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Synthetic and Structural Investigations on Some New 1,2,4,5-$(CH_2)_4C_6H_2$ Moiety-Containing Butterfly Fe/S Cluster Complexes from Reactions of Tetrathiol 1,2,4,5-$(HSCH_2)_4C_6H_2$ with $Fe_3(CO)_{12}$ or with $Fe_3(CO)_{12}$ in the Presence of Et_3N

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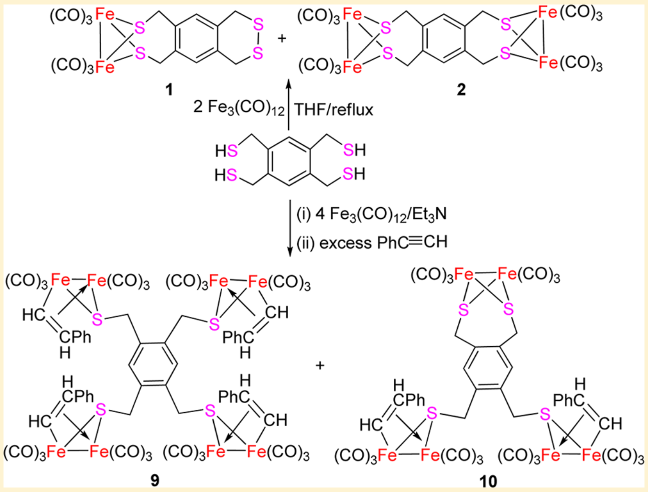
S *Supporting Information*



ABSTRACT: The 1,2,4,5-$(CH_2)_4C_6H_2$ moiety-containing butterfly Fe/S complexes $[1,2\text{-}(CH_2S_2CH_2)\text{-}4,5\text{-}(\mu\text{-}SCH_2)_2C_6H_2][Fe_2(CO)_6]$ (**1**), $[1,2,4,5\text{-}(\mu\text{-}SCH_2)_4C_6H_2][Fe_2(CO)_6]_2$ (**2**), and $[(1,2\text{-}Me_2)\text{-}4,5\text{-}(\mu\text{-}SCH_2)_2C_6H_2][Fe_2(CO)_6]$ (**3**) have been prepared by the reaction of tetrathiol 1,2,4,5-$(HSCH_2)_4C_6H_2$ with $Fe_3(CO)_{12}$ under different conditions. Treatment of complex **1** with PPh_3 or PMe_3 in the presence of Me_3NO or with the in situ generated N-heterocyclic carbene I_{Mes} (I_{Mes} = 1,3-bis(mesityl)imidazol-2-ylidene) afforded the corresponding monosubstituted single-butterfly complexes $[1,2\text{-}(CH_2S_2CH_2)\text{-}4,5\text{-}(\mu\text{-}SCH_2)_2C_6H_2][Fe_2(CO)_5L]$ (**4**, L = PPh_3; **5**, L = PMe_3; **6**, L = I_{Mes}). However, in contrast to the above-mentioned reaction of tetrathiol 1,2,4,5-$(HSCH_2)_4C_6H_2$ with $Fe_3(CO)_{12}$, the reactions of 1,2,4,5-$(HSCH_2)_4C_6H_2$ with $Fe_3(CO)_{12}$ in the presence of Et_3N, followed by treatment with PhCOCl or PhC(Cl)=NPh, resulted in formation of the quadruple- and triple-butterfly complexes $[(\mu\text{-}PhC{=}O)Fe_2(CO)_6]_4[1,2,4,5\text{-}(\mu\text{-}SCH_2)_4C_6H_2]$ (**7**) and $[(\mu\text{-}PhC{=}NPh)Fe_2(CO)_6]_2[Fe_2(CO)_6][1,2,4,5\text{-}(\mu\text{-}SCH_2)_4C_6H_2]$ (**8**), whereas the same tetrathiol reaction system reacted with PhC≡CH to give quadruple- and triple-butterfly complexes $[(\mu\text{-}\sigma,\pi\text{-}PhCH{=}CH)Fe_2(CO)_6]_4[1,2,4,5\text{-}(\mu\text{-}SCH_2)_4C_6H_2]$ (**9**) and $[(\mu\text{-}\sigma,\pi\text{-}PhCH{=}CH)Fe_2(CO)_6]_2[Fe_2(CO)_6][1,2,4,5\text{-}(\mu\text{-}SCH_2)_4C_6H_2]$ (**10**). More interestingly, the dithioformato ligand-containing quadruple-butterfly complex $[(\mu\text{-}S{=}CSCH_2Ph)Fe_2(CO)_6]_4[1,2,4,5\text{-}(\mu\text{-}SCH_2)_4C_6H_2]$ (**11**) could be prepared by the reaction of the tetrathiol system with CS_2, followed by treatment with $PhCH_2Br$, but the same tetrathiol/CS_2 system reacted with $CpFe(CO)_2I$ to afford the triple-butterfly complex $[(\mu\text{-}S{=}CSFe(CO)_2Cp)Fe_2(CO)_6]_2[Fe_2(CO)_6][1,2,4,5\text{-}(\mu\text{-}SCH_2)_4C_6H_2]$ (**12**). The possible pathways for production of complexes **1**−**3** and **7**−**12** are proposed, and the suggested intermediate $[1,2\text{-}(HSCH_2)_2\text{-}4,5\text{-}(\mu\text{-}SCH_2)_2C_6H_2][Fe_2(CO)_6]$ (**M$_6$**) for formation of complex **1** has been successfully isolated under anaerobic conditions. The structures of complexes **1**, **3**, **4**, **8**, **9**, and **11** have been confirmed by X-ray crystallography.

INTRODUCTION

Butterfly Fe/S cluster complexes have attracted growing interest during recent years, presumably owing to their rich chemistry[1−5] and particularly their close relationships with the active site of [FeFe]-hydrogenases.[6−10] Since 1928, when Reihlen prepared the first dinuclear butterfly Fe/S cluster complex $(\mu\text{-}EtS)_2Fe_2(CO)_6$,[11] a great number of butterfly Fe/S cluster complexes have been prepared by various synthetic methods, such as the old method involving reactions of various thiols with iron(0) carbonyls[12−15] and the new method involving reactions of various thiols with $Fe_3(CO)_{12}$ and Et_3N, followed by treatment with electrophiles.[16−21] To develop the organometallic synthetic methodology and to prepare the new type of butterfly Fe/S cluster complexes, we recently launched a comparative study of the direct reaction of tetrathiol 1,2,4,5-$(HSCH_2)_4C_6H_2$ with $Fe_3(CO)_{12}$ and the sequential reactions of the same tetrathiol with $Fe_3(CO)_{12}$ in the presence of Et_3N, followed by treatment with electrophiles. Interestingly, through such a study, we have expanded the applied scope of the aforementioned two synthetic methods and thus prepared some new types of 1,2,4,5-$(SCH_2)_4C_6H_2$ moiety-containing butterfly Fe/S cluster complexes. Herein, we report these interesting results from this study.

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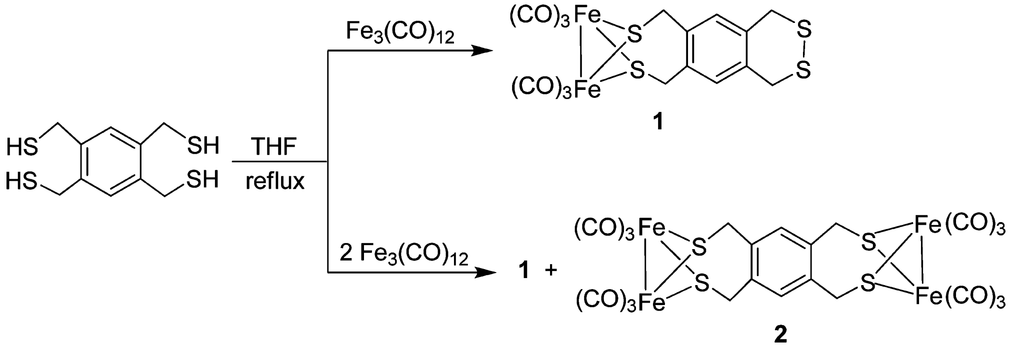
Scheme 1

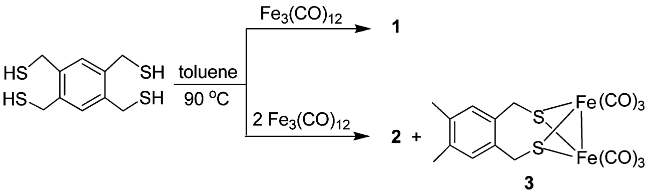


RESULTS AND DISCUSSION

Reaction of Tetrathiol 1,2,4,5-$(HSCH_2)_4C_6H_2$ with $Fe_3(CO)_{12}$. Synthesis and Characterization of Single- and Double-Butterfly Complexes [1,2-$(CH_2S_2CH_2)$-4,5-(μ-$SCH_2)_2C_6H_2$][$Fe_2(CO)_6$] (1), [1,2,4,5-(μ-$SCH_2)_4C_6H_2$][$Fe_2(CO)_6$]$_2$ (2), and [(1,2-Me_2)-4,5-(μ-$SCH_2)_2C_6H_2$]-[$Fe_2(CO)_6$] (3). Although the direct reactions of mono-, di-, and trithiols with $Fe_3(CO)_{12}$ are known to give the corresponding butterfly Fe/S cluster complexes,[12−15,22,23] no report has so far appeared in the literature regarding the direct reaction of tetrathiol with $Fe_3(CO)_{12}$. However, we found that simple treatment of tetrathiol 1,2,4,5-$(HSCH_2)_4C_6H_2$ with $Fe_3(CO)_{12}$ in a 1:1 molar ratio in refluxing THF, after the open-air TLC separation, gave rise to the S−S bond-containing single-butterfly Fe/S cluster complex **1** in 20% yield, whereas the same tetrathiol reacted with $Fe_3(CO)_{12}$ in a 1:2 molar ratio under the same conditions and through the same separation procedure to give not only the single-butterfly Fe/S complex **1** in 8% yield but also a double-butterfly Fe/S complex **2** in 18% yield, respectively (Scheme 1).

Similarly, it was further found that the reaction of 1,2,4,5-$(HSCH_2)_4C_6H_2$ with $Fe_3(CO)_{12}$ in a 1:1 molar ratio in toluene at 90 °C also afforded single-butterfly complex **1** in a nearly identical yield (19%), whereas the tetrathiol reacted with $Fe_3(CO)_{12}$ in a 1:2 molar ratio under the same conditions to give the double-butterfly complex **2** in 22% yield and another type of single-butterfly Fe/S complex **3** in 5% yield (Scheme 2).

Scheme 2



It follows that the types and yields of the products obtained from such direct reactions can be considerably influenced by the molar ratio of the starting materials and the reaction temperature in different solvents.

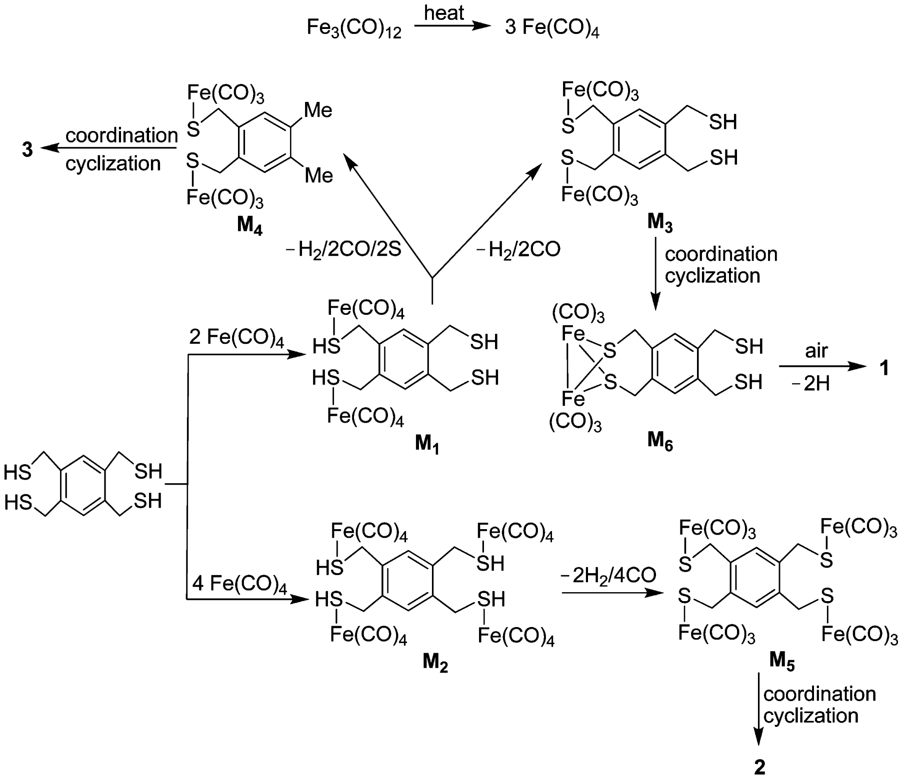
A possible pathway for formation of complexes **1**−**3** is shown in Scheme 3. That is, in the first step, the unsaturated 16e species $Fe(CO)_4$ is generated by thermal decomposition of $Fe_3(CO)_{12}$. Addition of two or four $Fe(CO)_4$ species to the tetrathiol then affords the coordinatively saturated diiron intermediate $\mathbf{M_1}$ and tetrairon intermediate $\mathbf{M_2}$. In the third step, the coordinatively unsaturated diiron intermediates $\mathbf{M_3}$/$\mathbf{M_4}$ and tetrairon intermediate $\mathbf{M_5}$ are produced by loss of the corresponding H atoms, S atoms, and CO ligands from intermediates $\mathbf{M_1}$ and $\mathbf{M_2}$. The intramolecular coordination/cyclization of $\mathbf{M_3}$, $\mathbf{M_4}$, and $\mathbf{M_5}$ affords dithiol intermediate $\mathbf{M_6}$ and products **3** and **2**, and the oxidation of the dithiol intermediate $\mathbf{M_6}$ by air results in formation of product **1**.

It is worth noting that, although some details regarding this parthway need to be further studied, it appears to be plausible. This is because (i) the thermal reactions of $Fe_3(CO)_{12}$ with thiols to give the butterfly $(\mu\text{-}S)_2Fe_2(CO)_6$ cluster-unit-containing complexes accompanied by evolution of H_2 and CO gases are precedented,[13,24] (ii) the suggested dithiol intermediate $\mathbf{M_6}$ could be isolated in an anaerobic glovebox by TLC and was characterized by elemental analysis and spectroscopy, and (iii) when a toluene solution of the isolated $\mathbf{M_6}$ was heated at about 90 °C for 10 min in air, **1** was obtained in 71% yield.

Complexes **1**−**3** are air-stable red solids, which have been characterized by elemental analysis and spectroscopy. For example, the IR spectra of **1**−**3** showed three absorption bands in the range of 2073−1985 cm^{-1} for their terminal carbonyls. The ^{1}H NMR spectra of **1**−**3** displayed a singlet at ca. 6.85 ppm for the two protons bound to their benzene rings, whereas **1** and **3** exhibited two doublets at ca. 3.09 and 3.80 ppm for the two methylene groups attached to their single-butterfly Fe/S cluster cores and **2** showed two multiplets in the range of 2.91−3.82 ppm for the four methylene groups attached to the double-butterfly cluster core, indicative of the different influences of the two single-butterfly cluster moieties in **2**. In addition, the ^{13}C NMR spectra of **1**−**3** showed one or two singlets in the range of 207−209 ppm for their terminal carbonyls.

Fortunately, the structures of **1** and **3** were confirmed by X-ray crystallography. The molecular structures of **1** and **3** are shown in Figures 1 and 2, whereas their selected bond lengths and angles are presented in Table 1. As can be seen in Figures 1 and 2, complexes **1** and **3** are structurally very similar; both of them contain a butterfly cluster unit $(\mu\text{-}S)_2Fe_2(CO)_6$ that is connected via its two sulfur atoms (namely, S1 and S2) to the two neighboring α-carbon atoms (namely, C7/C16 for **1** and C7/C14 for **3**) of the corresponding benzene ring. However, they do have some differences. That is, while the two neighboring α-carbon atoms of the benzene ring in **3** (namely, C10/C11) are connected to two methyl groups, the corresponding two α-carbon atoms in **1** (namely, C11/C12) are linked to S3 and S4 atoms to construct a chair-shaped C10C11S4S3C12C13 six-membered ring. It is noteworthy that the single bond length S3−S4 in complex **1** is 2.0294 Å, which

Scheme 3



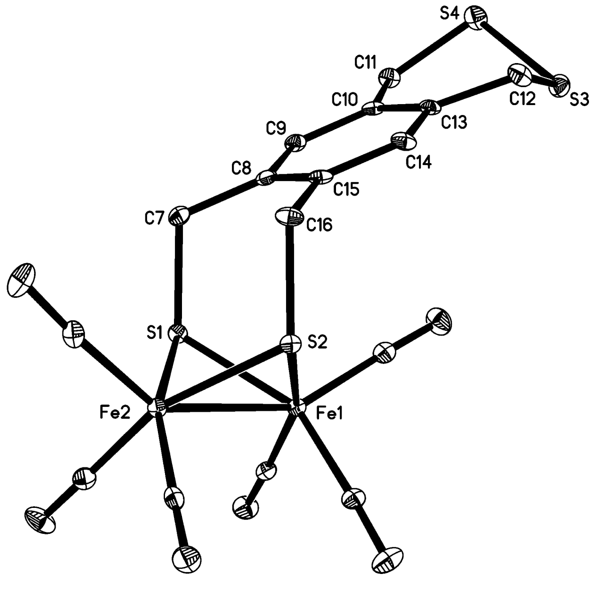


Figure 1. Molecular structure of **1** with 30% probability level ellipsoids.

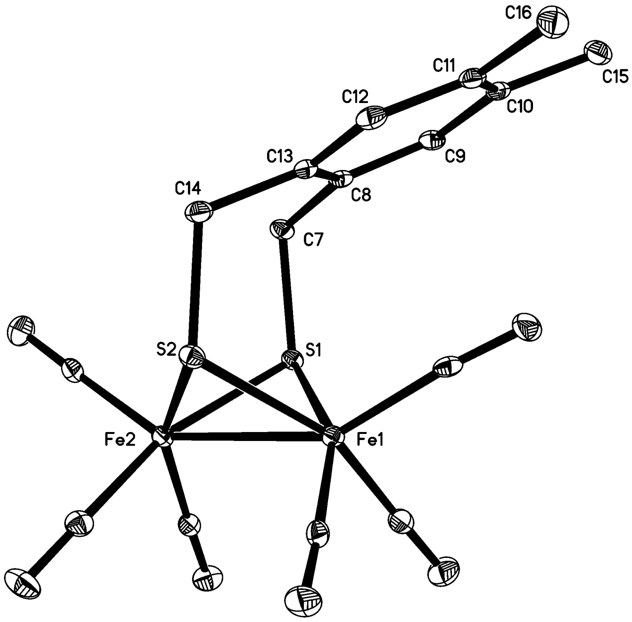


Figure 2. Molecular structure of **3** with 30% probability level ellipsoids.

is almost the same as the S−S bond length (2.01 Å) in tetrahedral cluster ($(\mu\text{-}S_2)Fe_2(CO)_6$).[25]

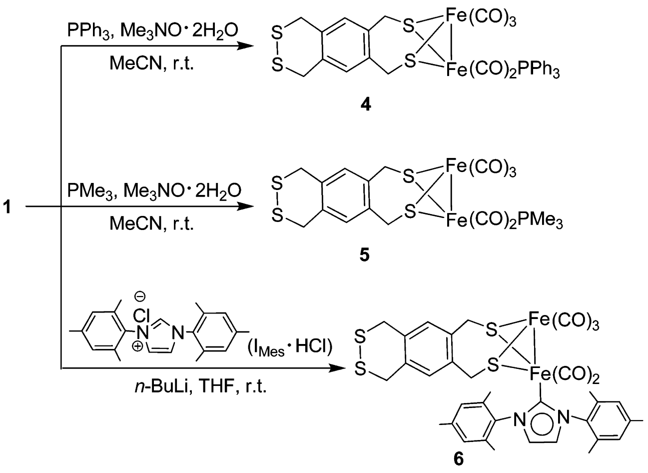
Reactions of Single-Butterfly Complex 1 with PPh_3, PMe_3, and I_{Mes}. Synthesis and Characterization of [1,2-($CH_2S_2CH_2$)-4,5-(μ-SCH_2)$_2C_6H_2$][$Fe_2(CO)_5L$] (4, L = PPh_3; 5, L = PMe_3; 6, L = I_{Mes}). The substituted derivatives of single-butterfly complex **1** were found to be prepared by CO substitution reactions. For instance, while **1** reacted with PPh_3 or PMe_3 in the presence of decarbonylating agent Me_3NO to give the PPh_3- and PMe_3-monosubstituted complexes **4** and **5** in ca. 29% yields, treatment of **1** with the N-heterocyclic carbene I_{Mes} (I_{Mes} = 1,3-bis(mesityl)imdazol-2-ylidene) generated in situ from imidazolium salt I_{Mes}·HCl and *n*-BuLi in THF at room temperature gave the I_{Mes}-monosubstituted complex **6** in 22% yield (Scheme 4).

Complexes **4**−**6** are also air-stable red solids, which have been characterized by elemental analysis and IR and ^1H (^{13}C) NMR spectroscopy. For example, the IR spectra of **4**−**6** showed three to four absorption bands in the region of 2044−1914 cm^{-1} for their terminal carbonyls. It follows that the $\nu_{C\equiv O}$

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 1 and 3

compound **1**			
Fe(1)−S(2)	2.2461(9)	Fe(1)−S(1)	2.2491(11)
Fe(2)−S(2)	2.2511(11)	Fe(1)−Fe(2)	2.5101(10)
S(3)−S(4)	2.0294(11)	Fe(2)−S(1)	2.2494(8)
S(1)−C(7)	1.842(2)	S(2)−C(16)	1.833(2)
Fe(1)−C(1)	1.805(2)	Fe(2)−C(6)	1.787(3)
C(7)−S(1)−Fe(1)	117.49(8)	C(7)−S(1)−Fe(2)	112.76(8)
S(1)−Fe(2)−S(2)	87.25(3)	S(2)−Fe(2)−Fe(1)	55.98(4)
S(1)−Fe(2)−Fe(1)	56.08(3)	S(2)−Fe(1)−S(1)	87.38(4)
Fe(1)−S(2)−Fe(2)	67.86(3)	Fe(1)−S(1)−Fe(2)	67.83(3)
C(12)−S(3)−S(4)	96.47(9)	C(11)−S(4)−S(3)	99.21(8)
compound **3**			
Fe(1)−C(1)	1.815(2)	Fe(2)−C(6)	1.803(2)
Fe(1)−S(2)	2.2594(18)	Fe(1)−S(1)	2.2686(18)
Fe(2)−S(2)	2.2699(18)	Fe(2)−S(1)	2.2516(13)
Fe(1)−Fe(2)	2.5139(16)	S(2)−C(14)	1.851(2)
S(1)−C(7)	1.852(2)	C(7)−C(8)	1.491(3)
C(7)−S(1)−Fe(1)	115.50(7)	C(14)−S(2)−Fe(1)	114.69(6)
S(1)−Fe(2)−S(2)	87.23(5)	S(2)−Fe(1)−S(1)	87.08(3)
S(2)−Fe(1)−Fe(2)	56.48(6)	S(1)−Fe(1)−Fe(2)	55.89(2)
S(1)−Fe(2)−Fe(1)	56.53(5)	S(2)−Fe(2)−Fe(1)	56.09(4)
Fe(2)−S(1)−Fe(1)	67.58(5)	Fe(1)−S(2)−Fe(2)	67.43(3)

Scheme 4



frequencies of **4**−**6**, relative to those of their parent complex **1**, are shifted toward lower frequencies by 28−76 cm^{-1}, which is consistent with PPh_3, PMe_3, and the NHC ligand I_{Mes} being stronger σ-donors than terminal carbonyls. In the ^1H NMR spectra, complex **4** showed a singlet at 6.62 ppm for the two protons attached to its benzene ring, **5** displayed a doublet at 1.43 ppm for the nine protons of the three methyl groups attached to its P atom, and **6** exhibited a singlet at 7.13 ppm for the two imidazole protons in its I_{Mes} ligand. In the ^{13}C NMR spectra, complex **4** showed two singlets at 208.3 and 212.5 ppm for its terminal carbonyl C atoms, **5** displayed a doublet at 19.7 ppm for the carbon atoms of its three methyl groups attached to the P atom, and **6** exhibited a singlet at 195.6 ppm for its carbene C atom. In addition, the ^{31}P NMR spectra of **4** and **5** displayed a singlet at 64.53 and 26.26 ppm, respectively.

The molecular structure of complex **4** has been unequivocally confirmed by X-ray crystallography. While its ORTEP drawing is depicted in Figure 3, Table 2 presents the selected bond lengths and angles. As shown in Figure 3, the monophosphine ligand PPh_3 is located at the apical position of the square-pyramidal iron atom and trans to its $(1,2\text{-}CH_2S_2CH_2)C_6H_2$ moiety in order to avoid the strong steric repulsion between them. In addition, the S3−S4 bond length (2.0370 Å) in **4** is slightly longer than that in its parent complex **1**, which is very close to those S−S single bond lengths of 2.01 Å in $(\mu\text{-}S)_2Fe_2(CO)_6$[25] and 2.04 Å in S_2Cl_2 and S_8.[26,27] The Fe1−Fe2 bond length (2.5106 Å) and the Fe1−P1 bond length (2.2512 Å) are close to the corresponding bond lengths in similar monophosphine-substituted Fe/S cluster complexes.[28−31]

Reactions of Tetrathiol System $1,2,4,5\text{-}(HSCH_2)_4C_6H_2/Fe_3(CO)_{12}/Et_3N$ with PhCOCl, Ph(Cl)C═NPh, and PhC≡CH. Synthesis and Characterization of Quadruple- and Triple-Butterfly Complexes $[(\mu\text{-}PhC{=}O)Fe_2(CO)_6]_4[1,2,4,5\text{-}(\mu\text{-}SCH_2)_4C_6H_2]$ (7), $[(\mu\text{-}PhC{=}NPh)Fe_2(CO)_6]_2[Fe_2(CO)_6][1,2,4,5\text{-}(\mu\text{-}SCH_2)_4C_6H_2]$ (8), $[(\mu\text{-}\sigma,\pi\text{-}PhCH{=}CH)Fe_2(CO)_6]_4[1,2,4,5\text{-}(\mu\text{-}SCH_2)_4C_6H_2]$ (9), and $[(\mu\text{-}\sigma,\pi\text{-}PhCH{=}CH)Fe_2(CO)_6]_2[Fe_2(CO)_6][1,2,4,5\text{-}(\mu\text{-}SCH_2)_4C_6H_2]$ (10). We previously reported that reaction of tetrathiol $1,2,4,5\text{-}(HSCH_2)_4C_6H_2$ with $Fe_3(CO)_{12}$ and Et_3N in a 1:4:4 molar ratio in THF at room temperature afforded the $[Et_3NH]_4$ salt of tetraanion $\{[(\mu\text{-}CO)Fe_2(CO)_6]_4[1,2,4,5\text{-}(\mu\text{-}SCH_2)_4C_6H_2]\}^{4-}$ (**A**) and the $[Et_3NH]_2$ salt of dianion $\{[(\mu\text{-}CO)Fe_2(CO)_6]_2[Fe_2(CO)_6][1,2,4,5\text{-}(\mu\text{-}SCH_2)_4C_6H_2]\}^{2-}$ (**B**), which were reacted in situ with electrophiles 2-furancarbonyl chloride and Ph_2PCl to give the corresponding furan ring-containing quadruple-butterfly and Ph_2P ligand-containing triple-butterfly complexes (Scheme 5).[21]

To develop this new method for synthesis of the other new types of butterfly Fe/S cluster complexes, we continued to study the in situ reactions of such a tetrathiol system with electrophiles PhCOCl, PhC(Cl)═NPh, and PhC≡CH. Interestingly, it was found that this tetrathiol system could react in situ with PhCOCl under similar conditions to produce quadruple-butterfly complex $[(\mu\text{-}PhC{=}O)Fe_2(CO)_6]_4[1,2,4,5\text{-}(\mu\text{-}SCH_2)_4C_6H_2]$ (**7**) in 22% yield, whereas it reacted with PhC(Cl)═NPh to afford triple-butterfly complex $[(\mu\text{-}PhC{=}NPh)Fe_2(CO)_6]_2[Fe_2(CO)_6][1,2,4,5\text{-}(\mu\text{-}SCH_2)_4C_6H_2]$ (**8**) in

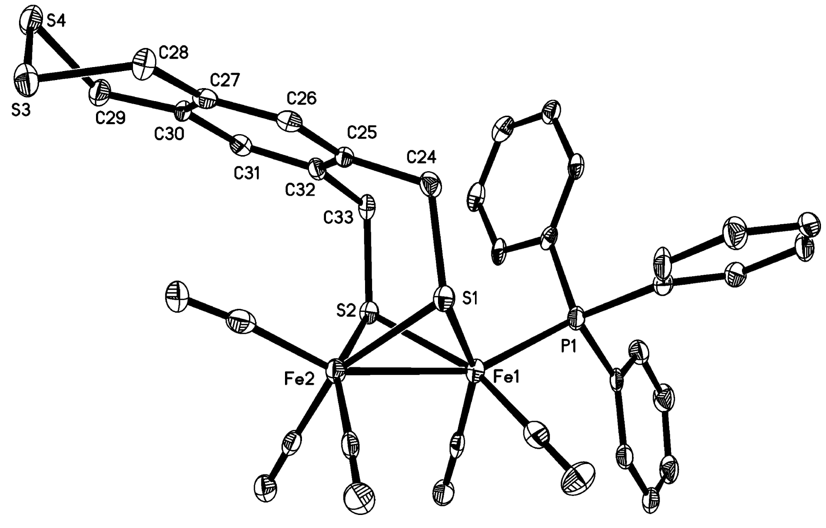
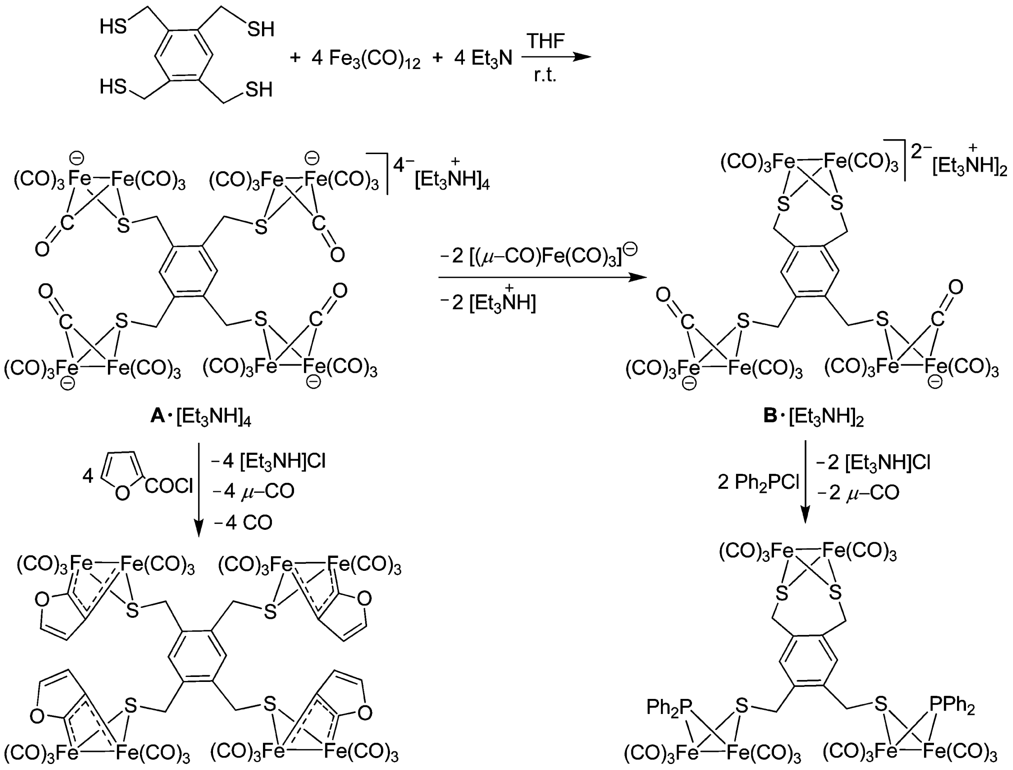


Figure 3. Molecular structure of **4** with 30% probability level ellipsoids.

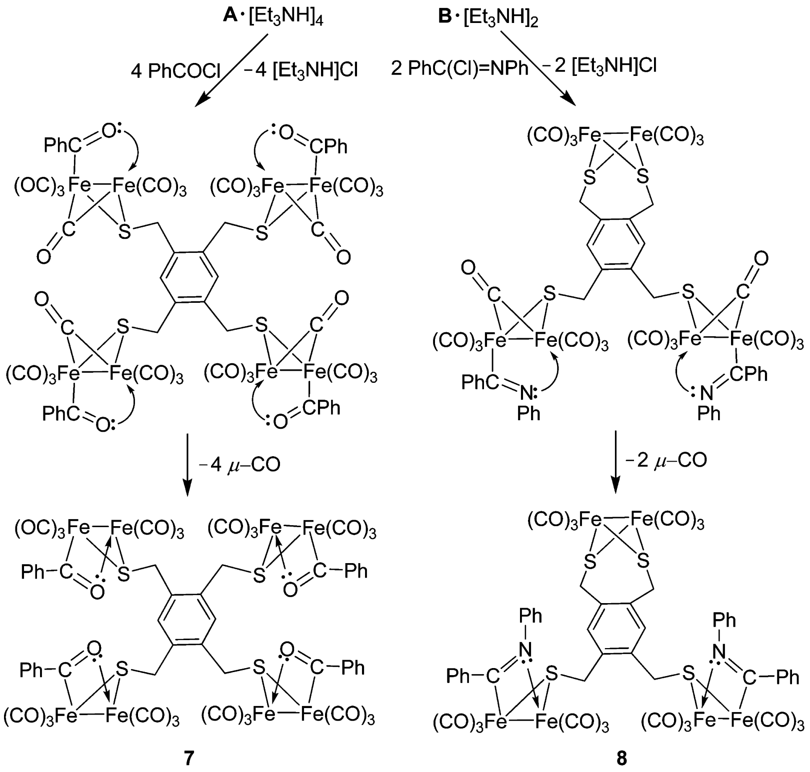
Table 2. Selected Bond Lengths (Å) and Angles (deg) for 4

Fe(1)–S(2)	2.2876(15)	Fe(1)–S(1)	2.2846(14)
Fe(1)–P(1)	2.2512(16)	Fe(1)–Fe(2)	2.5106(14)
Fe(2)–S(2)	2.2906(14)	Fe(2)–S(1)	2.2679(15)
S(1)–C(24)	1.859(4)	S(2)–C(33)	1.845(4)
P(1)–C(6)	1.842(4)	S(3)–S(4)	2.0370(19)
P(1)–Fe(1)–S(1)	110.94(5)	P(1)–Fe(1)–S(2)	104.26(5)
S(1)–Fe(1)–S(2)	86.22(5)	P(1)–Fe(1)–Fe(2)	155.07(5)
S(1)–Fe(1)–Fe(2)	56.22(4)	S(2)–Fe(1)–Fe(2)	56.80(4)
S(1)–Fe(2)–S(2)	86.54(5)	Fe(2)–S(1)–Fe(1)	66.94(5)
Fe(1)–S(2)–Fe(2)	66.51(5)	C(28)–S(3)–S(4)	97.23(14)

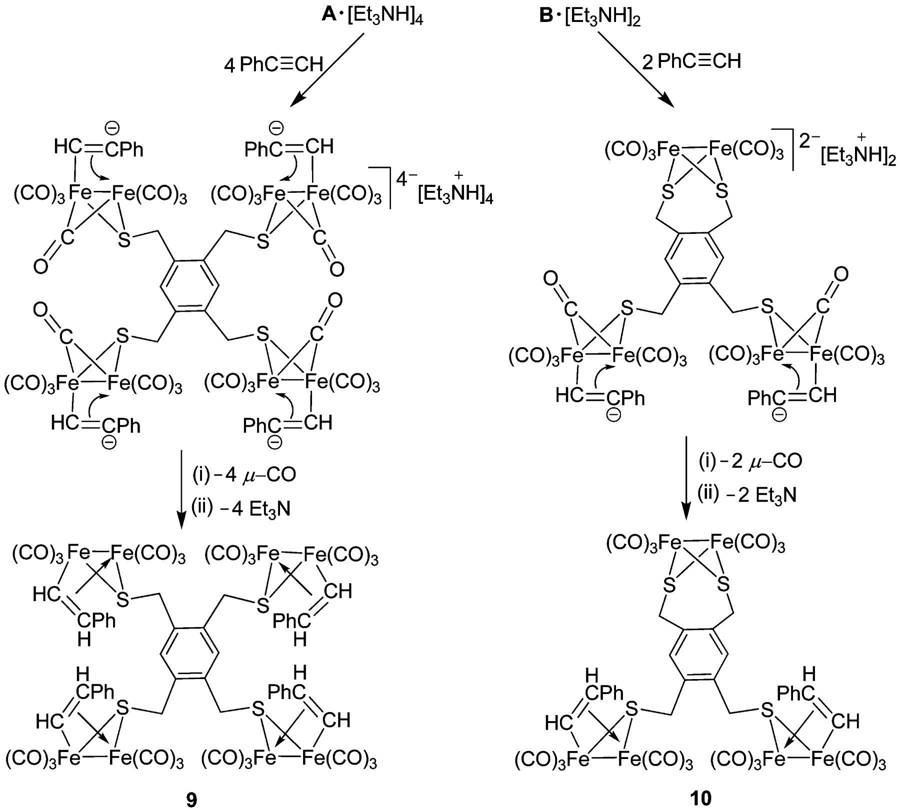
Scheme 5



Scheme 6



Scheme 7



18% yield (Scheme 6). Apparently, the formation of complex **7** is most likely via the nucleophilic attack of the four negatively charged Fe atoms in **A** at the leaving group (Cl^-)-attached C atoms in four molecules of PhCOCl, followed by displacement of the four μ-CO ligands in **A** and by subsequent intramolecular O atom coordination of the four PhCO ligands.[16,19] Similarly, the nucleophilic attack of the two negatively charged Fe atoms in **B** at the leaving group (Cl^-)-attached C atoms in two molecules of PhC(Cl)═NPh, followed by displacement of the two μ-CO ligands in **B** by intramolecular N atom coordination of the two PhC═NPh ligands, resulted in formation of triple-butterfly complex **8**.[32−34]

Particularly interesting is that, in contrast to the aforementioned electrophiles with a leaving group, the electrophile PhC≡CH without a leaving group was found to react with the $[Et_3NH]_4$ salt of tetraanion **A** and the $[Et_3NH]_2$ salt of dianion **B** to give both quadruple- and triple-butterfly complexes $[(\mu$-σ,π-PhCH═CH)$Fe_2(CO)_6]_4$[1,2,4,5-(μ-$SCH_2)_4C_6H_2$] (**9**) and [(μ-σ,π-PhCH═CH)$Fe_2(CO)_6]_2[Fe_2(CO)_6]$[1,2,4,5-($\mu$-$SCH_2)_4C_6H_2$] (**10**) in 12% and 25% yields, respectively (Scheme 7). Complex **9** might be produced by nucleophilic attack of the four negatively charged Fe atoms in **A** at β-C atoms of four phenyl acetylene molecules (both steric considerations and the ability of the phenyl group to stabilize α-carbanions favor β attack of the iron centered nucleophile), followed by loss of four μ-CO ligands from the initially formed $[Et_3NH]_4$ salt of the C-centered tetraanion and subsequent intramolecular protonation by its $[Et_3NH]_4$ cations. In addition, the nucleophilic attack of the negatively charged Fe atoms in the $[Et_3NH]_2$ salt of dianion **B** at β-C atoms of phenylacetylene molecules, followed by loss of its two μ-CO ligands and subsequent intramolecular protonation of the corresponding C-centered dianion, resulted in formation of triple-butterfly complex **10**.[35]

Complexes **7**−**10** are air-stable red solids, whose elemental analysis and spectroscopic data are consistent with the structures shown in Schemes 6 and 7. The IR spectra of **7**−**10** showed three absorption bands in the range of 2074−1985 cm $^{-1}$ for their terminal carbonyls and one absorption band at 1464, 1554, and 1495 or 1496 cm^{-1} for their bridged C═O, C═N, and C═C double bonds, respectively. The ^1H NMR spectra of **7**−**10** exhibited the corresponding signals for the protons in their H-containing groups, such as **9** and **10** showing two doublets at ca. 4.3 and 8.4 ppm for the two protons in their bridged CH═CH groups. The ^{13}C NMR of **7**−**10** displayed the corresponding signals for their carbon atoms, such as **7** showing a singlet at 292.1 ppm for its bridged C═O groups,[36] **8** showing a singlet at 232.5 ppm for its bridged C═N groups,[32] and **9**/**10** showing two singlets at ca. 96 and 144 ppm for their PhCH═CHFe groups.[37] The molecular structure of **8** was confirmed by X-ray diffraction analysis. Its ORTEP plot is shown in Figure 4, whereas Table 3 lists the selected bond lengths and angles. Figure 4 shows that complex **8** is indeed a triple-butterfly complex, which contains a closed butterfly subcluster $(\mu\text{-S})_2Fe_2(CO)_6$ and two identical open butterfly subclusters (μ-S)(μ-PhC═NPh)$Fe_2(CO)_6$, which are connected to the methylene carbon atoms of the central moiety 1,2,4,5-$(CH_2)_4C_6H_2$. All the two phenyl groups bound to a C═N bond in the two open subclusters lie in a cis manner. The N1−C28 (1.285 Å) and N2−C48 (1.269 Å) bonds in the two μ-iminoacyl ligands of complex **8** could be best assigned to the C═N double bonds, but not the C−N single bonds, since the normal bond lengths of a C−N single bond and a C═N double bond are 1.47 and 1.28 Å,[38] respectively. Actually, such a type of C═N double bond was also observed in other μ-iminoacyl bridged Fe/E (E = S, Se, Te) cluster complexes.[32−34]

An ORTEP drawing of **9** is shown in Figure 5, whereas its selected bond lengths and angles are given in Table 3. Complex **9** possesses a symmetric center, namely, the center of the benzene ring. As can be seen in Figure 5, complex **9** contains four identical butterfly subclusters [(μ-σ,π-PhCH═CH)$Fe_2(CO)_6(\mu\text{-S})]_4$, which are connected through their μ-S atoms to each α-C atom of the central benzene ring by an equatorial type of bond[2,39] (the angle C21−S1⋯C13 = 149.2°, and the angle C25−S2⋯C26 = 152.4°). It is noteworthy that the C−C bond lengths of the bridging substituted vinyl ligands (C13−C14 = 1.360 Å, C26−C27 = 1.391 Å) are obviously longer than the normal value for a C═C double bond, which demonstrates that the C═C double bond in each of the bridging substituted vinyl ligands is coordinated to the two iron atoms in a σ, π manner (Fe1−C13 σ-bond length is 1.974 Å; Fe2−C13 and Fe2−C14 π-bond lengths are 2.066 and 2.266 Å, respectively; Fe3−C26 σ-bond length is 1.975 Å; Fe4−C26 and Fe4−C27 π-bond lengths are 2.086 and 2.232 Å, respectively).[35,37]

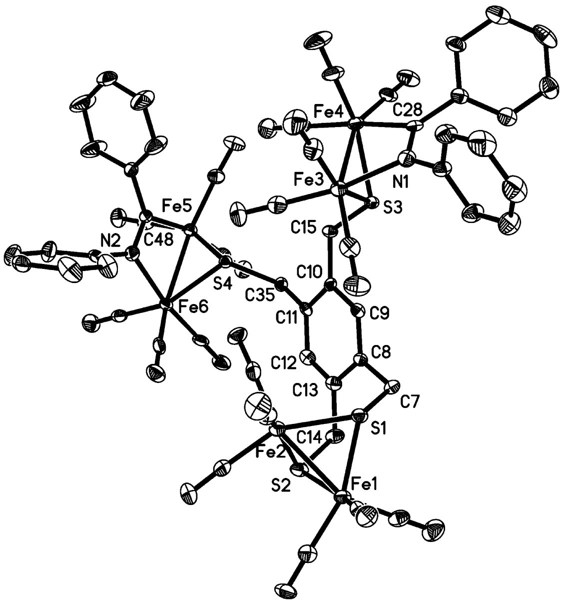


Figure 4. Molecular structure of **8** with 30% probability level ellipsoids.

Reactions of Tetrathiol System 1,2,4,5-$(HSCH_2)_4$-C_6H_2/$Fe_3(CO)_{12}$/Et_3N with CS_2, Followed by Treatment of $PhCH_2Br$ and $CpFe(CO)_2I$. Synthesis and Characterization of Quadruple- and Triple-Butterfly Complexes [(μ-S═$CSCH_2Ph)Fe_2(CO)_6]_4$[1,2,4,5-(μ-$SCH_2)_4C_6H_2$] (11) and [(μ-S═$CSFe(CO)_2Cp)Fe_2(CO)_6]_2[Fe_2(CO)_6]$[1,2,4,5-($\mu$-$SCH_2)_4C_6H_2$] (12). We further found that, when excess CS_2 was added to the tetrathiol system containing tetraanion **A** and dianion **B**, the dithioformato ligand-containing intermediates tetraanion **C** and dianion **D** were formed in a manner similar to those reactions of the other μ-CO-containing Fe/S cluster anions with CS_2;[17,19,40] further treatment of the intermediates **C** and **D** with $PhCH_2Br$ and $CpFe(CO)_2I$ afforded the quadruple- and triple-butterfly complexes **11** and **12** in 30% and 12% yields, respectively (Scheme 8).

Complexes **11** and **12** are also air-stable red solids, whose elemental analysis and spectroscopic data are in good agreement with the structures shown in Scheme 8. The IR spectra of **11** and **12** showed three strong absorption bands in the range of 2067−1985 cm^{-1} for their terminal carbonyls and one absorption band at 1015 and 1004 cm^{-1} for their C═S functional groups coordinated to iron atoms. It is due to such a coordination mode that the absorption bands of the thiocarbonyl μ-S═C−S groups in complexes **11** and **12** lie at a much lower frequency than that of C═S in free CS_2 (1533

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **8** and **9**

compound **8**			
Fe(1)−S(1)	2.2513(19)	Fe(1)−Fe(2)	2.5167(14)
Fe(3)−N(1)	1.992(6)	Fe(3)−S(3)	2.249(2)
Fe(3)−Fe(4)	2.5872(14)	Fe(6)−N(2)	1.992(6)
Fe(5)−Fe(6)	2.5737(13)	Fe(6)−S(4)	2.2438(17)
N(1)−C(28)	1.285(9)	N(2)−C(48)	1.269(8)
S(1)−Fe(1)−S(2)	87.49(7)	Fe(2)−S(1)−Fe(1)	68.02(6)
N(1)−Fe(3)−S(3)	81.31(19)	N(1)−Fe(3)−Fe(4)	70.77(19)
N(2)−Fe(6)−S(4)	79.95(16)	N(2)−Fe(6)−Fe(5)	71.11(19)
S(3)−Fe(4)−Fe(3)	55.03(6)	S(4)−Fe(5)−Fe(6)	54.94(5)
C(28)−Fe(4)−S(3)	81.47(17)	C(28)−N(1)−Fe(3)	109.4(5)
compound **9**			
Fe(1)−C(13)	1.974(8)	Fe(2)−C(13)	2.066(9)
Fe(1)−Fe(2)	2.546(2)	Fe(2)−C(14)	2.266(8)
Fe(1)−S(1)	2.252(3)	Fe(3)−Fe(4)	2.553(3)
Fe(2)−S(1)	2.261(2)	Fe(3)−S(2)	2.213(3)
Fe(4)−S(2)	2.278(3)	C(13)−C(14)	1.360(12)
S(1)−Fe(1)−Fe(2)	55.82(7)	S(2)−Fe(3)−Fe(4)	56.56(7)
Fe(1)−S(1)−Fe(2)	68.68(8)	Fe(3)−S(2)−Fe(4)	69.28(19)
S(1)−Fe(2)−Fe(1)	55.50(7)	S(2)−Fe(4)−Fe(3)	54.16(8)
C(13)−Fe(1)−Fe(2)	52.6(2)	C(13)−Fe(1)−S(1)	83.9(3)
Fe(1)−C(13)−Fe(2)	78.1(3)	C(13)−Fe(2)−C(14)	36.2(3)

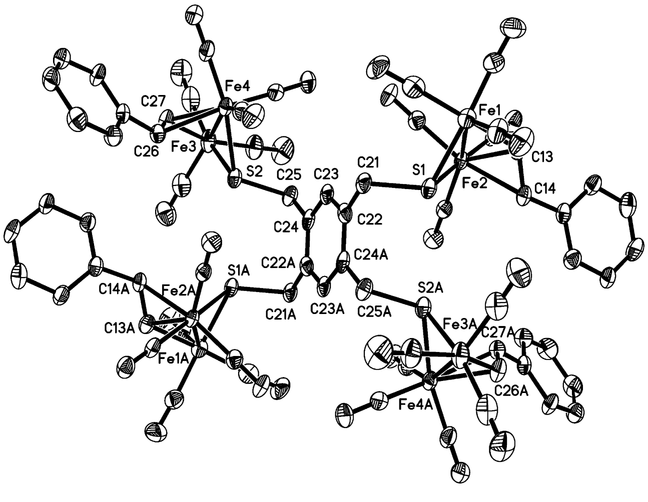


Figure 5. Molecular structure of **9** with 30% probability level ellipsoids.

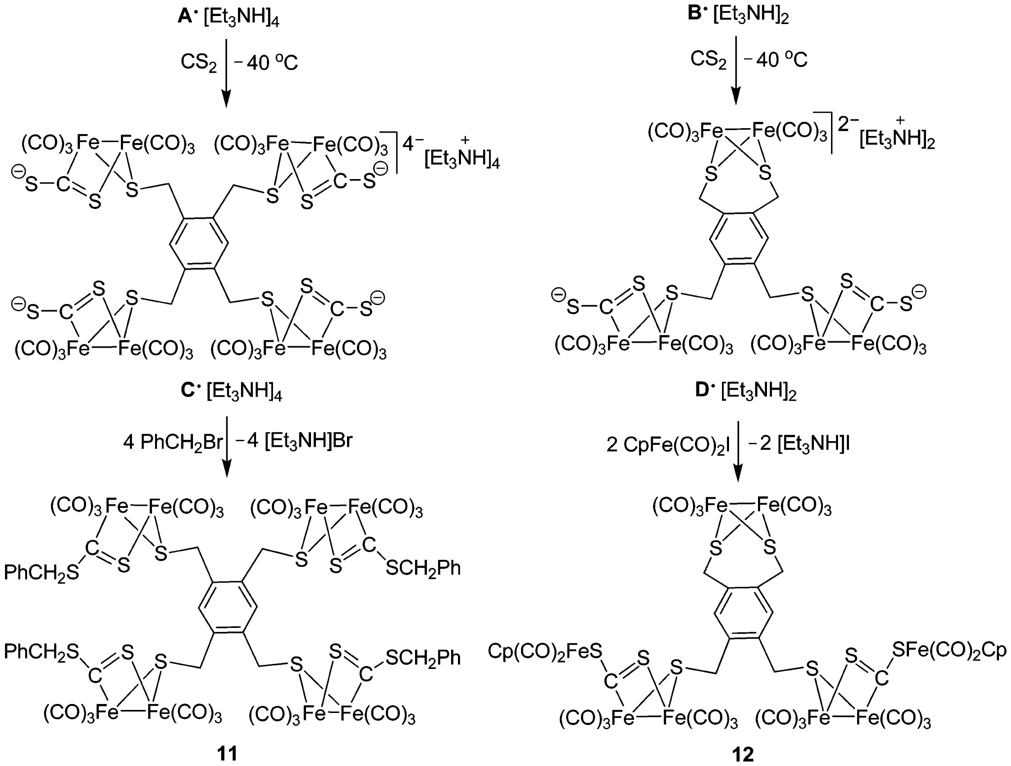
cm^{-1}) and falls within the range of 1120−860 cm^{-1} exhibited by the coordinated C═S in some other transition-metal complexes.[19,41] The ^1H NMR spectrum of **11** exhibited a multiplet centered at 4.25 ppm for the methylene protons attached to its phenyl groups, whereas **12** displayed one singlet at 4.97 ppm for its cyclopentadienyl ligands. In addition, the ^{13}C NMR spectra of **11** and **12** exhibited four and six singlets in the region of 206−213 ppm for their terminal carbonyls and one singlet in the range of 303−319 ppm for their C═S groups.[17]

The molecular structure of complex **11** was further confirmed by X-ray crystallography. Its ORTEP plot is shown in Figure 6, and Table 4 lists its selected bond lengths and angles. As can be seen in Figure 6, complex **11** is centrosymmetric and consists of four identical butterfly $[(\mu\text{-}S{=}CSCH_2Ph)Fe_2(CO)_6(\mu\text{-}S)]_4$ cluster units. The bridged C═S double bonds (for example, the double bond C1═S1 = 1.650 Å) is slightly shorter than its neighboring single bond S2−C1 (1.694 Å), but considerably shorter than the remote single bonds S2−C2 (1.79 Å). In addition, the four identical cluster units in **11** are joined together by connecting their μ-S atoms with four benzylic C atoms of the central benzene ring by equatorial-type bonds[2,39] (for example, the nonbonded angle C13−S4······S5 = 160.93°) in order to reduce the strong steric repulsions between these bulky cluster moieties. It is worth pointing out that, although some starlike triple-butterfly Fe_2S_2C clusters with a central 1,3,5-trimethylenebenzene moiety[40] and some quadruple-butterfly clusters with a central 1,2,4,5-tetramethylenebenzene moiety[21] are known, complex **11** is the first prepared and crystallographically characterized quadruple-butterfly cluster in which its four butterfly Fe_2S_2C cluster cores are connected to the central 1,2,4,5-tetramethylenebenzene moiety.

■ CONCLUSIONS

A comparative study of the reactions of tetrathiol 1,2,4,5-$(HSCH_2)_4C_6H_2$ with $Fe_3(CO)_{12}$ or with $Fe_3(CO)_{12}$ in the presence of Et_3N has allowed us to obtain a variety of the 1,2,4,5-$(CH_2)_4C_6H_2$ moiety-containing new butterfly Fe/S cluster complexes. Thus, the reaction of tetrathiol 1,2,4,5-$(HSCH_2)_4C_6H_2$ with $Fe_3(CO)_{12}$ is found to give the single-butterfly complex **1** or single- and double-butterfly complexes **1**/**2** or **2**/**3**, mainly dependent upon the molar ratio of the starting materials and the reaction temperature in different solvents. In addition, it is also found that further treatment of **1** with PPh_3, PMe_3, or N-heterocyclic carbene I_{Mes} affords its monosubstituted derivatives **4**, **5**, and **6**, respectively. More interestingly, the quadruple-butterfly complex **7** can be obtained by the reaction of 1,2,4,5-$(HSCH_2)_4C_6H_2$ with $Fe_3(CO)_{12}$ in the presence of Et_3N, followed by treatment of the intermediate μ-CO-containing tetraanion **A** with PhCOCl, and the triple-butterfly complex **8** is produced by reaction of PhC(Cl)═NPh with the μ-CO-containing dianion **B**, which is generated in situ from the initially formed tetraanion **A**. Similarly, the quadruple- and triple-butterfly complexes **9** and **10** are obtained by the reactions of PhC≡CH with tetraanion

Scheme 8



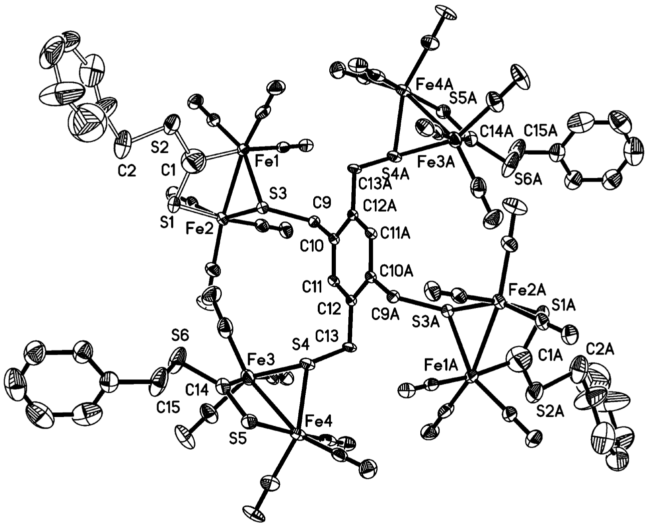


Figure 6. Molecular structure of **11** with 30% probability level ellipsoids.

A and dianion **B**. Particularly interesting is that the dithioformato ligand-containing quadruple-butterfly complex **11** can be obtained by the reaction of $PhCH_2Br$ with tetraanion **C** (which is generated in situ from tetraanion **A** and CS_2), whereas the organometallic halide $CpFe(CO)_2I$ reacts with dianion **D** (which is generated in situ from dianion **B** and CS_2) to give the corresponding triple-butterfly complex **12**. While complexes **1**−**12** have been characterized by elemental analysis, various spectroscopic methods, and some of them by X-ray crystallography, the suggested dithiol intermediate $[1,2\text{-}(HSCH_2)_2\text{-}4,5\text{-}(\mu\text{-}SCH_2)_2C_6H_2][Fe_2(CO)_6]$ ($\mathbf{M_6}$) is isolated in an anaerobic glovebox, and it has been proved to be able to convert to complex **1** by oxidation in air.

■ EXPERIMENTAL SECTION

General Comments. Unless otherwise stated, all reactions were carried out under an atmosphere of prepurified nitrogen by using standard Schlenk and vacuum-line techniques. Tetrahedrofuran (THF) and toluene were distilled from Na/benzophenone ketyl under nitrogen. $Fe_3(CO)_{12}$,[42] $1,2,4,5\text{-}(HSCH_2)_4C_6H_2$,[43] $PhC(Cl){=}NPh$,[44] and $CpFe(CO)_2I$,[45] and (1,3-bis(mesityl)imidazolium chlor-

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 11

Fe(1)−Fe(2)	2.6245(17)	Fe(4)−S(4)	2.244(2)
Fe(3)−Fe(4)	2.6405(18)	Fe(4)−S(5)	2.309(3)
Fe(2)−S(1)	2.255(4)	S(5)−C(14)	1.647(9)
Fe(2)−S(3)	2.250(2)	S(6)−C(14)	1.691(9)
Fe(3)−S(4)	2.258(3)	S(4)−C(13)	1.843(8)
S(3)−Fe(1)−Fe(2)	54.22(6)	S(3)−Fe(2)−Fe(1)	54.65(6)
S(3)−Fe(2)−S(1)	83.07(16)	Fe(2)−S(3)−Fe(1)	71.13(7)
S(1)−Fe(2)−Fe(1)	77.33(12)	Fe(4)−S(4)−Fe(3)	71.82(8)
S(4)−Fe(3)−Fe(4)	53.84(6)	C(1)−S(1)−Fe(2)	94.1(4)
S(4)−Fe(4)−S(5)	82.76(9)	S(1)−C(1)−S(2)	126.8(7)

ide[46] were prepared according to the literature procedures, whereas the other starting materials were of commercial origin and used without further purification. Preparative TLC was carried out on glass plates (25 × 15 × 0.25) coated with silica gel G (10−40 μm). IR spectra were recorded on a Bruker Vector 22 infrared spectrophotometer. ^{1}H (^{13}C, ^{31}P) NMR spectra were taken on a Bruker Avance 300 NMR or Bruker Avance 400 NMR spectrophotometer. Elemental analyses were preformed with an Elementar Vario EL analyzer. Melting points were determined on a Yanaco MP-500 apparatus and are uncorrected.

Preparation of [1,2-($CH_2S_2CH_2$)-4,5-(μ-SCH_2)$_2C_6H_2$][$Fe_2(CO)_6$] (1) via Reaction of 1,2,4,5-($HSCH_2$)$_4C_6H_2$ with $Fe_3(CO)_{12}$ in a 1:1 Molar Ratio in Refluxing THF. To a stirred solution of 1,2,4,5-($HSCH_2$)$_4C_6H_2$ (0.264 g, 1.00 mmol) in THF (20 mL) was added $Fe_3(CO)_{12}$ (0.504 g, 1.00 mmol), and then the mixture was refluxed for 1 h. After solvent was removed at reduced pressure, the residue was subjected to open-air TLC separation using petroleum ether/CH_2Cl_2 (2:1 v/v) as eluent to develop one major red band with many tiny bands. From the major red band, **1** (0.108 g, 20%) was obtained as a red solid. mp 158−159 °C. Anal. Calcd for $C_{16}H_{10}Fe_2O_6S_4$: C, 35.71; H, 1.87. Found: C, 35.76; H, 2.00. IR (KBr disk): $\nu_{C\equiv O}$ 2072 (s), 2031 (vs), 1990 (vs) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): 3.07 (d, 2H, J = 12.6 Hz, 2C*H*HSFe), 3.80 (d, 2H, J = 12.3 Hz, 2CH*H*SFe), 3.97 (s, 4H, 2CH_2S), 6.80 (s, 2H, C_6H_2) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): 34.2, 35.8 (2s, CH_2S), 131.2, 132.8, 137.8 (3s, C_6H_2), 207.0 (s, C≡O) ppm.

Preparation of Complex 1 and [1,2,4,5-(μ-SCH_2)$_4C_6H_2$]-[$Fe_2(CO)_6$]$_2$ (2) via Reaction of 1,2,4,5-($HSCH_2$)$_4C_6H_2$ with $Fe_3(CO)_{12}$ in a 1:2 Molar Ratio in Refluxing THF. To a stirred solution of 1,2,4,5-($HSCH_2$)$_4C_6H_2$ (0.132 g, 0.50 mmol) in THF (20 mL) was added $Fe_3(CO)_{12}$ (0.504 g, 1.00 mmol), and then the mixture was refluxed for 1 h. After the same workup as that for the above-described preparation of **1**, two major red bands were developed. From the upper red band, **1** (0.022 g, 8%) was obtained. From the lower red band, **2** (0.088 g, 18%) was obtained as a red solid. **2**: mp 191 °C (dec). Anal. Calcd for $C_{22}H_{10}Fe_4O_{12}S_4$: C, 32.30; H, 1.23. Found: C, 32.22; H, 1.32. IR (KBr disk): $\nu_{C\equiv O}$ 2073 (s), 2032 (vs), 1991 (vs) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): 2.91−3.06 (m, 4H, 4C*H*HSFe), 3.71−3.82 (m, 4H, 4CH*H*SFe), 6.92 (s, 2H, C_6H_2) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): 35.9, 37.6 (2s, CH_2S), 125.8, 132.3, 133.0, 135.8, 137.0, 140.2 (6s, C_6H_2), 207.0, 208.3 (2s, C≡O) ppm.

Preparation of Complex 1 via Reaction of 1,2,4,5-($HSCH_2$)$_4C_6H_2$ with $Fe_3(CO)_{12}$ in a 1:1 Molar Ratio in Toluene. While stirring, $Fe_3(CO)_{12}$ (0.504 g, 1.00 mmol) was added to a solution of 1,2,4,5-($HSCH_2$)$_4C_6H_2$ (0.264 g, 1.00 mmol) in toluene (20 mL). After the mixture continued to be stirred at about 90 °C for 1 h, solvent was removed at reduced pressure and the residue was subjected to TLC separation using petroleum ether/CH_2Cl_2 (2:1, v/v) as eluent. From the major red band, **1** (0.103 g, 19%) was obtained.

Preparation of Complex 2 and [(1,2-Me_2)-4,5-(μ-SCH_2)$_2C_6H_2$]-[$Fe_2(CO)_6$] (3) via Reaction of 1,2,4,5-($HSCH_2$)$_4C_6H_2$ with $Fe_3(CO)_{12}$ in a 1:2 Molar Ratio in Toluene. To a stirred solution of 1,2,4,5-($HSCH_2$)$_4C_6H_2$ (0.132 g, 0.50 mmol) in toluene (20 mL) was added $Fe_3(CO)_{12}$ (0.504 g, 1.00 mmol), and then the mixture was stirred at about 90 °C for 1 h. Through the same workup as that for the above-described preparation of **1**, two major bands were developed. From the lower red band, **2** (0.088 g, 22%) was obtained as a red solid. From the upper orange band, **3** (0.011 g, 5%) was obtained as an orange-red solid. **3**: mp 140−141 °C. Anal. Calcd for $C_{16}H_{12}Fe_2O_6S_2$: C, 40.37; H, 2.54. Found: C, 40.17; H, 2.47. IR (KBr disk): $\nu_{C\equiv O}$ 2071 (s), 2036 (vs), 1985 (vs) cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): 2.19 (s, 6H, 2CH_3), 3.08 (d, 2H, J = 12.8 Hz, 2C*H*HSFe), 3.79 (d, 2H, J = 12.8 Hz, 2CH*H*SFe), 6.83 (s, 2H, C_6H_2) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): 19.3 (s, CH_3), 36.0 (s, CH_2S), 131.0, 136.5, 136.7 (3s, C_6H_2), 207.3 (s, C≡O) ppm.

Isolation of Intermediate [1,2-($HSCH_2$)$_2$-4,5-(μ-SCH_2)$_2C_6H_2$]-[$Fe_2(CO)_6$] (M_6). A mixture of 1,2,4,5-($HSCH_2$)$_4C_6H_2$ (0.264 g, 1.00 mmol) and $Fe_3(CO)_{12}$ (0.504 g, 1.00 mmol) in toluene (15 mL) was stirred at about 90 °C for 1 h. After removal of solvent at reduced pressure, the residue was transferred to an anaerobic glovebox and subjected to TLC separation using deaerated petroleum ether/CH_2Cl_2 (2:1 v/v) as eluent to develop one major red band with many tiny bands. From the major red band, $\mathbf{M_6}$ (0.180 g, 33%) was obtained as a red air-stable solid (but in solution, it is air-sensitive). mp 111−113 °C. Anal. Calcd for $C_{16}H_{12}Fe_2O_6S_4$: C, 35.57; H, 2.24. Found: C, 35.38; H, 2.41. IR (KBr disk): $\nu_{C\equiv O}$ 2074 (vs), 2033 (vs), 1995 (vs) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): 1.82 (t, 2H, J = 7.1 Hz, 2SH), 3.07 (d, J = 12.9 Hz, 2H, 2C*H*HSFe), 3.76−3.86 (m, 6H, 2CH*H*SFe, 2CH_2SH), 7.00 (s, 2H, C_6H_2) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): 24.5 (s, CH_2SH), 34.8 (s, CH_2SFe), 130.1, 137.6, 137.8 (3s, C_6H_2), 206.0 (s, C≡O) ppm.

Conversion of Intermediate M_6 to Complex 1. A solution of $\mathbf{M_6}$ (0.108 g, 0.20 mmol) in toluene (10 mL) was stirred in air at 90 °C for about 10 min until TLC showed that $\mathbf{M_6}$ had completely disappeared. After removal of solvent at reduced pressure, the residue was subjected to TLC separation using petroleum ether/CH_2Cl_2 (2:1 v/v) to develop one major red band, from which **1** (0.076 g, 71%) was obtained.

Preparation of [1,2-($CH_2S_2CH_2$)-4,5-(μ-SCH_2)$_2C_6H_2$]-[$Fe_2(CO)_5PPh_3$] (4). A solution of **1** (0.108 g, 0.20 mmol), PPh_3 (0.052 g, 0.20 mmol), and $Me_3NO\cdot 2H_2O$ (0.022 g, 0.20 mmol) in MeCN (10 mL) was stirred at room temperature for 1 h. After solvent was removed under vacuum, the residue was subjected to open-air TLC separation using petroleum/CH_2Cl_2 (2:1 v/v) as eluent. From the major red band, **4** (0.045 g, 29%) was obtained as a red solid. mp 185−187 °C. Anal. Calcd for $C_{33}H_{25}Fe_2O_5PS_4$: C, 51.31; H, 3.26. Found: C, 51.25; H, 3.26. IR (KBr disk): $\nu_{C\equiv O}$ 2044 (vs), 1986 (vs), 1932 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): 3.07 (d, 2H, J = 10.8 Hz, 2C*H*HSFe), 3.83−3.97 (m, 6H, 2CH*H*SFe, 2CH_2S), 6.62 (s, 2H, C_6H_2), 7.46 (br s, 9H, 6*o*-H of 3C_6H_5, 3*p*-H of 3C_6H_5), 7.79 (br s, 6H, 6*m*-H of 3C_6H_5) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): 32.4, 34.2 (2s, CH_2S), 128.7, 128.8, 130.3, 130.9, 132.0, 133.5, 133.6, 135.2, 135.6, 138.8 (10s, C_6H_2, C_6H_5), 208.3, 212.5 (2s, C≡O) ppm. ^{31}P NMR ($CDCl_3$, 162 MHz, 85% H_3PO_4): 64.53(s) ppm.

Preparation of [1,2-($CH_2S_2CH_2$)-4,5-(μ-SCH_2)$_2C_6H_2$]-[$Fe_2(CO)_5PMe_3$] (5). The same procedure was followed as that for preparation of **4**, except PMe_3 (0.20 mL, 1M, 0.20 mmol) was employed in place of PPh_3. **5** (0.033 g, 28%) was obtained as a red solid. mp 170−172 °C. Anal. Calcd for $C_{18}H_{19}Fe_2O_5PS_4$: C, 36.88; H, 3.27. Found: C, 37.01; H, 3.50. IR (KBr disk): $\nu_{C\equiv O}$ 2037 (vs), 1980 (vs), 1964 (vs), 1920 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): 1.43 (d, 9H, J_{P-H} = 11.2 Hz, 3CH_3), 3.07 (br s, 2H, 2C*H*HSFe), 3.72 (br s, 2H, 2CH*H*SFe), 3.96 (br s, 4H, 2CH_2S), 6.75 (s, 2H, C_6H_2) ppm. ^{31}P NMR ($CDCl_3$, 162 MHz, 85%H_3PO_4): 26.26(s) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): 19.7(d, J_{P-C} = 29.5 Hz, PCH_3), 34.8, 37.7 (2s, CH_2S), 125.4, 125.7, 139.2, 139.4, 139.7, 139.9 (6s, C_6H_2), 209.4, 210.0 (2s, C≡O) ppm.

Preparation of [1,2-($CH_2S_2CH_2$)-4,5-(μ-SCH_2)$_2C_6H_2$]-[$Fe_2(CO)_5I_{Mes}$] (6). To a stirred suspension of 1,3-bis(mesityl)-imidazolium salt $I_{Mes}\cdot$HCl (0.341 g, 1.00 mmol) in THF (15 mL) was slowly added *n*-BuLi (0.40 mL, 2.5 M, 1.00 mmol in hexane) to give a yellowish solution. After it was stirred at room temperature for 20 min, the reaction mixture was filtered under anaerobic conditions through a Celite-packed column and eluted with THF (10 mL) to give a filtrate containing the air-sensitive carbene I_{Mes}. To the filtrate was added **1** (0.108 g, 0.20 mmol), and the new mixture was stirred at room temperature for 2 h. The resulting mixture was evaporated to dryness under vacuum to give a deep-red residue, which was subjected to open-air TLC separation using petroleum/CH_2Cl_2 (2:1 v/v) as eluent. From the brown-red band, **6** (0.036 g, 22%) was obtained as a red solid. mp 163−164 °C. Anal. Calcd for $C_{36}H_{34}Fe_2N_2O_5S_4$: C, 53.08; H, 4.21; N, 3.44. Found: C, 52.79; H, 4.30; N, 3.52. IR (KBr disk): $\nu_{C\equiv O}$ 2035 (s), 1973 (vs), 1914 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): 2.26 (s, 12H, 4*o*-CH_3 in 2C_6H_2 of I_{Mes}), 2.34 (s, 6H, 2*p*-CH_3 in 2C_6H_2 of I_{Mes}), 3.02 (d, 2H, J = 12.4 Hz, 2C*H*HSFe), 4.07 (d, 2H, J = 12.0 Hz, 2CH*H*SFe), 4.18−4.22 (m, 4H, 2CH_2S), 6.76 (s, 2H, C_6H_2), 7.03 (s, 4H, 4*m*-H of 2C_6H_2 in I_{Mes}), 7.13 (s, 2H, NCH=CHN) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): 18.6 (s, *o*-CH_3 of mesityl), 21.1 (s, *p*-CH_3 of mesityl), 33.7, 37.6 (2s, CH_2S), 125.1, 125.4 (2s, NCH=CHN), 128.3, 129.5, 130.1, 132.4, 136.2, 137.7,

Table 5. Crystal Data and Structure Refinement Details for 1, 3, and 4

	1	3	4
mol formula	$C_{16}H_{10}Fe_2O_6S_4$	$C_{16}H_{12}Fe_2O_6S_2$	$C_{33}H_{25}Fe_2O_5PS_4$
mol wt	538.18	476.08	772.44
cryst syst	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	7.4687(15)	8.767(7)	11.381(5)
b/Å	11.772(2)	9.768(8)	11.582(5)
c/Å	12.307(3)	11.476(10)	13.538(6)
α/deg	69.70(3)	97.411(8)	72.33(2)
β/deg	72.76(3)	106.071(17)	77.97(2)
γ/deg	85.42(3)	93.711(15)	74.449(18)
V/Å^3	968.9(3)	931.2(13)	1622.2(12)
Z	2	2	2
D_c/g·cm^{-3}	1.845	1.698	1.581
abs coeff/mm^{-1}	1.960	1.811	1.242
F(000)	540	480	788
index ranges	$-8 \leq h \leq 8$	$-10 \leq h \leq 11$	$-14 \leq h \leq 14$
	$-14 \leq k \leq 12$	$-12 \leq k \leq 12$	$-15 \leq k \leq 14$
	$-14 \leq l \leq 14$	$-15 \leq l \leq 15$	$-17 \leq l \leq 13$
no. of reflns	5586	10 760	15 836
no. of indep reflns	3373	4396	7627
$2\theta_{max}$/deg	50.04	55.82	55.86
R	0.0252	0.0234	0.0501
R_w	0.0622	0.0442	0.0791
goodness of fit	1.053	1.022	1.015
largest diff peak, hole/e Å^{-3}	0.374/−0.341	0.321/−0.451	0.646/−0.711

139.4, 139.9 (8s, benzene rings), 195.6 (s, NCN), 213.6, 215.8 (2s, C≡O) ppm.

Preparation of [(μ-PhC=O)$Fe_2(CO)_6$]$_4$[1,2,4,5-(μ-SCH_2)$_4C_6H_2$] (7). A mixture of 1,2,4,5-$(HSCH_2)_4C_6H_2$ (0.132 g, 0.50 mmol), $Fe_3(CO)_{12}$ (1.00 g, 2.0 mmol), Et_3N (0.28 mL, 2.0 mmol), and THF (20 mL) was stirred at room temperature for 0.5 h to give a brown-red solution. To this solution was added PhCOCl (0.53 mL, 4.0 mmol), and then the new mixture was stirred at room temperature for 24 h. After solvent was removed at reduced pressure, the residue was subjected to open-air TLC separation using petroleum ether/CH_2Cl_2 (5:1 v/v) as eluent to develop a major red band with many tiny bands. From the major red band, 7 (0.202 g, 22%) was obtained as a red solid. mp 92 °C (dec). Anal. Calcd for $C_{62}H_{30}Fe_8O_{28}S_4$: C, 41.42; H, 1.68. Found: C, 41.21; H, 1.72. IR (KBr disk): $\nu_{C\equiv O}$ 2074 (s), 2032 (vs), 1996 (vs); $\nu_{C=O}$ 1464 (m) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): 3.00−3.94 (m, 8H, $4CH_2S$), 7.07−7.66 (m, 22H, C_6H_2, $4C_6H_5$) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): 35.9, 39.2 (2s, CH_2S), 127.3, 128.4, 128.9, 131.1, 132.2, 133.7, 134.0, 134.1, 137.8, 139.3, 139.9, 144.5 (12s, C_6H_2, C_6H_5), 207.0, 209.7, 211.1, 211.7(4s, C≡O), 292.1 (s, C=O)ppm.

Preparation of [(μ-PhC=NPh)$Fe_2(CO)_6$]$_2$[$Fe_2(CO)_6$][1,2,4,5-(μ-SCH_2)$_4C_6H_2$] (8). The same procedure was followed as for 7, except that PhC(Cl)=NPh (0.862 g, 4.0 mmol) was used instead of PhCOCl. From the major red band, 8 (0.132 g, 18%) was obtained as a red solid. mp 104−105 °C. Anal. Calcd for $C_{54}H_{30}Fe_6N_2O_{18}S_4$: C, 44.48; H, 2.07; N, 1.92. Found: C, 44.55; H, 2.09; N, 2.11. IR (KBr disk): $\nu_{C\equiv O}$ 2065 (s), 2025(vs), 1984 (vs); $\nu_{C=N}$ 1554 (w) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 3.18 (d, 2H, J = 14.0 Hz, 2CH*H*SFeS), 3.91−4.16 (m, 6H, $2CH_2SFeN$, 2CH*H*SFeS), 6.51−7.17 (m, 22H, C_6H_2, $4C_6H_5$) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): 36.1, 40.5 (2s, CH_2S), 122.2, 123.7, 126.2, 127.7, 128.0, 128.9, 131.2, 137.9, 139.6, 146.7, 153.1(11s, C_6H_2, C_6H_5), 207.1, 208.7, 210.6, 213.4 (4s, C≡O), 232.5 (s, C=N) ppm.

Preparation of [(μ-σ,π-PhCH=CH)$Fe_2(CO)_6$]$_4$[1,2,4,5-(μ-SCH_2)$_4C_6H_2$] (9) and [(μ-σ,π-PhCH=CH)$Fe_2(CO)_6$]$_2$[$Fe_2(CO)_6$]-[1,2,4,5-(μ-SCH_2)$_4C_6H_2$] (10). The same procedure was followed as for 7, except that PhC≡CH (0.44 mL, 4.0 mmol) was utilized instead of PhCOCl, and the new mixture was stirred at reflux for 1 h and at room temperature for 3 h. From the lower major red band, **9** (0.108 g, 12%) was obtained as a dark-red solid. mp 78−79 °C. Anal. Calcd for $C_{66}H_{38}Fe_8O_{24}S_4$: C, 44.28; H, 2.14. Found: C, 44.19; H, 2.31. IR (KBr disk): $\nu_{C\equiv O}$ 2070 (s), 2034 (vs), 1986 (vs); $\nu_{C=C}$ 1495 (w) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 3.61 (s, 8H, $4CH_2S$), 4.26 (d, 4H, J = 14.0 Hz, $4C_6H_5$*CH*), 7.09−7.29 (m, 22H, C_6H_2, $4C_6H_5$), 8.42 (d, 4H, J = 13.6 Hz, 4FeCH) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): 39.9 (s, CH_2S), 95.7 (s, PhCH=CHFe), 125.8, 127.3, 127.9, 129.0, 129.5, 132.1, 138.0, 139.0 (8s, C_6H_2, C_6H_5), 143.5 (s, PhCH=CHFe), 209.3 (s, C≡O) ppm. From the upper band, **10** (0.161 g, 25%) was obtained as an orange-red solid. mp 135−137 °C. Anal. Calcd for $C_{44}H_{24}Fe_6O_{18}S_4$: C, 40.53; H, 1.86. Found: C, 40.78; H, 1.95. IR (KBr disk): $\nu_{C\equiv O}$ 2071 (s), 2033 (vs), 1987 (vs); $\nu_{C=C}$ 1496 (w) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 3.08 (d, 2H, J = 12.4 Hz, 2CH*H*SFeS), 3.46−3.58 (m, 4H, $2CH_2SFeC$), 3.83 (d, 2H, J = 13.6 Hz, 2C*H*HSFeS), 4.24 (d, 2H, J = 13.6 Hz, $2C_6H_5$*CH*), 6.96−7.19 (m, 12H, C_6H_2, $2C_6H_5$), 8.42 (d, 2H, J = 13.6 Hz, 2FeCH) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): 35.9, 39.6 (2s, CH_2S), 95.7 (s, PhCH=CHFe), 125.8, 127.3, 127.9, 128.0, 129.0, 129.5, 131.4, 137.1, 139.0, 140.0 (10s, C_6H_2, C_6H_5), 143.4 (s, PhCH=CHFe), 207.0, 209.3 (2s, C≡O) ppm.

Preparation of [(μ-S=CSCH$_2$Ph)$Fe_2(CO)_6$]$_4$[1,2,4,5-(μ-SCH_2)$_4C_6H_2$] (11). A mixture of 1,2,4,5-$(HSCH_2)_4C_6H_2$ (0.132 g, 0.50 mmol), $Fe_3(CO)_{12}$ (1.00 g, 2.0 mmol), Et_3N (0.28 mL, 2.0 mmol), and THF (20 mL) was stirred at room temperature for 0.5 h to give a brown-red solution. To this solution was added CS_2 (0.24 mL, 4.0 mmol), and then the mixture was stirred at −40 °C for about 0.5 h. After $PhCH_2Br$ (0.24 mL 2.0 mmol) was added, the new mixture was stirred at room temperature for 24 h, and then solvent was removed at reduced pressure to give a residue. The residue was subjected to open-air TLC separation using petroleum ether/CH_2Cl_2 (5:1 v/v) as eluent to develop a major red band with many tiny bands. From the major red band, **11** (0.305 g, 30%) was obtained as a red solid. mp 107−109 °C. Anal. Calcd for $C_{66}H_{38}Fe_8O_{24}S_{12}$: C, 38.73; H, 1.87. Found: C, 38.47; H, 1.89. IR (KBr disk): $\nu_{C\equiv O}$ 2067 (s), 2028 (vs), 1991 (vs), $\nu_{C=S}$ 1015 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): 3.88−3.93 (m, 8H, $4CH_2S$), 4.24−4.30 (m, 8H, $4CH_2Ph$), 7.07−7.29 (m, 22H, C_6H_2, $4C_6H_5$) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): 36.0,

Table 6. Crystal Data and Structure Refinement Details for 8, 9, and 11

	8	9	11
mol formula	$C_{54}H_{30}Fe_6N_2O_{18}S_4·1.5CHCl_3$	$C_{66}H_{38}Fe_8O_{24}S_4·3CHCl_3$	$C_{66}H_{38}Fe_8O_{24}S_{12}$
mol wt	1637.19	2148.11	2046.48
cryst syst	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$C2/c$
a/Å	14.683(3)	13.034(3)	22.827(3)
b/Å	15.6757(16)	14.132(3)	29.547(4)
c/Å	17.2812(11)	14.763(3)	13.0206(18)
α/deg	102.0350(12)	107.99(3)	90
β/deg	109.7940(13)	107.29(3)	101.027(2)
γ/deg	109.8450(15)	109.66(3)	90
V/Å^3	3276.7(8)	2177.4(8)	8620(2)
Z	2	1	4
D_c/g·cm^{-3}	1.659	1.638	1.577
abs coeff/mm^{-1}	1.672	1.734	1.664
F(000)	1638	1072	4104
index ranges	$-17 \leq h \leq 16$	$-15 \leq h \leq 15$	$-22 \leq h \leq 27$
	$-16 \leq k \leq 18$	$-16 \leq k \leq 16$	$-35 \leq k \leq 23$
	$-19 \leq l \leq 20$	$-17 \leq l \leq 17$	$-15 \leq l \leq 11$
no. of reflns	21760	16520	21584
no. of indep reflns	11429	7601	7592
$2\theta_{max}$/deg	50.04	50.04	50.02
R	0.0723	0.0903	0.0823
R_w	0.1850	0.2373	0.2075
goodness of fit	1.052	1.064	1.040
largest diff peak, hole/e Å^{-3}	0.867/−1.376	1.451/−1.145	3.213/−0.869

41.8, 45.8 (3s, CH_2S), 128.2, 129.1, 131.1, 133.2, 137.6, 137.7, 139.8 (7s, C_6H_2, C_6H_5), 206.7, 207.1, 210.6, 210.7 (4s, C≡O), 303.0 (s, C=S) ppm.

Preparation of [(μ-S=CSFe(CO)$_2$Cp)Fe$_2$(CO)$_6$]$_2$[Fe$_2$(CO)$_6$]-[1,2,4,5-(μ-SCH$_2$)$_4$C$_6$H$_2$] (12). The same procedure was taken as for **11**, but $CpFe(CO)_2I$ (1.261 g, 4.0 mmol) was used instead of $PhCH_2Br$. From the major red band, **12** (0.100 g, 12%) was obtained as a red solid. mp 128 °C (dec). Anal. Calcd for $C_{44}H_{20}Fe_8O_{22}S_8$: C, 32.95; H, 1.26. Found: C, 32.71; H, 1.41. IR (KBr disk): $\nu_{C\equiv O}$ 2062 (s), 2022 (vs), 1985 (vs); $\nu_{C=S}$ 1004 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): 3.16 (d, 2H, J = 13.2 Hz, 2CHHSFeS), 3.79–3.94 (m, 6H, 2CHHSFeS, 2CH$_2$SFeC), 4.97 (s, 10H, 2C$_5$H$_5$), 7.09, 7.12 (2s, 2H, C_6H_2) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): 36.0, 42.0 (2s, CH_2S), 85.9 (s, C_5H_5), 131.1, 138.2, 139.1 (3s, C_6H_2), 207.2, 207.7, 210.4, 210.6, 211.8, 212.7 (6s, C≡O), 317.8, 318.1(2s, C=S) ppm.

X-ray Structure Determinations of 1, 3, 4, 8, 9, and 11. Single crystals suitable for X-ray diffraction analyses were grown by slow evaporation of the $CHCl_3$/hexane solutions of **1**, **8** and **9** or CH_2Cl_2/hexane solutions of **3**, **4**, and **11** at −4 °C. A single crystal of **1**, **3**, **4**, **8**, or **9** was mounted on a Rigaku MM-007 (rotating anode) diffractometer equipped with a Saturn 70CCD. Data were collected at 113 K by using a graphite monochromator with Mo Kα radiation (λ = 0.71073) in the $\omega-\phi$ scanning mode. Absorption correction was performed by the CRYSTALCLEAR program.[47] A single crystal of **11** was mounted on a Bruker APEX-II CCD diffractometer. Data were collected at 173 K by using a graphite monochromator with Mo Kα radiation (λ = 0.71073) in the $\omega-\phi$ scanning mode. Absorption correction was performed by the SADABS program.[48] All the structures were solved by direct methods using the SHELXS-97 program[49] and refined by full-matrix least-squares techniques (SHELXL-97)[50] on F^2. Hydrogen atoms were located using the geometric method. Details of crystal data, data collections, and structure refinements are summarized in Tables 5 and 6.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Full tables of crystal data, atomic coordinates and thermal parameters, and bond lengths and angles for **1**, **3**, **4**, **8**, **9**, and **11** as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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