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# Binuclear Cyclooctatetraene-Iron Carbonyl Complexes: Examples of Fluxionality and Valence Tautomerism

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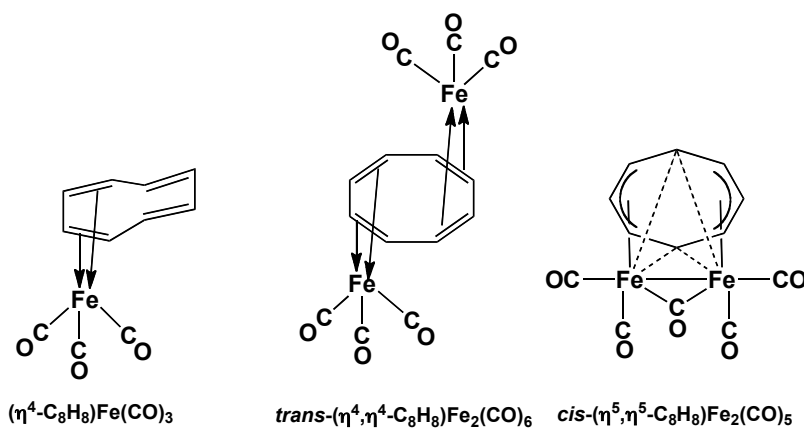
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## Abstract

Reactions of cyclooctatetraene with iron carbonyls under various conditions give not only the monomeric  $(\eta^4\text{-C}_8\text{H}_8)\text{Fe}(\text{CO})_3$  but three  $\text{C}_8\text{H}_8\text{Fe}_2(\text{CO})_6$  isomers and one  $\text{C}_8\text{H}_8\text{Fe}_2(\text{CO})_5$  isomer. Density functional theory on the  $\text{C}_8\text{H}_8\text{Fe}_2(\text{CO})_6$  system shows the *trans*- $(\eta^4, \eta^4\text{-C}_8\text{H}_8)\text{Fe}_2(\text{CO})_6$  isomer to be the lowest energy isomer. The *cis*- $(\eta^3, \eta^3\text{-C}_8\text{H}_8)\text{Fe}_2(\text{CO})_6$  isomer with an Fe–Fe bond and an uncomplexed C=C double bond in the  $\text{C}_8\text{H}_8$  ring lying  $\sim 11$  kcal/mol in energy above *trans*- $(\eta^4, \eta^4\text{-C}_8\text{H}_8)\text{Fe}_2(\text{CO})_6$  appears to correspond to one of the metastable  $\text{C}_8\text{H}_8\text{Fe}_2(\text{CO})_6$  isomers obtained under relatively mild conditions. However, the *cis*- $(\eta^4, \eta^4\text{-C}_8\text{H}_8)\text{Fe}_2(\text{CO})_6$  structure without an Fe–Fe bond suggested for the other metastable isomer appears to be a high-energy structure with a large imaginary vibrational frequency. Following the corresponding normal mode leads to *cis*- $(\eta^3, \eta^3\text{-C}_8\text{H}_8)\text{Fe}_2(\text{CO})_6$ . For  $\text{C}_8\text{H}_8\text{Fe}_2(\text{CO})_5$  the two lowest energy structures are singly bridged *cis*- $\text{C}_8\text{H}_8\text{Fe}_2(\text{CO})_4(\mu\text{-CO})$  structures differing only by a  $22.5^\circ$  rotation of the  $\text{C}_8\text{H}_8$  ring around the central  $\text{Fe}_2$  unit. One of these structures is the experimental  $\text{C}_8\text{H}_8\text{Fe}_2(\text{CO})_5$  structure. The closeness in energy of these two  $\text{C}_8\text{H}_8\text{Fe}_2(\text{CO})_5$  structures is consistent with the experimentally observed fluxionality of this molecule in the NMR spectrum at low temperatures. The unsaturated  $\text{C}_8\text{H}_8\text{Fe}_2(\text{CO})_n$  ( $n = 4, 3$ ) structures obtained by further decarbonylation of  $\text{C}_8\text{H}_8\text{Fe}_2(\text{CO})_5$  retain the bridging bis(tetrahapto) or bis(pentahapto)  $\text{C}_8\text{H}_8$  rings of  $\text{C}_8\text{H}_8\text{Fe}_2(\text{CO})_5$  and provide examples of structures with formal Fe=Fe double bonds with the lowest energy such structures having triplet rather than singlet spin states. Viable carbonyl-rich  $(\eta^2, \eta^2\text{-C}_8\text{H}_8)\text{Fe}_2(\text{CO})_8$  and  $(\eta^4, \eta^2\text{-C}_8\text{H}_8)\text{Fe}_2(\text{CO})_7$  structures represent possible intermediates in the formation of the various  $\text{C}_8\text{H}_8\text{Fe}_2(\text{CO})_n$  ( $n = 6, 5$ ) species from cyclooctatetraene and iron carbonyls.

## 1. Introduction

The seminal discoveries of ferrocene in 1951<sup>1,2</sup> and of dibenzenechromium in 1955<sup>3</sup> suggested the possibility of synthesizing transition metal complexes of larger cyclopolyolefins. In this connection three independent research groups<sup>4,5,6,7</sup> in 1959 reported the reaction of cyclooctatetraene with iron carbonyls under various conditions. Three major products were obtained from such reactions. The major product was the mononuclear complex  $(\eta^4\text{-C}_8\text{H}_8)\text{Fe}(\text{CO})_3$  as a red, air-stable sublimable solid. X-ray crystallography indicated the 1,2,3,4-tetrahapto structure with two adjacent (conjugated) C=C double bonds coordinated to the  $\text{Fe}(\text{CO})_3$  group (Figure 1).<sup>8</sup> The NMR spectrum of  $(\eta^4\text{-C}_8\text{H}_8)\text{Fe}(\text{CO})_3$  was initially a mystery since only a single sharp proton resonance was found under ambient conditions despite the non-equivalence of the protons in the solid state structure. However, cooling the  $(\eta^4\text{-C}_8\text{H}_8)\text{Fe}(\text{CO})_3$  solution to  $-150^\circ\text{C}$  led to splitting of this single proton resonance into the four proton resonances expected for the tetrahapto structure.<sup>9,10</sup> The single proton resonance of  $(\eta^4\text{-C}_8\text{H}_8)\text{Fe}(\text{CO})_3$  at ambient conditions was attributed to the  $\text{Fe}(\text{CO})_3$  moiety “whizzing” around the C=C double bonds of the  $\text{C}_8\text{H}_8$  ring at a fast rate relative to the NMR time scale. Compounds such as  $(\eta^4\text{-C}_8\text{H}_8)\text{Fe}(\text{CO})_3$  were designated as “ring whizzers” as descriptive of this process and represented early examples of fluxional molecules.<sup>11</sup> The 1,2,5,6 tetrahapto  $(\eta^{2,2}\text{-C}_8\text{H}_8)\text{Fe}(\text{CO})_3$  isomer with two opposite (non-conjugated) C=C double bonds of the cyclooctatetraene coordinated to the  $\text{Fe}(\text{CO})_3$  remains unknown. Density functional theory shows this isomer to lie  $\sim 15$  kcal/mol in energy above the known 1,2,3,4-tetrahapto isomer  $(\eta^4\text{-C}_8\text{H}_8)\text{Fe}(\text{CO})_3$ .<sup>12</sup>

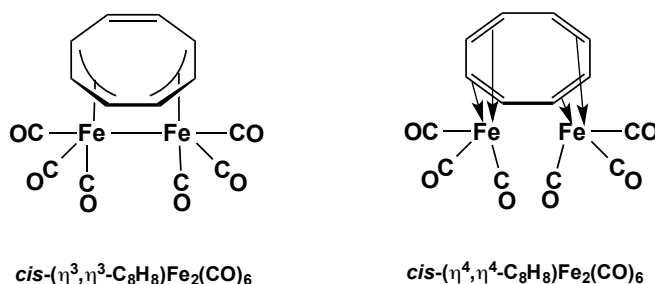


**Figure 1.** The products from the reaction of  $\text{Fe}(\text{CO})_5$  with cyclooctatetraene.

Two binuclear iron carbonyl derivatives of cyclooctatetraene were also found as minor products in the cyclooctatetraene/ $\text{Fe}(\text{CO})_5$  reaction mixture (Figure 1). Yellow *trans*- $(\eta^4, \eta^4\text{-C}_8\text{H}_8)\text{Fe}_2(\text{CO})_6$  is clearly derived from  $(\eta^4\text{-C}_8\text{H}_8)\text{Fe}(\text{CO})_3$  by bonding the two uncomplexed C=C double bonds to a second  $\text{Fe}(\text{CO})_3$  moiety. In *trans*- $(\eta^4, \eta^4\text{-C}_8\text{H}_8)\text{Fe}_2(\text{CO})_6$  the two  $\text{Fe}(\text{CO})_3$  units are located on opposite sides of the  $\text{C}_8\text{H}_8$  ring to reduce steric hindrance. The second binuclear cyclooctatetraene iron carbonyl was a black solid originally incorrectly formulated as the heptacarbonyl “ $(\text{C}_8\text{H}_8)\text{Fe}_2(\text{CO})_7$ ” but subsequently shown by X-ray crystallography to be the pentacarbonyl *cis*- $(\eta^5, \eta^5\text{-C}_8\text{H}_8)\text{Fe}_2(\text{CO})_4(\mu\text{-CO})$ .<sup>13</sup> The bis(pentahapto) coordination of the  $\eta^5, \eta^5\text{-C}_8\text{H}_8$  ring in this structure necessarily results in two of the  $\text{C}_8\text{H}_8$  carbon atoms bridging the pair of iron atoms. This *cis*- $(\eta^5, \eta^5\text{-C}_8\text{H}_8)\text{Fe}_2(\text{CO})_4(\mu\text{-CO})$  structure has one of its five CO groups bridging an iron-iron bond of length 2.776 Å. Considering this Fe–Fe bond as a formal single bond gives each iron atom in *cis*- $(\eta^5, \eta^5\text{-C}_8\text{H}_8)\text{Fe}_2(\text{CO})_4(\mu\text{-CO})$  the favored 18-electron configuration if the  $\text{C}_8\text{H}_8$  ring is assumed to contribute four of its eight  $\pi$  electrons to each iron atom. The species *cis*- $(\eta^5, \eta^5\text{-C}_8\text{H}_8)\text{Fe}_2(\text{CO})_4(\mu\text{-CO})$  exhibited a single sharp proton NMR peak indicating another example of a fluxional cyclooctatetraene iron carbonyl derivative.

In order to gain some insight into possible cyclooctatetraene iron carbonyl intermediates leading particularly to the binuclear derivatives *trans*- $(\eta^4, \eta^4\text{-C}_8\text{H}_8)\text{Fe}_2(\text{CO})_6$  and *cis*- $(\eta^5, \eta^5\text{-C}_8\text{H}_8)\text{Fe}_2(\text{CO})_4(\mu\text{-CO})$  (Figure 1) Pettit and coworkers in 1965<sup>14</sup> investigated the reaction of cyclooctatetraene with  $\text{Fe}_2(\text{CO})_9$  under much milder conditions than those previously used<sup>4,5,6,7</sup> for the reaction of cyclooctatetraene with  $\text{Fe}(\text{CO})_5$ . In addition to  $(\eta^4\text{-C}_8\text{H}_8)\text{Fe}(\text{CO})_3$  three  $\text{C}_8\text{H}_8\text{Fe}_2(\text{CO})_6$  isomers were obtained. One of these  $\text{C}_8\text{H}_8\text{Fe}_2(\text{CO})_6$  isomers was the same *trans*- $(\eta^4, \eta^4\text{-C}_8\text{H}_8)\text{Fe}_2(\text{CO})_6$  derivative as obtained from the cyclooctatetraene/ $\text{Fe}(\text{CO})_5$  reaction (Figure 1). The other two  $\text{C}_8\text{H}_8\text{Fe}_2(\text{CO})_6$  isomers were red-orange solids with the same melting point (90–93°) but distinctly different proton NMR spectra (Figure 2). The isomer exhibiting four NMR peaks of equal intensities was formulated as the bis(trihapto) derivative *cis*- $(\eta^3, \eta^3\text{-C}_8\text{H}_8)\text{Fe}_2(\text{CO})_6$  with an uncomplexed C=C double bond in the  $\text{C}_8\text{H}_8$  ring. The isomer exhibiting only two NMR peaks of equal intensity was formulated as the derivative *cis*- $(\eta^4, \eta^4\text{-C}_8\text{H}_8)\text{Fe}_2(\text{CO})_6$  without an Fe–Fe bond but with a bis(tetrahapto) mode of bonding of the  $\text{C}_8\text{H}_8$  ring to the central  $\text{Fe}_2$  unit similar to that in the *trans*- $(\eta^4, \eta^4\text{-C}_8\text{H}_8)\text{Fe}_2(\text{CO})_6$  isomer obtained from cyclooctatetraene and  $\text{Fe}(\text{CO})_5$ . These two *cis*- $\text{C}_8\text{H}_8\text{Fe}_2(\text{CO})_6$  isomers interconvert rapidly in solution. Furthermore, more prolonged standing of these *cis*- $\text{C}_8\text{H}_8\text{Fe}_2(\text{CO})_6$  isomers in solution leads to loss of one CO group to give the same *cis*- $(\eta^5, \eta^5\text{-C}_8\text{H}_8)\text{Fe}_2(\text{CO})_4(\mu\text{-CO})$  derivative as obtained directly

from  $\text{Fe}(\text{CO})_5$  and cyclooctatetraene. This facile decarbonylation of the  $\text{cis}\text{-C}_8\text{H}_8\text{Fe}_2(\text{CO})_6$  derivatives to  $\text{cis}\text{-}(\eta^5, \eta^5\text{-C}_8\text{H}_8)\text{Fe}_2(\text{CO})_4(\mu\text{-CO})$  is consistent with their *cis* stereochemistries.



**Figure 2.** The proposed structures based on proton NMR spectra for the two *cis*- $\text{C}_8\text{H}_8\text{Fe}_2(\text{CO})_6$  derivatives obtained from cyclooctatetraene and  $\text{Fe}_2(\text{CO})_9$ .

The structure assignments of the two *cis*- $\text{C}_8\text{H}_8\text{Fe}_2(\text{CO})_6$  isomers (Figure 2) is based purely on their proton NMR spectra.<sup>14</sup> Neither of these isomers has been structurally characterized by X-ray crystallography, possibly owing to the difficulty of growing single crystals without decomposition into  $\text{cis}\text{-}(\eta^5, \eta^5\text{-C}_8\text{H}_8)\text{Fe}_2(\text{CO})_4(\mu\text{-CO})$ . Furthermore, these two *cis*- $\text{C}_8\text{H}_8\text{Fe}_2(\text{CO})_6$  isomers do not appear to have been investigated further since their original report more than 50 years ago in 1965. In view of these circumstances we have undertaken a density functional theory investigation of the  $\text{C}_8\text{H}_8\text{Fe}_2(\text{CO})_6$  systems as well as the  $\text{C}_8\text{H}_8\text{Fe}_2(\text{CO})_5$  system in order to provide insight into the chemistry of these interesting fluxional molecules. We have also explored the chemistry of the unsaturated  $\text{C}_8\text{H}_8\text{Fe}_2(\text{CO})_n$  ( $n = 4, 3$ ) systems in order to find possible examples of iron-iron double and triple bonds in binuclear cyclooctatetraene iron carbonyl complexes. Note that the 18-electron rule suggests the *cis*- $\text{C}_8\text{H}_8\text{Fe}_2(\text{CO})_4$  and *cis*- $\text{C}_8\text{H}_8\text{Fe}_2(\text{CO})_3$  systems to be possible candidates for binuclear iron carbonyl complexes with formal  $\text{Fe}=\text{Fe}$  double bonds and  $\text{Fe}\equiv\text{Fe}$  triple bonds, respectively. In addition the carbonyl-rich  $\text{C}_8\text{H}_8\text{Fe}_2(\text{CO})_n$  ( $n = 8, 7$ ) systems are investigated as possible intermediates for the formation of the known  $\text{C}_8\text{H}_8\text{Fe}_2(\text{CO})_n$  ( $n = 6, 5$ ) derivatives from cyclooctatetraene and iron carbonyls.

## 2. Theoretical Methods

During the past 20 years, the B3LYP and BP86 functionals have been used extensively to model organometallic compounds.<sup>15,16,17,18,19,20,21</sup> However, Gusev<sup>22</sup> recently stated that the continuing use of the B3LYP method may be related to a lack of confidence in the newer methods rather than its performance. Furthermore, Gusev

demonstrated that the M06-L functional is a good quality and relatively fast local density functional for computational work in organometallic chemistry and catalysis. For this reason the newer M06-L method<sup>23</sup> as well as the older B3LYP<sup>24,25</sup> and BP86<sup>26,27</sup> methods were used to study the structures of the binuclear cyclooctatetraene-iron carbonyl complexes reported in this paper. All calculations were carried out in Gaussian 09 with tight optimizations and the ultrafine integration grid (99,590) grid).<sup>28</sup>

Double- $\xi$  plus polarization (DZP) basis sets were used in the present study. For carbon, one set of pure spherical harmonic d functions with orbital exponents  $\alpha_d(\text{C}) = 0.75$  and  $\alpha_d(\text{O}) = 0.85$  was added to the standard Huzinaga-Dunning contracted DZ set,<sup>29</sup> designated as (9s5p1d/4s2p1d). For hydrogen, a set of p polarization functions  $\alpha_p(\text{H}) = 0.75$  was added to the Huzinaga-Dunning DZ set. The loosely contracted DZP basis set for iron uses the Wachters' primitive sets augmented by two sets of p functions and one set of d functions and contracted following Hood et al. leading to a (14s11p6d/10s8p3d) basis set.<sup>30,31</sup>

The stationary points of the *cis*- and *trans*- $\text{C}_8\text{H}_8\text{Fe}_2(\text{CO})_n$  ( $n = 8, 7, 6, 5, 4, 3$ ) structures were optimized in their lowest energy electronic singlet and triplet states by using the above methods. Frequency calculations were performed at the same levels to confirm the stationary points and to obtain the zero-point energy corrections (ZPC). 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.<sup>32,33,34</sup> Thus, an imaginary vibrational frequency of magnitude less than  $50i \text{ cm}^{-1}$  should imply that there is a minimum with an energy very similar to that of the stationary point in question. All of the final optimized structures reported in this paper have only real vibrational frequencies unless otherwise indicated.

The structures are designated as **N-cis/trans-aX**, where **N** is the number of CO groups, **a** orders the structures according to relative energies by the M06-L method, and **X** designates the spin states, using **S** and **T** for singlets and triplets, respectively. The B3LYP, BP86, and M06-L methods were found to give consistent results for the binuclear cyclooctatetraene-iron carbonyl derivatives. Therefore only the M06-L results are discussed in the text. Further details regarding the results with the B3LYP and BP86 methods are presented in the Supporting Information.

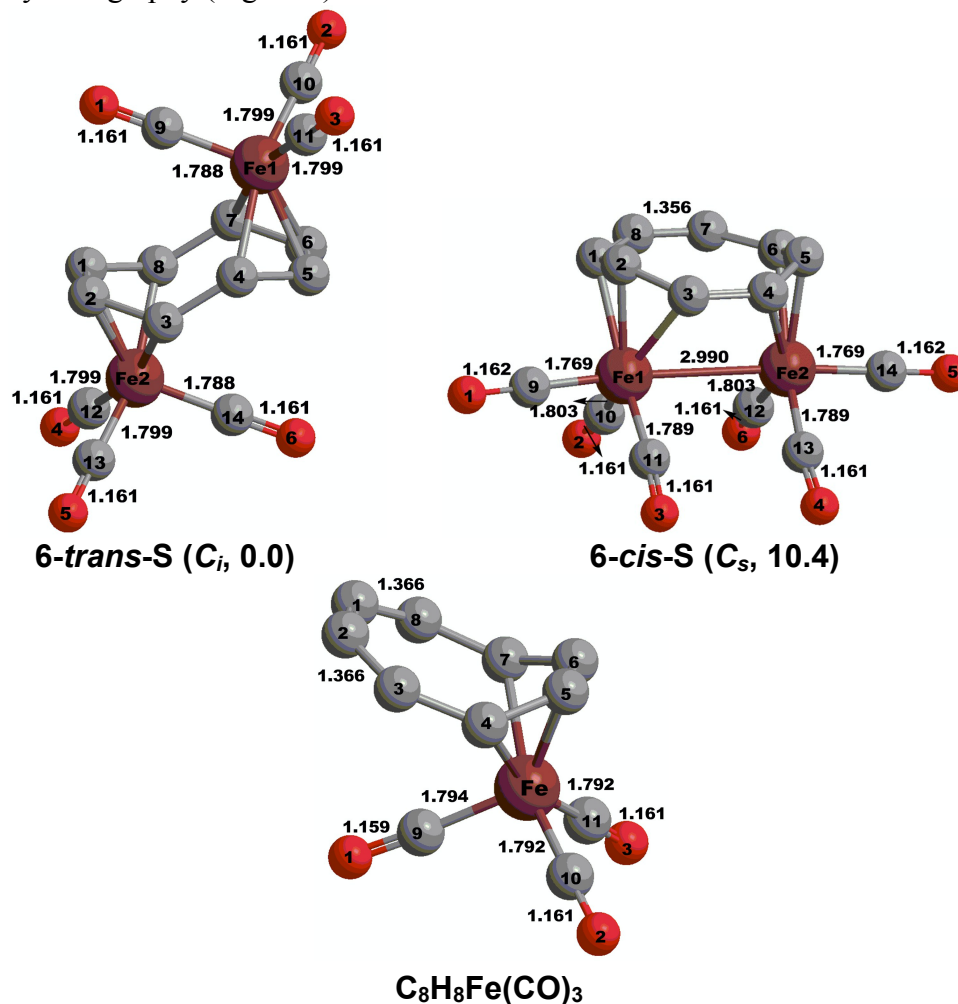
### 3. Results

#### 3.1 Molecular structures

**3.1.1  $\text{C}_8\text{H}_8\text{Fe}_2(\text{CO})_6$  structures.** Both singlet and triplet *cis*- and *trans*- structures were optimized for  $\text{C}_8\text{H}_8\text{Fe}_2(\text{CO})_6$ . However, the triplet structures were found to have energies



more than 15 kcal/mol higher than the lowest energy singlet structure and thus are not discussed in this paper. The Fe–C distances in the lowest energy  $C_8H_8Fe_2(CO)_6$  structure **6-trans-S** indicate that each iron atom is bonded to the  $C_8H_8$  ligand as a tetrahapto ligand corresponding to the experimentally known structure (Figure 1). The singlet *cis*-( $\eta^3, \eta^3$ - $C_8H_8$ ) $Fe_2(CO)_6$  structure **6-cis-S** with the  $C_8H_8$  ligand bonded to each iron atom as a trihapto ligand lies 10.4 kcal/mol in energy above **6-trans-S** (Figure 3). This leaves a relatively short uncomplexed C=C double bond of length 1.356 Å in the  $C_8H_8$  ring. The Fe–Fe distance of 2.99 Å in **6-cis-S** can be interpreted as a formal single bond thereby giving each iron atom the favored 18-electron configuration. The **6-cis-S** structure appears to correspond to one of the less stable  $C_8H_8Fe_2(CO)_6$  isomers obtained from cyclooctatetraene and  $Fe_2(CO)_9$ , which has not been structurally characterized by X-ray crystallography (Figure 2).<sup>14</sup>



**Figure 3.** Optimized geometries for the  $C_8H_8Fe_2(CO)_6$  and  $C_8H_8Fe(CO)_3$  structures. In Figures 3 to 7, the symmetry point groups and relative energies ( $\Delta E$ , in kcal/mol) obtained by the M06-L/DZP method are given in parentheses.

An attempt was made to optimize the *cis*-( $\eta^4, \eta^4$ -C<sub>8</sub>H<sub>8</sub>)Fe<sub>2</sub>(CO)<sub>6</sub> structure presumed to be the third (C<sub>8</sub>H<sub>8</sub>)Fe(CO)<sub>3</sub> isomer obtained from cyclooctatetraene and Fe<sub>2</sub>(CO)<sub>9</sub>.<sup>14</sup> Starting from the *cis*-( $\eta^4, \eta^4$ -C<sub>8</sub>H<sub>8</sub>)Fe<sub>2</sub>(CO)<sub>6</sub> structure, the optimized structure change into *cis*-( $\eta^2, \eta^2$ -C<sub>8</sub>H<sub>8</sub>)Fe<sub>2</sub>(CO)<sub>6</sub>, which was found to lie 36 kcal/mol in energy above **6-trans-S** with a large imaginary vibrational frequency of 132i cm<sup>-1</sup>. Following the corresponding normal mode leads to **6-cis-S**.

**Table 1.** Comparison of predicted intramolecular distances (in Å) and angles (deg) of *trans*-C<sub>8</sub>H<sub>8</sub>Fe<sub>2</sub>(CO)<sub>6</sub> and C<sub>8</sub>H<sub>8</sub>Fe(CO)<sub>3</sub> with the experimental structures determined by X-ray crystallography.<sup>35</sup>

	<i>trans</i> -C <sub>8</sub> H <sub>8</sub> Fe <sub>2</sub> (CO) <sub>6</sub> (singlet)				C <sub>8</sub> H <sub>8</sub> Fe(CO) <sub>3</sub> (singlet)			
	Exp.	M06L	B3LYP	BP86	Exp.	M06L	B3LYP	BP86
FeC(COT)								
Fe1-C4	2.15(3)	2.108	2.139	2.140	2.18(1)	2.202	2.218	2.249
Fe1-C5	2.04(2)	2.056	2.077	2.075	2.05(1)	2.051	2.073	2.066
Fe1-C6	2.03(3)	2.056	2.077	2.075	2.05(1)	2.051	2.073	2.066
Fe1-C7	2.17(3)	2.108	2.139	2.141	2.18(1)	2.202	2.218	2.249
C(COT)C(COT)								
C1-C2	1.39(4)	1.408	1.411	1.421	1.49(3)	1.426	1.438	1.435
C2-C3	1.40(4)	1.439	1.441	1.450	1.34(2)	1.366	1.367	1.383
C3-C4	1.50(4)	1.501	1.514	1.514	1.45(2)	1.447	1.461	1.456
C4-C5	1.40(4)	1.439	1.441	1.450	1.42(1)	1.438	1.441	1.450
FeC(CO)								
Fe1-C9	1.81(3)	1.788	1.788	1.780	1.79(1)	1.794	1.795	1.784
Fe1-C10	1.76(3)	1.799	1.804	1.786	1.80(2)	1.792	1.798	1.781
Fe1-C11	1.73(3)	1.799	1.804	1.786	1.80(2)	1.792	1.798	1.781
CO								
C9-O1	1.13(3)	1.161	1.158	1.173	1.12(2)	1.159	1.156	1.171
C10-O2	1.20(3)	1.161	1.157	1.173	1.13(1)	1.161	1.158	1.175
C11-O3	1.13(3)	1.161	1.157	1.173	1.13(1)	1.161	1.158	1.175
∠								
∠C1C2C3	119(2)	118.9	119.5	119.1	131.8(7)	131.4	131.2	131.2
∠C2C3C4	129(3)	129.3	129.6	129.7	133.2(12)	134.6	134.6	134.7
∠C9Fe1C10	94(1)	99.6	99.2	99.1	100.7(5)	99.6	99.4	98.6
∠C10Fe1C11	90(1)	91.6	91.8	90.3	92.7(7)	93.3	93.2	92.5
∠C9Fe1C11	94(1)	99.6	99.1	98.9	100.7(5)	99.6	99.4	98.6

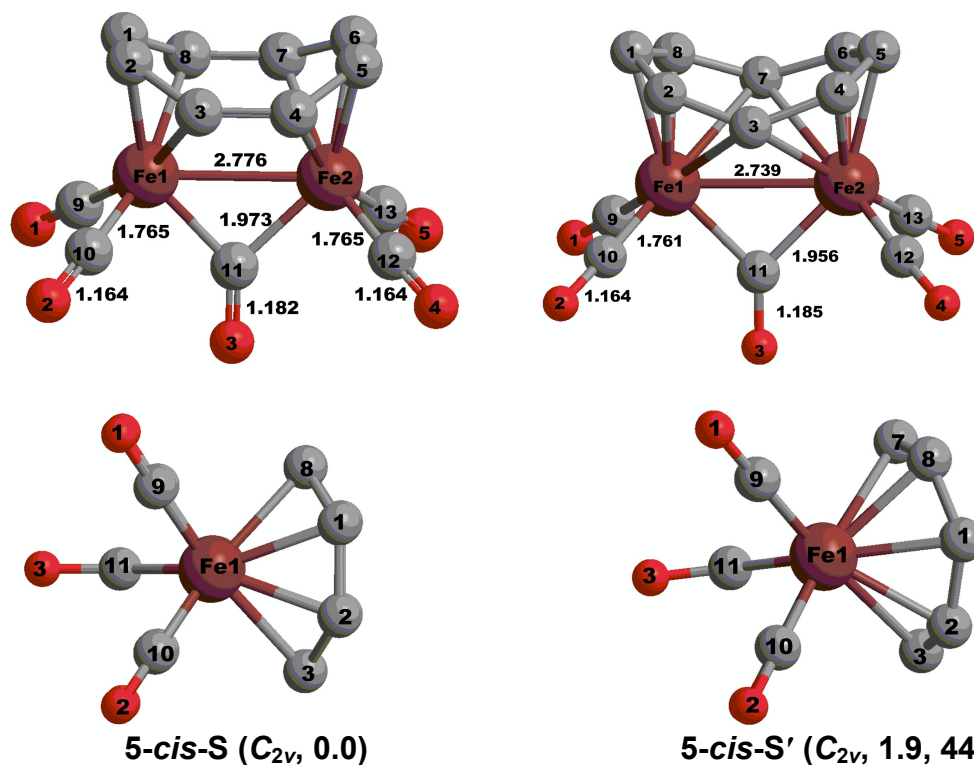
The chair conformation of the C<sub>8</sub>H<sub>8</sub> ring and the Fe–C, C–C bond distances in **6-trans-S** predicted by the M06-L density functional method agree well with the experimental C<sub>8</sub>H<sub>8</sub>Fe<sub>2</sub>(CO)<sub>6</sub> structure as determined by X-ray crystallography (Table 1).<sup>8</sup>



In addition the singlet and triplet spin state structures of the mononuclear  $C_8H_8Fe(CO)_3$  were optimized for comparison of the predicted bond distances and angles with the experimental values determined by X-ray crystallography. The singlet  $C_8H_8Fe(CO)_3$  structure, lying 20.9 kcal/mol in energy below the isomeric triplet  $C_8H_8Fe(CO)_3$  structure, has the  $C_8H_8$  ligand bonded to the iron atom as a tetrahapto ligand using four adjacent carbon atoms. This leaves two uncomplexed conjugated C=C double bonds shorter than 1.4 Å in the  $C_8H_8$  ring and gives the iron atom the favored 18-electron configuration.

**3.1.2  $C_8H_8Fe_2(CO)_5$  structures.** The  $C_{2v}$  singlet *cis*- $C_8H_8Fe_2(CO)_5$  structure **5-cis-S** having a single bridging CO group is predicted to be the lowest energy isomer (Figure 4). The Fe–C distances in **5-cis-S** indicate that the  $C_8H_8$  ring is bonded to each iron atom as a tetrahapto ligand with each carbon atom within bonding distance of a single iron atom. The 2.776 Å Fe–Fe bond distance in **5-cis-S** is very close to the experimental Fe–Fe distance of 2.742 Å determined by X-ray crystallography<sup>13</sup> and suggests a formal single bond. This gives each iron atom in **5-cis-S** the favored 18-electron configuration. However, the bonding of the  $C_8H_8$  ring to the central  $Fe_2$  unit in **5-cis-S** is different from the experimental  $C_8H_8Fe_2(CO)_5$  structure. In the experimental  $C_8H_8Fe_2(CO)_5$  structure a bent  $C_8H_8$  ring functions as a pentahapto ligand to each iron atom with two opposite ring carbon atoms each bridging the Fe–Fe bond. These two carbon atoms lie on the mirror plane in the experimental  $C_8H_8Fe_2(CO)_5$  structure. However, in **5-cis-S** the mirror plane is located differently to bisect two opposite C–C bonds of the  $C_8H_8$  ring. Thus in **5-cis-S** the  $C_8H_8$  ring is rotated 22.5° relative to the  $C_8H_8$  ring in the experimental structure. Using the M06-L method, a  $C_8H_8Fe_2(CO)_5$  structure **5-cis-S'** similar to the experimental  $C_8H_8Fe_2(CO)_5$  structure was found, lying only 1.9 kcal/mol in energy above **5-cis-S** before zero-point energy corrections (ZPC). A small imaginary vibrational frequency of 44i  $cm^{-1}$  in **5-cis-S'** corresponds to the  $C_8H_8$  ring rotation required to convert **5-cis-S'** into **5-cis-S**.

The triplet *cis*- $C_8H_8Fe_2(CO)_5$  structure **5-cis-T**, lying 20.9 kcal/mol in energy above **5-cis-S**, has a single bridging CO group similar to like **5-cis-S** (Figure S1). The  $C_8H_8$  ring in **5-cis-T** is bonded to each iron atom as a trihapto ligand leaving one uncomplexed C=C double bond of length 1.377 Å. The singlet and triplet *trans*- $C_8H_8Fe_2(CO)_5$  structures lie 21.2 kcal/mol above **5-cis-S** (Figure S1). The  $C_8H_8$  rings in **5-trans-S** and **5-trans-T** are bonded as a hexahapto-tetrahapto ligand and a pentahapto-trihapto ligand, respectively. This gives each iron atom in the singlet structure **5-trans-S** the favored 18-electron configuration and each iron atom in the triplet structure **5-trans-T** the 17-electron configuration for a binuclear triplet.

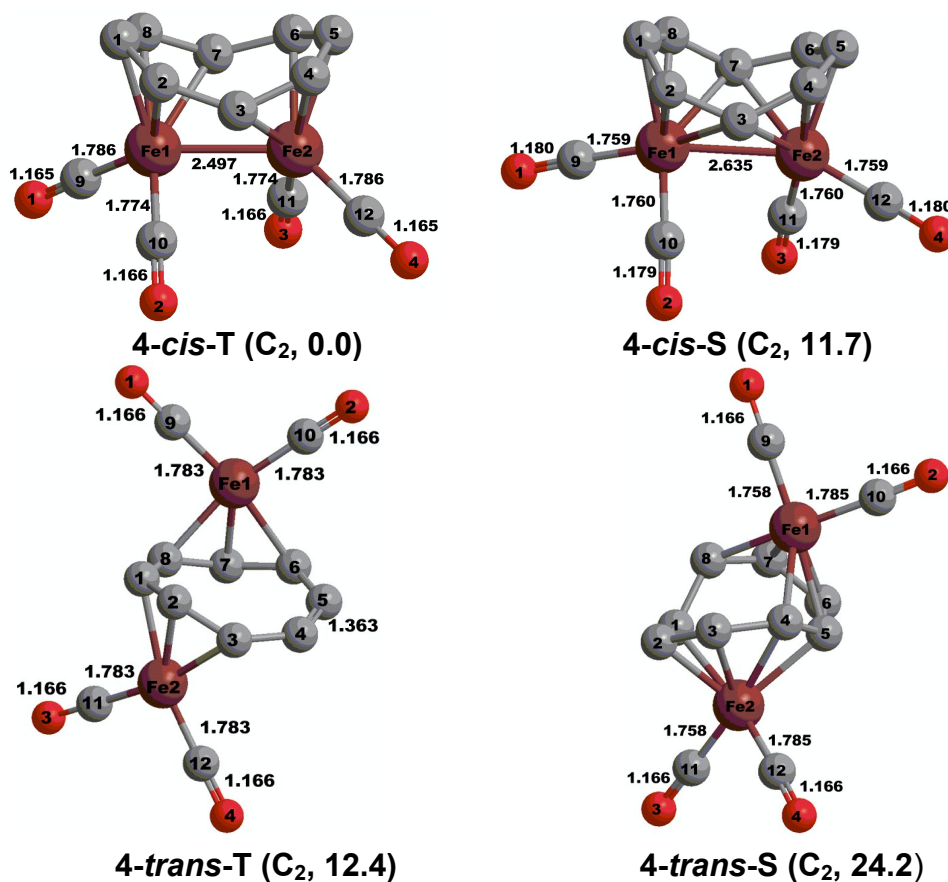


**Figure 4.** Two views of the geometries for the lowest energy  $C_8H_8Fe_2(CO)_5$  structures.

**Table 2.** Comparison of predicted intramolecular distances (in Å) of *cis*- $C_8H_8Fe_2(CO)_5$  with the experimental structure determined by X-ray crystallography.<sup>13</sup>

	<b>5-<i>cis</i>-S (<math>C_{2v}</math>)</b>			<b>5-<i>cis</i>-S' (<math>C_{2v}</math>)</b>			
	Exp.	M06L	B3LYP	BP86	M06L	B3LYP	BP86
FeC(COT)							
Fe1-C7	2.494	2.981	3.023	3.010	2.436	2.549	2.487
Fe1-C8	2.123	2.214	2.254	2.234	2.131	2.165	2.143
Fe1-C1	2.113	2.105	2.125	2.116	2.131	2.137	2.141
Fe1-C2	2.136	2.105	2.125	2.116	2.131	2.165	2.143
Fe1-C3	2.496	2.214	2.254	2.234	2.436	2.549	2.487
C(COT)C(COT)							
C4-C5	1.432	1.423	1.424	1.437	1.411	1.416	1.425
C5-C6	1.410	1.408	1.413	1.420	1.411	1.416	1.425
C6-C7	1.392	1.423	1.424	1.437	1.433	1.431	1.444
C7-C8	1.392	1.435	1.443	1.448	1.433	1.431	1.444
FeC(CO)							
Fe1-C9	1.802	1.765	1.773	1.758	1.761	1.768	1.754
Fe1-C11	1.968	1.973	1.968	1.993	1.956	1.955	1.955
Fe1-C10	1.786	1.765	1.773	1.758	1.761	1.768	1.754

**3.1.3  $C_8H_8Fe_2(CO)_4$  structures.** The starting  $C_8H_8Fe_2(CO)_4$  structures were obtained by removing one CO group from the optimized  $C_8H_8Fe_2(CO)_5$  structures. The *cis*-structures obtained by removing the bridging carbonyl have imaginary frequencies. Following the corresponding normal modes reduces the  $C_{2v}$  symmetry to  $C_2$  symmetry. The lowest energy  $C_8H_8Fe_2(CO)_4$  structure is the triplet *cis*- $C_8H_8Fe_2(CO)_4$  structure **4-cis-T** (Figure 5). The next three  $C_8H_8Fe_2(CO)_4$  structures **4-cis-S**, **4-trans-T** and **4-trans-S**, lie 11.7, 12.4, and 24.2 kcal/mol respectively, in energy above **4-cis-T**.



**Figure 5.** Optimized geometries for the  $C_8H_8Fe_2(CO)_4$  structures.

The lowest energy  $C_8H_8Fe_2(CO)_4$  structure **4-cis-T** (Figure 5) has a bis(tetrahapto)  $\eta^4, \eta^4$ - $C_8H_8$  ring similar to that in the  $C_8H_8Fe_2(CO)_5$  structure **5-cis-S** (Figure 4). The Fe=Fe distance of 2.497 Å in **4-cis-T** is  $\sim 0.3$  Å shorter than the Fe–Fe single bond in **5-cis-S** and thus can be interpreted as a formal double bond. This gives each iron atom in **4-cis-T** the favored 18-electron configuration. The triplet spin state in **4-cis-T** arises from the Fe=Fe double bond being of the  $\sigma + \frac{1}{2} \pi$  type with unpaired electrons in two orthogonal  $\pi$  single-electron “half-bonds.” Such an Fe=Fe double bond is found in the

unsaturated binuclear cyclopentadienyliron carbonyls ( $\eta^5\text{-R}_5\text{C}_5$ )<sub>2</sub>Fe<sub>2</sub>( $\mu$ -CO)<sub>3</sub> (R = H, CH<sub>3</sub>),<sup>36,37,38</sup> which have been characterized by X-ray crystallography for R = CH<sub>3</sub>.<sup>39</sup>

The lowest energy singlet C<sub>8</sub>H<sub>8</sub>Fe<sub>2</sub>(CO)<sub>4</sub> structure **4-cis-S**, lying 11.7 kcal/mol in energy above **4-cis-T**, has the C<sub>8</sub>H<sub>8</sub> ring bonded to each iron atom as a pentahapto rather than a tetrahapto ligand (Figure 5) similar to the experimental structure **5-cis-S'** for the pentacarbonyl C<sub>8</sub>H<sub>8</sub>Fe<sub>2</sub>(CO)<sub>5</sub> (Figure 4). The Fe–Fe distance of 2.635 Å in **4-cis-S** is ~0.15 Å longer than the Fe=Fe double bond in the triplet structure **4-cis-T** and thus suggests the formal single bond required to give each iron atoms the favored 18-electron configuration.

The *trans*-C<sub>8</sub>H<sub>8</sub>Fe<sub>2</sub>(CO)<sub>4</sub> structures **4-trans-T** and **4-trans-S** are necessarily higher energy structures, since there is no possibility of an iron-iron bond to give the iron atoms favored 18-electron configurations for the singlet structure and 17-electron configurations for the triplet structure. (Figure 5) In the triplet *trans*-C<sub>8</sub>H<sub>8</sub>Fe<sub>2</sub>(CO)<sub>4</sub> structure **4-trans-T** the C<sub>8</sub>H<sub>8</sub> ring is bonded to each iron atom as a trihapto ligand leaving an uncomplexed C=C double bond of length 1.363 Å. This gives each iron atom a 15-electron configuration, which is reasonable for a triplet spin state structure. In the singlet structure **4-trans-S** the C<sub>8</sub>H<sub>8</sub> ring is bonded to each iron atom as a pentahapto ligand with two adjacent carbon atoms bridging the central Fe<sub>2</sub> unit.

**3.1.4 C<sub>8</sub>H<sub>8</sub>Fe<sub>2</sub>(CO)<sub>3</sub> structures.** Similar to the *cis*-C<sub>8</sub>H<sub>8</sub>Fe<sub>2</sub>(CO)<sub>5</sub> structures, the bridged C<sub>8</sub>H<sub>8</sub>Fe<sub>2</sub>(CO)<sub>3</sub> structures were optimized for the singlet and triplet spin states (Figure 6). The bridged structures are bisected by a mirror plane passing through two opposite carbon atoms of the C<sub>8</sub>H<sub>8</sub> ring and the bridging carbonyl group. The lowest energy C<sub>8</sub>H<sub>8</sub>Fe<sub>2</sub>(CO)<sub>3</sub> structure is the triplet **3-cis-T** structure in which the C<sub>8</sub>H<sub>8</sub> ring is bonded to each iron atom as a tetrahapto ligand with an Fe–Fe distance of 2.446 Å. Interpreting this Fe–Fe distance as a formal single bond gives each iron atom in **3-cis-T** a 17-electron configuration for a binuclear triplet. The C<sub>8</sub>H<sub>8</sub>-Fe<sub>2</sub> bonding in **3-cis-T** contrasts with that in the singlet *cis*-C<sub>8</sub>H<sub>8</sub>Fe<sub>2</sub>(CO)<sub>3</sub> structure **3-cis-S**, lying 7.7 kcal/mol in energy above **3-cis-T**, in which the C<sub>8</sub>H<sub>8</sub> ring is bonded to each iron atom as a pentahapto ligand with two opposite ring carbon atoms bridging the central Fe<sub>2</sub> unit. Interpreting the Fe=Fe distance of 2.24 Å in **3-cis-S** as a formal double bond gives each iron atom the favored 18-electron configuration. This Fe=Fe distance in **3-cis-S** is very close to the experimental 2.265 Å Fe=Fe double bond distance in ( $\eta^5\text{-Me}_5\text{C}_5$ )<sub>2</sub>Fe<sub>2</sub>( $\mu$ -CO)<sub>3</sub> as determined by X-ray crystallography.<sup>39</sup> The *trans*-C<sub>8</sub>H<sub>8</sub>Fe<sub>2</sub>(CO)<sub>3</sub> structures lie at least 20 kcal/mol in energy above **3-cis-T** and thus are not discussed in this paper.

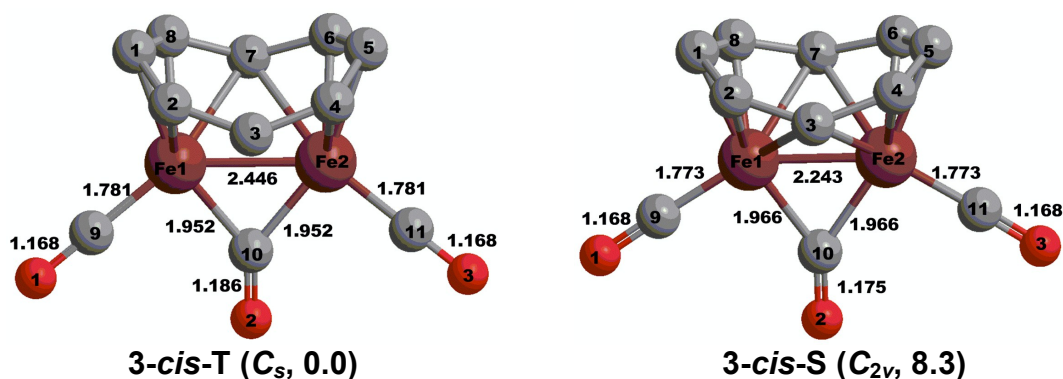


Figure 6. Optimized geometries for the  $C_8H_8Fe_2(CO)_3$  structures.

3.1.6 Carbonyl-rich  $C_8H_8Fe_2(CO)_8$  and  $C_8H_8Fe_2(CO)_7$  structures. Singlet and triplet *cis*- and *trans*- structures were optimized for the carbonyl-rich  $C_8H_8Fe_2(CO)_8$  and  $C_8H_8Fe_2(CO)_7$  systems. For the octacarbonyl *cis*- $C_8H_8Fe_2(CO)_8$  the  $C_{2v}$  singlet structure **8-cis-S** is the lowest energy structure (Figure 7). Each  $Fe(CO)_4$  moiety in **8-cis-S** is bonded to a C=C double bond of the  $C_8H_8$  ring leaving two non-conjugated uncomplexed C=C double bonds of lengths 1.349 Å. The very long  $Fe\cdots Fe$  distance 6.427 Å in **8-cis-S** clearly indicates the absence of a direct iron-iron bond. The triplet *cis*- $C_8H_8Fe_2(CO)_8$  structure and both *trans*- $C_8H_8Fe_2(CO)_8$  structures all lie more than 15 kcal/mol in energy above **8-cis-S**, and thus are not discussed in this paper.

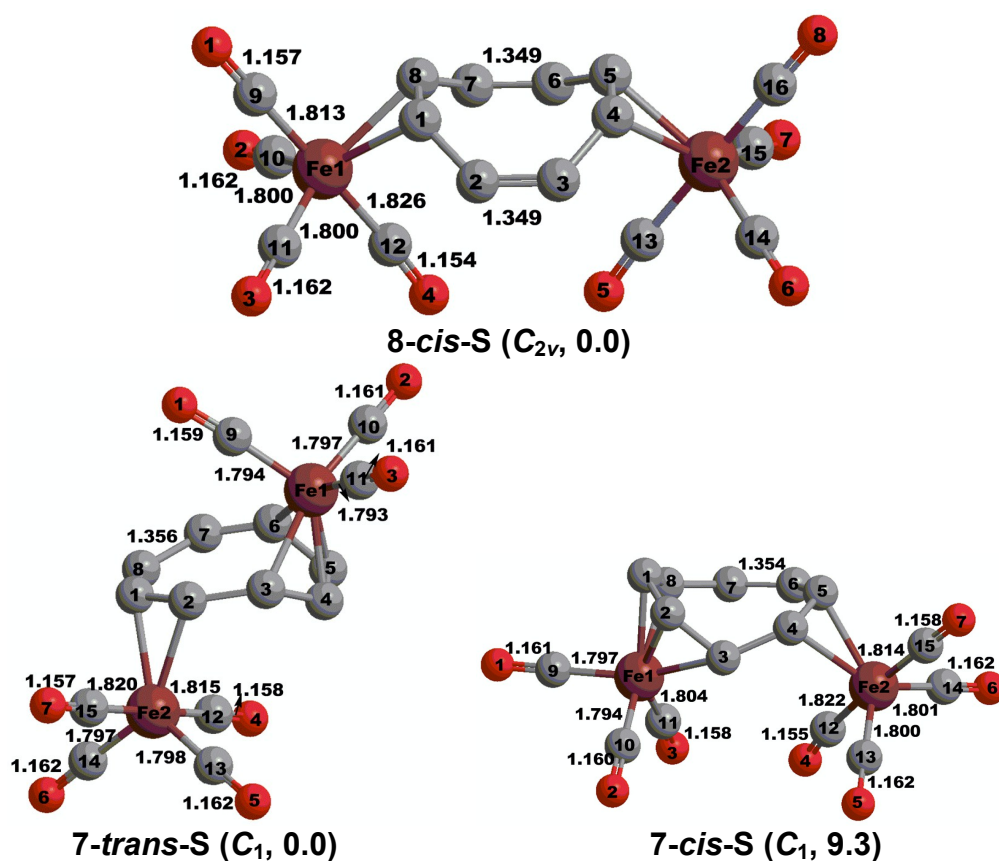
The lowest energy structure for the heptacarbonyl  $C_8H_8Fe_2(CO)_7$  is the singlet *trans* structure **7-trans-S**, in which one side of the  $C_8H_8$  ring is bonded to an  $Fe(CO)_3$  moiety as a tetrahapto ligand and the other side of the  $C_8H_8$  ring is bonded to the  $Fe(CO)_4$  moiety as a dihapto ligand (Figure 7). The singlet *cis*- $C_8H_8Fe_2(CO)_7$  structure **7-cis-S**, lying 9.3 kcal/mol in energy above **7-trans-S**, has similar bonding of the  $C_8H_8$  ring to the  $Fe(CO)_3$  and  $Fe(CO)_4$  moieties but both iron atoms are located on the same side of the  $C_8H_8$  ring. Each  $C_8H_8Fe_2(CO)_7$  structure has an uncomplexed C=C double bond of length  $\sim 1.36$  Å in their  $C_8H_8$  ring and an  $Fe\cdots Fe$  distance far too long for a direct bond. Triplet  $C_8H_8Fe_2(CO)_7$  structures lie more than 15 kcal/mol in energy above **7-trans-S** and thus are not considered in this paper.

### 3.2 Thermochemistry of Binuclear Cyclooctatetraene-iron Carbonyls

The CO dissociation energies ( $\Delta E_{\text{diss}}$ ) of the  $C_8H_8Fe_2(CO)_n$  ( $n = 8, 7, 6, 5, 4$ ) based on the lowest energy structures are listed in Table 3. For all of these systems the CO dissociation process is endothermic. However, the CO dissociation energies for the carbonyl-rich systems  $C_8H_8Fe_2(CO)_8$  of only  $\sim 6$  kcal/mol are much less than the  $\sim 20$  kcal/mol carbonyl dissociation energy of  $C_8H_8Fe_2(CO)_6$ , and the  $\sim 40$  kcal/mol



carbonyl dissociation energy of  $C_8H_8Fe_2(CO)_5$ . This is consistent with the isolation of  $C_8H_8Fe_2(CO)_6$  as the carbonyl-richest binuclear product from the thermal reaction of  $Fe(CO)_5$  with cyclooctatetraene. Furthermore, the CO dissociation energy of the *cis*-( $\eta^3, \eta^3$ - $C_8H_8$ ) $Fe_2(CO)_6$  isomer **6-cis-S** giving the lowest energy *cis*-( $\eta^5, \eta^5$ - $C_8H_8$ ) $Fe_2(CO)_4(\mu-CO)$  isomer **5-cis-S** is only  $\sim 7$  kcal/mol. This is consistent with the experimentally observed facile decarbonylation of **6-cis-S** to give **5-cis-S** in solution.<sup>14</sup> For comparison, the experimental CO dissociation energies of the stable simple metal carbonyls  $Ni(CO)_4$ ,  $Fe(CO)_5$ , and  $Cr(CO)_6$  are 27 kcal/mol, 41 kcal/mol, and 37 kcal/mol, respectively.<sup>40</sup>



**Figure 7.** Optimized geometries for the carbonyl-rich  $C_8H_8Fe_2(CO)_8$  and  $C_8H_8Fe_2(CO)_7$  structures.

The energies for the disproportionation reactions  $2(C_8H_8)Fe_2(CO)_n \rightarrow (C_8H_8)Fe_2(CO)_{n+1} + (C_8H_8)Fe_2(CO)_{n-1}$  ( $n = 6, 5, 4$ ) were also investigated in order to check the viability of binuclear cyclooctatetraene-iron carbonyls (Table 4). In this connection, the experimentally known  $(C_8H_8)Fe_2(CO)_5$  structure **5-cis-S** is clearly viable with respect to disproportionation into  $(C_8H_8)Fe_2(CO)_6 + (C_8H_8)Fe_2(CO)_4$  in which the



fragments were allowed to relax. However, the unknown  $(C_8H_8)Fe_2(CO)_4$  is disfavored relative to disproportionation into  $(C_8H_8)Fe_2(CO)_5 + (C_8H_8)Fe_2(CO)_3$ .

**Table 3.** Energies (kcal/mol) for carbonyl dissociation of  $(C_8H_8)Fe_2(CO)_n$  derivatives with the zero-point energy corrections (ZPC).

	M06-L	B3LYP	BP86
$(C_8H_8)Fe_2(CO)_8$ ( <b>8-cis-S</b> ) $\rightarrow$ $(C_8H_8)Fe_2(CO)_7$ ( <b>7-trans-S</b> ) + CO	5.5	7.7	8.5
$(C_8H_8)Fe_2(CO)_7$ ( <b>7 trans-S</b> ) $\rightarrow$ $(C_8H_8)Fe_2(CO)_6$ ( <b>6-trans-S</b> ) + CO	11.4	12.8	15.6
$(C_8H_8)Fe_2(CO)_6$ ( <b>6- trans-S</b> ) $\rightarrow$ $(C_8H_8)Fe_2(CO)_5$ ( <b>5-cis-S</b> ) + CO	17.6	14.1	17.6
$(C_8H_8)Fe_2(CO)_6$ ( <b>6-cis-S</b> ) $\rightarrow$ $(C_8H_8)Fe_2(CO)_5$ ( <b>5-cis-S</b> ) + CO	7.2	2.7	7.1
$(C_8H_8)Fe_2(CO)_5$ ( <b>5-cis-S</b> ) $\rightarrow$ $(C_8H_8)Fe_2(CO)_4$ ( <b>4-cis-T</b> ) + CO	36.7	26.3	48.8
$(C_8H_8)Fe_2(CO)_4$ ( <b>4-cis-T</b> ) $\rightarrow$ $(C_8H_8)Fe_2(CO)_3$ ( <b>3-cis-T</b> ) + CO	35.9	35.7	34.8

**Table 4.** Thermochemistry of the reactions  $2(C_8H_8)Fe_2(CO)_n \rightarrow (C_8H_8)Fe_2(CO)_{n+1} + (C_8H_8)Fe_2(CO)_{n-1}$  (energies in kcal/mol) with the zero-point energy corrections (ZPC).

	M06-L	B3LYP	BP86
$2(C_8H_8)Fe_2(CO)_6$ ( <b>6-trans-S</b> ) $\rightarrow$ $(C_8H_8)Fe_2(CO)_7$ ( <b>7-trans-S</b> ) + $(C_8H_8)Fe_2(CO)_5$ ( <b>5-cis-S</b> )	6.3	1.2	2.1
$2(C_8H_8)Fe_2(CO)_5$ ( <b>5-cis-S</b> ) $\rightarrow$ $(C_8H_8)Fe_2(CO)_6$ ( <b>6-trans-S</b> ) + $(C_8H_8)Fe_2(CO)_4$ ( <b>4-cis-T</b> )	19.0	12.2	31.2
$2(C_8H_8)Fe_2(CO)_4$ ( <b>4-cis-T</b> ) $\rightarrow$ $(C_8H_8)Fe_2(CO)_5$ ( <b>5-cis-S</b> ) + $(C_8H_8)Fe_2(CO)_3$ ( <b>3-cis-T</b> )	-0.8	9.4	-14.1

## 4. Discussion

Three  $C_8H_8Fe_2(CO)_6$  isomers have been synthesized.<sup>13,14</sup> The *trans*- $(\eta^4, \eta^4-C_8H_8)Fe_2(CO)_6$  isomer is obtained from the reaction of cyclooctatetraene with  $Fe(CO)_5$  at elevated temperatures,<sup>8</sup> which we also find to be the lowest energy structure **6-trans-S** (Figure 3) using density functional methods. Two readily interconverting metastable *cis*- $C_8H_8Fe_2(CO)_6$  isomers are isolated from the reaction of cyclooctatetraene with the more reactive  $Fe_2(CO)_9$ , which allows the reaction to proceed under milder conditions (Figure 2).<sup>14</sup> One of these metastable isomers is suggested to be *cis*- $(\eta^3, \eta^3-C_8H_8)Fe_2(CO)_6$  from the 2:2:2:2 pattern of peaks in its proton NMR spectrum.<sup>14</sup> This corresponds to our predicted  $C_8H_8Fe_2(CO)_6$  isomer **6-cis-S**, lying ~10 kcal/mol in energy above **6-trans-S** (Figure 3). The other metastable isomer was suggested to be *cis*- $(\eta^4, \eta^4-C_8H_8)Fe_2(CO)_6$  from the 4:4 pattern of peaks in its proton NMR spectrum.<sup>14</sup> However, attempts to optimize such a *cis*- $(\eta^4, \eta^4-C_8H_8)Fe_2(CO)_6$  structure using density functional methods, led to a high-energy structure at ~36 kcal/mol in energy above the global minimum with a large imaginary vibrational frequency. Following the

corresponding normal mode was found to give **6-cis-S**. This suggests that it is energetically preferable to have a metal-metal bond and six of the eight carbon atoms bonded to metal atoms as in **6-cis-S** rather than to have no metal-metal bond and all four ring carbon atoms bonded to metal atoms. Thus our theoretical data do not support the suggestion of two readily interconverting *cis*-C<sub>8</sub>H<sub>8</sub>Fe<sub>2</sub>(CO)<sub>6</sub> isomers of similar energies as proposed by Pettit and coworkers.<sup>13,14</sup> Further experimental work is needed on the metastable C<sub>8</sub>H<sub>8</sub>Fe<sub>2</sub>(CO)<sub>6</sub> isomers obtained under mild conditions, which were reported 50 years ago<sup>13</sup> and apparently not studied recently.

The metastable *cis*-(C<sub>8</sub>H<sub>8</sub>)Fe<sub>2</sub>(CO)<sub>6</sub> isomers lose CO in solution to give the pentacarbonyl *cis*-(η<sup>5</sup>,η<sup>5</sup>-C<sub>8</sub>H<sub>8</sub>)Fe<sub>2</sub>(CO)<sub>4</sub>(μ-CO) consistent with the low predicted CO dissociation energy of ~7 kcal/mol for **6-cis-S** (Table 2). The experimental *cis*-(η<sup>5</sup>,η<sup>5</sup>-C<sub>8</sub>H<sub>8</sub>)Fe<sub>2</sub>(CO)<sub>4</sub>(μ-CO) structure **5-cis-S'**, determined by X-ray crystallography, has a symmetry plane passing through the two carbon atoms bridging the central Fe<sub>2</sub> unit as well as the bridging CO group. The *cis*-(η<sup>5</sup>,η<sup>5</sup>-C<sub>8</sub>H<sub>8</sub>)Fe<sub>2</sub>(CO)<sub>4</sub>(μ-CO) structure **5-cis-S'** lies only ~2 kcal/mol in energy above the lowest energy C<sub>8</sub>H<sub>8</sub>Fe<sub>2</sub>(CO)<sub>5</sub> structure **5-cis-S**, which has its symmetry plane passing through a pair of opposite C–C bonds in the C<sub>8</sub>H<sub>8</sub> ring as well as through the bridging CO group. Structure **5-cis-S** was the structure originally suggested for (C<sub>8</sub>H<sub>8</sub>)Fe<sub>2</sub>(CO)<sub>5</sub> after the erroneous original heptacarbonyl formula<sup>5</sup> (C<sub>8</sub>H<sub>8</sub>)Fe<sub>2</sub>(CO)<sub>7</sub> was corrected. The closeness in energy of the *cis*-(η<sup>5</sup>,η<sup>5</sup>-C<sub>8</sub>H<sub>8</sub>)Fe<sub>2</sub>(CO)<sub>4</sub>(μ-CO) structures **5-cis-S** and **5-cis-S'** is consistent with the experimentally observed fluxional properties indicated by a single proton NMR peak even at –80°.

The carbonyl-rich (C<sub>8</sub>H<sub>8</sub>)Fe<sub>2</sub>(CO)<sub>*n*</sub> (*n* = 8, 7) systems were investigated in order to identify possible precursors to the formation of the experimentally observed C<sub>8</sub>H<sub>8</sub>Fe<sub>2</sub>(CO)<sub>*n*</sub> (*n* = 6, 5) structures. The lowest energy structure **8-cis-S** for the octacarbonyl (C<sub>8</sub>H<sub>8</sub>)Fe<sub>2</sub>(CO)<sub>8</sub> has two opposite C=C bonds in the C<sub>8</sub>H<sub>8</sub> ring bonded to Fe(CO)<sub>4</sub> units leaving two opposite uncomplexed C=C double bonds of lengths ~1.35 Å. Using opposite C=C bonds of the C<sub>8</sub>H<sub>8</sub> ring to bond to Fe(CO)<sub>4</sub> units minimizes steric interference between their carbonyl groups. For the heptacarbonyl C<sub>8</sub>H<sub>8</sub>Fe<sub>2</sub>(CO)<sub>7</sub> both *cis* and *trans* isomers were found with an Fe(CO)<sub>3</sub> moiety bonded to two conjugated C=C double bonds of the C<sub>8</sub>H<sub>8</sub> ring and the Fe(CO)<sub>4</sub> moiety bonded to a third double bond leaving an uncomplexed C=C double bond of length ~1.36 Å. The *cis*-(η<sup>4</sup>,η<sup>2</sup>-C<sub>8</sub>H<sub>8</sub>)Fe<sub>2</sub>(CO)<sub>7</sub> isomer **7-cis-S** lies ~9 kcal/mol in energy above the corresponding *trans* isomer **7-trans-S** consistent with greater steric interference between the CO groups in the *cis* isomer relative to the *trans* isomer. The CO dissociation energy of the octacarbonyl C<sub>8</sub>H<sub>8</sub>Fe<sub>2</sub>(CO)<sub>8</sub> **8-cis-S** to give the heptacarbonyl **7-trans-S** is

relatively low at  $\sim 5$  kcal/mol (M06-L). The CO dissociation energy of the heptacarbonyl **7-trans-S** of  $\sim 11$  kcal/mol to give the hexacarbonyl **6-trans-S**, although higher than that of **8-cis-S**, is still low compared with that required for further dissociation of **6-trans-S**.

The unsaturated  $C_8H_8Fe_2(CO)_n$  ( $n = 4, 3$ ) systems were investigated in search for cyclooctatetraene iron carbonyl structures having iron-iron multiple bonds. The lowest energy  $C_8H_8Fe_2(CO)_4$  structure **4-cis-T** is a triplet structure with a bent bis(tetrahapto)  $\eta^4, \eta^4-C_8H_8$  ring similar to that in **5-cis-S** and a  $\sigma + \frac{1}{2} \pi$  Fe=Fe double bond similar to that in  $Cp_2Fe_2(\mu-CO)_3$  derivatives.<sup>36,37,38,39</sup> The lowest energy singlet  $C_8H_8Fe_2(CO)_4$  structure **4-cis-S**, lying  $\sim 12$  kcal/mol in energy above **4-cis-T**, has a bis(pentahapto)  $\eta^5, \eta^5-C_8H_8$  ring similar to the experimental  $(\eta^5, \eta^5-C_8H_8)Fe_2(CO)_4(\mu-CO)$  structure. The Fe–Fe distance of  $\sim 2.6$  Å in **4-cis-S** can correspond to the formal single bond required to give each iron atom the favored 18-electron configuration if the  $\eta^5, \eta^5-C_8H_8$  ring effectively donates five electrons to each metal atom. For  $C_8H_8Fe_2(CO)_3$  the lowest energy structure is also a triplet, namely **3-cis-T** with the singlet structure **3-cis-S** lying  $\sim 8$  kcal/mol higher in energy. As in the  $C_8H_8Fe_2(CO)_4$  system, the triplet  $C_8H_8Fe_2(CO)_3$  structure **3-cis-T** has a bis(tetrahapto)  $\eta^4, \eta^4-C_8H_8$  ring whereas the singlet structure **3-cis-S** has a bis(pentahapto)  $\eta^5, \eta^5-C_8H_8$  ring. The short Fe=Fe distance of 2.243 Å in **3-cis-S** is similar in length to the Fe=Fe double bond in the  $Cp_2Fe_2(\mu-CO)_3$  structures. Interpreting the Fe=Fe interaction in **3-cis-S** as a formal double bond gives each iron atom the favored 18-electron configuration.

## 5. Summary

Three different  $C_8H_8Fe_2(CO)_6$  species have been obtained from cyclooctatetraene and iron carbonyls under various conditions.<sup>13,14</sup> The lowest energy  $C_8H_8Fe_2(CO)_6$  structure predicted by density functional theory is the experimentally known *trans*-( $\eta^4, \eta^4-C_8H_8$ ) $Fe_2(CO)_6$  structure, obtained from the reaction of cyclooctatetraene with  $Fe(CO)_5$ .<sup>35</sup> A bis(trihapto) *cis*-( $\eta^3, \eta^3-C_8H_8$ ) $Fe_2(CO)_6$  structure with an uncomplexed C=C bond in the  $C_8H_8$  ring and lying  $\sim 11$  kcal/mol in energy above *trans*-( $\eta^4, \eta^4-C_8H_8$ ) $Fe_2(CO)_6$  appears to correspond to one of the two metastable  $C_8H_8Fe_2(CO)_6$  species obtained from cyclooctatetraene and  $Fe_2(CO)_9$  under mild conditions. However, the *cis*-( $\eta^4, \eta^4-C_8H_8$ ) $Fe_2(CO)_6$  structure with all eight  $C_8H_8$  carbons bonded to an iron atom and no Fe–Fe bond is a high energy structure with a large imaginary vibrational frequency. This structure thus appears to be a transition state rather than a genuine minimum.

Two singlet  $C_8H_8Fe_2(CO)_4(\mu-CO)$  structures differing in energy by only  $\sim 2$  kcal/mol are found for the pentacarbonyl  $C_8H_8Fe_2(CO)_5$ . These structures are related

by a  $22.5^\circ$  rotation of the  $C_8H_8$  ring around the central  $Fe_2(CO)_4(\mu-CO)$  unit. The closeness in energy of these two  $C_8H_8Fe_2(CO)_4(\mu-CO)$  structures is consistent with the experimentally observed fluxionality of the  $C_8H_8Fe_2(CO)_5$  molecule. Further decarbonylation of  $C_8H_8Fe_2(CO)_5$  to give unsaturated  $C_8H_8Fe_2(CO)_n$  ( $n = 4, 3$ ) structures retains the bridging bis(tetrahapto) or bis(pentahapto)  $C_8H_8$  rings of  $C_8H_8Fe_2(CO)_5$  and provides examples of *cis*- $C_8H_8Fe_2(CO)_n$  ( $n = 4, 3$ ) structures with Fe=Fe double bonds. The lowest energy *cis*- $C_8H_8Fe_2(CO)_n$  ( $n = 4, 3$ ) structures are triplet rather than singlet spin state structures.

Viable carbonyl-rich  $(\eta^2, \eta^2-C_8H_8)Fe_2(CO)_8$  and  $(\eta^4, \eta^2-C_8H_8)Fe_2(CO)_7$  structures are found as possible intermediates in the formation of the various  $C_8H_8Fe_2(CO)_n$  ( $n = 6, 5$ ) from cyclooctatetraene and iron carbonyls.

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### Supporting Information.

Higher energy optimized  $C_8H_8Fe_2(CO)_n$  structures (Figures S1); Energies, relative energies, and iron-iron distances for the  $C_8H_8Fe_2(CO)_n$  ( $n = 8, 7, 6, 5, 4, 3$ ) structures by the M06L, B3LYP and BP86 methods (Table S1); Complete tables of iron-carbon and carbon-carbon distances (in Å) for the  $C_8H_8Fe_2(CO)_n$  ( $n = 8, 7, 6, 5, 4, 3$ ) structures (Tables S2) by the M06L, B3LYP and BP86 methods; Coordinates of the optimized  $(C_8H_8)Fe_2(CO)_n$  ( $n = 8, 7, 6, 5, 4, 3$ ) structures (Table S3) by the M06L method; Harmonic vibrational frequencies of the  $(C_8H_8)Fe_2(CO)_n$  ( $n = 8, 7, 6, 5, 4, 3$ ) structures (Table S4) by the M06L method; complete Gaussian reference.

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## Graphical Abstract

### **Binuclear Cyclooctatetraene-Iron Carbonyl Complexes: Examples of Fluxionality and Valence Tautomerism**

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Wang, and R. Bruce King<sup>\*</sup>

Fluxionality and valence tautomerism are studied in the experimentally observed *trans*-( $\eta^4, \eta^4$ -C<sub>8</sub>H<sub>8</sub>)Fe<sub>2</sub>(CO)<sub>6</sub>, *cis*-( $\eta^3, \eta^3$ -C<sub>8</sub>H<sub>8</sub>)Fe<sub>2</sub>(CO)<sub>6</sub>, and *cis*-C<sub>8</sub>H<sub>8</sub>Fe<sub>2</sub>(CO)<sub>4</sub>( $\mu$ -CO) structures using density functional theory

