(OC)_4$Mn–Mn$(CO)_5$ structure for $Mn_2(CO)_9$ has only slightly (<6 kcal/mol) higher energy with a somewhat shorter metal–metal distance of 2.77 Å. For $Mn_2(CO)_8$ the lowest energy structure is a D_{2d} unbridged structure with a 2.36 Å metal–metal distance suggesting the triple bond required for the favored 18-electron configuration for both metal atoms. However, the unbridged unsymmetrical $(CO)_3$Mn–Mn$(CO)_5$ structure with a metal–metal bond distance of 2.40 Å lies only 1 to 3 kcal/mol above this global minimum. The lowest energy structure of $Mn_2(CO)_7$ is an unbridged C_s structure with a short metal–metal distance of 2.26 Å. This is followed energetically by another C_s unbridged $Mn_2(CO)_7$ structure with a somewhat longer metal–metal distance of 2.38 Å.

1. Introduction

The only isolable homoleptic manganese carbonyl is $Mn_2(CO)_{10}$, which was discovered much more recently (1954) than most of the other stable homoleptic metal carbonyls of the first row transition metals because of the difficulty of its synthesis. Thus, $Mn_2(CO)_{10}$ was first isolated in <1% yield from the reaction of a MnI_2/Cu mixture with magnesium metal in diethyl ether under 200 atm of CO pressure.[1] More reasonable yields of $Mn_2(CO)_{10}$ were subsequently obtained by the reductive carbonylation at high CO pressures of suitable chosen manganese(II) derivatives with rather unusual reagents such as sodium benzophenone ketyl[2] or triisobutylaluminum.[3] The stability of $Mn_2(CO)_{10}$ is sufficiently high that it can be purified by steam distillation in air without significant decomposition. It became available commercially within a decade of its discovery although for a relatively high price compared with that of simple manganese compounds because of the difficulty of its synthesis.

X-ray diffraction studies have shown $Mn_2(CO)_{10}$ to have a structure with a direct manganese−manganese bond and no bridging carbonyls.[4−8] Consideration of the 18-electron rule requires the Mn−Mn bond to be a single bond so that $Mn_2(CO)_{10}$ may be regarded as the metal carbonyl analogue of ethane with the favorable octahedral coordination for each manganese atom.

Matrix isolation studies have provided spectroscopic evidence for unsaturated binuclear homoleptic manganese carbonyls formed by the low-temperature photolysis of Mn_2-

---

* To whom correspondence should be addressed. E-mail: HFSIII@uga.edu.
[†] University of Georgia.
[‡] Samsung Advanced Institute of Technology.

(1) Brimm, E. O.; Lynch, M. A.; Sesny, W. J. *J. Am. Chem. Soc.* **1954**, *76*, 3831.
(2) Closson, R. D.; Buzbee, L. R.; Ecke, G. C. *J. Am. Chem. Soc.* **1958**, *80*, 6167.
(3) Podall, H. E.; Dunn, J. H.; Shapiro, H. *J. Am. Chem. Soc.* **1960**, *82*, 1325.
(4) Dahl, L. F.; Ishishi, E.; Rundle, R. E. *J. Chem. Phys.* **1957**, *26*, 1750.
(5) Dahl, L. F.; Rundle, R. E. *Acta Crystallogr.* **1963**, *16*, 419.
(6) Almenningen, A.; Jacobsen, G. G.; Seip, H. M. *Acta Chem. Scand.* **1969**, *23*, 685.
(7) Churchill, M. R.; Amoh, K. N.; Wasserman, H. J. *Inorg. Chem.* **1981**, *20*, 1609.
(8) Martin, M.; Rees, B.; Mitschler, A. *Acta Crystallogr.* **1981**, *B38*, 6.

10.1021/ic030118r CCC: $25.00

$(CO)_{10}$. Thus, photolysis of $Mn_2(CO)_{10}$ in a frozen alkane matrix below 100 K[9,10] or in an argon matrix at 12 K[11] results in the loss of a single CO group to give a species with a bridging carbonyl group formulated as $Mn_2(CO)_9$. This species is also generated as a transient species by the flash photolysis of $Mn_2(CO)_{10}$ in hydrocarbon solution at room temperature.[12] More prolonged low-temperature photolysis of $Mn_2(CO)_{10}$ gives a more highly unsaturated product, $Mn_2(CO)_8$, shown by infrared spectroscopy to have only terminal carbonyls.[10]

The objective of this research is to examine the effect of unsaturation on the structure and bonding in the unsaturated manganese carbonyls $Mn_2(CO)_n$ ($n = 9, 8, 7$) using the density functional theory (DFT) methods previously used for homoleptic binuclear carbonyls[13] of copper,[14] nickel,[15] cobalt,[16] iron,[17] and chromium.[18,19]

2. Theoretical Methods

The most reliable DFT functional is generally considered to be 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) general gradient correlation functional.[20,21] Another 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).[22,23] It has been noted elsewhere[13−19] that the BP86 method may be somewhat more reliable than B3LYP for the type of organometallic systems considered in this paper.

The basis sets are also analogous to our previous studies.[13−19] The DZP basis for C and O atoms are Huzinage−Dunning's contracted double-ζ contraction sets[24−25] plus a set of spherical harmonic d polarization functions with orbital exponents $\alpha_d(C) = 0.75$ and $\alpha_d(O) = 0.85$. It may be designated as (9s5p1d/4s2p1d). For Mn, in our loosely contracted DZP basis set, the Wachters' primitive set[26] is used, but augmented by two sets of p functions and one set of d functions, contracted following Hood et al.,[27] and designated (14s11p6d/10s8p3d). For $Mn_2(CO)_{10}$, there are 398 contracted Gaussian functions in the present DZP basis set.

The geometries of all structures were optimized using the two DFT methods independently. The harmonic vibrational frequencies were obtained 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[28] in which the fine grid (75, 302) is the default for evaluating integrals numerically. Cases for which finer integration grids were used will be discussed later.

Table 1. Relative Energies (in kcal/mol) for the $Mn_2(CO)_{10}$ Isomers

	no. of bridging COs	B3LYP	BP86
9-1 (C_s) + CO		32.3	36.8
10-3 (D_{2h})	2	21.0	14.8
10-2 (D_{4h})	0	3.8	3.8
10-1 (D_{4d})	0	0.0	0.0

Generally speaking, imaginary vibrational frequencies of small magnitude are problematic. Recomputation with a finer numerical integration grid generally leaves the results unchanged within a few wavenumbers. A wealth of experience suggests that, in such cases, one should conclude that the structure in question is either (a) a genuine minimum, or (b) structurally similar to a genuine minimum. Pursuing such structures into lower symmetry is rarely profitable.

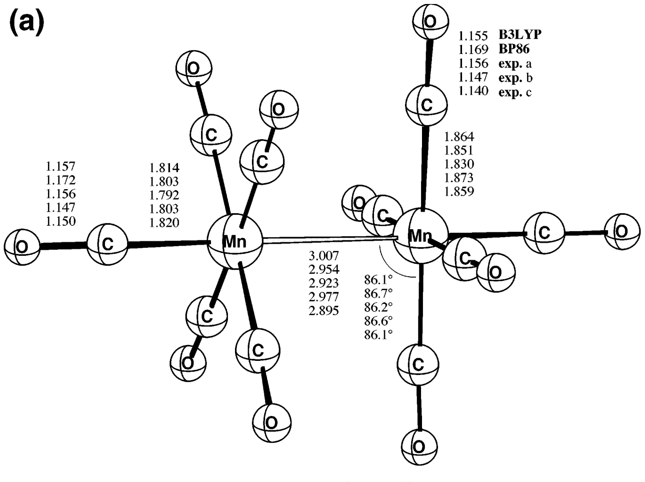
3. Results

3.1 $Mn_2(CO)_{10}$. In 1957, Dahl, Ishishi, and Rundle determined that $Mn_2(CO)_{10}$ has D_{4d} symmetry with a direct Mn−Mn bond.[4] Additional geometric parameters for $Mn_2(CO)_{10}$ were reported in 1963 by Dahl and Rundle.[5] Later, the structure of $Mn_2(CO)_{10}$ was also determined by gas-phase electron diffraction.[6] The carbonyl stretching frequencies of $Mn_2(CO)_{10}$ have been examined in some detail by infrared spectroscopy.[1,29−32] There are also a number of other experimental and theoretical studies on $Mn_2(CO)_{10}$.[33,34]

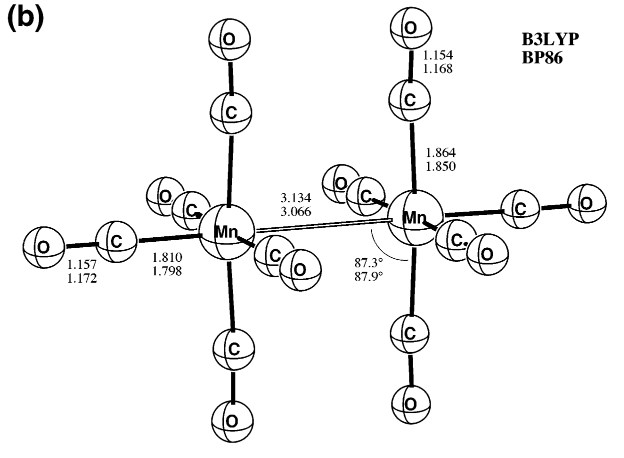
We have studied three structures for $Mn_2(CO)_{10}$, namely **10-1** (D_{4d}), **10-2** ($D_{4h,}$), and **10-3** (D_{2h}) (Figure 1 and Table 1). The staggered **10-1** (D_{4d}) structure was found (in agreement with experiment) to be the global minimum with all real vibrational frequencies (Table 2) computed by both B3LYP and BP86 methods. The Mn−Mn bond distance is computed to be 3.007 Å (B3LYP) or 2.954 Å (BP86) in good

---

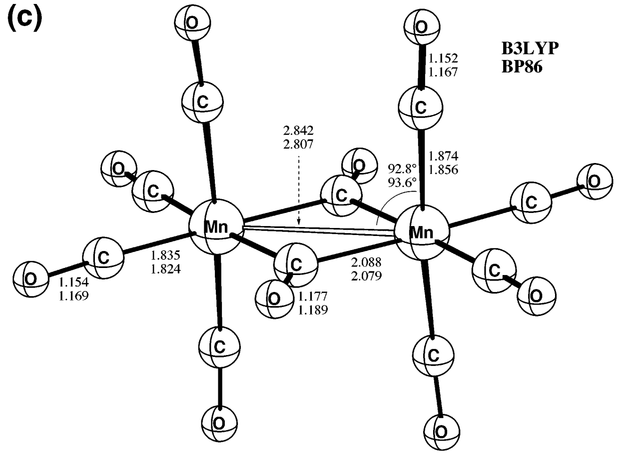
(9) Hepp, A. F.; Wrighton, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 5934.
(10) Kvietok, F. A.; Bursten, B. E. *Organometallics* **1995**, *14*, 2395.
(11) Dunkin, I. R.; Härter, P.; Shields, C. J. *J. Am. Chem. Soc.* **1984**, *106*, 7248.
(12) Church, S. P.; Hermann, H.; Grevels, F.-W.; Schaffner, K. *Chem. Commun.* **1984**, 785.
(13) Schaefer, H. F.; King, R. B. *Pure Appl. Chem.* **2001**, *73*, 1059.
(14) Li, Q.; Liu, Y.; Xie, Y.; King, R. B.; Schaefer, H. F. *Inorg. Chem.* **2001**, *40*, 5842.
(15) Ignatyev, I.; King, R. B.; Schaefer, H. F. *J. Am. Chem. Soc.* **2000**, *122*, 1989.
(16) Kenny, J.; King, R. B.; Schaefer, H. F. *Inorg. Chem.* **2001**, *40*, 900.
(17) Xie, Y.; King, R. B.; Schaefer, H. F. *J. Am. Chem. Soc.* **2000**, *122*, 8746.
(18) Richardson, N. R.; Xie, Y.; King, R. B.; Schaefer, H. F. *J. Phys. Chem. A* **2001**, *105*, 11134.
(19) Li, S.; Richardson, N. R.; Xie, Y.; King, R. B.; Schaefer, H. F.; *Faraday Discuss.*, in press.
(20) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
(21) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
(22) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.
(23) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.
(24) Dunning, T. H. *J. Chem. Phys.* **1970**, *53*, 2823.
(25) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293.
(26) Wachters, A. J. H. *J. Chem. Phys.* **1970**, *52*, 1033.
(27) Hood, D. M.; Pitzer, R. M.; Schaefer, H. F. *J. Chem. Phys.* **1979**, *71*, 705.
(28) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, revision B.3; Gaussian, Inc.: Pittsburgh, PA, 1995.
(29) Hileman, J. C.; Huggins, D. K.; Kaesz, H. D. *Inorg. Chem.* **1962**, *1*, 933.
(30) Flitcroft, N.; Huggins, D. K.; Kaesz, H. D. *Inorg. Chem.* **1964**, *3*, 1123.
(31) Haas, H.; Sheline, R. K. *J. Chem. Phys.* **1967**, *47*, 2996.
(32) Parker, D. J. *Spectrochim. Acta* **1983**, *39A*, 463.
(33) (a) Rosa, A.; Ricciarde, G.; Baerends, E. J.; Stufkens, D. J. *Inorg. Chem.* **1995**, *34*, 3425. (b) Rosa, A.; Ricciarde, G.; Baerends, E. J.; Stufkens, D. J. *Inorg. Chem.* **1996**, *35*, 2886.
(34) (a) Veillard, A.; Rohmer, M.-M. *Int. J. Quantum Chem.* **1992**, *42*, 965. (b) Decker, S. A.; Donini, O.; Klobukowski, M. *J. Phys. Chem. A* **1997**, *101*, 8734. (c) Liddell, M. J. *J. Organomet. Chem.* **1998**, *565*, 271. (d) van Gisbergen, S. J. A.; Groeneveld, J. A.; Rosa, A.; Snijders, J. G.; Baerends, E. J. *J. Phys. Chem. A* **1999**, *103*, 6835. (e) Barchholtz, T. A.; Bursten, B. E. *J. Organomet. Chem.* **2000**, *596*, 212. (f) Kuhn, O.; Hachey, M. R. D.; Rohmer, M. M.; Daniel, C. *Chem. Phys. Lett.* **2000**, *322*, 199.



10-1 (D_{4d})



10-2 (D_{4h})



10-3 (D_{2h})

Figure 1. The three isomers of $Mn_2(CO)_{10}$ found in this work: (a) ref 5; (b) ref 6; (c) ref 8.

agreement with gas electron diffraction (2.98 Å),[6] but slightly longer than that found by X-ray crystallography (2.92,[5] 2.895 Å[8]), similar to the isoelectronic $[Cr_2(CO)_{10}]^{2-}$.[18,19] The Mn−Mn bond in $Mn_2(CO)_{10}$ should be a single bond in order to satisfy the 18-electron rule. The eclipsed **10-2** structure of $Mn_2(CO)_{10}$ with D_{4h} symmetry has a slightly longer Mn−Mn bond distance by ~0.1 Å (Figure 1), and somewhat higher energy (~3.8 kcal/mol) than the global minimum (Table 1). It is a transition state with a small imaginary vibrational frequency (17i or 13i cm^{-1}, Table 3). The corresponding normal mode (a_{1u}) is related to the inner rotation around the Mn−Mn bond and leads to the **10-1** structure. The **10-3** (D_{2h}) structure has two bridging carbonyls, like the global minimum of $Cr_2(CO)_{10}$.[19] It lies substantially higher energetically than **10-1** by 21 (B3LYP) or 15 (BP86) kcal/mol (Table 1). Structure **10-3** has an imaginary vibrational frequency 145i (B3LYP) or 98i (BP86) cm^{-1} (Table 4), related to the cleavage of the CO bridges. Following this normal mode leads first to the D_{4h} structure **10-2** and then finally to the D_{4d} structure **10-1**.

Table 2. Harmonic Vibrational Frequencies (cm^{-1}) and Their Infrared Intensities (km/mol, in Parentheses) for the D_{4d} $Mn_2(CO)_{10}$ (**10-1**)[a]

	B3LYP		BP86		exptl	
a_1	97	(0)	95	(0)		
	148	(0)	148	(0)		
	405	(0)	425	(0)		
	485	(0)	499	(0)		
	693	(0)	692	(0)		
	2069	(0)	1989	(0)		
	2173	(0)	2091	(0)		
a_2	370	(0)	373	(0)		
b_1	42	(0)	43	(0)		
	372	(0)	375	(0)		
b_2	118	(3)	114	(3)		
	395	(33)	421	(14)		
	477	(3)	490	(1)		
	665	(683)	670	(553)		
	2057	(442)	1978	(742)	1983[b]	1992[c]
	2094	(2294)	2032	(1304)	2045[b]	2053[c]
e_1	56	(0)	53	(0)		
	98	(0)	95	(0)		
	106	(1)	103	(0)		
	421	(0)	416	(0)		
	469	(30)	480	(17)		
	565	(1)	554	(0)		
	667	(202)	664	(179)		
	2085	(2482)	2001	(2155)	2014[b]	2025[c]
e_2	70	(0)	62	(0)		
	99	(0)	95	(0)		
	411	(0)	428	(0)		
	476	(0)	464	(0)		
	560	(0)	544	(0)		
	2080	(0)	2005	(0)		
e_3	60	(0)	55	(0)		
	84	(0)	80	(0)		
	109	(0)	105	(0)		
	402	(0)	397	(0)		
	465	(0)	479	(0)		
	554	(0)	542	(0)		
	664	(0)	662	(0)		
	2051	(0)	1969	(0)		

[a] In this paper, the IR intensities for the degenerate modes (e.g., e_1, e_2, and e_3 in this table) refer to only one component. [b] Reference 31. [c] Reference 32.

Although there have been several infrared spectroscopic studies for structure **10-1** of $Mn_2(CO)_{10}$,[11,29−32] many fundamentals cannot be observed because several of the irreducible representations for D_{4d} symmetry (a_1, a_2, b_1, e_2, and e_3) are infrared forbidden. Nevertheless, as early as 1964, Flitcroft, Huggins, and Kaesz[30] assigned three fundamentals in the CO stretching region for $Mn_2(CO)_{10}$ in solution. Later, Haas and Sheline[31] reported the analogous IR absorptions:

Table 3. Harmonic Vibrational Frequencies (cm^{-1}) and Their Infrared Intensities (km/mol, in Parentheses) for the D_{4h} $Mn_2(CO)_{10}$ (**10-2**)

	B3LYP		BP86			B3LYP		BP86	
a_{1g}	115	(0)	115	(0)	a_{1u}	17i		13i	
	144	(0)	142	(0)		371	(0)	375	(0)
	406	(0)	425	(0)	a_{2u}	126	(3)	122	(3)
	486	(0)	501	(0)		396	(35)	421	(15)
	694	(0)	693	(0)		482	(8)	497	(0)
	2068	(0)	1989	(0)		676	(696)	682	(561)
	2174	(0)	2092	(0)		2057	(377)	1979	(637)
a_{2g}	368	(0)	372	(0)		2094	(2658)	2033	(1545)
b_{1g}	121	(0)	115	(0)	b_{1u}	93	(0)	89	(0)
	410	(0)	426	(0)		562	(0)	547	(0)
	475	(0)	463	(0)	b_{2u}	61	(0)	53	(0)
	2094	(0)	2016	(0)		410	(0)	426	(0)
b_{2g}	95	(0)	91	(0)		487	(0)	477	(0)
	562	(0)	547	(0)		2070	(0)	1994	(0)
e_g	42	(0)	36	(0)	e_u	68	(0)	66	(0)
	86	(0)	81	(0)		101	(1)	97	(1)
	110	(0)	106	(0)		131	(0)	128	(0)
	408	(0)	405	(0)		416	(0)	413	(0)
	470	(0)	483	(0)		472	(27)	483	(15)
	561	(0)	550	(0)		567	(0)	556	(0)
	666	(0)	665	(0)		670	(204)	667	(182)
	2051	(0)	1969	(0)		2089	(2459)	2004	(2133)

Table 4. Harmonic Vibrational Frequencies (cm^{-1}) and Their Infrared Intensities (km/mol, in Parentheses) for the D_{2h} $Mn_2(CO)_{10}$ (**10-3**)

	B3LYP		BP86			B3LYP		BP86	
a_{1g}	85	(0)	82	(0)	a_u	23	(0)	19	(0)
	107	(0)	100	(0)		91	(0)	88	(0)
	196	(0)	198	(0)		393	(0)	392	(0)
	352	(0)	355	(0)		570	(0)	552	(0)
	399	(0)	424	(0)	b_{1u}	59	(0)	54	(0)
	468	(0)	484	(0)		94	(1)	92	(0)
	554	(0)	542	(0)		344	(0)	355	(0)
	676	(0)	675	(0)		462	(2)	457	(4)
	1927	(0)	1859	(0)		473	(36)	476	(18)
	2091	(0)	2008	(0)		662	(189	662	(177)
	2170	(0)	2085	(0)		1876	(971)	1831	(710)
b_{1g}	84	(0)	81	(0)		2080	(1820)	2001	(1548)
	127	(0)	123	(0)	b_{2u}	52	(0)	44	(0)
	412	(0)	416	(0)		102	(1)	97	(1)
	472	(0)	488	(0)		114	(1)	108	(1)
	624	(0)	616	(0)		392	(0)	392	(0)
	2061	(0)	1972	(0)		448	(52)	464	(24)
b_{2g}	145i		98i			535	(13)	523	(13)
	58	(0)	54	(0)		650	(181)	644	(174)
	153	(0)	155	(0)		2092	(2530)	2002	(2210)
	309	(0)	316	(0)	b_{3u}	69	(1)	65	(0)
	464	(0)	473	(0)		107	(0)	103	(0)
	493	(0)	480	(0)		239	(15)	238	(14)
	680	(0)	677	(0)		392	(14)	419	(5)
	2075	(0)	1996	(0)		453	(75)	472	(56)
b_{3g}	67	(0)	60	(0)		530	(241)	519	(189)
	95	(0)	92	(0)		559	(178)	552	(196)
	371	(0)	372	(0)		657	(498)	657	(509)
	514	(0)	498	(0)		2081	(660)	1999	(464)
	575	(0)	558	(0)		2117	(1687)	2041	(1479)

Table 5. Relative Energies (in kcal/mol) for the $Mn_2(CO)_9$ Isomers

	no. of bridging CO	B3LYP	BP86
8-1 (D_{2d}) + CO		33.7	39.5
9-5 (C_{2v})	3	25.9	17.7
9-4 (C_2)	1 + 2 (semi)	22.6	15.5
9-3 (D_{3h}) triplet	3	16.0	12.2
9-2 (C_{2v})	0	5.8	7.2
9-1 (C_s)	1 (semi)	0.0	0.0

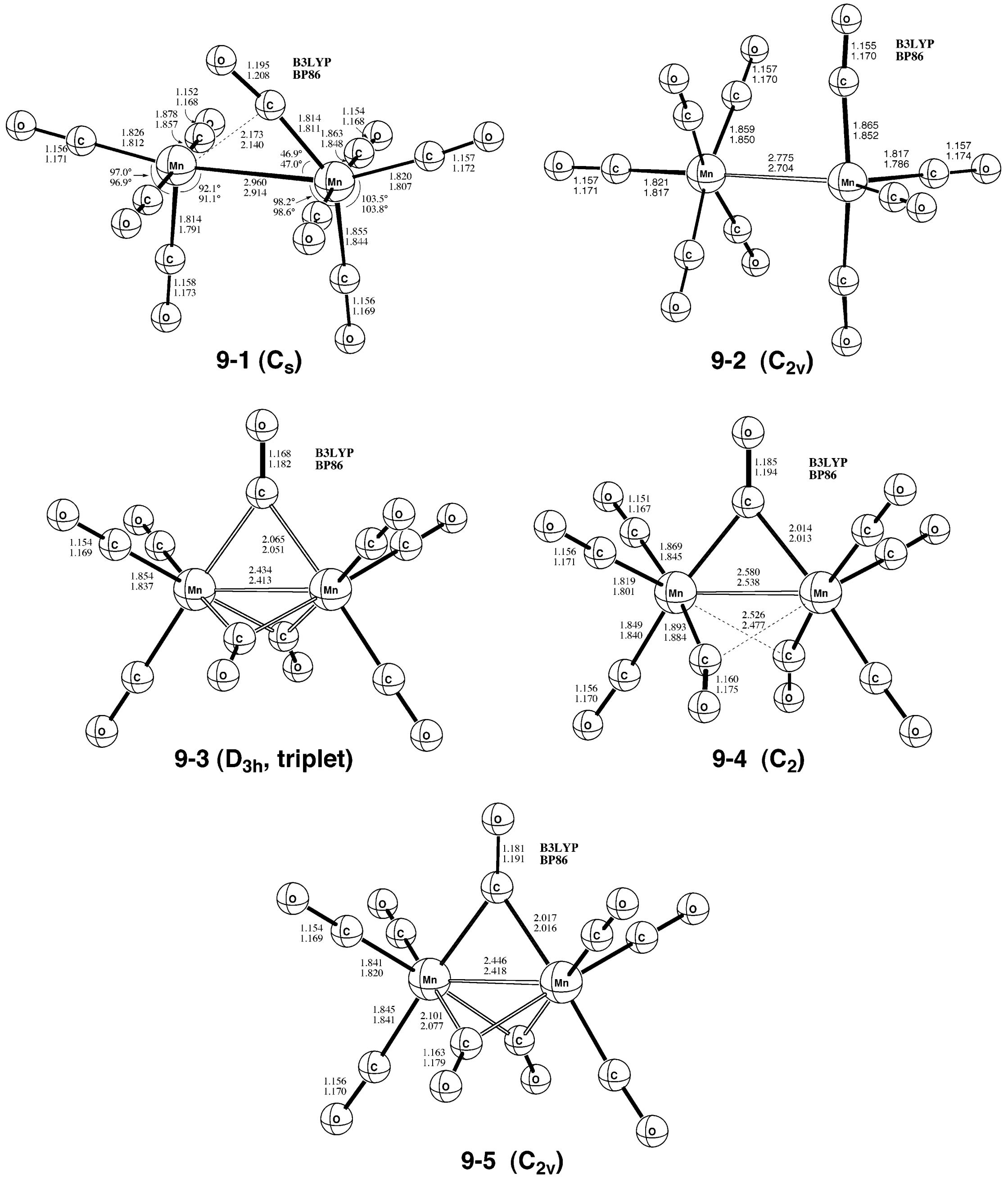
Table 6. Harmonic Vibrational Frequencies (cm^{-1}) and Their Infrared Intensities (km/mol, in Parentheses) for the C_s $Mn_2(CO)_9$ (**9-1**)

	B3LYP		BP86			B3LYP		BP86	
a′	47	(0)	43	(0)	a″	20	(0)	17	(0)
	50	(0)	50	(0)		71	(0)	65	(0)
	69	(0)	66	(0)		79	(0)	75	(0)
	78	(0)	79	(0)		91	(0)	88	(0)
	95	(0)	88	(0)		96	(0)	93	(0)
	103	(1)	97	(0)		111	(0)	106	(0)
	105	(0)	98	(0)		113	(0)	108	(0)
	108	(0)	105	(0)		157	(0)	152	(0)
	160	(0)	162	(0)		368	(0)	367	(0)
	263	(8)	263	(4)		396	(0)	397	(0)
	390	(5)	394	(1)		409	(0)	411	(0)
	400	(2)	418	(1)		416	(3)	419	(0)
	408	(2)	423	(2)		446	(42)	466	(31)
	426	(3)	433	(1)		469	(9)	481	(1)
	436	(1)	446	(1)		563	(0)	545	(0)
	464	(2)	465	(11)		576	(4)	562	(4)
	471	(27)	481	(10)		585	(1)	571	(1)
	479	(5)	496	(1)		635	(45)	632	(44)
	487	(7)	496	(5)		653	(122)	647	(105)
	501	(15)	499	(16)		2059	(9)	1970	(40)
	530	(1)	521	(2)		2091	(2512)	2000	(2178)
	538	(4)	534	(10)					
	643	(111)	651	(91)					
	668	(283)	674	(322)					
	683	(163)	680	(57)					
	687	(111)	683	(105)					
	1827	(416)	1767	(380)					
	2045	(75)	1966	(156)					
	2064	(1076)	1983	(853)					
	2073	(813)	1989	(502)					
	2085	(358)	2003	(395)					
	2106	(1584)	2034	(1197)					
	2163	(48)	2078	(46)					

1983 (b_2), 2014 (e_1), and 2045 (e_2) cm^{-1} for $Mn_2(CO)_{10}$ in *n*-hexane solution,[31] and then Parker observed these absorptions, 1992 (b_2), 2025 (e_1), and 2053 (e_2) cm^{-1}, in the gas phase.[32] Our theoretical predictions, especially the BP86 results, are in good agreement with these experimental observations (Table 2).

3.2 $Mn_2(CO)_9$. The global minimum of $Mn_2(CO)_9$ is the C_s structure **9-1** with an unsymmetrically bridging carbonyl group (Table 5 and Figure 2). This structure was suggested by Dunkin, Härter, and Shields,[11] who proposed a dative bond from a C−O π bond to the Mn atom leading to a bridging carbonyl group donating four rather than the usual two electrons. The Mn−Mn bond distance in **9-1** is 2.91−2.96 Å, which is slightly shorter than that in **10-1**, by about 0.04 Å. This Mn−Mn bond distance corresponds to the single bond required by the 18-electron rule if the bridging CO group is a four-electron donor. The harmonic vibrational frequencies of **9-1** (Table 6) are all real.

Another low-lying $Mn_2(CO)_9$ isomer has a nonbridged structure with C_{2v} symmetry (**9-2**). It lies above **9-1** by only 6−7 kcal/mol (Table 5). The Mn−Mn bond distance in **9-2** is 2.70−2.77 Å, which is shorter than that in **9-1** by 0.2 Å. This is consistent with a zwitterionic structure with a positive charge on the $Mn(CO)_5$ manganese (the "left" manganese in **9-2** of Figure 2) and a negative charge on the $Mn(CO)_4$ manganese (the "right" manganese in **9-2** of Figure 2) and the Mn=Mn double bond required by the 18-electron role. The B3LYP method computes all real vibrational frequencies for **9-2** (Table 7), indicating a genuine minimum, whereas the BP86 method computes two very small imaginary frequencies: 22i cm^{-1} (b_1) and 9i cm^{-1} (a_2). These very small



9-1 (C_s)

9-2 (C_{2v})

9-3 (D_{3h}, triplet)

9-4 (C_2)

9-5 (C_{2v})

Figure 2. The five isomers of $Mn_2(CO)_9$ found in this work.

imaginary frequencies might be considered as arising from the numerical integration errors. When the grid is increased from (75, 302) to a finer one (99, 590), one imaginary frequency is removed, and the other one becomes even smaller (17i cm^{-1}).

In 1996, Rosa et al. found the semibridged structure **9-1** of $Mn_2(CO)_9$ to be the global minimum using the DFT methods.[33] However, they also predicted three nonbridged structures with higher energies. In the present paper, structure c in Rosa's paper collapses to the global minimum **9-1**, and both structures a and b lead to our low-lying nonbridged structure **9-2**.

Besides these two energetically low-lying structures, we also tried to optimize a D_{3h} tribridged $Mn_2(CO)_9$ structure similar to the global minimum of $Fe_2(CO)_9$.[17] The singlet tribridged $Mn_2(CO)_9$ structure collapsed to a structure **9-4** with lower symmetry (C_2) and 16−22 kcal/mol energy above the global minimum. However, this C_2 structure is a transition state with one imaginary vibrational frequency 151i cm^{-1} (B3LYP) or 100i cm^{-1} (BP86) (Table S1 in Supporting Information). Following the corresponding mode leads to the energetically low-lying structure **9-2**.

The triplet tribridged $Mn_2(CO)_9$ **9-3** was found to be a local minimum. The BP86 method predicts all real vibrational frequencies, while the B3LYP method obtains a small imaginary frequency 49i cm^{-1} (e″ mode) (Table S2 in Supporting Information), which might be considered as a numerical error. The Mn−Mn bond distance of this tribridged structure is the shortest (2.41−2.43 Å) found for any of the isomers of $Mn_2(CO)_9$.

Table 7. Harmonic Vibrational Frequencies (cm^{-1}) and Their Infrared Intensities (km/mol, in Parentheses) for the C_{2v} $Mn_2(CO)_9$ (**9-2**)

	B3LYP		BP86			B3LYP		BP86	
a_1	79	(1)	78	(1)	b_1	23	(0)	22i	(0)
	90	(0)	86	(0)		68	(0)	63	(0)
	110	(1)	108	(1)		96	(1)	93	(0)
	118	(2)	115	(1)		104	(0)	99	(0)
	155	(2)	162	(2)		111	(0)	110	(0)
	399	(27)	419	(14)		398	(1)	394	(0)
	411	(1)	426	(2)		418	(2)	419	(1)
	457	(8)	479	(0)		474	(9)	483	(7)
	476	(1)	497	(0)		487	(34)	498	(22)
	562	(40)	544	(0)		562	(0)	548	(0)
	564	(103)	557	(109)		632	(55)	630	(50)
	670	(208)	677	(332)		667	(95)	662	(79)
	688	(196)	684	(0)		2038	(6)	1954	(52)
	2055	(274)	1973	(336)		2076	(2526)	1993	(2094)
	2069	(28)	1989	(182)	b_2	23	(0)	10	(0)
	2094	(2033)	2020	(1363)		68	(0)	65	(0)
	2160	(1)	2075	(22)		84	(1)	78	(1)
a_2	12	(0)	9i			93	(0)	92	(0)
	72	(0)	68	(0)		109	(0)	105	(0)
	90	(0)	88	(0)		382	(0)	393	(0)
	369	(0)	369	(0)		415	(0)	406	(0)
	373	(0)	374	(0)		474	(18)	490	(11)
	412	(0)	422	(0)		483	(10)	495	(2)
	470	(0)	458	(0)		552	(1)	533	(1)
	549	(0)	537	(0)		593	(22)	602	(21)
	2066	(0)	1996	(0)		666	(124)	657	(111)
						2051	(62)	1961	(195)
						2063	(2251)	1982	(1763)

Table 8. Relative Energies (in kcal/mol) for the $Mn_2(CO)_8$ Isomers

	no. of bridging CO	B3LYP	BP86
7-1 (C_s) + CO		45.5	47.7
8-9 (D_{2h})	4	80.8	60.6
8-8 (C_{2h})	4	42.4	27.5
8-7 (D_{4h})	0	41.9	45.3
8-6 (C_{2v})	2	18.5	12.7
8-5 (C_{2h})	2	15.2	6.3
8-4 (C_{2h})	2 (semi)	12.6	9.6
8-3 (C_2)	2 (semi)	6.4	5.8
8-2 (C_s)	0	1.6	2.6
8-1 (D_{2d})	0	0.0	0.0

Table 9. Harmonic Vibrational Frequencies (cm^{-1}) and Their Infrared Intensities (km/mol, in Parentheses) for the Nonbridged D_{2d} $Mn_2(CO)_8$ (**8-1**)

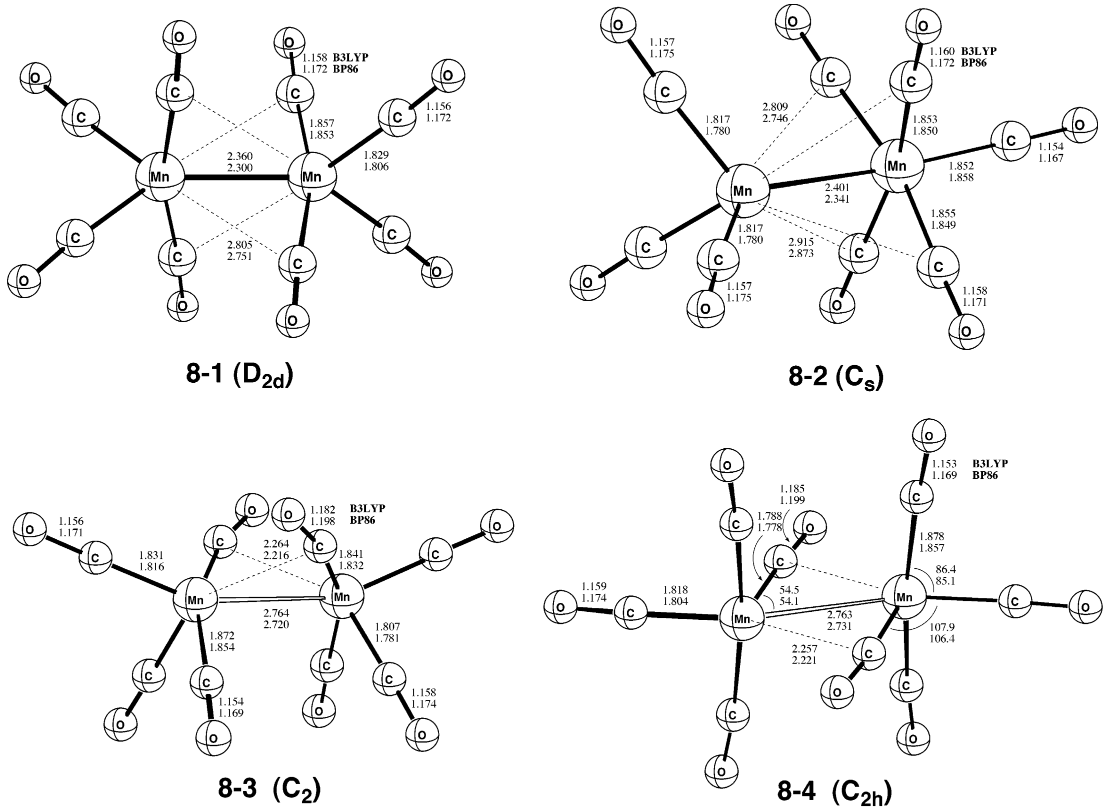
	B3LYP		BP86			B3LYP		BP86	
a_1	79	(0)	77	(0)	b_2	82	(3)	81	(3)
	88	(0)	87	(0)		115	(2)	111	(2)
	202	(0)	223	(0)		411	(55)	424	(26)
	422	(0)	428	(0)		451	(9)	482	(0)
	448	(0)	469	(0)		527	(232)	509	(182)
	564	(0)	547	(0)		652	(227)	655	(174)
	668	(0)	668	(0)		2051	(9)	1976	(67)
	2057	(0)	1977	(0)		2085	(2129)	2003	(1747)
	2147	(0)	2057	(0)	e	36	(0)	33	(0)
a_2	82	(0)	78	(0)		73	(1)	65	(1)
	368	(0)	364	(0)		85	(0)	80	(0)
	527	(0)	509	(0)		100	(0)	96	(0)
b_1	45	(0)	46	(0)		393	(0)	388	(0)
	84	(0)	81	(0)		395	(0)	400	(0)
	403	(0)	399	(0)		472	(17)	478	(4)
	526	(0)	509	(0)		497	(3)	499	(1)
						568	(32)	571	(42)
						628	(88)	619	(66)
						2037	(578)	1956	(161)
						2066	(1748)	1978	(1788)

Table 10. Harmonic Vibrational Frequencies (cm^{-1}) and Their Infrared Intensities (km/mol, in Parentheses) for the Nonbridged C_s $Mn_2(CO)_8$ (**8-2**)

	B3LYP		BP86			B3LYP		BP86	
a′	39	(0)	33	(0)	a″	6	(0)	21i	
	55	(1)	50	(1)		28	(0)	11	(0)
	85	(0)	82	(0)		39	(0)	37	(0)
	87	(0)	89	(0)		58	(1)	53	(0)
	95	(1)	91	(0)		86	(0)	83	(0)
	96	(0)	94	(0)		95	(1)	95	(0)
	110	(0)	102	(0)		110	(0)	103	(0)
	118	(0)	117	(0)		376	(0)	374	(0)
	193	(19)	210	(14)		378	(0)	377	(1)
	395	(1)	379	(1)		391	(0)	395	(0)
	402	(0)	408	(0)		400	(1)	400	(0)
	412	(19)	418	(26)		411	(0)	413	(0)
	450	(5)	459	(7)		454	(0)	444	(0)
	458	(13)	491	(4)		485	(19)	491	(4)
	485	(18)	497	(1)		490	(11)	509	(8)
	489	(12)	509	(8)		534	(9)	522	(8)
	535	(9)	522	(7)		616	(31)	626	(58)
	564	(0)	541	(0)		661	(100)	653	(57)
	616	(30)	626	(56)		2036	(250)	1947	(144)
	661	(103)	652	(62)		2048	(335)	1985	(446)
	674	(97)	694	(10)		2063	(1706)	1975	(1300)
	691	(253)	667	(294)					
	2035	(248)	1947	(116)					
	2060	(1960)	1977	(1709)					
	2071	(146)	1999	(65)					
	2091	(1980)	2008	(1704)					
	2145	(7)	2058	(91)					

We also investigated a singlet tribridged structure with C_{2v} symmetry, **9-5**, and found it to be a stationary point with rather high energy: 18 or 26 kcal/mol above **9-1** (Table 5). Structure **9-5** has two (a_2 and b_2 with B3LYP) or three (a_2, b_1, and b_2 with BP86) imaginary vibrational frequencies (Table S3 in Supporting Information), and the corresponding normal modes lead to either the **9-4** or **9-2** structure.

3.3 $Mn_2(CO)_8$. We have found no less than nine stationary points for the $Mn_2(CO)_8$ stoichiometry (Table 8). The global minimum is a nonbridged D_{2d} structure (**8-1**, Figure 3). The Mn−Mn bond distance (2.30−2.36 Å) is much shorter than that in **9-1**, indicating a higher bond order. The vibrational analysis shows that **8-1** is a genuine minimum with all real vibrational frequencies (Table 9). Another low-lying $Mn_2(CO)_8$ isomer is also nonbridged (**8-2**, Figure 3, Table 10), which lies only 1−3 kcal/mol above **8-1**. It has an unsymmetrical $(OC)_3Mn-Mn(CO)_5$ structure with C_s symmetry, and its Mn−Mn bond distance (2.34−2.40 Å) is slightly longer than that for **8-1**. The B3LYP method computes all real vibrational frequencies. However, the BP86 method computes a very small imaginary frequency (21i cm^{-1}, Table 10), which might be considered as a numerical noise. The third $Mn_2(CO)_8$ isomer (**8-3**, Figure 3) is also a relatively energetically low-lying species, only 5.8−6.4 kcal/mol above the global minimum **8-1**. The Mn−Mn bond distance in **8-3** (2.72−2.76 Å) is longer than those for **8-1** and **8-2**. However, there are short distances (2.22−2.26 Å) from each Mn atom to a C atom on the other Mn atom thereby suggesting dative bonds from the π orbital of the CO group to the Mn atom (dashed lines in Figure 3) similar to the bridging CO group in **9-1**. Thus, the two bridging CO groups in **8-3** appear to be four-electron donor bridges, so that only a Mn−Mn single bond is required to give the manganese atoms the favored



8-1 (D_{2d})

8-2 (C_s)

8-3 (C_2)

8-4 (C_{2h})

Figure 3. The four energetically lowest lying isomers of $Mn_2(CO)_8$ found in this work.

Table 11. Harmonic Vibrational Frequencies (cm^{-1}) and Their Infrared Intensities (km/mol, in Parentheses) for the Nonbridged C_2 $Mn_2(CO)_8$ (**8-3**)

	B3LYP		BP86			B3LYP		BP86	
a	36	(0)	31	(0)	b	53	(0)	51	(0)
	50	(0)	50	(0)		77	(0)	75	(0)
	74	(0)	70	(0)		80	(0)	79	(0)
	82	(0)	80	(0)		88	(0)	84	(0)
	98	(1)	95	(0)		104	(0)	101	(0)
	107	(0)	102	(0)		122	(0)	119	(0)
	150	(0)	146	(0)		134	(0)	144	(0)
	165	(0)	166	(0)		392	(3)	391	(8)
	190	(0)	197	(0)		399	(7)	399	(6)
	371	(0)	365	(0)		412	(22)	418	(4)
	400	(1)	405	(0)		423	(1)	432	(7)
	428	(0)	430	(0)		443	(10)	452	(6)
	436	(0)	442	(0)		467	(9)	483	(3)
	453	(6)	461	(4)		476	(9)	491	(13)
	478	(7)	485	(5)		535	(20)	528	(3)
	484	(8)	496	(6)		562	(17)	554	(10)
	529	(16)	528	(3)		627	(131)	634	(78)
	561	(13)	554	(8)		642	(245)	642	(72)
	625	(87)	628	(68)		647	(165)	653	(306)
	652	(23)	652	(27)		1885	(496)	1808	(459)
	663	(4)	663	(0)		2051	(190)	1968	(277)
	1891	(452)	1807	(393)		2074	(1538)	1988	(1199)
	2051	(249)	1969	(170)		2093	(2146)	2011	(1698)
	2070	(980)	1982	(864)					
	2141	(207)	2054	(202)					

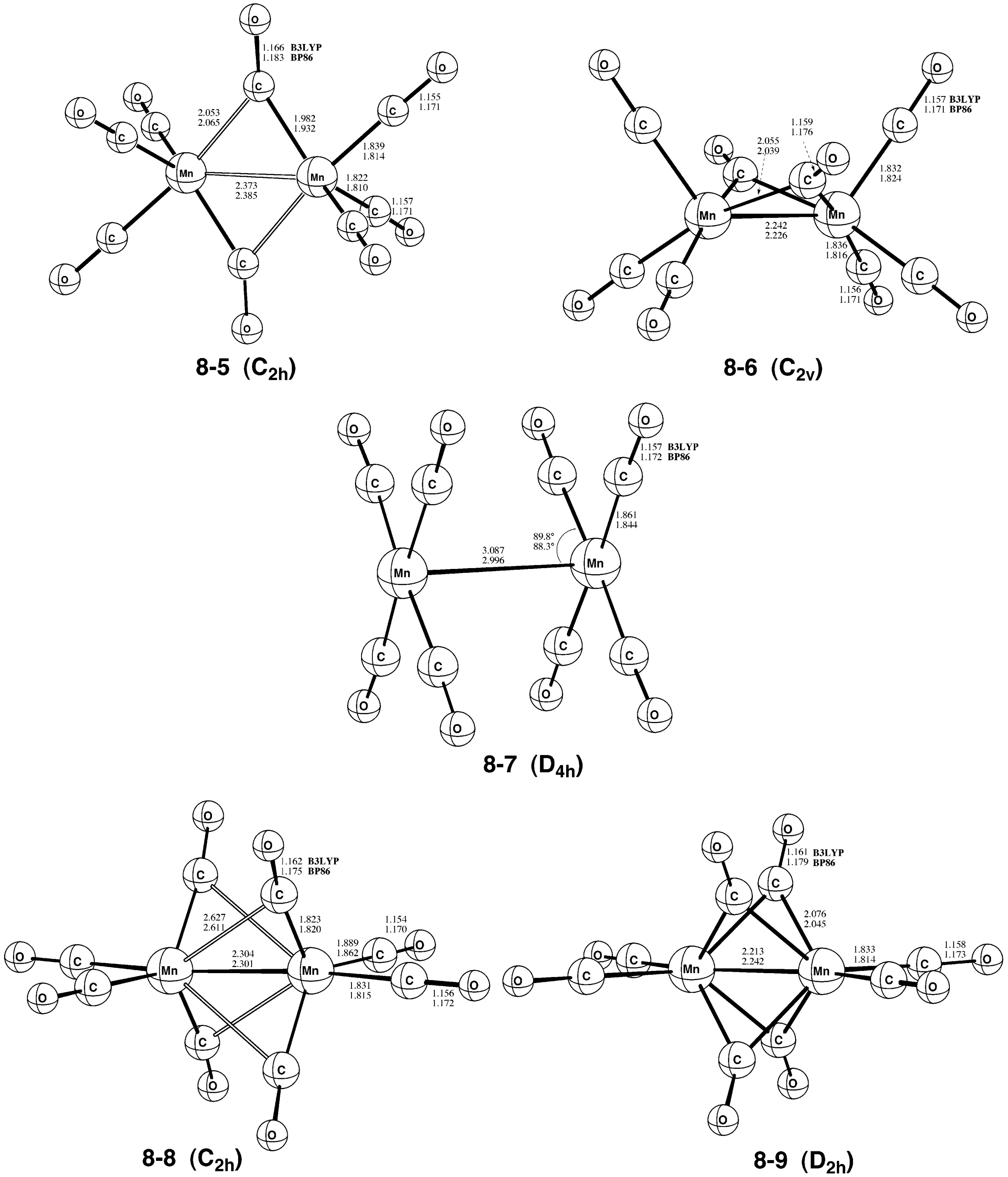
Table 12. Harmonic Vibrational Frequencies (cm^{-1}) and Their Infrared Intensities (km/mol, in Parentheses) for the Nonbridged C_{2h} $Mn_2(CO)_8$ (**8-4**)

	B3LYP		BP86			B3LYP		BP86	
a_g	52	(0)	53	(0)	a_u	50	(0)	47	(0)
	88	(0)	85	(0)		69	(0)	64	(0)
	97	(0)	94	(0)		106	(0)	102	(0)
	169	(0)	169	(0)		137	(1)	127	(1)
	191	(0)	191	(0)		368	(1)	363	(1)
	390	(0)	397	(0)		409	(6)	410	(3)
	408	(0)	422	(0)		433	(65)	449	(41)
	464	(0)	470	(0)		594	(2)	581	(0)
	503	(0)	511	(0)		632	(100)	627	(90)
	523	(0)	520	(0)		2086	(2663)	1988	(2318)
	628	(0)	636	(0)	b_u	39	(1)	44	(0)
	681	(0)	678	(0)		82	(3)	82	(2)
	1885	(0)	1821	(0)		86	(2)	85	(2)
	2059	(0)	1974	(0)		112	(3)	116	(4)
	2151	(0)	2062	(0)		388	(11)	412	(46)
b_g	88	(0)	86	(0)		421	(76)	418	(11)
	110	(0)	106	(0)		471	(123)	482	(118)
	114	(0)	108	(0)		482	(11)	499	(3)
	377	(0)	375	(0)		526	(66)	526	(77)
	413	(0)	421	(0)		626	(182)	633	(149)
	448	(0)	458	(0)		653	(229)	660	(175)
	568	(0)	554	(0)		1877	(935)	1822	(866)
	627	(0)	621	(0)		2051	(1822)	1967	(1252)
	2056	(0)	1961	(0)		2101	(1129)	2019	(1089)

18-electron configuration. Structure **8-3** is a genuine minimum with all real vibrational frequencies (Table 11).

The fourth nonbridged isomer of $Mn_2(CO)_8$, **8-4**, has C_{2h} symmetry with two four-electron donor CO bridges, as indicated by the short distances (2.22−2.25 Å) between a manganese atom and a carbon atom on the other manganese (shown by dashed lines in Figure 3). This $Mn_2(CO)_8$ isomer (**8-4**) lies energetically above the global minimum **8-1** by 9−13 kcal/mol and is a genuine minimum with all real vibrational frequencies (Table 12) obtained by both B3LYP and BP86 methods. In **8-4**, the Mn−Mn bond distance is 2.73−2.76 Å, indicative of the single bond required for both Mn atoms to have the favored 18-electron configuration in the presence of two four-electron donor bridging CO groups.

Two $Mn_2(CO)_8$ isomers having two normal two-electron



8-5 (C_{2h})

8-6 (C_{2v})

8-7 (D_{4h})

8-8 (C_{2h})

8-9 (D_{2h})

Figure 4. The five remaining isomers of $Mn_2(CO)_8$ found in this work.

donor bridging CO groups were found, namely **8-5** (C_{2h}) and **8-6** (C_{2v}) (Figure 4). B3LYP predicts the lower energy structure **8-5** to lie 12.6 kcal/mol above the global minimum **8-1**, while BP86 computes only 6.3 kcal/mol (Table 8). Structure **8-6** has a slightly higher energy, namely 12−19 kcal/mol above **8-1**. The manganese−manganese bond distances in these dibridged species are rather short (2.37−2.39 Å for **8-5**, and 2.23−2.24 Å for **8-6**), consistent with the Mn≡Mn triple bonds required for 18-electron Mn configurations. However, both the C_{2h} and C_{2v} structures are stationary points with several imaginary vibrational frequencies (Tables 13 and S4). The C_{2h} structure **8-5** has two imaginary frequencies computed by B3LYP, and one by BP86. Following the corresponding normal modes leads to the lower energy nonbridged structures **8-1** and **8-2**. The C_{2v} structure **8-6** has four imaginary vibrational frequencies by both DFT methods. Following the corresponding normal modes leads again to the structures **8-1** and **8-2**.

The energetically highest lying minima found for $Mn_2(CO)_8$ (Figure 4) are the highly symmetric D_{4h} nonbridged structure **8-7** and two tetrabridged structures **8-8** (C_{2h}) and **8-9** (D_{2h}). Structure **8-7** has 42−45 kcal/mol higher energy than **8-1**, and a rather long manganese−manganese distance (3.00−3.09 Å) suggesting a Mn−Mn single bond and Mn atoms with 16-electron rather than 18-electron configurations. The two tetrabridged structures lie far above the global

Table 13. Harmonic Vibrational Frequencies (cm^{-1}) and Their Infrared Intensities (km/mol, in Parentheses) for the Dibridged C_{2h} $Mn_2(CO)_8$ (**8-5**)

	B3LYP		BP86			B3LYP		BP86	
a$_g$	75	(0)	72	(0)	b$_g$	21	(0)	40	(0)
	98	(0)	93	(0)		97	(0)	93	(0)
	135	(0)	127	(0)		131	(0)	121	(0)
	201	(0)	208	(0)		386	(0)	386	(0)
	230	(0)	257	(0)		428	(0)	423	(0)
	285	(0)	321	(0)		455	(0)	452	(0)
	369	(0)	391	(0)		526	(0)	530	(0)
	452	(0)	467	(0)		635	(0)	632	(0)
	477	(0)	479	(0)		2053	(0)	1968	(0)
	527	(0)	528	(0)	b$_u$	52i		58	(0)
	608	(0)	606	(0)		89	(2)	82	(2)
	652	(0)	641	(0)		115	(0)	111	(0)
	1973	(0)	1865	(0)		137	(0)	200	(1)
	2070	(0)	1985	(0)		212	(1)	243	(3)
	2141	(0)	2052	(0)		385	(1)	402	(0)
a$_u$	73i		64i			449	(3)	441	(15)
	12	(0)	21	(0)		454	(14)	469	(3)
	61	(0)	54	(0)		505	(81)	507	(12)
	99	(0)	95	(0)		598	(77)	599	(88)
	362	(0)	353	(1)		643	(236)	637	(162)
	384	(0)	378	(0)		1977	(1024)	1883	(798)
	449	(0)	439	(0)		2073	(1399)	1987	(1076)
	527	(75)	533	(26)		2091	(2702)	2015	(2037)
	597	(40)	603	(58)					
	2061	(2073)	1975	(1854)					

Table 14. Relative Energies (in kcal/mol) for the $Mn_2(CO)_7$ Isomers

	no. of bridging CO	B3LYP	BP86
7-5 (C_{2v})	3	21.9	9.3
7-4 (C_{2v})	1	15.3	11.9
7-3 (C_{2v})	2 (semi)	−1.2	4.4
7-2 (C_s)	0	0.1	3.0
7-1 (C_s)	0	0.0	0.0

Table 15. Harmonic Vibrational Frequencies (cm^{-1}) and Their Infrared Intensities (km/mol, in Parentheses) for the Nonbridged C_s $Mn_2(CO)_7$ (**7-1**)

	B3LYP		BP86			B3LYP		BP86	
a′	30	(0)	36	(0)	a″	8	(0)	10	(0)
	55	(0)	53	(0)		56	(0)	54	(0)
	73	(0)	73	(0)		70	(0)	67	(0)
	88	(0)	88	(0)		91	(1)	89	(1)
	91	(1)	89	(1)		94	(0)	90	(0)
	109	(0)	104	(0)		108	(0)	103	(0)
	118	(0)	116	(0)		362	(1)	354	(1)
	225	(20)	248	(6)		368	(1)	364	(0)
	365	(2)	354	(1)		390	(0)	401	(0)
	394	(0)	402	(0)		417	(1)	420	(2)
	409	(14)	419	(12)		475	(32)	478	(11)
	417	(0)	421	(2)		499	(14)	522	(5)
	461	(5)	449	(1)		563	(0)	540	(1)
	463	(1)	478	(11)		619	(51)	618	(73)
	477	(27)	493	(0)		634	(24)	632	(1)
	500	(15)	526	(7)		2023	(79)	1937	(121)
	620	(50)	618	(72)		2049	(2472)	1970	(1898)
	634	(23)	622	(129)					
	639	(163)	631	(0)					
	678	(2)	677	(4)					
	2023	(98)	1937	(136)					
	2044	(1811)	1967	(1716)					
	2058	(627)	1983	(151)					
	2069	(1156)	1987	(1043)					
	2135	(11)	2048	(14)					

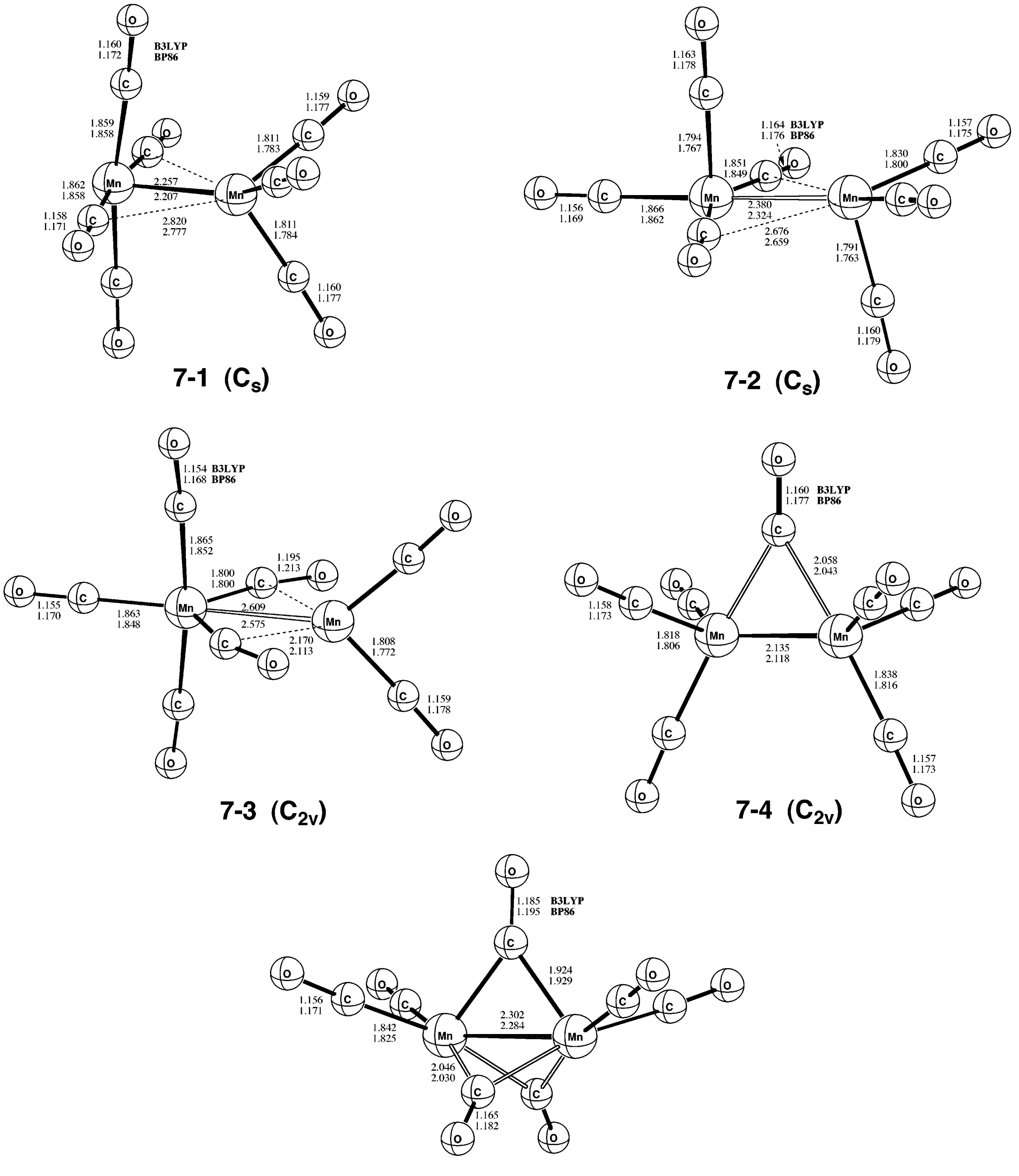
Table 16. Harmonic Vibrational Frequencies (cm^{-1}) and Their Infrared Intensities (km/mol, in Parentheses) for the Nonbridged C_s $Mn_2(CO)_7$ (**7-2**)

	B3LYP		BP86			B3LYP		BP86	
a′	19	(1)	21	(1)	a″	29	(0)	28	(0)
	69	(1)	61	(1)		45	(0)	47	(0)
	78	(1)	74	(0)		71	(0)	70	(0)
	87	(0)	85	(1)		85	(0)	84	(0)
	93	(1)	90	(0)		93	(1)	90	(1)
	105	(0)	101	(0)		111	(0)	104	(0)
	115	(0)	114	(0)		356	(0)	360	(0)
	191	(9)	206	(2)		387	(0)	376	(0)
	372	(7)	377	(9)		397	(0)	401	(0)
	407	(30)	409	(19)		404	(0)	413	(0)
	414	(14)	422	(15)		476	(44)	478	(11)
	440	(16)	449	(13)		479	(0)	488	(22)
	446	(2)	464	(3)		517	(13)	513	(0)
	486	(11)	483	(9)		598	(20)	588	(21)
	500	(10)	514	(1)		627	(44)	625	(32)
	510	(20)	529	(29)		2000	(938)	1929	(235)
	601	(216)	593	(83)		2056	(1396)	1956	(1641)
	609	(53)	621	(92)					
	630	(17)	643	(18)					
	659	(9)	658	(2)					
	2014	(176)	1937	(125)					
	2036	(1094)	1946	(1035)					
	2038	(410)	1965	(211)					
	2074	(2506)	1984	(2219)					
	2126	(20)	2031	(7)					

minimum **8-1** (27−42 kcal/mol for **8-8** and 61−81 kcal/mol for **8-9**, Table 8). Structure **8-7** has only one very small imaginary frequency (25i cm^{-1} with B3LYP and 24i cm^{-1} with BP86, Table S5 in Supporting Information) suggesting that it is a minimum or close to a genuine minimum. The two tetrabridged structures **8-8** and **8-9** are both saddle points with several large imaginary frequencies (Tables S6 and S7). Following the related modes, the D_{2h} structure **8-9** collapses to the C_{2h} structure **8-8** and then to structures **8-3** and **8-5**. The latter finally go to **8-1** and **8-2**.

3.4 $Mn_2(CO)_7$. There are three energetically low-lying $Mn_2(CO)_7$ structures (**7-1**, **7-2**, and **7-3** in Figure 5) having nearly the same energies within 5 kcal/mol (Table 14). The $(OC)_3Mn-Mn(CO)_4$ structures **7-1** and **7-2** can be derived from $(OC)_3Mn-Mn(CO)_5$ (**8-2**) by removal of an axial or equatorial CO group, respectively. The $(OC)_2Mn-Mn(CO)_5$ structure **7-3** can also be obtained by removal of a CO group from **8-2**, but from the other side. Structure **7-1** has the lowest energy, but **7-2** lies only 0.1 (B3LYP) or 3.0 (BP86) kcal/mol higher than **7-1**. Structure **7-3** is computed to have a higher energy by the BP86 method, but the B3LYP method predicts an even lower energy for **7-3** than **7-1** (Table 14). These structures thus appear to be nearly energetically degenerate after considering the accuracy of DFT methods. The manganese−manganese bond distance in **7-1** is very short (2.21−2.26 Å), which is about 0.1 Å shorter than that of **8-1**, suggesting strong metal−metal bonding. This is consistent with the metal−metal bond order of four required for an 18-electron configuration for both manganese atoms in $Mn_2(CO)_7$. Both structures **7-1** and **7-2** are genuine minima with all real vibrational frequencies (Tables 15 and 16). Structure **7-3** has a tiny imaginary vibrational frequency (43i or 44i cm^{-1}, Table 17), which might be considered a consequence of numerical integration errors.

There are two higher-lying structures for $Mn_2(CO)_7$ with bridging CO groups. Structure **7-4** with C_{2v} symmetry has one bridging CO group. It lies above **7-1** by 12 (B3LYP) or 15 (BP86) kcal/mol (Table 14). The Mn−Mn distance is very



7-1 (C_s)

7-2 (C_s)

7-3 (C_{2v})

7-4 (C_{2v})

7-5 (C_{2v})

Figure 5. The five isomers of $Mn_2(CO)_7$ found in this work.

short (2.12−2.14 Å, Figure 5), again suggestive of a metal−metal quadruple bond. However, structure **7-4** has one imaginary vibrational frequency (135i or 46i cm^{-1}, Table S8 in Supporting Information). Following this imaginary frequency leads to the global BP86 minimum **7-1**. Structure **7-5** with C_{2v} symmetry is a tribridged structure, which lies above **7-1** by 22 kcal/mol with the B3LYP method, but about 9 kcal/mol with the BP86 method. Its Mn−Mn bond distance (2.28 or 2.30 Å) is still short but slightly longer than that for the monobridged structure (**7-4**). The BP86 method computes one imaginary vibrational frequency (96i cm^{-1}, a_2) for **7-5**, while the B3LYP method predicts two larger frequencies (209i and 181i cm^{-1}, a_2 and b_1, Table S9 in Supporting Information). Structure **7-5** collapses along the a_2 mode to the monobridged structure **7-4**.

4. Discussion

The DFT computational methods used in this paper are similar to those used in our previous studies of the homoleptic carbonyls of the other 3d transition metals from chromium to copper.[13] The agreement between the computed and experimental values for the geometry of the known $Mn_2(CO)_{10}$ (e.g., the Mn−Mn bond distance and infrared ν(CO) frequencies) provides an additional indication of the validity, accuracy, and relevance of the DFT methods used in this work.

Of particular interest are the structures found for the unsaturated manganese carbonyls $Mn_2(CO)_x$ ($x = 9, 8, 7$). In principle, unsaturated binuclear metal carbonyls can be divided into three general structural types:[13] (1) The first type includes structures containing formal metal−metal multiple

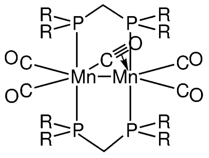
Table 17. Harmonic Vibrational Frequencies (cm^{-1}) and Their Infrared Intensities (km/mol, in Parentheses) for the Nonbridged C_{2v} $Mn_2(CO)_7$ (**7-3**)

	B3LYP		BP86			B3LYP		BP86	
a_1	80	(0)	79	(0)	b_1	44	(0)	40	(0)
	92	(1)	91	(1)		85	(0)	85	(0)
	196	(4)	212	(1)		106	(0)	105	(0)
	203	(7)	232	(1)		231	(0)	246	(0)
	411	(0)	429	(4)		400	(0)	381	(0)
	427	(3)	439	(10)		440	(10)	433	(4)
	459	(71)	472	(57)		509	(7)	493	(10)
	486	(26)	506	(1)		517	(11)	525	(6)
	587	(0)	601	(1)		707	(128)	704	(85)
	665	(7)	684	(51)		1801	(668)	1718	(454)
	675	(339)	656	(268)	b_2	43i		44i	
	1838	(464)	1747	(287)		60	(0)	58	(0)
	2076	(1800)	1979	(1469)		98	(0)	95	(0)
	2079	(362)	1994	(307)		147	(0)	149	(0)
	2135	(152)	2053	(271)		355	(0)	361	(0)
a_2	56	(0)	56	(0)		383	(0)	389	(0)
	111	(0)	109	(0)		467	(15)	471	(5)
	363	(0)	350	(0)		516	(32)	566	(17)
	443	(0)	458	(0)		555	(0)	532	(0)
	556	(0)	536	(0)		641	(108)	636	(94)
						2039	(630)	1937	(623)
						2082	(1712)	2002	(1350)

bonds with the favored 18-electron rare gas electronic configuration for each metal atom. This would imply metal−metal double, triple, and quadruple bonds for $Mn_2(CO)_9$, $Mn_2(CO)_8$, and $Mn_2(CO)_7$, respectively. (2) The second type includes structures containing four-electron bridging carbonyl groups and with a lower metal−metal bond order than otherwise required to accommodate the unsaturation. Such four-electron bridging carbonyl groups are more likely to occur with the more oxophilic early transition metals. (3) The third type includes structures in which one or both of the metal atoms have less than the favored 18-electron configuration, so that the metal−metal bond order is lower than otherwise required to accommodate the unsaturation. Such structures are more likely to occur with the late transition metals and are particularly prevalent in the optimized structures found for the formally unsaturated copper carbonyls $Cu_2(CO)_x$ ($x = 5$, 4, 3, 2, and 1).[14]

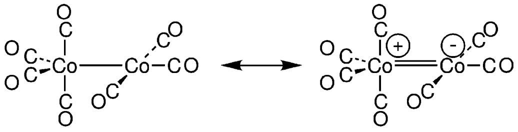
All three of these structural types were found in this DFT study of the unsaturated manganese carbonyls $Mn_2(CO)_x$ ($x = 9$, 8, 7). The variety of structure types found for the unsaturated homoleptic binuclear manganese carbonyls may relate to the central position of manganese among the first row transition metals. Thus, examples of characteristic early and late transition metal behavior are both found with manganese. The structures found for individual stoichiometries are considered in the following paragraphs.

4.1 $Mn_2(CO)_9$. The global minimum energy structure for $Mn_2(CO)_9$ is $[(OC)_4Mn]_2(\mu\text{-}\eta^2\text{-}CO)$, **9-1**, which has a unique four-electron bridging carbonyl group so that the Mn−Mn bond order is 1 as in $Mn_2(CO)_{10}$. In fact, the Mn−Mn bond distance of 2.960 Å (B3LYP) or 2.914 Å (BP86) computed for **9-1** is only ∼0.04 Å shorter than the Mn−Mn bond distances computed for $Mn_2(CO)_{10}$, which clearly has a Mn−Mn single bond. Although $Mn_2(CO)_9$ is only known in matrix isolation experiments, analogous small bite bidentate chelating phosphine derivatives $[R_2PCH_2PR_2]_2Mn_2(CO)_4(\mu\text{-}\eta^2\text{-}CO)$ (**I**, $R = C_6H_5$) have been isolated and characterized structurally by X-ray diffraction.[35,36]



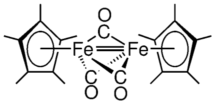
I

A second low-lying structure **9-2** for $Mn_2(CO)_9$ lies only 6−7 kcal/mol above the global minimum **9-1**. This structure has only terminal carbonyl groups. The shorter metal−metal bond distance of 2.775 Å (B3LYP) or 2.704 Å (BP86) relative to **9-1** is consistent with the Mn═Mn double bond required to give each metal atom the favored 18-electron configuration. Structure **9-2** is analogous to structure **II** found[16] as a global minimum for $Co_2(CO)_7$.

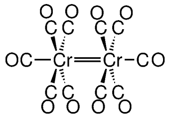


II

A third local minimum computed for $Mn_2(CO)_9$ is the triplet structure $[(OC)_3Mn]_2(\mu\text{-}CO)_3$ (**9-3**) with a Mn═Mn double bond similar to the O═O bond in triplet dioxygen. The Mn═Mn bond distance of 2.434 Å (B3LYP) or 2.413 Å (BP86) is approximately 0.5 Å shorter than the Mn−Mn distance in **9-1** indicative of a double bond shortened further by the three CO bridges. A similar triplet structure is found the isolable complex $(\eta^5\text{-}Me_5C_5Fe)_2(\mu\text{-}CO)_3$ (**III**) whose structure has been determined by X-ray diffraction.[37] The structure found experimentally for **III** is directly related to the structure of **9-3** by the isolobal relationship $\eta^5\text{-}Me_5C_5Fe \longleftrightarrow Mn(CO)_3$. In addition, a triplet structure **IV** with a Cr═Cr double bond was computed[19] to be a local minimum for $Cr_2(CO)_{10}$.



III



IV

In summary, all three structural types for unsaturated binuclear metal carbonyls have been found for the stoichiometry $Mn_2(CO)_9$. Thus, in **9-1** the unsaturation leads to a four-electron donor bridging CO group whereas in **9-2** the unsaturation leads to a coordinately unsaturated (16-electron) $Mn(CO)_4$ unit. Furthermore, in **9-3** the unsaturation leads to a metal−metal double bond as a triplet state with a σ component and two orthogonal single electron π bonds.

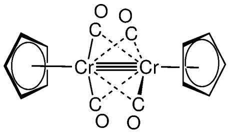
---

(35) Colton, R.; Commons, C. J. *Aust. J. Chem.* **1975**, *28*, 1673.

(36) Commons, C. J.; Hoskins, B. F. *Aust. J. Chem.* **1975**, *28*, 1663.

(37) Blaha, J. P.; Bursten, B. E.; Dewan, J. C.; Frankel, R. B.; Randolph, C. L.; Wilson, B. A.; Wrighton, M. A. *J. Am. Chem. Soc.* **1985**, *107*, 4561.

4.2 $Mn_2(CO)_8$. Barkholtz and Bursten[38] reported some DFT calculations on $Mn_2(CO)_8$, and our comparable results are in essential agreement with their work. Thus, the global energy minimum for $Mn_2(CO)_8$ is the unbridged symmetrical structure **8-1**. The very short Mn$\equiv$Mn distance of 2.360 Å (B3LYP) or 2.300 Å (BP86) is indicative of the triple bond required to give each manganese atom the favored 18-electron configuration. The structure of **8-1** is closely related to that of the well-known isolable $(\eta^5\text{-}R_5C_5)_2Cr_2(CO)_4$ derivatives (**V**, R = H, CH_3),[39] also with a metal−metal triple bond, through the isolobal substitution $(\eta^5\text{-}R_5C_5)Cr(CO)_2 \longleftrightarrow Mn(CO)_4$.



V

A second minimum for $Mn_2(CO)_8$ lying only 1−3 kcal/mol above **8-1** is the unbridged unsymmetrical structure $(OC)_5Mn{\equiv}Mn(CO)_3$, **8-2**. Again, the short Mn$\equiv$Mn distance of 2.401 Å (B3LYP) or 2.341 Å (BP86) suggests a metal−metal triple bond. However, in this case, the two orthogonal π components of the triple bond need to be dative bonds from the $Mn(CO)_5$ group to the $Mn(CO)_3$ group in order to give both manganese atoms the favored 18-electron rare gas electronic configuration.

The next two higher lying structures for $Mn_2(CO)_8$, namely **8-3** and **8-4**, each appear to have two four-electron donor bridging groups similar to the bridging CO in **9-1**. In both cases, the Mn−Mn distances are significantly longer (~2.7 Å) than the Mn$\equiv$Mn distances interpreted as triple bonds in **8-1** and **8-2**. This is consistent with a Mn−Mn single bond being sufficient to give both metal atoms the favored 18-electron configuration in **8-3** and **8-4** when there are two four-electron donor bridging CO groups.

4.3 $Mn_2(CO)_7$. The two lowest lying structures **7-1** and **7-2** may each be derived from the unsymmetrical **8-2** structure for $Mn_2(CO)_8$ by removal of an axial or an equatorial CO group, respectively. Removal of an axial CO group from **8-2** to give **7-1** leads to a reduction of the metal−metal bond distance by ~0.14 Å. This suggests the increase in the metal−metal bond order from 3 in **8-2** to 4 required to give both metal atoms in **7−1** the favored 18-electron rare gas configuration. However, removal of an equatorial CO group from **8-2** to give **7-2** leads to only a 0.02 Å decrease in the metal−metal bond distance. This suggests retention of the metal−metal bond order of 3 and a 16-electron configuration for one of the manganese atoms, probably the $Mn(CO)_4$ metal atom with approximate square pyramidal coordination. The other structure for $Mn_2(CO)_7$ without substantial ($>50i\ cm^{-1}$) imaginary frequencies is **7-3** with two four-electron bridging CO groups and a Mn=Mn distance of 2.609 Å (B3LYP) or 2.575 Å (BP88). This is consistent with the double bond required to give both manganese atoms the favored 18-electron rare gas configuration.

Acknowledgment. This research was supported by the U.S. National Science Foundation Grants CHE-0136186 and CHE-0209857.

Supporting Information Available: Additional tables. This material is available free of charge via the Internet at http://pubs.acs.org.

IC030118R

---

(38) Barckholtz, T. A.; Bursten, B. E. *J. Am. Chem. Soc.* **1998**, *120*, 1926

(39) Curtis, M. D.; Butler, W. M. *J. Organomet. Chem.* **1978**, *155*, 131.