The diversity of structural features in binuclear cyclobutadiene manganese carbonyls: Relationship to homoleptic manganese carbonyls and cyclopentadienyl chromium carbonyls

Xiaohong Chen [a], Quan Du [a], Rong Jin [a], Hao Feng [a,*], Yaoming Xie [b], R. Bruce King [b,*]

[a] School of Physics and Chemistry, Research Center for Advanced Computation, Xihua University, Chengdu 610039, China
[b] Department of Chemistry and Center for Computational Quantum Chemistry, University of Georgia, Athens, GA 30602, USA

ABSTRACT

The structures and energetics of the cyclobutadiene manganese carbonyls $(C_4H_4)_2Mn_2(CO)_n$ (n = 6, 5, 4, 3) have been investigated using density functional theory. In this connection the lowest energy $(C_4H_4)_2Mn_2(CO)_6$ structure consists of two $C_4H_4Mn(CO)_3$ units coupled through an Mn–Mn bond of length ~3.0 Å. This rather fragile dimer is predicted to dissociate readily into $C_4H_4Mn(CO)_3$ radicals. A higher energy $(C_4H_4)_2Mn_2(CO)_6$ structure has an agostic hydrogen atom and an Mn···Mn distance of ~4.3 Å, too long for a direct bond. The unsaturated pentacarbonyl $(C_4H_4)_2Mn_2(CO)_5$ system resembles its $(C_5H_5)_2Cr_2(CO)_5$ counterpart by having low energy triplet spin state structures and being disfavored relative to $(C_4H_4)_2Mn_2(CO)_6$ + $(C_4H_4)_2Mn_2(CO)_4$. A singlet tetracarbonyl $(C_4H_4)_2Mn_2(CO)_4$ structure is found with a short Mn≡Mn distance of ~2.2 Å suggesting a formal triple bond analogous to the known $(C_5H_5)_2Cr_2(CO)_4$ structure. However, the lowest energy $(C_4H_4)_2Mn_2(CO)_4$ state is a novel triplet spin state octahedral Mn_2C_4 cluster with $Mn(CO)_3$ and $(\eta^4-C_4H_4)Mn(CO)$ vertices. The lowest energy $(C_4H_4)_2Mn_2(CO)_3$ structure by ~13 kcal/mol is an unsymmetrical triplet spin state structure with a C_4H_4 ligand bridging a dative formal Mn≡Mn triple bond connecting an $Mn(CO)_3$ group to a $(\eta^4-C_4H_4)Mn$ group.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Several types of cyclobutadiene derivatives of the first row transition metals have been synthesized (Fig. 1). The first cyclobutadiene metal carbonyl to be synthesized was the iron derivative $(\eta^4-C_4H_4)Fe(CO)_3$, which is obtained from the reaction of $Fe_2(CO)_9$ with 3,4-dichlorocyclobutene [1]. Photolysis of $(\eta^4-C_4R_4)Fe(CO)_3$ is found to give an interesting binuclear derivative $(\eta^4-C_4R_4)_2Fe_2$ (μ-CO)_3 (R = H [2], CH_3 [3]), suggested to have a formal Fe≡Fe triple bond on the basis of a short Fe≡Fe distance. For cobalt, the binuclear tetramethylcyclobutadiene cobalt carbonyl derivative $(\eta^4-Me_4C_4)_2Co_2(CO)_4$ has been synthesized in relatively low yield and characterized by elemental analysis, mass spectrometry, and infrared $\nu(CO)$ frequencies [4]. It is presumed to have a trans doubly bridged structure (Fig. 1), but this has not been confirmed by X-ray crystallography. Related $(\eta^4-diene)_2Co_2(CO)_4$ complexes are known [5] with other dienes such as butadiene, 1,3-cyclohexadiene, and norbornadiene. In addition, the binuclear

cyclobutadiene complex $(\eta^4-C_4H_4)Co_2(CO)_6$ (Fig. 1), i.e. $(\eta^4-C_4H_4)$-$Co(CO)_2Co(CO)_4$, is known [6,7] in which only one of the two cobalt atoms bears a cyclobutadiene ring.

We have now explored the chemistry of binuclear cyclobutadiene manganese carbonyls $(C_4H_4)_2Mn_2(CO)_n$ (n = 6, 5, 4, 3) using well-established density functional theory methods. Such $(C_4H_4)_2Mn_2(CO)_n$ derivatives may be regarded as substitution products of $Mn_2(CO)_n$ (n = 10, 9, 8, 7) by replacement of two pairs of CO groups with two cyclobutadiene ligands. In addition, the $(C_4H_4)_2Mn_2(CO)_n$ derivatives bear a close relationship to binuclear cyclopentadienyl-chromium carbonyls of which $(\eta^5-C_5R_5)_2Cr_2(CO)_n$ (R = H, CH_3; n = 6, 4) have been isolated and structurally characterized by X-ray crystallography (Fig. 2). The tetracarbonyls [8–10] $(\eta^5-C_5R_5)_2Cr_2(CO)_4$ and their molybdenum analogues [11,12] are of historical interest in providing the first examples of formal M≡M triple bonds in metal carbonyl derivatives. Both the $Mn_2(CO)_n$ and $(C_5H_5)_2Cr_2(CO)_n$ systems have been the subject of previous comprehensive density functional theory studies [13–15]. In addition to $(C_4H_4)_2Mn_2(CO)_n$ structures analogous to $Mn_2(CO)_n$ and $(\eta^5-C_5R_5)_2Cr_2(CO)_n$ derivatives, other unusual types of structures were found. Of particular interest is the low-energy triplet cluster structure for $(C_4H_4)_2Mn_2(CO)_4$ having a central C_4Mn_2 octahedron.

* Corresponding authors. Tel.: +1 7065421901; fax: +1 7065429454 (R.B. King).
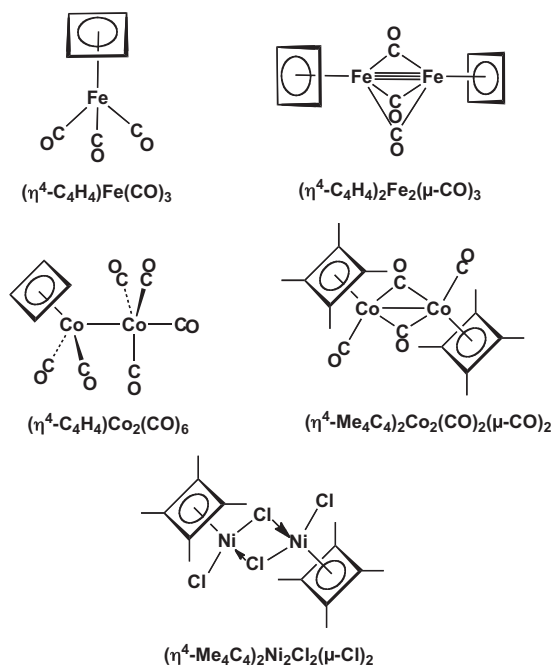E-mail addresses: Fenghao@mail.xhu.edu.cn (H. Feng), rbking@chem.uga.edu (R.B. King).

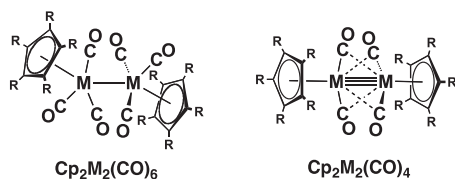Fig. 1. Some known cyclobutadiene and tetramethylcyclobutadiene complexes of the first row transition metals.

Fig. 2. The stable binuclear cyclopentadienylmetal carbonyls of chromium and molybdenum (M = Mo, W; R = H, CH$_3$).

Other unusual (C$_4$H$_4$)$_2$Mn$_2$(CO)$_n$ structure provide examples of agostic C–H–Mn interactions not found in the chemistry of (η^5-C$_5$R$_5$)$_2$Cr$_2$(CO)$_n$ derivatives or even other binuclear cyclopentadienylmetal carbonyls.

2. Theoretical methods

Electron correlation effects were considered by employing density functional theory (DFT) methods, which have been a practical and effective computational tool, especially for organometallic compounds [16–19]. Thus two DFT methods were first tried in this study. The first functional is the B3LYP method, which is the hybrid HF/DFT method combining the three parameter Becke functional (B3) with the Lee–Yang–Parr (LYP) correlation functional [20,21]. The next DFT method is BP86, which combines Becke's 1988 exchange functional (B) with Perdew's 1986 gradient corrected correlation functional method (P86) [22,23]. In the present study, the B3LYP and BP86 methods agree with each other fairly well in predicting the structural characteristics of the (C$_4$H$_4$)$_2$Mn$_2$(CO)$_n$ derivatives. However, in the present study, the B3LYP and BP86 methods predict different singlet–triplet splittings. Fortunately, this discrepancy has been thoroughly studied by Reiher et al., [24] and they have shown that the true value should lie between the B3LYP and BP86 values. For this reason, they proposed a new parametrization for the B3LYP functional, named B3LYP*, which provides electronic state orderings in better agreement with experiment [25]. Therefore, we also used the B3LYP* method to give

more reliable energy differences between the singlet and triplet structures. We will discuss mainly the B3LYP* results in the text so that unless otherwise indicated the distances in the discussion are B3LYP* distances. The B3LYP and BP86 results are listed in the Supplementary data.

All computations were performed using the double-ζ plus polarization (DZP) basis sets. The DZP basis sets used for carbon and oxygen add one set of pure spherical harmonic d functions with orbital exponents α_d(C) = 0.75 and α_d(O) = 0.85 to the standard Huzinaga–Dunning contracted DZ sets [26,27] and are designated (9s5p1d/4s2p1d). For hydrogen, a set of p polarization functions α_p(H) = 0.75 is added to the Huzinaga–Dunning DZ set. The loosely contracted DZP basis set for manganese is the Wachters primitive set [28] augmented by two sets of p functions and a set of d functions, contracted following Hood et al. [29], designated (14s11p6d/10s8p3d).

The geometries of all structures were fully optimized using the three DFT methods. The vibrational frequencies and the corresponding infrared intensities were determined analytically. All of the computations were carried out with the GAUSSIAN 09 program [30] exercising the fine grid option (75 radial shells, 302 angular points) for evaluating integrals numerically [31].

3. Results

3.1. Molecular structures

3.1.1. (C$_4$H$_4$)$_2$Mn$_2$(CO)$_6$

Two low-lying singlet structures were found for (C$_4$H$_4$)$_2$Mn$_2$(CO)$_6$ (Fig. 3 and Table 1). Triplet (C$_4$H$_4$)$_2$Mn$_2$(CO)$_6$ structures were found to have energies more than 30 kcal/mol above the lowest energy singlet structure and thus are not reported in this paper. The lowest energy (C$_4$H$_4$)$_2$Mn$_2$(CO)$_6$ structure **6S-1** by the B3LYP* method lies only ~0.1 kcal/mol below the next lowest energy structure **6S-2** so that these two structures can be regarded as essentially degenerate in energy.

The (C$_4$H$_4$)$_2$Mn$_2$(CO)$_6$ structure **6S-1** has four terminal CO groups and two semibridging CO groups (Fig. 3 and Table 1). However, these semibridging CO groups are only very weakly semibridging with short Mn–C distances of 1.835 Å and relatively long Mn–C distances of 2.844 Å. The C$_4$H$_4$ ligands are terminal tetrahapto ligands. The predicted Mn–Mn distance in **6S-1** of 3.037 Å, although slightly longer than the experimental unbridged Mn–Mn distance of 2.8950(6) Å in Mn$_2$(CO)$_{10}$ by the most recent X-ray crystallography study [32] nevertheless suggests a formal single bond thereby giving each Mn atom the favored 18-electron configuration.

The essentially isoenergetic (C$_4$H$_4$)$_2$Mn$_2$(CO)$_6$ structure **6S-2** is very different from **6S-1** (Fig. 3 and Table 1). Thus **6S-2** has six terminal CO groups, one terminal tetrahapto η^4-C$_4$H$_4$ ligand, and one bridging η^1,η^4-C$_4$H$_4$ ligand bonded to one Mn atom as a tetrahapto ligand and to the other Mn atom through an agostic hydrogen atom in a C–H–Mn bridge. The agostic hydrogen atom in **6S-2** is indicated by a ν(Mn–H) frequency of 1078 cm^{-1} (BP86). Three terminal CO groups are bonded to each Mn atom. The Mn$\cdots$Mn distance of 4.318 Å is too long for a direct bond. However, each Mn atom has the favored 18-electron configuration since in terms of electron bookkeeping the C–H–Mn agostic interaction is equivalent to an Mn–Mn bond.

3.1.2. (C$_4$H$_4$)$_2$Mn$_2$(CO)$_5$

Four low-lying structures (two singlets and two triplets) were found for (C$_4$H$_4$)$_2$Mn$_2$(CO)$_5$ (Fig. 4, Table 2). The lowest energy (C$_4$H$_4$)$_2$Mn$_2$(CO)$_5$ structure is the C_1 triplet structure **5T-1**. Structure **5T-1** has two terminal η^4-C$_4$H$_4$ rings, three terminal