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Binuclear Pentalene Iron Carbonyl Complexes

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The bicyclic hydrocarbon pentalene, although unstable in the free state, forms a stable iron carbonyl derivative *cis*-(η^5,η^5-C_8H_6)$Fe_2(CO)_4$(μ-CO). In this connection, the series of binuclear pentalene iron carbonyl derivatives $C_8H_6Fe_2(CO)_n$ (n = 7, 6, 5, 4) have been investigated by density functional theory. The lowest energy $C_8H_6Fe_2(CO)_6$ structure is predicted to be *trans*-(η^5,η^5-C_8H_6)$Fe_2(CO)_6$ without an iron–iron bond. However, a *cis*-(η^5,η^1-C_8H_6)$Fe_2(CO)_6$ structure with an uncomplexed pentalene C=C double bond and a formal Fe–Fe bond of length 2.646 Å (BP86) lies only ca. 3 kcal/mol above this global minimum. The CO dissociation energy of $C_8H_6Fe_2(CO)_6$ to give $C_8H_6Fe_2(CO)_5$ is predicted to be only ca. 12 kcal/mol, explaining the formation of $C_8H_6Fe_2(CO)_5$ rather than $C_8H_6Fe_2(CO)_6$ in reactions of dihydropentalene with iron carbonyls. In addition, the experimentally known *cis*-(η^5,η^5-C_8H_6)$Fe_2(CO)_4$(μ-CO) structure is found to be the lowest energy $C_8H_6Fe_2(CO)_5$ structure by more than 25 kcal/mol (BP86). For the tetracarbonyl two triplet and two singlet *cis*-$C_8H_6Fe_2(CO)_4$ structures lie within 7 kcal/mol of each other (BP86) with the triplet structures being of slightly lower energies. The singlet $C_8H_6Fe_2(CO)_4$ structure is predicted to be thermodynamically unfavorable with respect to disproportionation into $C_8H_6Fe_2(CO)_5$ + $C_8H_6Fe_2(CO)_3$.

1. Introduction

Organometallic compounds containing two or more metal carbonyl units simultaneously coordinated to a polycyclic hydrocarbon are of interest because of several possible types of electronic interactions between the metal centers. For metal carbonyl derivatives such interactions can include not only metal-metal bonding but also bridging carbonyl groups of various types. For unsaturated derivatives the latter can include formal metal-metal multiple bonds as well as carbonyl groups donating more than the usual two-electrons because of metal-oxygen interactions as well as metal-carbon interactions.

One of the simplest planar non-benzenoid hydrocarbons as a possible ligand for such binuclear metal complexes is pentalene, the lower homolog of naphthalene consisting of two fused five-membered rings. However, the instability of pentalene under ambient conditions,[1,2] precludes the synthesis of pentalene metal carbonyl complexes by the direct reaction of pentalene with metal carbonyls. Despite the instability of free pentalene, Armit and Robinson[3] suggested in 1922 that pentalene (C_8H_6) might possess aromatic character. This suggestion has attracted much attention from both experimental[4–9] and theoretical[10,11] chemists.

Organometallic derivatives of pentalene were first synthesized in 1963 by Katz and co-workers[12] using the pentalene dianion as the pentalene source. However, because of synthetic difficulties, including the instability of free pentalene, the organometallic chemistry of pentalene has developed only in recent years.[13,14] Like cyclobutadiene,[15] heptafulvene,[16] trimethylenemethane[17] and some other highly reactive organic molecules that can be stabilized by coordinating to transition metals, the substituted or unsubstituted pentalene systems are also stabilized by coordination to transition metals. The resulting pentalene metal complexes exhibit a diverse array of coordination modes, thereby showing great flexibility in adapting to the electronic requirements of the metal center.[18] Examples of such complexes include the mononuclear transition metal derivatives (C_8H_6)V(C_9H_7), (η^8-C_8H_6)M(η^5-C_5H_5) (M = V, Ti, Zr), (η^8-C_8H_6)$_2$M (M = Ti, Zr, Hf) and (η^3-C_3H_5)$_2$Zr(η^8-C_8H_6) having a pentalene ligand bonded to a single metal atom as an octahapto ligand,[19–22] as well as the binuclear pentalene metal carbonyl derivatives *cis*-(η^5,η^5-C_8H_6)$Fe_2(CO)_5$,[6] *trans*-(η^5,η^5-C_8H_6)[M(CO)$_3$]$_2$ (M = Mn, Re),[7] and $Ru_2(MMe_3)_2(CO)_4(C_8H_6)$.[5] Within the last few years the chemistry of pentalene metal complexes has expanded with the development by O'Hare and co-workers of methods for the synthesis of permethylpentalene precursors in quantity.[18] This has allowed the synthesis of stable hexameth-

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ylpentalene metal carbonyl complexes[4] including the metal carbonyl derivatives *cis*-(η^5,η^5-C_8Me_6)$Fe_2(CO)_5$ and *cis*-(η^5,η^5-C_8Me_6)$Co_2(CO)_4$[4] as well as the bis(hexamethylpentalene)metal derivatives $(C_8Me_6)_2M_2$ (M = V, Cr, Mn, Co, Ni).[23] In addition Cloke and co-workers[24–26] have synthesized the silylated bis(pentalene)metal derivatives $Mo_2[C_8H_4(SiPr_3)_2]_2$, $Cr_2[C_8H_4(SiPr_3)_2]_2$, and $Mn_2[C_8H_4(SiPr_3)_2]_2$.

Among the pentalene metal carbonyl derivatives, the pentalene iron carbonyls (Figure 1) have been studied in the greatest detail. Either dihydropentalene[1,2,4,27] or pentalene dimer[6] can be used as the source of the pentalene ligand in thermal reactions with $Fe(CO)_5$. In all cases *cis*-(η^5,η^5-pentalene)$Fe_2(CO)_4$(μ-CO) derivatives are obtained with two terminal carbonyl groups on each iron atom as well as a single carbonyl group bridging the two iron atoms. The iron atoms in such (η^5,η^5-pentalene)$Fe_2(CO)_4$(μ-CO) derivatives have the favored 18-electron configuration if the pentalene ligand donates all eight of its π-electrons to the Fe_2 system and there is a formal iron–iron single bond. The donation of all eight pentalene π-electrons to the pair of iron atoms is supported by all eight carbon atoms of the pentalene ligand being within bonding distance of at least one of the iron atoms (Figure 1).

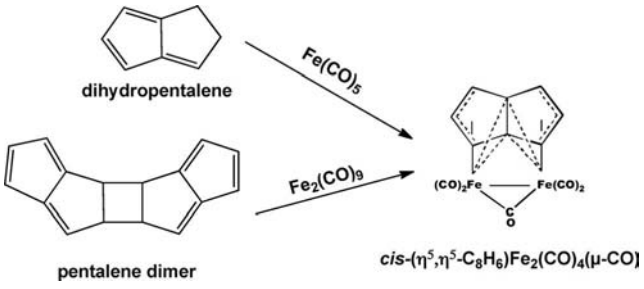

Figure 1. Synthesis of *cis*-(η^5,η^5-C_8H_6)$Fe_2(CO)_4$(μ-CO).

The presence of an iron–iron single bond in the (η^5,η^5-pentalene)$Fe_2(CO)_4$(μ-CO) derivatives is more controversial. Thus, despite a typical Fe–Fe single bond length of 2.69 Å in (η^5,η^5-C_8Me_6)$Fe_2(CO)_4$(μ-CO), O'Hare and co-workers[4] suggest the absence of an iron–iron bond on the basis of electron-population studies. This may relate to the difficulty in finding evidence for a direct iron–iron bond in $Fe_2(CO)_9$, which has a triply bridged $Fe_2(CO)_6(\mu\text{-}CO)_3$ structure, also requiring a formal Fe–Fe single bond to give both iron atoms the favored 18-electron configuration.[28] The (η^5,η^5-pentalene)$Fe_2(CO)_4$(μ-CO) complexes can be considered to have a similar triply bridging structure to $Fe_2(CO)_9$, since the two carbon atoms shared by the two pentalene five-membered rings form the second and third bridges by being within bonding distance of each iron atom (Figure 1).

This paper reports a density functional theory study of the binuclear pentalene-iron carbonyl complexes (C_8H_6)$Fe_2(CO)_n$ (n = 7, 6, 5, 4). The hexacarbonyl complex (C_8H_6)$Fe_2(CO)_6$ was included in this study since this is a possible structure arising from the four pentalene C=C double bonds functioning as two independent η^4-diolefin units towards separate $Fe(CO)_3$ moieties. The tetracarbonyl (C_8H_6)$Fe_2(CO)_4$ was included in this study because it is the most likely unsaturated (C_8H_6)$Fe_2(CO)_n$ derivative to be synthesized, e.g., by photolysis of the known (η^5,η^5-pentalene)$Fe_2(CO)_4$(μ-CO) or its substitution products. The tetracarbonyl (C_8H_6)$Fe_2(CO)_4$ is also of interest since it could provide in principle a possible structure with a formal Fe=Fe double bond or a four-electron donor bridging η^2-μ-CO group to give both iron atoms the favored 18-electron configuration.

2. Theoretical Methods

In this work the double-ζ plus polarization (DZP) basis sets used for carbon and oxygen add one set of pure spherical harmonic d functions with orbital exponents $\alpha_d(C)$ = 0.75 and $\alpha_d(O)$ = 0.85 to the Huzinaga–Dunning standard contracted DZ sets and are designated (9s5p1d/4s2p1d).[29,30] For H, a set of p polarization functions $\alpha_p(H)$ = 0.75 is added to the Huzinaga-Dunning DZ sets. For iron, in our loosely contracted DZP basis set, the Wachters' primitive set is used but is augmented by two sets of p functions and one set of d functions, contracted following Hood et al., and designated (14s11p6d/10s8p3d).[31,32]

Electron correlation effects have been included by employing density functional theory (DFT) methods, which have been shown to be a practical and effective computation tool, especially for organometallic compounds.[33–47] Two DFT methods, B3LYP and BP86, were used in our present study. The reliability of such density functional theory (DFT) methods is governed by the quality of the approximate exchange–correlation (XC) energy functional. The B3LYP and the BP86 methods are constructed in very different ways. The B3LYP method is a hybrid HF/DFT method using a combination of the three-parameter Becke functional (B3) with the Lee–Yang–Parr (LYP) generalized gradient correlation functional.[48,49] This method includes exact exchanges and is calibrated by fitting three parameters to a set of experimental results. The BP86 method combines Becke's 1988 exchange functional (B) with Perdew's 1986 gradient corrected correlation functional method (P86).[50,51] This method does not include exact exchange and is mainly deduced by forcing the functional to satisfy certain exact constraints based on first principles. When these two very different DFT methods agree, confident predictions can be made. For most the compounds investigated in this work, both methods agree quite well. However, for the relative energies of different spin states, these two functionals give different results. The B3LYP method favors the high-spin states and BP86 favors the low-spin states. This phenomenon was thoroughly studied by Reiher and co-workers who found the true values to lie between the results predicted by the two methods.[52,53]

The geometries of all structures were fully optimized using both the DZP B3LYP and DZP BP86 methods. The harmonic vibrational frequencies were determined at the same levels by evaluating analytically the second derivatives of the energy with respect to the nuclear coordinates. The

corresponding infrared intensities were evaluated analytically as well. All of the computations were carried out with the Gaussian 09 program,[54] in which the fine grid (75, 302) is the default for evaluating integrals numerically, and the tight designation is the default for the energy convergence.

In this paper each $C_8H_6Fe_2(CO)_a$ structure is designated as **aX-b** where **a** is the number of CO groups, **X** relates to the spin state (**S** = singlet or **T** = triplet), and **b** orders the structures according to their BP86 relative energies. Thus the lowest energy (predicted by BP86) singlet structure of $C_8H_6Fe_2(CO)_5$ is designated **5S-1**.

3. Results

3.1 Molecular Structures

3.1.1 $C_8H_6Fe_2(CO)_7$

Two singlet structures, namely **7S-1** and **7S-2**, were obtained for $C_8H_6Fe_2(CO)_7$ (see Figure 2, Table 1 and Table S44; in Figures 2–7 the upper distances were obtained by the B3LYP method and the lower distances by the BP86 method). Both structures have one $Fe(CO)_3$ group and one $Fe(CO)_4$ group. The predicted global minimum is the singlet *trans*-(η^5,η^1-C_8H_6)$Fe_2(CO)_7$ structure **7S-1**. The Fe–C distances in **7S-1** indicate that one five-membered ring functions as a monohapto ligand bonding to the iron atom in the $Fe(CO)_4$ moiety and the other ring functions as a pentahapto ligand bonding to the iron atom in the $Fe(CO)_3$ moiety. The relatively short C7=C8 distance of 1.382 Å (B3LYP) or 1.389 Å (BP86) in the pentalene unit of **7S-1** corresponds to an uncomplexed double bond. The very long Fe···Fe distance of 5.283 Å (B3LYP) or 5.185 Å (BP86) in **7S-1** indicates no direct interaction between the two iron atoms. The second singlet *cis*-$C_8H_6Fe_2(CO)_7$ structure **7S-2** is similar to **7S-1**, except for *cis* rather than *trans* geometry. Structure **7S-2** lies only 3.7 kcal/mol (B3LYP) or 5.0 kcal/mol (BP86) above the global minimum **7S-1**. The Fe···Fe distance in **7S-2**, namely 4.428 Å (B3LYP) or 4.390 Å (BP86), is far too long for direct interaction between the two iron atoms. Both iron atoms in **7S-1** and **7S-2** have the favored 18-electron configuration if the $Fe(CO)_3$ iron atom has a formal positive charge and the $Fe(CO)_4$ iron has a formal negative charge.

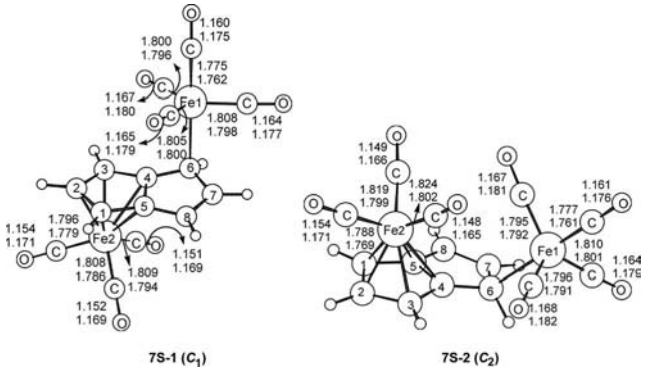

Figure 2. Two optimized structures of $C_8H_6Fe_2(CO)_7$. In Figures 2, 3, 4, 5, 6, and 7 the upper distances were obtained by the B3LYP method and the lower distances by the BP86 method.

Table 1. Total energies (E, Hartree), relative energies (ΔE, kcal/mol), Fe–Fe bond lengths (Å), and numbers of imaginary vibrational frequencies (Nimg) for the (pentalene)$Fe_2(CO)_7$ structures.

	7S-1 (C_1)		**7S-2** (C_1)	
	B3LYP	BP86	B3LYP	BP86
Fe–Fe	5.283	5.185	4.428	4.390
E + 3629	–0.52362	–1.02848	–0.51770	–1.02059
ΔE	0.0	0.0	3.7	5.0
Nimg	none	none	none	none

3.1.2 $C_8H_6Fe_2(CO)_6$

The *cis* and *trans* structures consisting of two $Fe(CO)_3$ groups bonded to the pentalene molecule were used as the starting geometries for optimization. Three singlet structures and three triplet structures of $C_8H_6Fe_2(CO)_6$ were obtained. (Figure 3, Table 2 and Table S45). The global minimum **6S-1** is a singlet *trans*-$C_8H_6Fe_2(CO)_6$ structure with C_{2h} symmetry. It has two $Fe(CO)_3$ groups bonded to the two pentahapto five-membered rings. The Fe–C distances to the carbon atoms bonded to a single iron atom in **6S-1**, namely C1, C2, C3, C6, C7, and C8 in Figure 3, fall in the range 2.01 to 2.16 Å. Since the carbon atoms C4 and C5 are linked to both Fe atoms simultaneously, each Fe atom actually obtains only four electrons from a pentahapto five-

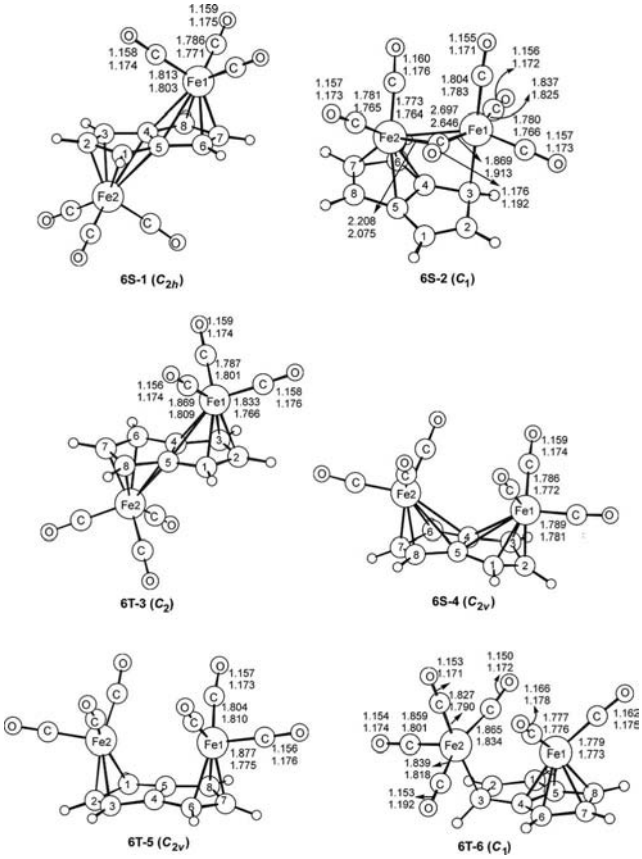

Figure 3. Six optimized structures of $C_8H_6Fe_2(CO)_6$.

Table 2. Total energies (E, Hartree), relative energies (ΔE, kcal/mol), Fe–Fe bond lengths (Å), numbers of imaginary vibrational frequencies (Nimg), and spin expectation values $\langle S^2 \rangle$ for the (pentalene)$Fe_2(CO)_6$ structures.

Singlet	**6S-1** (C_{2h})		**6S-2** (C_1)		**6S-4** (C_{2v})	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
Fe–Fe	4.870	4.833	2.697	2.646	4.187	4.182
E + 3516	–0.17994	–0.68765	–0.17655	–0.68309	–0.13908	–0.65110
ΔE	0.0	0.0	2.1	2.9	25.6	22.9
Nimg	none	none	none	none	2(73i, 54i)	1(40i)
Triplet	**6T-3** (C_2)		**6T-5** (C_{2v})		**6T-6** (C_1)	
	B3LYP	BP86	3516.15137	3516.64265	B3LYP	BP86
Fe–Fe	4.824	4.840	3.854	3.714	3.791	3.263
E + 3516	–0.16172	–0.65174	–0.15137	–0.64265	–0.15209	–0.63028
ΔE	11.4	22.6	18.0	28.3	17.5	36.0
Nimg	none	none	1(10i)	1(65i)	none	none
$\langle S^2 \rangle$	2.09	2.04	2.07	2.04	2.07	2.03

membered ring. Consequently, the corresponding four Fe–C bonds are weaker than others, with longer Fe–C distances (ca. 2.5 Å). The long Fe···Fe distance forced by the *trans* stereochemistry of **6S-1** necessarily indicates the lack of a direct iron–iron bond. All six carbonyls in **6S-1** are terminal groups with ν(CO) vibrational frequencies from 1960 to 2025 cm^{-1}. Each iron atom in **6S-1** has the favored 18-electron configuration assuming that the eight pentalene π-electrons are split equally between the two $Fe(CO)_3$ groups.

The singlet *cis*-$C_8H_6Fe_2(CO)_6$ structure **6S-2** with five terminal carbonyls and one bridging carbonyl, lies only 2.1 kcal/mol (B3LYP) or 2.9 kcal/mol (BP86) higher in energy than **6S-1**. The pentalene ligand in **6S-2** is unusual, since one of the five-membered rings functions as a pentahapto ligand whereas the other ring functions as a monohapto ligand. Two pentalene carbon atoms, namely C1 and C2 in Figure 3, are more than 3.4 Å from either iron atom and thus correspond to an uncomplexed C=C double bond of length 1.372 Å (B3LYP) or 1.387 Å (BP86). This C=C bond is shorter than any other C–C bonds in the pentalene ring system of **6S-2** by ca. 0.05 Å in agreement with expectation. Thus only six of the eight π-electrons of the pentalene ligand are donated to the pair of iron atoms in **6S-2**. The Fe–Fe distance of 2.697 Å (B3LYP) or 2.646 Å (BP86) in **6S-2** is consistent with the singly CO-bridged formal single bond required to give each iron atom the favored 18-electron configuration if the Fe_2 unit receives only six of the eight π-electrons from the pentalene ligand. This singly bridged Fe–Fe distance in **6S-2** is ca. 0.15 Å shorter than the experimental unbridged Fe–Fe distance of 2.782 Å in the somewhat related azulene complex *cis*-η^5,η^3-$C_{10}H_8Fe_2(CO)_5$, determined by X-ray crystallography.[55] This appears to be a consequence of the single bridging carbonyl group in **6S-2**. The ν(CO) frequency corresponding to the bridging carbonyl is 1842 cm^{-1}, and the ν(CO) frequencies corresponding to the terminal carbonyl groups fall in the range from 1955 to 2037 cm^{-1}.

A third singlet *cis*-$C_8H_6Fe_2(CO)_6$ structure **6S-4** lies at the much higher energy of 25.6 kcal/mol (B3LYP) or 22.9 kcal/mol (BP86) above **6S-1** (Figure 3 and Table 2). In **6S-4** each pentalene ring functions as a pentahapto ligand towards an $Fe(CO)_3$ group. In **6S-4** two small imaginary vibrational frequencies (73*i* and 54*i* cm^{-1}) are found by the B3LYP method and one small imaginary vibrational frequency (40*i* cm^{-1}) is found by the BP86 method.

The triplet $C_8H_6Fe_2(CO)_6$ structures are found to lie at much higher energies than the corresponding singlet structures, particularly by the BP86 method (Figure 3 and Table 2). Thus the lowest energy triplet *trans*-$C_8H_6Fe_2(CO)_6$ structure **6T-3** lies 11.4 kcal/mol (B3LYP) or 22.6 kcal/mol (BP86) above the global minimum **6S-1**. Structure **6T-3** is very similar to that of **6S-1** except for the spin state.

The triplet *cis*-$C_8H_6Fe_2(CO)_6$ structures **6T-5** and **6T-6**, despite their *cis* stereochemistries, have Fe···Fe distances of 3.854 Å (B3LYP) or 3.714 Å (BP86) for **6T-5** and 3.791 Å (B3LYP) or 3.263 Å (BP86) for **6T-6** (Figure 3 and Table 2). These long Fe···Fe distances clearly indicate the lack of direct iron–iron bonds. The C_{2v} triplet *cis*-$C_8H_6Fe_2(CO)_6$ structure **6T-5** lies 18.0 kcal/mol (B3LYP) or 28.2 kcal/mol (BP86) above the lowest energy structure **6S-1**. In **6T-5** two $Fe(CO)_3$ groups are bonded to two trihapto five-membered rings with Fe–C distances in the range 2.05 to 2.23 Å. The Fe–C distances to the remaining two carbons of the pentalene system in **6T-5**, i.e., C4 and C5 in Figure 3, are significantly longer, in the range 2.63 to 2.71 Å and thus are assumed to be formally non-bonding. The triplet *cis*-$C_8H_6Fe_2(CO)_6$ structure **6T-6** is predicted to lie 17.5 kcal/mol (B3LYP) or 34.9 kcal/mol (BP86) above **6S-1**. In **6T-6**, one of the pentalene rings is bonded to an $Fe(CO)_4$ group as a monohapto ligand whereas the other pentalene ring is bonded to an $Fe(CO)_2$ group as a pentahapto ligand, thereby giving both iron atoms the 17-electron configuration for a binuclear triplet with no direct iron–iron bond.

3.1.3 $C_8H_6Fe_2(CO)_5$

The $C_8H_6Fe_2(CO)_5$ system is of particular interest since (pentalene)$Fe_2(CO)_5$ derivatives have been synthesized and characterized structurally.[4,6] In the theoretical study reported here, a total of four low-lying $C_8H_6Fe_2(CO)_5$ structures were found, namely, the singlet *cis* and *trans* structures **5S-1** and **5S-2**, as well as the triplet *cis* and *trans* structures **5T-3** and **5T-4** (Figure 4, Table 3 and Table S46). Structure **5S-1** lies >25 kcal/mol by the BP86 method below any of

Table 3. Bond lengths (Å), total energies (E, Hartree), relative energies (ΔE, kcal/mol), and spin expectation values $\langle S^2 \rangle$ for the $C_8H_6Fe_2(CO)_5$ structures.

	5S-1 (C_s)		**5S-2** (C_1)		**5T-3** (C_1)		**5T-4** (C_s)	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
Fe–Fe	2.770	2.753	4.419	4.399	4.581	4.547	2.734	2.652
E + 3402	–0.83690	–1.33665	–0.79419	–1.29635	–0.81475	–1.28649	–0.80002	–1.28612
ΔE	0.0	0.0	26.8	25.3	12.2	31.5	23.1	31.7
Nimg	none	none	none	none	none	none	1(55i)	none
$\langle S^2 \rangle$	0.00	0.00	0.00	0.00	2.08	2.03	2.10	2.04

the other $C_8H_6Fe_2(CO)_5$ structures, suggesting that it is a highly favored structure. This is consistent with the recent experimental observation of **5S-1** structures for the (pentalene)$Fe_2(CO)_5$ derivatives that have been synthesized by O'Hare and co-workers.[4]

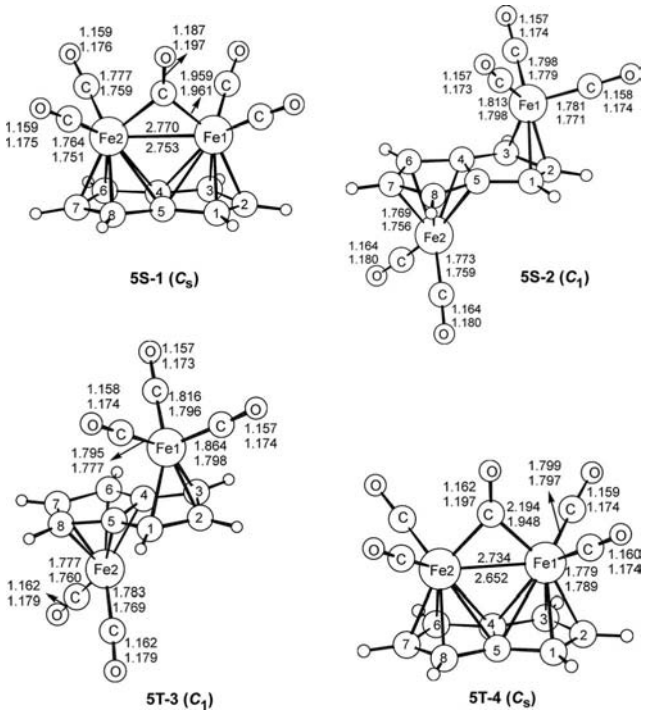

Figure 4. The four optimized $C_8H_6Fe_2(CO)_5$ structures.

The global minimum **5S-1** is a singlet *cis*-$C_8H_6Fe_2(CO)_5$ structure with four terminal carbonyl groups, one bridging carbonyl group, and two pentahapto five-membered rings (Figure 4 and Table 3). This geometry is in agreement with the structure suggested by Hunt and Russell[1] as well as the experimental structure of the related permethylpentalene iron carbonyl complex $C_8Me_6Fe_2(CO)_5$, determined by O'Hare and co-workers using X-ray crystallography.[4] Our predicted Fe–Fe distance of 2.770 Å (B3LYP) or 2.753 Å (BP86) for the $C_8H_6Fe_2(CO)_5$ structure **5S-1** is somewhat longer than the experimental Fe–Fe distance of 2.687 Å for the permethylated derivative $C_8Me_6Fe_2(CO)_5$, possibly because of the effects of multiple methyl substitution. In **5S-1** each Fe atom accepts four electrons from pentalene thereby acquiring the favored 18-electron configuration. In **5S-1** the ν(CO) frequency for the bridging carbonyl is predicted to be 1811 cm^{-1} and those for the terminal carbonyls are predicted to be 1958, 1967, 1993, and 2019 cm^{-1} (BP86, Table S46). These theoretical harmonic ν(CO) frequencies are comparable with the experimentally observed 1750, 1945, 1985, and 2030 cm^{-1} obtained in a KBr pellet.[6]

The singlet *trans*-$C_8H_6Fe_2(CO)_5$ structure **5S-2** is predicted to lie 26.8 kcal/mol (B3LYP) or 25.3 kcal/mol(BP86) above the global minimum **5S-1** (Figure 4 and Table 3). The predicted Fe–C distances in **5S-2** suggest that one pentalene ring is bonded to the $Fe(CO)_2$ group as a pentahapto ligand and the other pentalene ring is bonded to the $Fe(CO)_3$ group as a trihapto ligand. In **5S-2** the iron atom of the $Fe(CO)_3$ group has the favored 18-electron configuration but the iron atom of the $Fe(CO)_2$ group has only a 16-electron configuration.

The triplet *trans*-$C_8H_6Fe_2(CO)_5$ structure **5T-3** is predicted to lie 12.2 kcal/mol (B3LYP) or 31.5 kcal/mol (BP86) in energy above the global minimum **5S-1** (Figure 4 and Table 3). As we mentioned above, the two methods predict different relative energies for different spin states. The true value should lie between the predictions of the two methods. The Fe–C distances in **5T-3** indicate that the five-membered ring bonded to a $Fe(CO)_3$ group functions as a trihapto ligand and the five-membered ring bonded to the $Fe(CO)_2$ group functions as a pentahapto ligand. Each iron atom has the 17-electron configuration, which is consistent with a binuclear triplet.

The C_s triplet *cis*-$C_8H_6Fe_2(CO)_5$ structure **5T-4** is predicted to lie much higher in energy at 23.1 kcal/mol (B3LYP) or 31.7 kcal/mol (BP86) above **5S-1** (Figure 4 and Table 3). The B3LYP method predicts a small imaginary vibrational frequency (55*i* cm^{-1}), whereas the BP86 method predicts all real frequencies. The Fe–C distances in this structure suggest that each five-membered ring functions as a pentahapto ligand to one of the iron atoms. The Fe–Fe distance of 2.734 Å (B3LYP) or 2.652 Å (BP86) is consistent with a formal single bond.

3.1.4 $C_8H_6Fe_2(CO)_4$

Four *cis* (Figure 5 and Table 4) and three *trans* (Figure 6 and Table 5) structures are obtained for $C_8H_6Fe_2(CO)_4$. None of these structures exhibits any imaginary vibrational frequencies. All seven structures thus are genuine minima. The global minimum predicted by the BP86 method is the triplet *cis*-$C_8H_6Fe_2(CO)_3(\mu\text{-}CO)$ structure **4T-1**, which has one bridging carbonyl group and three terminal carbonyl groups. In **4T-1** an FeCO group is bonded to a pentahapto five-membered ring and an $Fe(CO)_2$ group is bonded to a trihapto five-membered ring. The predicted Fe–Fe distance

Table 4. Bond lengths (Å), total energies (*E*, Hartree), relative energies (Δ*E*, kcal/mol), and spin expectation values $\langle S^2 \rangle$ for the *cis*-$C_8H_6Fe_2(CO)_4$ structures.

	4T-1 (C_1)		**4T-2** (C_2)		**4S-3** (C_1)		**4S-4** (C_s)	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
Fe–Fe	2.683	2.629	2.597	2.499	2.621	2.568	2.641	2.677
E + 3289	–0.45708	–0.92834	–0.46379	–0.92741	–0.43683	–0.92625	–0.43224	–0.91746
Δ*E*	0.0	0.0	–4.2	0.6	12.7	1.3	15.6	6.8
$\langle S^2 \rangle$	2.26	2.04	2.09	2.03	0.00	0.00	0.00	0.00

of 2.683 Å (B3LYP) or 2.629 Å (BP86) can be interpreted as a formal single bond, which gives each iron the 17-electron configuration, consistent with the binuclear triplet.

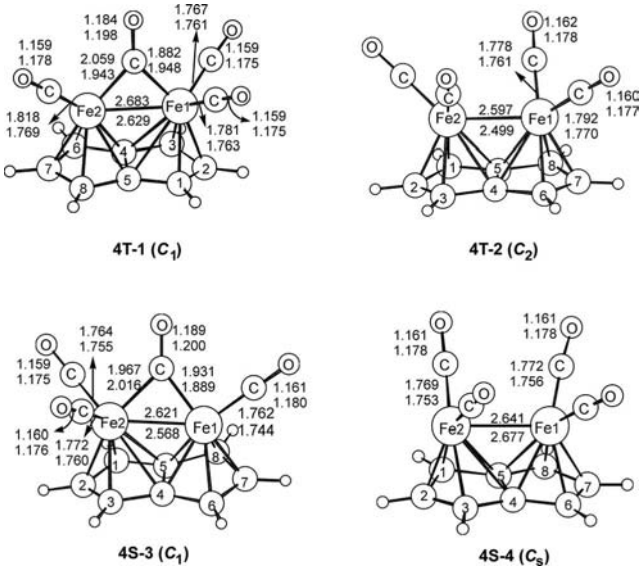

Figure 5. The four optimized *cis*-$C_8H_6Fe_2(CO)_4$ structures.

A second triplet *cis*-$C_8H_6Fe_2(CO)_4$ structure **4T-2** is predicted to have essentially the same energy as **4T-1**, lying only 0.6 kcal/mol above **4T-1** by BP86, but 4.2 kcal/mol below **4T-1** by B3LYP (Figure 5 and Table 4). In **4T-2** each pentalene ring is bonded to an $Fe(CO)_2$ moiety as a pentahapto ligand. The predicted Fe=Fe distance of 2.597 Å (B3LYP) or 2.499 Å (BP86) in **4T-2** is consistent with a formal double bond, which gives each iron atom the 18-electron configuration. This Fe=Fe double bond is of the σ + $^2/_2\pi$ type with one σ "full bond" and two orthogonal π "half-bonds," similar to the double bonds in triplet dioxygen or the organometallic[56] $(\eta^5\text{-}Me_5C_5)_2Fe_2(\mu\text{-}CO)_3$. The triplet spin state of **4T-2** arises from the unpaired single electrons in each of the two π "half-bonds." This analysis of the Fe=Fe bonding is supported by an investigation of the singly occupied molecular orbitals (SOMOs).

Table 5. Bond lengths (Å), total energies (*E*, Hartree), relative energies (Δ*E*, kcal/mol), and spin expectation values $\langle S^2 \rangle$ for the *trans*-$C_8H_6Fe_2(CO)_4$ structures.

	4T-5 (C_{2h})		**4S-6** (C_{2h})		**4T-7** (C_1)	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
Fe–Fe	4.421	4.298	4.272	4.243	4.652	4.526
E + 3289	–0.46183	–0.91336	–0.39908	–0.89546	–0.43442	–0.88061
Δ*E*	–3.0	9.4	36.4	20.6	14.2	30.0
$\langle S^2 \rangle$	2.06	2.03	0.00	0.00	3.05	2.34

The singlet *cis*-$C_8H_6Fe_2(CO)_4$ structure **4S-3** is predicted to lie 12.7 kcal/mol (B3LYP) or only 1.3 kcal/mol (BP86) in energy above the global minimum **4T-1** (Figure 6 and Table 4). Again, it should not be surprising to have different relative energies between different spin states predicted by the B3LYP and BP86 methods. The true value is estimated to be between the two predicted values.[52,53] The bridging carbonyl group in **4S-3** exhibits a low ν(CO) frequency at 1804 cm^{-1} relative to the ν(CO) frequencies of the terminal carbonyl groups (Table S47). The predicted Fe–C bonds with the distances of 2.06 to 2.30 Å in **4S-3** suggest one trihapto ring and one pentahapto ring (Figure 5). The predicted Fe=Fe distance of 2.621 Å (B3LYP) or 2.568 Å (BP86) can be interpreted as the formal double bond required to give each iron atom the favored 18-electron configuration. The other singlet *cis*-$C_8H_6Fe_2(CO)_4$ structure

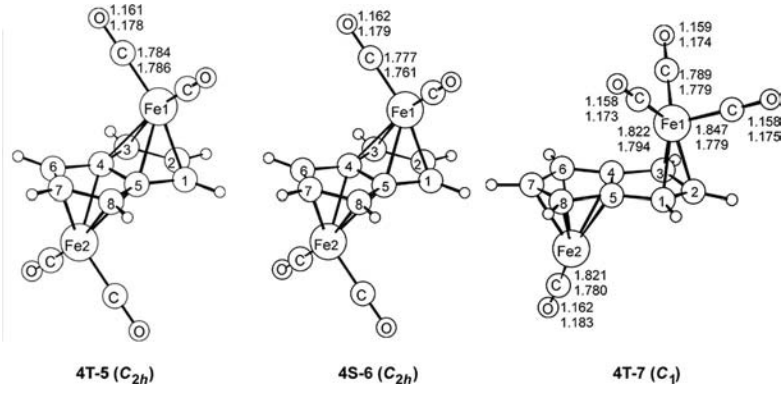

Figure 6. The three optimized *trans*-$C_8H_6Fe_2(CO)_4$ structures.

4S-4 with all terminal carbonyls is predicted to lie 15.6 kcal/mol (B3LYP) or 6.8 kcal/mol (BP86) above **4T-1** (Figure 5 and Table S47). For **4S-4** the Fe–C distances indicate a pentahapto five-membered ring bonded to a $Fe(CO)_2$ group and a trihapto five-membered ring bonded to the other $Fe(CO)_2$ group. The predicted Fe–Fe distance of 2.641 Å (B3LYP) or 2.677 Å (BP86) can be interpreted as a formal single bond thereby giving the iron atom bonded to the pentahapto ring the favored 18-electron configuration but the iron bonded to the trihapto ring only a 16-electron configuration. The LUMO for **4S-4** is mainly a d orbital centered on Fe2, thereby confirming that the Fe2 atom is electron-deficient from the closed-shell 18-electron configuration.

The *trans*-$C_8H_6Fe_2(CO)_4$ structures (Figure 6 and Table 5) lie higher in energy than the *cis*-$C_8H_6Fe_2(CO)_4$ structures, at least by the more reliable BP86 method. The C_{2h} triplet *trans*-$C_8H_6Fe_2(CO)_4$ structure **4T-5** is predicted to lie in energy 3.0 kcal/mol below (B3LYP) or 9.4 kcal/mol above (BP86) than the global minimum **4T-1** predicted by BP86. In **4T-5** the Fe–C distances indicate both five-membered rings are pentahapto rings, and both iron atoms in this *trans* structure have 16-electron configurations. The other triplet *trans*-$C_8H_6Fe_2(CO)_4$ structure **4T-7** has a relatively large spin contamination of 3.05 (B3LYP) or 2.34 (BP86) and is predicted to lie 14.2 kcal/mol (B3LYP) or 30.0 kcal/mol (BP86) above **4T-1**. Structure **4T-7** has a trihapto five-membered ring bonded to an $Fe(CO)_3$ group and a pentahapto five-membered ring bonded to an Fe(CO) group. This leads to a 15-electron configuration for one of the iron atoms and a 17-electron configuration for the other iron atom, consistent with a binuclear triplet. The singlet *trans*-$C_8H_6Fe_2(CO)_4$ structure **4S-6** is predicted to lie 36.4 kcal/mol (B3LYP) or 20.6 kcal/mol (BP86) above **4T-1**. In the *trans*-$C_8H_6Fe_2(CO)_4$ structure **4S-6** each pentalene ring is bonded to an $Fe(CO)_2$ moiety as a pentahapto ligand.

3.1.5 $C_8H_6Fe_2(CO)_3$

A total of 11 $C_8H_6Fe_2(CO)_3$ structures were found within ca. 20 kcal/mol of the global minimum by the BP86 method, indicating a very complicated potential energy surface. The lowest-lying singlet $C_8H_6Fe_2(CO)_3$ structure **3S** (Figure 7) is reported here, since its energy is required for some of the thermochemistry discussed later in this paper. Structure **3S** has a single bridging carbonyl group, a terminal carbonyl group on each iron atom, and two equivalent pentahapto five-membered rings, one bonded to each iron atom. The predicted Fe≡Fe distance in **3S** of 2.277 Å (B3LYP) or 2.304 Å (BP86) is significantly shorter than the iron–iron distances in any of the $C_8H_6Fe_2(CO)_n$ (n = 6, 5, 4) derivatives. This short Fe≡Fe distance can be interpreted as the formal triple bond required to give each iron atom the favored 18-electron configuration. The ν(CO) frequency of the bridging carbonyl group in **3S** is a typical 1825 cm^{-1}. The total energy of –3176.04678 (B3LYP) or –3176.53092 (BP86) for **3S** is used to determine the energies for CO dissociation and disproportionation of $C_8H_6Fe_2(CO)_4$.

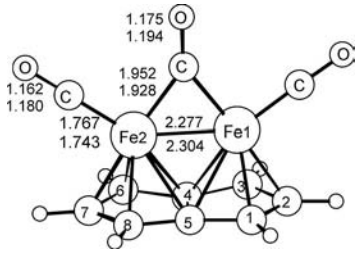

Figure 7. The lowest energy singlet structure **3S** for $C_8H_6Fe_2(CO)_3$.

3.2 Dissociation Energies

The predicted dissociation energy (Table 6) for the loss of one CO group from *trans*-$C_8H_6Fe_2(CO)_7$ (**7S-1**) to give *trans*-$C_8H_6Fe_2(CO)_6$ (**6S-1**) is rather low at 9.4 kcal/mol (B3LYP) or 8.5 kcal/mol (BP86). The predicted dissociation energy (Table 6) for the loss of one CO group from *trans*-$C_8H_6Fe_2(CO)_6$ (**5S-1**) to give *cis*-$C_8H_6Fe_2(CO)_5$ (**5S-1**) is also rather low at 9.0 kcal/mol (B3LYP) or 14.9 kcal/mol (BP86). However, further dissociation of a CO group from *cis*-$C_8H_6Fe_2(CO)_5$ (**5S-1**) to give *cis*-$C_8H_6Fe_2(CO)_4$ (**4S-3**) requires the much higher energy of 44.8 kcal/mol (B3LYP) or 52.2 kcal/mol (BP86). This demonstrates that structure *cis*-$C_8H_6Fe_2(CO)_5$ (**5S-1**) is energetically viable. These CO dissociation energies can account for the experimental observation[4,6] of **5S-1** as a product from thermal reactions of dihydropentalenes or pentalene dimer with iron carbonyls.

The high stability of the experimentally observed *cis*-$C_8H_6Fe_2(CO)_5$ (**5S-1**) is also proven by the high energy of 35.8 kcal/mol (B3LYP) or 37.3 kcal/mol (BP86) required for

Table 6. Bond dissociation energies (kcal/mol) for removal of one carbonyl group and disproportionation energies of the $C_8H_6Fe_2(CO)_n$ derivatives.

	B3LYP	BP86
trans-$C_8H_6Fe_2(CO)_7$ (**7S-1**) → *trans*-$C_8H_6Fe_2(CO)_6$ (**6S-1**) + CO	9.4	8.5
trans-$C_8H_6Fe_2(CO)_6$ (**6S-1**) → *cis*-$C_8H_6Fe_2(CO)_5$ (**5S-1**) + CO	9.0	14.9
cis-$C_8H_6Fe_2(CO)_5$ (**5S-1**) → *cis*-$C_8H_6Fe_2(CO)_4$ (**4S-3**) + CO	44.8	52.2
cis-$C_8H_6Fe_2(CO)_4$ (**4S-3**) → *cis*-$C_8H_6Fe_2(CO)_3$ (**3S**) + CO	38.5	42.7
2 *trans*-$C_8H_6Fe_2(CO)_6$ (**6S-1**) → *trans*-$C_8H_6Fe_2(CO)_6$ (**7S-1**) + *cis*-$C_8H_6Fe_2(CO)_4$ (**5S-1**)	–0.4	6.4
2 *cis*-$C_8H_6Fe_2(CO)_5$ (**5S-1**) → *trans*-$C_8H_6Fe_2(CO)_6$ (**6S-1**) + *cis*-$C_8H_6Fe_2(CO)_4$ (**4S-5**)	35.8	37.3
2 *cis*-$C_8H_6Fe_2(CO)_4$ (**4S-5**) → *cis*-$C_8H_6Fe_2(CO)_5$ (**5S-1**) + *cis*-$C_8H_6Fe_2(CO)_3$ (**3S**)	–6.3	–9.5

its disproportionation into a mixture of *trans*-$C_8H_6Fe_2(CO)_6$ (**6S-1**) and *cis*-$C_8H_6Fe_2(CO)_4$ (**4S-3**). However, the analogous disproportionation of the tetracarbonyl *cis*-$C_8H_6Fe_2(CO)_4$ (**4S-5**) into *cis*-$C_8H_6Fe_2(CO)_5$ (**5S-1**) and *cis*-$C_8H_6Fe_2(CO)_3$ (**3S**) is predicted to be exothermic, with an energy of –6.3 kcal/mol (B3LYP) or –9.5 kcal/mol (BP86). This suggests that *cis*-$C_8H_6Fe_2(CO)_4$ (**4S-5**) is not likely to be synthetically accessible.

4. Discussion

Simple electron counting suggests that a stable $PnFe_2(CO)_6$ structure (Pn = pentalene or substituted pentalene ligand) would have the pentalene system functioning as a bis(1,3-diene) with each pair of double bonds bonded to an $Fe(CO)_3$ unit analogous to the long-known butadiene-iron tricarbonyl,[57] η^4-$C_4H_6Fe(CO)_3$. In such a structure each pentalene ring would function as a tetrahapto ligand. However, in the lowest energy $PnFe_2(CO)_6$ structure **6S-1** (Figure 3) each pentalene ring functions as a pentahapto ligand rather than a tetrahapto ligand so that the two carbons common to both pentalene rings are bonded to each iron atom. However, these Fe–C distances of ca. 2.5 Å are significantly longer than the ca. 2.0 to ca. 2.2 Å Fe–C distances to the other six pentalene carbon atoms that are within bonding distance of one of the two iron atoms.

A $PnFe_2(CO)_6$ structure with all eight pentalene carbon atoms bonded to iron atoms does not require an iron–iron bond for each iron atom to have the favored 18-electron configuration. In fact, five of the six $PnFe_2(CO)_6$ structures found in this work, namely **6S-1**, **6T-3**, **6S-4**, **6T-5**, and **6T-6**, have all eight pentalene carbon atoms within bonding distance of at least one of the two iron atoms and the iron atoms too far apart for a formal direct iron–iron bond. However, a relatively low energy $PnFe_2(CO)_6$ structure **6S-2** (Figure 3) is found with a formal Fe–Fe single bond of ca. 2.66 Å and only six of the eight pentalene carbon atoms within bonding distance of at least one iron atom. In structure **6S-2** one of the pentalene five-membered rings functions as a typical pentahapto ligand, while the other pentalene ring functions as only a monohapto ligand with an uncomplexed C=C double bond. The relatively low energy of the $PnFe_2(CO)_6$ structure **6S-2** at only ca. 3 kcal/mol above the **6S-1** global minimum suggests that the energy of forming an Fe–Fe bond is comparable to forming an olefin-Fe bond from one of the C=C double bonds of a pentalene ring.

The carbonyl dissociation energy of $PnFe_2(CO)_6$ to give $PnFe_2(CO)_5$ is relatively low at about 12 kcal/mol (Table 6). Furthermore, the $PnFe_2(CO)_5$ structure **5S-1** (Figure 4) is predicted to lie >25 kcal/mol below any other $PnFe_2(CO)_5$ structure using the more reliable BP86 method. This is consistent with the observation that reactions of dihydropentalenes with iron carbonyls[1,2,6,7] lead directly to $PnFe_2(CO)_5$ complexes with **5S-1** structures. Also the $PnFe_2(CO)_5$ structure **5S-1** (Figure 4) may be derived from the $PnFe_2(CO)_6$ structure **6S-2** (Figure 3) by loss of a carbonyl group from the iron atom bonded to the monohapto pentalene ring, with concurrent conversion of the monohapto pentalene ring to a pentahapto ring. During the conversion of **6S-2** to **5S-1** the Fe–Fe distance (BP86) lengthens by ca. 0.1 Å from 2.646 Å in **6S-2** to 2.753 Å in **5S-1**.

The carbonyl dissociation energy of $PnFe_2(CO)_5$ (**5S-1**) to give $PnFe_2(CO)_4$ is relatively high at 48 kcal/mol (Table 6). This again is consistent with the experimental observation of $PnFe_2(CO)_5$ as the product from reactions of dihydropentalenes with iron carbonyls. For $PnFe_2(CO)_4$ both triplet structures such as **4T-1** and **4T-2** and singlet structures such as **4S-3** and **4S-4** lie within 7 kcal/mol of each other by the BP86 method with the triplet structures lying slightly below the singlet structures in energy. The tetracarbonyl $PnFe_2(CO)_4$, at least in the singlet spin state, is predicted to be thermodynamically unfavorable with respect to disproportionation into $PnFe_2(CO)_5$ + $PnFe_2(CO)_3$.

The more highly unsaturated $PnFe_2(CO)_n$ (n = 3, 2, 1) were also investigated. However, their potential surfaces are considerably more complicated with 11 structures for $PnFe_2(CO)_3$ and 12 structures for $PnFe_2(CO)_2$. These structures include not only singlet and triplet state structures but also quintet state structures. Only the lowest energy singlet structure **3S** for $PnFe_2(CO)_3$ is reported here (Figure 7). The energy of this $PnFe_2(CO)_3$ is used to calculate the carbonyl dissociation and disproportionation energies of $PnFe_2(CO)_4$. Structure **3S** for $PnFe_2(CO)_3$ is also of interest since its very short Fe≡Fe distance of ca. 2.3 Å is consistent with the formal triple bond required to give both iron atoms the favored 18-electron configuration. The lowest energy singlet structures for $PnFe_2(CO)_5$ (**5S-1**), $PnFe_2(CO)_4$ (**4S-3**), and $PnFe_2(CO)_3$ (**3S**) thus form a sequence of singly carbonyl-bridged structures where the formal iron–iron bond order increases from one in **5S-1**, to two in **4S-3**, and then to three in **3S** in order to maintain the favored 18-electron configuration for both iron atoms. The iron–iron distances in this series decrease correspondingly from 2.753 Å in **5S-1**, to 2.568 Å in **4S-3**, and then 2.304 Å in **3S**.

It is also instructive to compare these binuclear pentalene iron carbonyl complexes with the binuclear azulene iron carbonyl complexes.[58] Binuclear iron carbonyl complexes of the type $LFe_2(CO)_5$ (L = azulene or pentalene) are known experimentally for both azulene and pentalene. In essentially all of the (azulene)$Fe_2(CO)_n$ (n = 6, 5, 4, 3, 2, 1) complexes all of the carbons of the five-membered ring are within bonding distance of an iron atom, whereas the seven-membered azulene ring exhibits variable hapticity with one or two uncomplexed C=C double bonds in some structures. Even the experimentally known *cis*-η^5,η^3-$C_{10}H_8Fe_2(CO)_5$ has one uncomplexed C=C double bond in the seven-membered azulene ring. For almost all of the binuclear pentalene iron carbonyl derivatives reported here, all eight carbon atoms are within bonding distance of at least one iron atom. The major exception is the $PnFe_2(CO)_6$ structure **6S-2** in which one of the pentalene rings is bonded to an iron atom as a monohapto ligand leaving an uncomplexed C=C double bond. In many of the $PnFe_2$-

$(CO)_n$ structures the two carbon atoms shared by both five membered rings bridge the pair of iron atoms. Thus the known $PnFe_2(CO)_4(\mu\text{-}CO)$ derivative **5S-1** may be regarded as an analogue of $Fe_2(CO)_9$, having a $Fe_2(CO)_6(\mu\text{-}CO)_3$ structure with three bridging carbonyl groups.

5. Conclusion

The lowest energy structure of the hexacarbonyl complex $PnFe_2(CO)_6$ is predicted to be *trans*-$(\eta^5,\eta^5\text{-}C_8H_6)Fe_2(CO)_6$ without an iron–iron bond and in which the pentalene unit bonds to each iron atom as a pentahapto ligand. However, an alternative *cis*-$(\eta^5,\eta^1\text{-}C_8H_6)Fe_2(CO)_6$ structure with an uncomplexed pentalene C=C double bond and a direct iron–iron bond lies only ca. 3 kcal/mol above this global minimum for $PnFe_2(CO)_6$. In this latter structure the pentalene system is bonded to one iron atom as a pentahapto ligand but to the other iron atom as only a monohapto ligand.

The CO dissociation energy of $PnFe_2(CO)_6$ to give $PnFe_2(CO)_5$ is predicted to be only ca. 12 kcal/mol. This can account for the formation of the pentacarbonyl rather than the hexacarbonyl in thermal reactions of dihydropentalene with iron carbonyls. The *cis*-$(\eta^5,\eta^5\text{-}C_8H_6)Fe_2(CO)_4(\mu\text{-}CO)$ global minimum structure for the pentacarbonyl complex with an iron–iron bond bridged by a carbonyl group corresponds to the structure found experimentally and is favored over any other possible $PnFe_2(CO)_5$ structures by more than 25 kcal/mol.

Two triplet and two singlet structures within 7 kcal/mol of each other are found for $PnFe_2(CO)_4$ with the triplet structures being of slightly lower energies. The singlet $PnFe_2(CO)_4$ structure is predicted to be thermodynamically disfavored with respect to disproportionation into $PnFe_2(CO)_5 + PnFe_2(CO)_3$.

Supporting Information (see footnote on the first page of this article): Tables S1 to S19: Atomic coordinates of the optimized structures for the $C_8H_6Fe_2(CO)_n$ (n = 7, 6, 5, 4) complexes; Tables S20 to S38: Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses in km/mol) for the $C_8H_6Fe_2(CO)_n$ (n = 7, 6, 5, 4) complexes; Tables S39 to S43: Fe–C(pentalene) distances in the $C_8H_6Fe_2(CO)_n$ (n = 7, 6, 5, 4) complexes; Tables S44–S47: ν(CO) frequencies (in cm^{-1}) predicted for the $C_8H_6Fe_2(CO)_n$ (n = 7, 6, 5, 4) structures by the BP86 method; complete Gaussian09 reference (ref.[54]).

Acknowledgments

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