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Theoretical Studies on the Desulfurization of Benzothiophene (Thianaphthene) and Thienothiophene (Thiophthene) by Carbon-Sulfur Bond Cleavage: Binuclear Iron Carbonyl Intermediates

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Abstract

Thiophene is known experimentally to be desulfurized by $\text{Fe}_3(\text{CO})_{12}$ under mild conditions to give the tricarbonyl ferrole ($\eta^4, \eta^2\text{-C}_4\text{H}_4$) $\text{Fe}_2(\text{CO})_6$. A similar reaction of benzothiophene (thianaphthene) with $\text{Fe}_3(\text{CO})_{12}$ gives a $(\text{C}_8\text{H}_6\text{S})\text{Fe}_2(\text{CO})_6$ complex in which an iron carbonyl moiety has inserted into the thiophene ring to give a thiaferranaphthalene ligand. Density functional theory shows this experimental structure to be the lowest energy structure. Furthermore, the lowest energy structures of the diiron pentacarbonyl $(\text{C}_8\text{H}_6\text{S})\text{Fe}_2(\text{CO})_5$ are simply derived from this $(\text{C}_8\text{H}_6\text{S})\text{Fe}_2(\text{CO})_6$ by loss of a CO group retaining the thiaferranaphthalene ligand. However, a higher energy isomeric ($\eta^6, \eta^2\text{-C}_8\text{H}_6\text{S}$) $\text{Fe}_2(\text{CO})_5$ structure retains the original benzothiophene ligand with the C_6 ring bonded to an $\text{Fe}(\text{CO})_2$ moiety as a hexahapto ligand and the $\text{C}=\text{C}$ double bond of the C_4S ring bonded to an $\text{Fe}(\text{CO})_3$ moiety as a dihapto ligand with an $\text{Fe}\rightarrow\text{Fe}$ dative bond between the iron atoms. Similar insertion of an iron atom into a thiophene ring to give a thiaferrabenzene ring is predicted to occur in the lowest energy $(\text{C}_6\text{H}_4\text{S}_2)\text{Fe}_2(\text{CO})_6$ structure derived from either the *anti* or *syn* isomers of thienothiophene. However, the bonding of the exocyclic iron atom to the resulting thiaferrabenzothiophene ligand involves atoms in both rings in contrast to the $(\text{C}_8\text{H}_6\text{S})\text{Fe}_2(\text{CO})_6$ complex where the benzene ring is not involved in the ligand-iron bonding.

1. Introduction

Transition metal complexes of sulfur heterocycles are of interest because of their possible roles in removal of sulfur from petroleum.¹ In this connection, the first metal carbonyl complex of thiophene to be synthesized was the chromium derivative $(\eta^5\text{-C}_4\text{H}_4\text{S})\text{Cr}(\text{CO})_3$, obtained by a simple thermal reaction of $\text{Cr}(\text{CO})_6$ with thiophene.^{2,3} In this complex the thiophene ring is retained and bonds to the $\text{Cr}(\text{CO})_3$ moiety analogous to the benzene-chromium bond in benzene chromium tricarbonyl, $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$.^{4,5,6,7,8} An analogous reaction of $\text{Fe}_3(\text{CO})_{12}$ with thiophene gave a product, initially, but incorrectly, reported as the analogous thiophene iron dicarbonyl.⁹ However, the absence of sulfur in this presumed thiophene metal complex proved an early and obvious clue that soon led to the reformulation of this complex as the sulfur-free tricarbonylferrole iron tricarbonyl, $(\eta^4, \eta^2\text{-C}_4\text{H}_4)\text{Fe}_2(\text{CO})_6$,¹⁰ previously obtained from acetylene and iron carbonyl (Figure 1).¹¹ This reaction was the first demonstration of the desulfurization of a sulfur heterocycle with a metal carbonyl derivative.

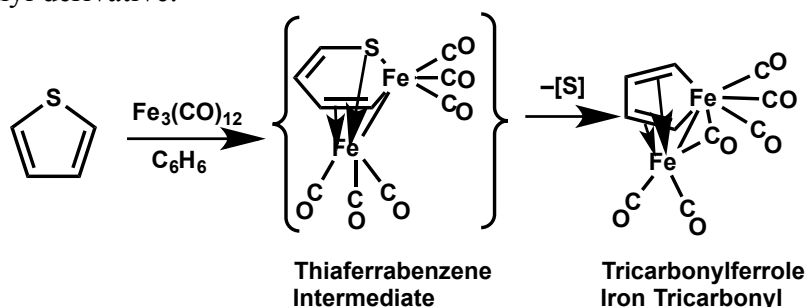


Figure 1. Desulfurization of thiophene with iron carbonyl to give a tricarbonylferrole derivative.

The erroneous report of “thiophene iron dicarbonyl” stimulated an early investigation of the reaction of benzothiophene (thianaphthene) with $\text{Fe}_3(\text{CO})_{12}$. In this case the resulting binuclear iron carbonyl complex clearly contained sulfur. Since benzothiophene appeared to be a potential donor of ten electrons to a pair of metal atoms, this iron complex was initially but incorrectly formulated as a diiron pentacarbonyl¹² $(\text{C}_8\text{H}_6\text{S})\text{Fe}_2(\text{CO})_5$, based on the 18-electron rule.^{13,14,15,16,17} However, shortly thereafter the reactions of $\text{Fe}_3(\text{CO})_{12}$ with vinyl sulfides, $\text{RSCH}=\text{CH}_2$, were shown to result in cleavage of the vinyl-sulfur bond to give compounds with bridging vinyl groups of the type $(\eta^2\text{-CH}_2=\text{CH})\text{Fe}_2(\text{CO})_6(\text{SR})$ (Figure 2).¹⁸ Since benzothiophene is effectively a cyclic vinyl sulfide, this suggested what turned out to be the correct formulation as a thiaferranaphthalene derivative, $(\eta^3, \eta^2\text{-C}_6\text{H}_4\text{SC}_2\text{H}_2)\text{Fe}_2(\text{CO})_6$ (Figure 3).

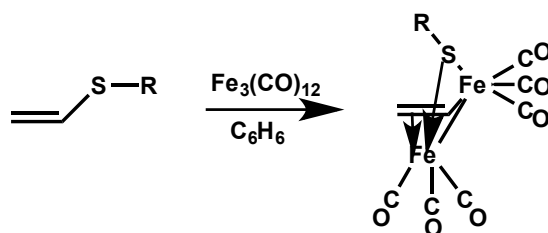


Figure 2. Cleavage of a carbon-sulfur bond in an alkyl vinyl sulfide by reaction with $\text{Fe}_3(\text{CO})_{12}$.

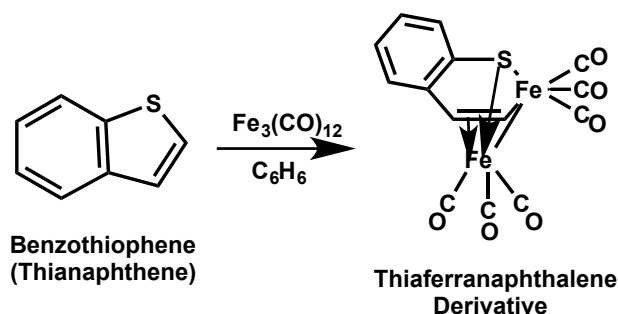


Figure 3. Reaction of benzothiophene with iron carbonyl to give a thiaferranaphthalene derivative.

These early studies on iron carbonyl reactions with thiophene and benzothiophene around 1960 predated the availability of X-ray structure determinations on a routine basis. In 1988 Rauchfuss and co-workers reinvestigated these and related systems.¹⁹ They used X-ray crystallography to confirm the thiaferranaphthalene structure of the triphenylphosphine derivative $(\eta^3, \eta^2\text{-C}_6\text{H}_4\text{SC}_2\text{H}_2)\text{Fe}_2(\text{CO})_5(\text{PPh}_3)$. However, the parent $(\eta^3, \eta^2\text{-C}_6\text{H}_4\text{SC}_2\text{H}_2)\text{Fe}_2(\text{CO})_6$ has not been amenable to X-ray structural studies. The bonding of the thianaphthene ligand to the Fe_2 unit does not involve the carbon atoms of the benzene ring. Therefore related iron carbonyl complexes should be accessible without the fused benzene ring. In this connection Rauchfuss and co-workers¹⁹ have synthesized a stable thiaferrabenzene iron carbonyl derivative without a fused benzene ring. This suggests an intermediate of this type in the desulfurization of thiophene with $\text{Fe}_3(\text{CO})_{12}$ (Figure 1).

This manuscript describes the use of density functional theory to explore the structures and thermochemistry of binuclear iron carbonyl derivatives derived from two types of sulfur heterocycles. The first system is the benzothiophene (thianaphthene) system that has been investigated experimentally. The experimentally observed thiaferranaphthalene structure $(\text{C}_8\text{H}_6\text{S})\text{Fe}_2(\text{CO})_6$, in which a C-S bond of the benzothiophene ligand has been cleaved,^{18,19} is shown to be the lowest energy structure by a substantial margin. This structure does not involve the benzene ring of the benzothiophene ligand in the

bonding to the iron carbonyl unit. In addition, a $(C_8H_6S)Fe_2(CO)_5$ pentacarbonyl structure is found with an intact benzothiophene ligand at potentially accessible energies.

Iron carbonyl complexes of the two thienothiophene (thiophthene) isomers consisting of a pair of fused thiophene rings (Figure 4) were also included in this study. This system leads to unique lowest energy structures for both the hexacarbonyl $(C_6H_4S_2)Fe_2(CO)_6$ and the pentacarbonyl $(C_6H_4S_2)Fe_2(CO)_5$ by substantial margins. The behaviors of the *syn* and *anti* thienothiophene isomers are completely analogous so only one of the isomers is discussed in detail in the text although the results with both isomers are presented in the Supporting Information. The predicted nature of the binuclear iron carbonyl thienothiophene complexes is very different from those derived from benzothiophene since both thiophene rings in the thienothiophene heterocycles are involved in the interaction with the iron carbonyl system.

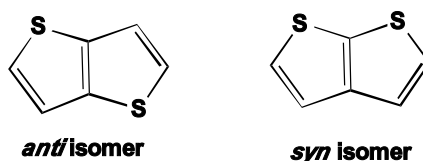


Figure 4. Stereoisomers of thienothiophene (thiophthene).

2. Theoretical Methods

Electron correlation effects were considered by employing density functional theory (DFT) methods, which have evolved as a practical and effective computational tool, especially for organometallic compounds.^{20,21,22,23,24,25,26} Thus three DFT methods were used in this study. The first DFT method is B3LYP, which is the popular hybrid HF/DFT method using the combination of the three parameter Becke functional with the Lee–Yang–Parr generalized gradient correlation functional.^{27,28} The second DFT method is BP86, which combines Becke’s 1988 exchange functional with Perdew’s 1986 gradient corrected correlation functional.^{29,30} The third is a newer hybrid meta-GGA DFT method, M06-L, developed by Truhlar’s group,³¹ which is constructed using three strategies: constraint satisfaction, modeling the exchange-correlation hole, and empirical fits. In comparing the first two DFT methods Reiher and collaborators found that B3LYP always overestimates the energy of high-spin states and BP86 overestimates the energies of low-spin states for a series of the Fe(II)-S complexes.³² King and collaborators³³ found that the M06-L method predicts an intermediate energy difference, anticipated to be closer to experiment. Since various spin state structures were involved in this paper, we therefore adopt the energy order predicted by the M06-L method, but report the BP86 and B3LYP results in the Supporting Information.

All computations were performed using 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 $\alpha_d(\text{C}) = 0.75$ and $\alpha_d(\text{O}) = 0.85$ to the standard Huzinaga–Dunning contracted DZ sets^{34,35} and are designated (9s5p1d/4s2p1d). For hydrogen, a set of p polarization functions $\alpha_p(\text{H}) = 0.75$ is added to the Huzinaga–Dunning DZ set. The loosely contracted DZP basis set for iron is the Wachters primitive set³⁶ augmented by two sets of p functions and a set of d functions, contracted following Hood, Pitzer, and Schaefer,³⁷ designated (14s11p6d/10s8p3d).

All optimizations were carried out using the Gaussian 09 program³⁸ with the fine grid option for evaluating integrals numerically. Unless otherwise indicated, the optimized structures are genuine minima with no imaginary vibrational frequencies. The vibrational frequencies and infrared intensities were determined analytically. Since the BP86 method has been shown to predict vibrational frequencies closer to experimental values without using any scaling factors, we discuss only the BP86 $\nu(\text{CO})$ frequencies in the text. The results by the other methods are reported in the Supporting Information.

In the present paper each benzothiophene complex $(\text{C}_8\text{H}_6\text{S})\text{Fe}_2(\text{CO})_n$ is designated as **BTha-b** where *a* is the number of CO groups, and *b* orders the structures according to their M06-L relative energies. Thus the lowest energy $(\text{C}_8\text{H}_6\text{S})\text{Fe}_2(\text{CO})_6$ structure is designated **BTh6-1**. Similarly each thienothiophene complex $(\text{C}_6\text{H}_4\text{S}_2)\text{Fe}_2(\text{CO})_n$ is designated as **ThTha-b**, so that the lowest energy structure of $(\text{C}_6\text{H}_4\text{S}_2)\text{Fe}_2(\text{CO})_6$ is designated **ThTh6-1**.

3. Results and Discussion

3.1 Benzothiophene (Thianaphthene) complexes $(\text{C}_8\text{H}_6\text{S})\text{Fe}_2(\text{CO})_n$ ($n = 6,5$)

Only one low energy structure **BTh6-1** was found for the benzothiophene (thianaphthene) diiron hexacarbonyl $(\text{C}_8\text{H}_6\text{S})\text{Fe}_2(\text{CO})_6$ (Figure 5 and Table 1). Other possible $(\text{C}_8\text{H}_6\text{S})\text{Fe}_2(\text{CO})_6$ structures were also studied, but their energies were so high (more than 27 kcal/mol above **BTh6-1**) that these structures are not likely to be chemically significant and thus not discussed in this paper.

The unique $(\text{C}_8\text{H}_6\text{S})\text{Fe}_2(\text{CO})_6$ structure **BTh6-1** corresponds to the experimental structure as indicated by X-ray diffraction of its triphenylphosphine complex $(\text{C}_8\text{H}_6\text{S})\text{Fe}_2(\text{CO})_5(\text{PPh}_3)$.¹⁹ Thus, the predicted Fe–Fe distance of 2.536 Å for **BTh6-1** is close to the experimental Fe–Fe distance of 2.550(2) Å in $(\text{C}_8\text{H}_6\text{S})\text{Fe}_2(\text{CO})_5(\text{PPh}_3)$. The predicted Fe–S distances of 2.335 and 2.322 Å in **BTh6-1** are somewhat longer than the experimental Fe–S distances of 2.297(2) and 2.254(2) Å in $(\text{C}_8\text{H}_6\text{S})\text{Fe}_2(\text{CO})_5(\text{PPh}_3)$. This may be an effect of substituting one of the CO groups in **BTh6-1** with the weaker back-bonding triphenylphosphine ligand.

In **BTh6-1** as well as the experimental $(C_8H_6S)Fe_2(CO)_5(PPh_3)$ structure, an iron atom has inserted into a C–S bond of the thiophene ring to convert the benzothiophene ligand into a thiaferranaphthalene ligand. The sulfur atom in **BTh6-1** is a three-electron donor to the pair of iron atoms forming an S→Fe dative bond (2.322 Å) to donate two electrons to one iron atom and a regular covalent S–Fe bond (2.335 Å) to donate a single electron to the other iron atom. The latter iron atom also accepts a pair of electrons from the C=C bond in the original thiophene ring, as indicated by two short Fe–C distances. The six terminal CO groups in **BTh6-1** are evenly distributed between the two iron atoms leading to two $Fe(CO)_3$ moieties. The predicted Fe–Fe distance of 2.536 Å in **BTh6-1** suggests a formal single bond, thereby giving each iron atom the favored 18-electron configuration. The predicted medium to strong $\nu(CO)$ frequencies for **BTh6-1** of 1978, 1987, 1991, 2021, and 2049 cm^{-1} are in reasonable agreement with the experimental frequencies in hexane solution¹⁹ for $(C_8H_6S)Fe_2(CO)_6$, namely 1961, 1994, 2006, 2044, and 2077 cm^{-1} .

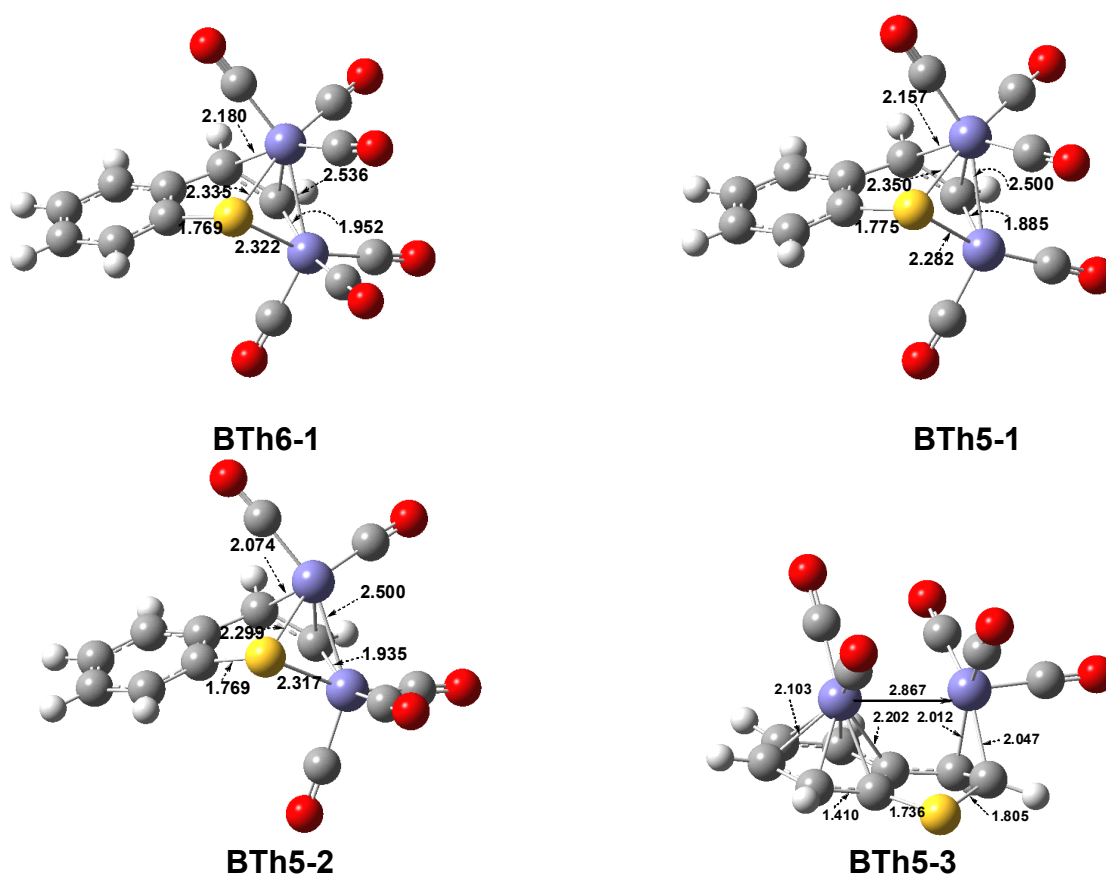


Figure 5. The lowest energy $(C_8H_6S)Fe_2(CO)_n$ ($n = 6, 5$) structures indicating distances predicted by the M06-L method.

Table 1. Total energies (E, in hartree), relative energies (ΔE , in kcal/mol), and Fe–Fe and S–Fe distances (in Å) predicted by the M06-L method for the $(C_8H_6S)Fe_2(CO)_6$ and $(C_8H_6S)Fe_2(CO)_5$ structures.

	BTh6-1 ($C_1, ^1A$)	BTh5-1 ($C_1, ^1A$)	BTh5-2 ($C_1, ^1A$)	BTh5-3 ($C_1, ^1A$)
–E	3914.241814	3800.858136	3800.846878	3800.846562
ΔE	—	0.0	7.1	7.3
Fe–Fe	2.536	2.500	2.500	2.867
Fe–S	2.322, 2.335	2.282, 2.350	2.317, 2.299	3.262, 3.498

For the diiron pentacarbonyl $(C_8H_6S)Fe_2(CO)_5$ three low-lying singlet structures, namely, **BTh5-1**, **BTh5-2**, and **BTh5-3**, were found (Figure 5 and Table 1). Structures **BTh5-1** and **BTh5-2** are thiaferranaphthalene structures derived from **BTh6-1** by loss of a CO group. Structure **BTh5-1**, as well as **BTh5-2**, lying 7.1 kcal/mol in energy above **BTh5-1**, both have an $Fe(CO)_3$ and an $Fe(CO)_2$ moiety and differ only in the distribution of the CO groups. The Fe–Fe distances of ~ 2.50 Å in both pentacarbonyls **BTh5-1** and **BTh5-2** are only ~ 0.04 Å shorter than that in the hexacarbonyl **BTh6-1**, thereby suggesting formal single bonds in the pentacarbonyls as well as the hexacarbonyls. Thus in **BTh5-1** and **BTh5-2** only the $Fe(CO)_3$ iron atoms have the favored 18-electron configuration whereas the $Fe(CO)_2$ iron atoms have only a 16-electron configuration.

The $(C_8H_6S)Fe_2(CO)_5$ structure **BTh5-3**, lying 7.3 kcal/mol in energy above **BTh5-1**, differs from **BTh5-1** and **BTh5-2** by having an intact benzothiophene (thianaphthene) $\eta^6, \eta^2-C_8H_6S$ ligand with no cleavage of the C–S bonds by the iron atoms (Figure 5 and Table 1). The six-membered C_6 ring of the benzothiophene ligand is bonded to an $Fe(CO)_2$ moiety whereas the C=C double bond unique to the five-membered C_4S ring is bonded to an $Fe(CO)_3$ moiety. A long $Fe \cdots S$ distance of ~ 3.3 Å clearly indicates the lack of a direct iron-sulfur bond. The $Fe \rightarrow Fe$ distance of 2.867 Å in **BTh5-3** is ~ 0.3 Å longer than the formal Fe–Fe single bonds in **BTh6-1**, **BTh5-1**, and **BTh5-2** but can be interpreted as a dative bond from the $Fe(CO)_2$ moiety to the $Fe(CO)_3$ fragment. This interpretation of the $Fe \rightarrow Fe$ bond as a dative bond in **BTh5-3** gives each iron atom the favored 18-electron configuration.

3.2 Thienothiophene complexes $(C_6H_4S_2)Fe_2(CO)_n$ ($n = 6, 5$)

The binuclear iron carbonyl complexes $(C_6H_4S_2)Fe_2(CO)_n$ ($n = 6, 5$) derived from both the *anti* and *syn* thienothiophene isomers (Figure 4) were optimized. For each thienothiophene isomer several isomeric $(C_6H_4S_2)Fe_2(CO)_n$ ($n = 6, 5$) structures were

obtained. However, in all cases one isomer was significantly lower in energy by at least 11 kcal/mol relative to the other isomers. Furthermore, these lowest energy **ThTh6-1** and **ThTh5-1** structures (Figure 6) with the two sulfur atoms in the *anti* and *syn* positions (Figure 4) were found to be nearly degenerate in energy with the *anti* structures having slightly lower energies. Thus the energy difference between the *anti* and *syn* isomers of **ThTh6-1** is 0.5, 1.0, and 0.2 kcal/mol and that for **ThTh5-1** is 0.5, 0.5, and 0.3 kcal/mol predicted by the M06-L, BP86, and B3LYP methods, respectively. This indicates that the relative position of the two sulfur atoms in the $C_6H_4S_2$ ligand has little effect on the energies of the corresponding $(C_6H_4S_2)Fe_2(CO)_n$ ($n = 6, 5$) complexes. For this reason only the very slightly lower energy *anti* isomers are discussed in the text. The corresponding information on the *syn* isomers is presented in the Supporting Information.

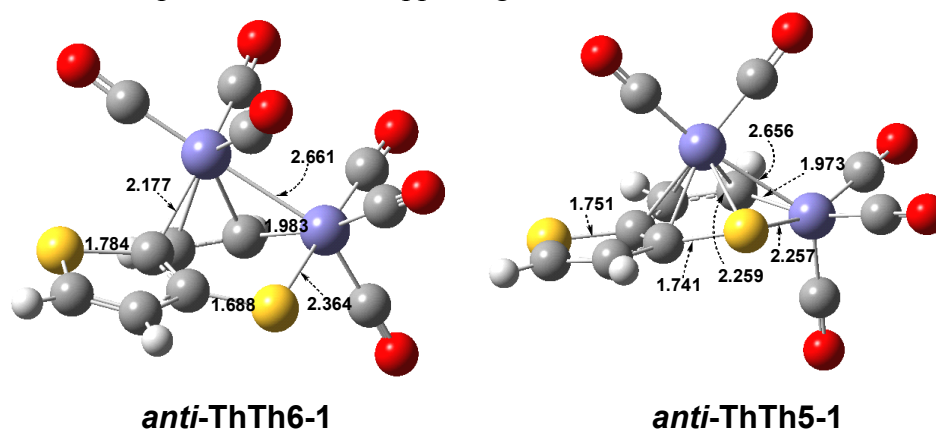


Figure 6. The lowest-lying *anti*-($C_6H_4S_2$) $Fe_2(CO)_n$ ($n = 6, 5$) structures.

The lowest energy *anti*-($C_6H_4S_2$) $Fe_2(CO)_6$ structure **ThTh6-1** has an iron atom inserted into a C-S bond to give a thiaferrabenzene ring (Figure 6) similar to the $(C_8H_6S)Fe_2(CO)_6$ structure **BTh6-1** (Figure 5). However, the sulfur atom from the cleaved C-S bond is not within bonding distance of the other iron atom, in contrast to **BTh6-1**. Instead this other iron atom, i. e., the exocyclic iron atom, is bonded to three adjacent carbon atoms of the thienothiophene ligand, including one of the carbon atoms common to both C_4S rings. This bonding scheme is depicted in Figure 7. Note that in **ThTh6-1** the C=S distance to the non-bridging sulfur atom of ~ 1.69 Å is significantly shorter than the other C-S distances of 1.74 to 1.77 Å suggesting a formal double bond in the former case. In the lowest energy diiron pentacarbonyl *anti*-($C_6H_4S_2$) $Fe_2(CO)_5$ structure **ThTh5-1**, the C=S double bond in **ThTh6-1** displaces a CO group so that its sulfur atom bridges the Fe_2 unit in **ThTh5-1** (Figure 7). The Fe-Fe distances of ~ 2.66 Å in both **ThTh6-1** and **ThTh5-1** can be interpreted as the formal single bonds required to give each iron atom the favored 18-electron configuration.

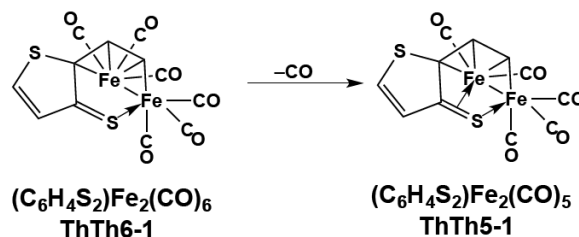


Figure 7. The bonding schemes in the $(\text{C}_6\text{H}_4\text{S}_2)\text{Fe}_2(\text{CO})_n$ structures **ThTh6-1** and **ThTh5-1**.

4. Summary

The lowest energy structure for the benzothiophene diiron hexacarbonyl $(\text{C}_8\text{H}_6\text{S})\text{Fe}_2(\text{CO})_6$ by a substantial margin is the experimentally observed thiaferranaphthalene structure in which an iron atom has inserted into a C-S bond of the thiophene ring of the ligand. In this structure the benzene ring of the original benzothiophene ligand does not participate in the metal-ligand bonding. The lowest energy structures for the benzothiophene diiron pentacarbonyl $(\text{C}_8\text{H}_6\text{S})\text{Fe}_2(\text{CO})_5$ are simply derived from this structure by loss of a terminal CO group. However, the original benzothiophene ligand remains intact in a higher energy $(\text{C}_8\text{H}_6\text{S})\text{Fe}_2(\text{CO})_5$ structure, at ~ 7 kcal/mol above the global minimum. In this last structure the benzothiophene is an octahapto ligand to the Fe_2 unit with the benzene ring bonded to an $\text{Fe}(\text{CO})_2$ moiety as a hexahapto ligand and the C=C bond of the thiophene ring bonded to an $\text{Fe}(\text{CO})_3$ moiety as a dihapto ligand. An $\text{Fe} \rightarrow \text{Fe}$ dative bond from the $\text{Fe}(\text{CO})_2$ moiety to the $\text{Fe}(\text{CO})_3$ moiety in this structure gives both iron atoms the favored 18-electron configuration.

The nature of the binuclear iron carbonyl complexes from thienothiophene is very different from those of benzothiophene since both rings of the bicyclic heterocycle are involved in the interaction with the iron atoms. Thus in the lowest energy structure for the thienothiophene diiron hexacarbonyl $(\text{C}_6\text{H}_4\text{S}_2)\text{Fe}_2(\text{CO})_6$, like that of $(\text{C}_8\text{H}_6\text{S})\text{Fe}_2(\text{CO})_6$, one of the iron atoms has inserted into a C-S bond of a thiophene ring to give a thiaferrabenzene ring. However, the sulfur atom in this expanded ring is not within bonding distance of the exocyclic iron atom. Instead that iron atom is bonded to three carbon atoms of the thiaferrabenzothiophene ligand including a carbon atom shared by the two rings (Figure 7). This $(\text{C}_6\text{H}_4\text{S}_2)\text{Fe}_2(\text{CO})_6$ structure has an uncomplexed C=S double bond in the thiaferrabenzene ring. In the conversion of the hexacarbonyl $(\text{C}_6\text{H}_4\text{S}_2)\text{Fe}_2(\text{CO})_6$ derived from thienothiophene to the corresponding pentacarbonyl, this C=S double bond displaces one of the CO groups bonded to the exocyclic iron atom. The structures of these binuclear iron carbonyl complexes are completely analogous for both the *anti* and *syn* stereoisomers of thienothiophene.

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Supporting Information. Tables S1 to S4: Harmonic vibrational frequencies and infrared intensities for the $(C_8H_6S)Fe_2(CO)_n$ ($n = 6, 5$) structures **BTh6-1**, **BTh5-1**, **BTh5-2**, and **BTh5-3**; Tables S5 to S8: Harmonic vibrational frequencies and infrared intensities for the $(C_6H_4S_2)Fe_2(CO)_n$ ($n = 6, 5$) structures *anti-ThTh6-1*, *anti-ThTh5-1*, *anti-ThTh5-2* and *anti-ThTh5-3*; Tables S9 to S12: Harmonic vibrational frequencies and infrared intensities for the $(C_6H_4S_2)Fe_2(CO)_n$ ($n = 6, 5$) structures *syn-ThTh6-1*, *syn-ThTh5-1*, *syn-ThTh5-2* and *syn-ThTh5-3*; Tables S13 to S16: Cartesian coordinates and total energies for the $(C_8H_6S)Fe_2(CO)_n$ ($n = 6, 5$) structures **Bth6-1**, **Bth5-1**, **Bth5-2**, and **Bth5-3**; Tables S17 to S20: Cartesian coordinates and total energies for the $(C_6H_4S_2)Fe_2(CO)_n$ ($n = 6, 5$) structures *anti-ThTh6-1*, *anti-ThTh5-1*, *anti-ThTh5-2* and *anti-ThTh5-3*; Tables S21 to S24: Cartesian coordinates and total energies for the *syn* $(C_6H_4S_2)Fe_2(CO)_n$ ($n = 6, 5$) structures *syn-ThTh6-1*, *syn-ThTh5-1*, *syn-ThTh5-2* and *syn-ThTh5-3*; Table S25: Total energies, relative energies, and Fe–Fe and S–Fe distances for the structures of $(C_8H_6S)Fe_2(CO)_6$ and $(C_8H_6S)Fe_2(CO)_5$ **BTh6-1**, **BTh5-1**, **BTh5-2**, and **BTh5-3**; Table S26: Total energies, relative energies, and Fe–Fe and S–Fe distances for the $(C_6H_4S_2)Fe_2(CO)_6$ structures **ThTh6-1** and *syn-ThTh6-1*; Table S27: Total energies, relative energies, and Fe–Fe and S–Fe distances for the $(C_6H_4S_2)Fe_2(CO)_5$ structures **ThTh5-n** ($n = 1, 2, 3$) and the *syn*- $(C_6H_4S_2)Fe_2(CO)_5$ structures *syn-ThTh5-n* ($n = 1$ to 3); Table S28: Harmonic $\nu(CO)$ vibrational frequencies predicted for the $(C_8H_6S)Fe_2(CO)_n$ and $(C_6H_4S_2)Fe_2(CO)_n$ ($n = 6, 5$) structures; Complete Gaussian reference; Figure S1: The $(C_8H_6S)Fe_2(CO)_6$ and $(C_8H_6S)Fe_2(CO)_5$ structures **BTh6-1**, **BTh5-1**, **BTh5-2**, and **BTh5-3**; Figure S2: The lowest-lying $(C_6H_4S_2)Fe_2(CO)_6$ and $(C_6H_4S_2)Fe_2(CO)_5$ structures *anti-ThTh6-1* and *anti-ThTh5-1*; Figure S3: The $(C_6H_4S_2)Fe_2(CO)_5$ structures *anti-ThTh5-2* and *anti-ThTh5-3*; Figure S4: The lowest-lying *syn*- $(C_6H_4S_2)Fe_2(CO)_6$ and *syn*- $(C_6H_4S_2)Fe_2(CO)_5$ structures *syn-ThTh6-1* and *syn-ThTh5-1*; Figure S5: The *syn*- $(C_6H_4S_2)Fe_2(CO)_5$ structures *syn-ThTh5-2* and *syn-ThTh5-3*.

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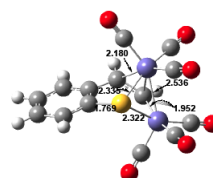
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Table of Contents Synopsis

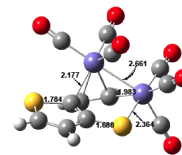
Theoretical Studies on the Desulfurization of Benzothiophene (Thianaphthene) and Thienothiophene (Thiophthene) by Carbon-Sulfur Bond Cleavage: Binuclear Iron Carbonyl Intermediates

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The lowest energy $(C_8H_6S)Fe_2(CO)_n$ and $(C_6H_4S_2)Fe_2(CO)_n$ structures ($n = 6, 5$) derived from benzothiophene and thienothiophene, respectively, have an iron atom inserted into C-S bond of the ligand thiophene ring.



$C_8H_6SFe_2(CO)_6$



$C_6H_4S_2Fe_2(CO)_6$