On the Possible Structures of $Mn_2(CO)_8$: Theoretical Support for an Unprecedented Asymmetric Unbridged Isomer

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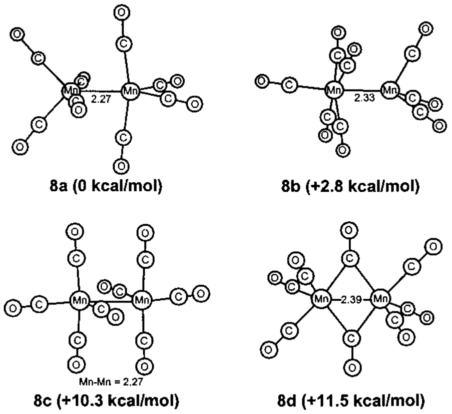
In the 1980s, it was shown that $Mn_2(CO)_{10}$ (**10**) and $Cp_2Fe_2(CO)_2(\mu\text{-}CO)_2$ (Cp = η^5-C_5H_5) can dissociate a carbonyl ligand upon irradiation and that this process competes with photochemical metal−metal bond homolysis.[1] Matrix and solution studies showed that the CO-loss product from **10**, $Mn_2(CO)_9$ (**9**), has a C−O stretching frequency of 1759 cm^{-1}, indicative of a semibridging CO.[2] The CO-loss product from $Cp_2Fe_2(CO)_4$ has three symmetrically bridging CO ligands and a triplet ground state.[3] We recently used low-temperature matrix experiments to show that the initial CO loss photoproducts are also photoactive; upon irradiation, they lose a second CO to form $Mn_2(CO)_8$ (**8**)[4] and $Cp_2Fe_2(CO)_2$.[5] The infrared spectrum of **8** shows that is has only terminal COs.[4] Dark back-reaction of **8** produces IR spectra that contain peaks corresponding to the known form of **9** along with new peaks in the terminal C−O region and a new semibridging CO stretch at 1728 cm^{-1}. We tentatively attributed the new peaks to a second isomer of **9**.[4] To provide further insight into the photochemical processes of **10** and its products, we have used density functional theory (DFT) to calculate the structures, relative energies, and IR spectra of many possible isomers of **8** and **9**.

DFT calculations that incorporate nonlocal corrections have successfully reproduced the crystal structure geometries of **10**,[6] $Fe_2(CO)_9$,[7] and $Co_2(CO)_8$.[6] Recently, Baerends et al. have used DFT to calculate the structure of **9** and the energies and chemistry of the excited states of **10**.[8] These studies have shown that DFT is more accurate than Hartree−Fock,[9] MP2,[10] and CI[11] methods at calculating the geometries of **10** and **9**, especially with respect to the Mn−Mn bond length. Recent calculations of the vibrational frequencies of $Fe_2(CO)_9$ and $Fe_2(CO)_8$ also give credibility to DFT calculations on dinuclear carbonyl complexes.[7] We therefore are confident that DFT can be successfully applied to study the structure, energetics, and infrared spectra of **8**.



8a (0 kcal/mol) **8b (+2.8 kcal/mol)** **8c (+10.3 kcal/mol)** **8d (+11.5 kcal/mol)**

Figure 1. Optimized geometries of **8a**, **8b**, **8c**, and **8d** at the gradient-corrected Becke−Perdew (BP) level. Bond lengths are in angstroms; relative energies are in kcal/mol. Full details are given in the Supporting Information.

Twelve possible structures for **8** were considered and optimized at the relatively inexpensive LDA level[12] (Figure 1S of the Supporting Information). Four structures (**8a**−**d**) were found to be significantly lower in energy than the rest.[13] These four structures were optimized at the gradient-corrected BP level, and their frequencies were calculated at the minima (Table 1 and Supporting Information).[14] As a test of the theory, the geometries and frequencies of the paradigms **10**, **9**, $Fe_2(CO)_9$, and $Co_2(CO)_8$ were also calculated with the BP methodology.

The optimized BP geometries and relative energies of **8a**−**d** are shown in Figure 1. On going from the LDA to the BP calculations, the relative energies of the four isomers change slightly, but not enough to warrant higher-level calculations on the higher-energy structures. Thus, the less-expensive LDA calculations can be used to eliminate geometries that are too high in energy. We have corroborated this approach via calculations on a number of isomers of **10**, **9**, and $Co_2(CO)_8$.[15]

The BP energies of the four isomers suggest that only **8a** and **8b** are likely to be observed experimentally. Because of the small difference in energy between the two isomers (comparable to the expected error in the calculated energies), we have used frequency calculations to help determine which isomer corresponds to the experimentally observed molecule. Although neither isomer gives a perfect correlation with the experimental spectra, isomer **8b** provides a better match than does isomer **8a**. Because no other all-terminal isomers of **8** are even close to **8b** in energy, we propose that the all-terminal structure of **8** observed in the matrix isolation experiments is the unprecedented asymmetric isomer **8b**.

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[12] Computational details: All calculations were performed with the Amsterdam Density Functional program.[12a] Two different functionals were used: the local density approximation (LDA) functional[12b] and the LDA functional plus the nonlocal corrections of Becke[12c] and Perdew (BP).[12d] Complete computational details are given in the Supporting Information. (a) ADF 2.1, Theoretical Chemistry; Vrije Universiteit, Amsterdam (Baerends, E. J.; Ellis, D. E.; Ros, P. *Chem. Phys.* **1973**, *2*, 41−51. te Velde, G.; Baerends, E. J. *J. Comput. Phys.* **1992**, *99*, 84−98). (b) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200. (c) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (d) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.

[13] Structures **8e**, **8f**, and **8g** were also relatively low in energy but will not be considered in this contribution. For **8e** and **8f**, an internal rotation of one of the $Mn(CO)_3$ fragments converts them to **8d**. Thus, we felt it necessary to calculate only one of the isomers at a higher level. Isomer **8g** is the only isomer that has a triplet ground state at the LDA level. Higher-level calculations on this isomer indicate that it will be significantly higher in energy (ca. 22 kcal/mol) than isomer **8a**.

[14] Only the ν(C−O) values are given in Table 1. Complete frequencies for **8a**−**d** are given in the Supporting Information.

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Table 1. Experimental and Calculated C−O Stretching Frequencies for $Mn_2(CO)_n$ (n = 10, 9, 8) and Related Compounds[a]

compound	experimental ν(C−O)	ref	calculated ν(C−O)
$Mn_2(CO)_{10}$ (**10**)	**2116**, 2046 (47), **2024**, 2015 (100), **1997**, 1984 (16), **1981**	4, 20	2096, 2036 (56), 2004, 2001 (100), 1987, 1976 (37), 1968
$Mn_2(CO)_9$ (**9**)	2105 (4), 2055 (63), 2016 (100), 2003 (8), 2000 (15), 1986 (29), 1963 (8), 1759 (12)	4, 2a	2083 (2), 2036 (51), 2001 (100), 2002 (20), 1985 (21), 1981 (41), 1968 (2), 1960 (10), 1780 (19)
$Mn_2(CO)_8$ (**8a**)			2059, 2003 (88), 1975 (100), 1974, 1973 (4), 1952 (4)
$Mn_2(CO)_8$ (**8b**)	2048 (56), *1977 (21)*, 1952 (100), 1940 (88)	4	2062 (7), 2009 (92), 1997 (5), 1980 (23), 1974 (100), 1972 (76), 1940 (8), 1939 (10)
$Mn_2(CO)_8$ (**8c**)	2088 (24), 2027 (94), *2013 (100), 2001 (94), 1984 (47)*, 1728 (12)	4	2067, 2021 (44), 1990 (100), 1970, 1962 (58), 1959, 1831 (40), 1829
$Mn_2(CO)_8$ (**8d**)			2054, 2013 (100), 1981 (58), 1977, 1971 (93), 1964, 1884 (42), 1866
$Fe_2(CO)_9$	**2112**, 2064 (100), 2037 (84), **1990**, **1891**, 1847 (36)	21	2083, 2039 (100), 2011 (76), 2006, 1894, 1868 (42)
$Co_2(CO)_8$ (C_{2v})	2110 (1), 2076 (100), 2050 (19), 2048 (78), 1868 (27), 1857 (42)	22	2086 (1), 2048 (90), 2021 (100), 2020 (84), 2013 (1), 2010, 1878 (18), 1868 (46)
$Co_2(CO)_8$ (D_{3d})	2074 (36), 2027 (100), 2052 (16)	22	2090, 2050 (82), 2016, 2009 (100), 1996 (12), 1992

[a] Values in italic were tentatively assigned in the experimental work. Relative IR intensities are given in parentheses. No value in parenthesis indicates the mode is not IR active, by symmetry. Bold-faced values are from Raman studies of the solid samples; the IR data are from matrix experiments.

We demonstrated that the all-terminal form of **8** undergoes a dark reaction in the matrix, during which it is converted to a new species that contains a semibridging CO [ν(C−O) = 1728 cm^{-1}]. We proposed that this species was a new form of **9**.[4] Our present search of the $Mn_2(CO)_9$ potential energy surface yields no structure consistent with that proposed earlier; every alternative structure with a semibridging CO collapses to the structure previously calculated for **9**.[8,11] However, molecule **8c** could be responsible for the 1728 cm^{-1} band. Isomer **8c** contains two semibridging COs, and only the antisymmetric stretch of these is IR active under C_{2h} symmetry.[16] The calculated C−O stretching frequencies for **8c** are given in Table 1 and compare favorably with the experimental data for the new species of reference 4. Therefore, we now propose that the carrier of the 1728 cm^{-1} absorption is not a new isomer of **9**, but rather **8c**.

There are two problems with the assignments of **8b** and **8c** as the species responsible for the $Mn_2(CO)_8$ spectra. First, the thermal reaction of **8b** to **8c** occurs with a net decrease in the IR absorbance of free CO, indicating consumption of CO in the reaction.[4] It is likely that both **8b** and **8c** can react directly with CO to form **9**. Thus, the thermal process that begins with only **8b** involves several reactions, which when combined can give rise to both the new species **8c** and consumption of CO.

The second problem with our proposed assignments is that the calculated relative energies are in disagreement with the proposed experimental processes. Why would **8b** convert to structure **8c**, which is 8 kcal/mol higher in energy? In our calculation of the relative energies of different isomers of **10**, **9**, and $Co_2(CO)_8$,[10] we found that the error in the calculation of the relative energies using the BP method was approximately 3 kcal/mol.[15] Therefore, the computed difference of 8 kcal/mol cannot be ignored and must be explained.

Our calculations are performed on isolated molecules in the gas phase, while the experiments involve molecules frozen in an "inert" hydrocarbon matrix. As is now well established, many organometallic complexes are able to bind hydrocarbon solvent molecules as ligands.[17] Indeed, the solvated form of $Mn_2(CO)_9$ in a 3-methylpentane matrix has been characterized by its IR spectrum.[18] For the group 6 pentacarbonyls $M(CO)_5L$, the M−L binding energies range from a few kcal/mol for L = methane or a noble gas up to 12 kcal/mol for L = heptane, cyclohexane, and octane.[17] An inspection of the calculated geometries of **8** shows that **8a** has no unoccupied coordination sites on either metal, **8b** has one open site on the $Mn(CO)_3$ fragment, **8c** has an open site on each Mn, and **8d** has no open sites available for binding of a solvent molecule. If we assume that the binding energy of a 3-methylpentane ligand (RH) to these open sites is 10 kcal/mol, then the estimated relative energies become **8c**·$(RH)_2$ (0 kcal/mol), **8b**·(RH) (+2 kcal/mol), **8a** (+10 kcal/mol), and **8d** (+21 kcal/mol). These relative energies thus rationalize the observation of **8b** rather than **8a** as the initial all-terminal form of **8** and the conversion of **8b** to **8c** during the thermal process. The presence of the alkane ligands would also account for the somewhat poorer agreement between the calculated and experimental CO stretching frequencies for **8b** and **8c** than is found for the benchmark molecules.[19]

The proposed isomer $(OC)_5Mn-Mn(CO)_3$ (**8b**) has unprecedented asymmetry for dinuclear binary carbonyls. Given past precedent in metal−carbonyl chemistry, it seems surprising that such a nonintuitive "5−3" isomer of **8** would have an energy comparable to the more intuitive "4−4" isomers. We will provide a detailed discussion of the bonding in isomer **8b** in a subsequent publication.

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Supporting Information Available: Computational details (6 pages). See any current masthead page for ordering information and Web access instructions.

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[16] All else being equal, the antisymmetric stretch of the semibridging CO ligands of **8c** is expected to occur at lower energy than the 1759 cm^{-1} stretch of the semibridging CO in **9**.

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