Organometallics **2000,** *19,* 3909−3915

Synthesis and Characterization of Double- and Triple-Butterfly Fe/S Cluster Complexes Obtained from the Novel Butterfly Cluster Anions $\{(\mu\text{-RS})(\mu\text{-CO})[\mathrm{Fe_2(CO)_6}]_2(\mu_4\text{-S})\}^-$ and $(\mu\text{-RS})(\mu\text{-S}^-)[\mathrm{Fe_2(CO)_6}]_3(\mu_4\text{-S})_2$. Crystal Structures of $(\mu\text{-MeS})(\mu\text{-PhNHC{=}S})[\mathrm{Fe_2(CO)_6}]_2(\mu_4\text{-S})$, $(\mu\text{-MeS})(\mu\text{-MeSC{=}S})[\mathrm{Fe_2(CO)_6}]_2(\mu_4\text{-S})$, and $(\mu\text{-PhCH_2S})_2[\mathrm{Fe_2(CO)_6}]_3(\mu_4\text{-S})_2$

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The novel reaction of $(\mu\text{-RS})(\mu\text{-S}^-)\mathrm{Fe_2(CO)_6}$ (**1**) with $\mathrm{Fe_3(CO)_{12}}$ gives a new type of anion, $\{(\mu\text{-RS})(\mu\text{-CO})[\mathrm{Fe_2(CO)_6}]_2(\mu_4\text{-S})\}^-$ (**4**). While anions **4** (R = Me, Et) react with $\mathrm{PhNCS/CF_3CO_2H}$ to give the neutral double-cluster complexes $(\mu\text{-RS})(\mu\text{-PhNHC{=}S})[\mathrm{Fe_2(CO)_6}]_2(\mu_4\text{-S})$ (**6**, R = Me; **7**, R = Et), the reaction of **4** (R = Me, Ph, $p\text{-MeC_6H_4}$) with $\mathrm{CS_2/MeI}$ or $\mathrm{PhCH_2Br}$ affords the neutral double-cluster complexes $(\mu\text{-RS})(\mu\text{-MeSC{=}S})[\mathrm{Fe_2(CO)_6}]_2(\mu_4\text{-S})$ (**8**, R = Me; **10**, R = $p\text{-MeC_6H_4}$; **12**, R = Ph), and $(\mu\text{-RS})(\mu\text{-PhCH_2SC{=}S})$ $[\mathrm{Fe_2(CO)_6}]_2(\mu_4\text{-S})$ (**9**, R = Me; **11**, R = $p\text{-MeC_6H_4}$), respectively. More interestingly, reaction of anions **4** with $\mu\text{-S_2Fe_2(CO)_6}$ produces another new type of anion, $(\mu\text{-RS})(\mu\text{-S}^-)[\mathrm{Fe_2(CO)_6}]_3(\mu_4\text{-S})_2$ (**5**), which reacts further with MeI, EtBr, or $\mathrm{PhCH_2Br}$ to give the neutral triple-cluster complexes $(\mu\text{-RS})(\mu\text{-MeS})[\mathrm{Fe_2(CO)_6}]_3(\mu_4\text{-S})_2$ (**13**, R = Me; **14**, R = $p\text{-MeC_6H_4}$), $(\mu\text{-}p\text{-MeC_6H_4S})(\mu\text{-EtS})[\mathrm{Fe_2(CO)_6}]_3(\mu_4\text{-S})_2$ (**15**), and $(\mu\text{-PhCH_2S})_2[\mathrm{Fe_2(CO)_6}]_3(\mu_4\text{-S})_2$ (**16**), respectively. All these new double- and triple-butterfly clusters have been characterized by combustion analyses and spectroscopy as well as by X-ray diffraction for clusters **6**, **8**, and **16**.

Introduction

Over the past 15−20 years single-butterfly Fe/S cluster anions containing a $\mu\text{-S}^-$ ligand, $(\mu\text{-RS})(\mu\text{-S}^-)\mathrm{Fe_2(CO)_6}$ (**1**)[1−11] (Chart 1), and the corresponding anions containing a μ-CO ligand, $[(\mu\text{-RS})(\mu\text{-CO})\mathrm{Fe_2(CO)_6}]^-$ (**2**)[12−23] (Chart 1), have been demonstrated to play an important role in the development of the chemistry of Fe/S cluster complexes.[1−23] More recently, double-butterfly Fe/S cluster anions containing a $\mu\text{-S}^-$ ligand, $(\mu\text{-RS})(\mu\text{-S}^-)[\mathrm{Fe_2(CO)_6}]_2(\mu_4\text{-S})$ (**3**), a higher homologue of **1** (Chart 1), have been also shown to be important in the development of Fe/S cluster chemistry.[24−26] Closely related to these known anions **1**−**3**, one might naturally ask if the

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Scheme 1

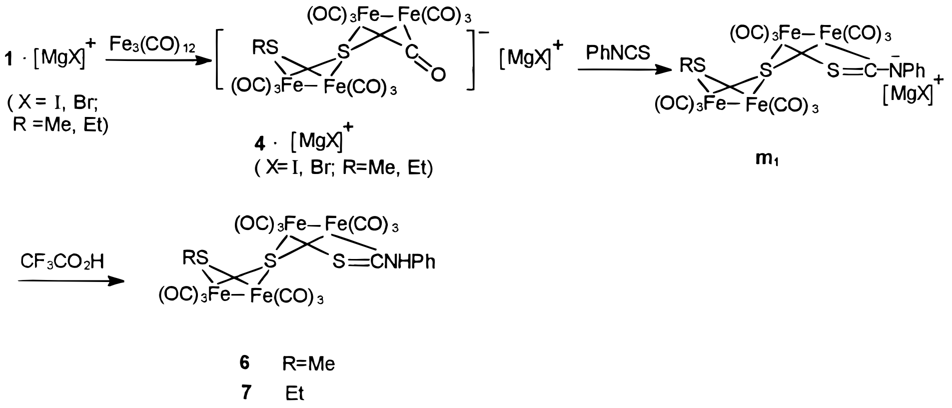
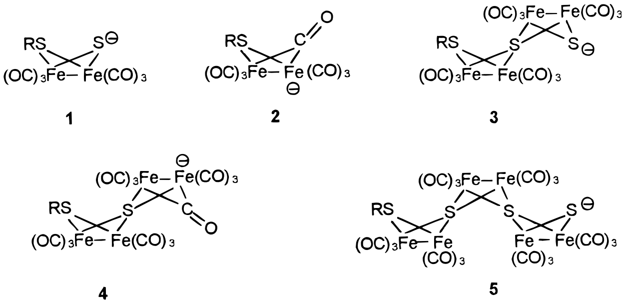


Chart 1



higher homologue of **2**, namely, the double-butterfly Fe/S cluster anions $\{(\mu\text{-RS})(\mu\text{-CO})[Fe_2(CO)_6]_2(\mu_4\text{-S})\}^-$ (**4**), and that of **3**, i.e., the triple-butterfly Fe/S cluster anions $\{(\mu\text{-RS})(\mu\text{-S}^-)[Fe_2(CO)_6]_3(\mu_4\text{-S})_2\}^-$ (**5**) (Chart 1), could also be prepared and if these compounds would be rich in chemical reactivities. It is evident that such questions are both challenging and interesting for further development of the Fe/S cluster chemistry. This article will answer these questions by describing the formation of the novel double- and triple-butterfly cluster anions **4** and **5**, as well as their nucleophilicity toward various electrophiles leading to a series of neutral double- and triple-butterfly Fe/S cluster complexes.

Results and Discussion

Reaction of the Anions $\{(\mu\text{-RS})(\mu\text{-CO})[Fe_2(CO)_6]_2(\mu_4\text{-S})\}^-$ (4) Leading to $(\mu\text{-RS})(\mu\text{-PhNHC=S})[Fe_2(CO)_6]_2(\mu_4\text{-S})$ (6, R = Me; 7, R = Et). Crystal Structure of 6. It was found that the $[MgX]^+$ (X = I, Br) salts of the anions $(\mu\text{-RS})(\mu\text{-S}^-)Fe_2(CO)_6$ (**1**; R = Me, Et) prepared from the complex $\mu\text{-}S_2Fe_2(CO)_6$ and the Grignard reagent MeMgI or EtMgBr[5] reacted in situ with $Fe_3(CO)_{12}$ in THF to give the double-butterfly Fe/S cluster anions **4** (R = Me, Et) as their $[MgX]^+$ (X = I, Br) salts, which reacted in situ further, in a manner similar to their homologue **2**,[27] with the electrophile PhNCS followed by treatment of the intermediate $\mathbf{m_1}$ with CF_3CO_2H to give the double-butterfly Fe/S clusters **6** and **7**, each containing a thiocarbamato ligand, as shown in Scheme 1.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 6

Fe(1)–S(1)	2.251(1)	Fe(1)–S(2)	2.254(1)
Fe(2)–S(1)	2.241(1)	Fe(2)–S(2)	2.267(1)
Fe(3)–S(1)	2.225(1)	Fe(3)–S(3)	2.312(1)
Fe(3)–Fe(4)	2.627(1)	Fe(4)–S(1)	2.250(2)
N(1)–C(1)	1.316(6)	S(2)–C(2)	1.801(5)
S(1)–Fe(1)–S(2)	77.65(5)	S(1)–Fe(1)–Fe(2)	55.37(4)
Fe(3)–S(1)–Fe(2)	134.85(6)	Fe(3)–S(1)–Fe(4)	71.91(4)
Fe(2)–S(1)–Fe(4)	127.56(6)	Fe(2)–S(1)–Fe(1)	68.87(4)
Fe(1)–S(2)–Fe(2)	68.37(4)	N(1)–C(1)–Fe(4)	125.3(4)
S(3)–C(1)–Fe(4)	114.6(2)	S(1)–Fe(2)–S(2)	77.59(5)
S(1)–Fe(2)–Fe(1)	55.76(4)	S(2)–Fe(2)–Fe(1)	55.56(4)
S(1)–Fe(3)–S(3)	86.20(5)	S(3)–Fe(3)–Fe(4)	77.28(4)

Products **6** and **7** derived from anions **4** have been characterized by elemental and spectroscopic analyses, and in particular by an X-ray crystallographic study of **6**. The IR spectra of **6** and **7** showed several absorption bands in the range 2079–1953 cm^{-1} for their terminal carbonyls[28] and one absorption band at about 950 cm^{-1} for their coordinated C=S bonds.[29] In addition, the ^1H NMR spectra of **6** and **7** displayed a singlet at about 8.65 ppm for their NH groups and corresponding signals for their methyl, ethyl, and phenyl groups. To confirm the structures of **6** and **7**, a single-crystal diffraction analysis of **6** was undertaken. Selected bond lengths and angles of **6** are given in Table 1. Figure 1 illustrates its molecular structure, which shows that it has the double-butterfly cluster skeleton Fe(1)Fe(2)S(1)S(2) and Fe(3)-Fe(4)S(1)C(1)S(3) joined to a spiro type of μ_4-S[S(1)] atom. On this double-cluster skeleton, each Fe atom is attached to three terminal carbonyls, whereas the S(2) and C(1) atoms are bonded to an Me group and the N(1) atom of the PhNH group, respectively. While the geometric parameters of the subcluster core Fe(1)-Fe(2)S(1)S(2) are very similar to those of the butterfly Fe_2S_2 cluster cores present in crystallographically characterized double clusters, such as $[(\mu\text{-MeS})Fe_2(CO)_6]_2(\mu_4\text{-S})$[30] and $[(\mu\text{-EtS})Fe_2(CO)_6]_2(\mu_4\text{-S})$,[7] the geometric parameters of another subcluster core, Fe(3)Fe(4)S(1)C-(1)S(3), are similar to those of butterfly Fe_2CSSe (or S) cluster cores present in the single clusters, such as $(\mu\text{-PhSe})(\mu\text{-PhCH}_2\text{SC=S})Fe_2(CO)_6$.[20] For example, the bond

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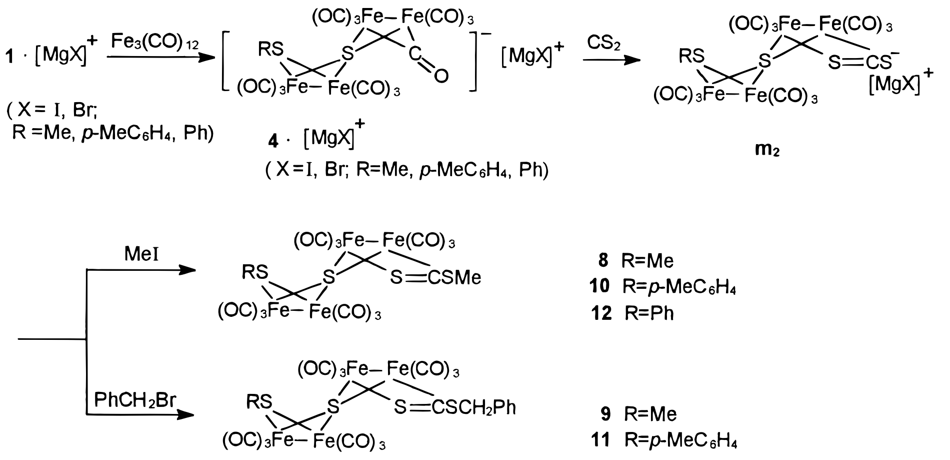
Scheme 2



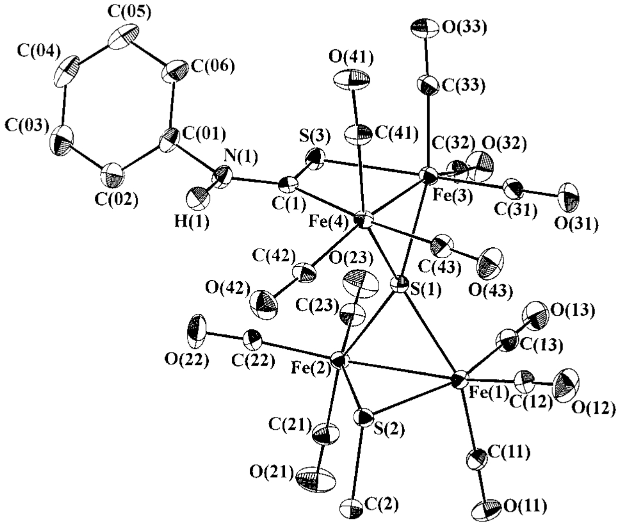
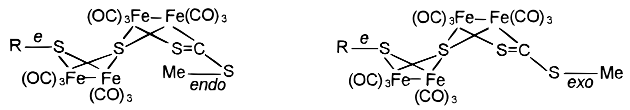


Figure 1. ORTEP drawing of **6** with atom-labeling scheme.

length of Fe(3)−Fe(4) in the subcluster core Fe(3)-Fe(4)S(1)C(1)S(3) of **6** (2.627(1) Å) is slightly shorter than that of Fe−Fe (2.648(3) Å) in the subcluster core Fe_2CSSe of (μ-PhSe)(μ-$PhCH_2SC{=}S$)$Fe_2(CO)_6$,[20] and the bond length of the thiocarbonyl C(1)−S(3) in **6** (1.698(5) Å) is slightly longer than the corresponding thiocarbonyl C=S in (μ-PhSe)(μ-$PhCH_2SC{=}S$)$Fe_2(CO)_6$ (1.63(1) Å).[20] In addition, it can be seen from Figure 1 that C(2) is bonded to S(2) by an equatorial (abbreviated as *e* hereafter) bond; that is, the methyl group is at an equatorial position and thus **6** belongs to an *e*-type of isomer.[31]

Reaction of the Anions {(μ-RS)(μ-CO)[$Fe_2(CO)_6$]$_2$-(μ_4-S)}$^-$ (4) Leading to (μ-RS)(μ-$MeSC{=}S$)[$Fe_2(CO)_6$]$_2$-(μ_4-S) (8, R = Me; 10, R = p-MeC_6H_4; 12, R = Ph) and (μ-RS)(μ-$PhCH_2SC{=}S$)[$Fe_2(CO)_6$]$_2$(μ_4-S) (9, R = Me; 11, R = p-MeC_6H_4). Crystal Structure of 8. We further found that the $[MgX]^+$ (X = I, Br) salts of the anions (μ-RS)(μ-S^-)$Fe_2(CO)_6$ (**1**; R = Me, p-MeC_6H_4, Ph) prepared from μ-$S_2Fe_2(CO)_6$ and the Grignard reagent MeMgI, p-MeC_6H_4MgBr, or PhMgBr[5] reacted in situ with $Fe_3(CO)_{12}$ in THF to give the $[MgX]^+$ (X = I, Br) salts of the anions **4** (R = Me, p-MeC_6H_4, Ph), whose subsequent in situ reaction with CS_2, in a fashion similar to their analogue **2**,[27] followed by treatment of the intermediate $\mathbf{m_2}$ with MeI or $PhCH_2Br$ afforded the double-butterfly clusters **8**−**12**, each containing a dithioformato ligand, as shown in Scheme 2.

Chart 2



Clusters **8**−**12** have been fully characterized by combustion analysis and IR and ^1H NMR spectroscopy, as well as by X-ray diffraction techniques for **8**. The IR spectra of **8**−**12**, similar to those of **6** and **7**, displayed several absorption bands in the range 2084−1983 cm^{-1} for their terminal carbonyls[28] and one absorption band at ca. 1010 cm^{-1} for their coordinated C=S bonds.[29] It is worth pointing out that the ^1H NMR spectra demonstrated that while **8**, **10**, and **12** contain two isomers, **9** and **11** contain only one. This is because the methyl groups attached to S atoms of the dithioformato ligands in the former showed two singlets in the range 2.57−2.69 ppm, whereas the methylenes of benzyl groups in the dithioformato ligands in the latter displayed only one quartet (due to coupling between the two magnetically nonequivalent protons of the CH_2 group) at 4.35 and 4.41 ppm, respectively. As we know, the R group in μ_4-S-containing clusters **8**−**12** should be attached to the bridged S atom only by an equatorial bond to avoid the strong axial−axial steric repulsions.[22,31] In addition, the Me and $PhCH_2$ groups attached to the S atom of dithioformato ligands in **8**−**12** could be located either inside or outside the butterfly subcluster core $Fe_2SC{=}S$, or more exactly, the inside or outside of the dihedral angle of the two wings of the butterfly cluster core Fe_2-$SC{=}S$. Therefore, the two isomers for **8**, **10**, and **12** would be *e*(R) *endo*(Me) and *e*(R) *exo*(Me), as shown in Chart 2. The one isomer for **9** and **11** might be *e*(R) *exo*($PhCH_2$), and the other isomer *e*(R) *endo*($PhCH_2$) for **9** and **11** was not obtained, possibly due to the strong steric repulsions between the larger $PhCH_2$ group and the bulky subcluster moiety (μ-RS)$Fe_2(CO)_6$(μ_4-S).

Fortunately, for **8** one of its two isomers, i.e., isomer *e*(Me) *exo*(Me), has been separated by recrystallization of its isomer mixture (not being separated by TLC) in

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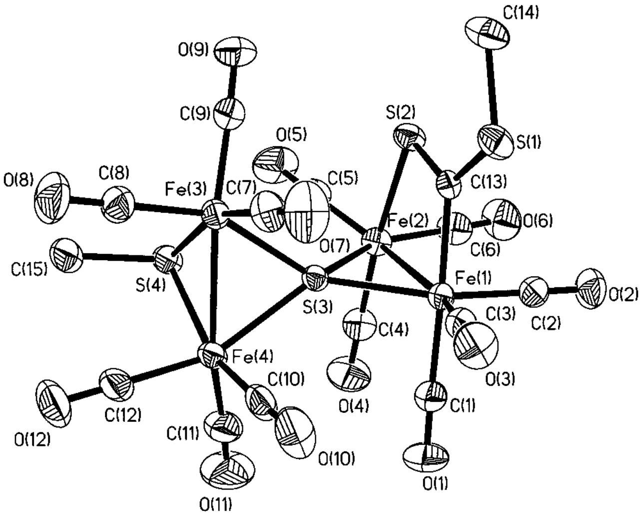


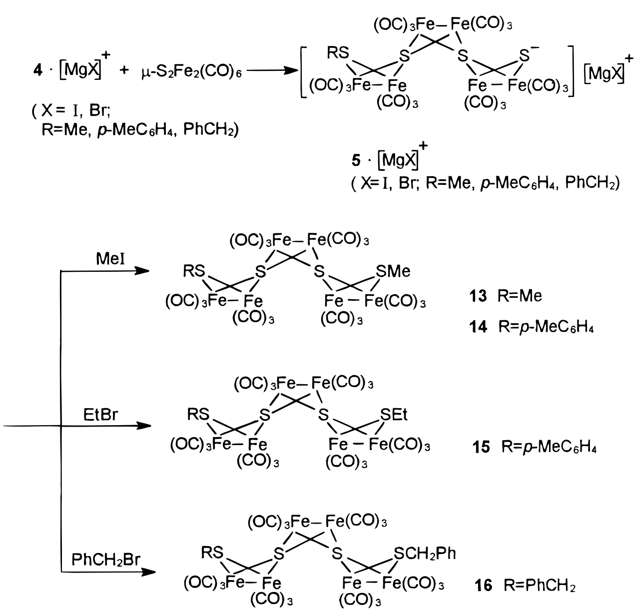
Figure 2. ORTEP drawing of **8** with atom-labeling scheme.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 8

Fe(1)−S(3)	2.2455(10)	Fe(1)−Fe(2)	2.6496(7)
Fe(3)−S(3)	2.2584(10)	Fe(3)−S(4)	2.2768(11)
Fe(3)−Fe(4)	2.5376(8)	Fe(2)−S(3)	2.2433(10)
Fe(2)−S(2)	2.3100(11)	Fe(4)−S(3)	2.2615(9)
Fe(4)−S(4)	2.2660(11)	S(1)−C(14)	1.803(4)
S(3)−Fe(3)−S(4)	76.76(4)	S(3)−Fe(3)−Fe(4)	55.90(3)
S(4)−Fe(3)−Fe(4)	55.84(3)	S(3)−Fe(2)−S(2)	85.91(4)
S(3)−Fe(2)−Fe(1)	53.86(3)	S(2)−Fe(2)−Fe(1)	75.65(3)
S(3)−Fe(4)−S(4)	76.91(4)	S(3)−Fe(4)−Fe(3)	55.79(3)
S(4)−Fe(4)−Fe(3)	56.24(3)	Fe(2)−S(3)−Fe(1)	72.35(3)
Fe(3)−S(3)−Fe(4)	68.31(3)	Fe(4)−S(4)−Fe(3)	67.92(3)

CH_2Cl_2/petroleum ether. This isomer was characterized by ^1H NMR spectroscopy (one singlet at 2.25 ppm for μ-MeS and another singlet at 2.65 ppm for μ-MeSC=S) and was confirmed by X-ray diffraction analysis. The molecular structure of **8** is shown in Figure 2, and its selected bond lengths and angles are presented in Table 2. Figure 2 shows that **8** is very similar to **6**, which consists of the two butterfly subcluster cores Fe(1)Fe(2)S(3)C(13)S(2) and Fe(3)Fe(4)S(3)S(4) joined together to a spiro type of μ_4-S atom, i.e., S(3). Indeed, as seen intuitively from Figure 2, the S(4) atom is bonded to C(15) of the Me group by an equatorial type of bond[31] and C(14) of another Me group is located outside the subcluster core Fe(1)Fe(2)S(3)C(13)S(2); that is, **8** is an *e*(Me) *exo*(Me) isomer. Interestingly, it can be seen from Figure 1 that **6** is also an *e*/*exo* type of isomer: i.e., the *e*(Me) *exo*(PhNH) isomer. Similarly to **9** and **11**, cluster **6** exists only as one such isomer in order to avoid the strong steric repulsions between the larger PhNH group and the subcluster moiety (μ-MeS)$Fe_2(CO)_6$(μ_4-S) in the isomer *e*(Me) *endo*(PhNH). The corresponding geometric parameters of **6** and **8** are very similar. For example, in **6** the bond lengths are Fe(1)−Fe(2) = 2.540(1) Å, Fe(3)−Fe(4) = 2.627(1) Å, and C(1)−S(3) = 1.698(5) Å, whereas in **8** they are Fe(3)−Fe(4) = 2.5376(8) Å, Fe(1)−Fe(2) = 2.6496(7) Å, and C(13)−S(2) = 1.672(4) Å. In addition, in **6** the dihedral angles between Fe(1)Fe(2)S(1) and Fe(1)Fe(2)S(2) and between Fe(3)Fe(4)S(1) and Fe(3)Fe(4)C(1)S(3) are 81.28 and 84.28°, whereas in **8** the angles between Fe(3)Fe(4)S(3) and Fe(3)Fe(4)S(4) and between Fe(1)Fe(2)S(3) and Fe(1)Fe(2)C(13)S(2) are 82.82 and 84.45°. It follows that the coordinated thiocarbonyl in **8** (C(13)−S(2)) is slightly shorter than that of **6** (C(1)−S(3)) but slightly longer than that of (μ-PhSe)(μ-$PhCH_2SC$=S)$Fe_2(CO)_6$ (1.63(1) Å),[20] which are all much longer than that of a typical C=S double bond in free CS_2 (1.554 Å).[32]

Scheme 3



Reaction of the Anions (μ-RS)(μ-S^-)$[Fe_2(CO)_6]_3$(μ_4-S)$_2$ (5) Leading to (μ-RS)(μ-MeS)$[Fe_2(CO)_6]_3$(μ_4-S)$_2$ (13, R = Me; 14, R = *p*-MeC_6H_4), (μ-*p*-MeC_6H_4S)(μ-EtS)$[Fe_2(CO)_6]_3$(μ_4-S)$_2$ (15), and (μ-$PhCH_2S$)$_2$$[Fe_2(CO)_6]_3$($\mu_4$-S)$_2$ (16). Crystal Structure of 16. More interestingly, it was also found that the $[MgX]^+$ (X = I, Br) salts of anions **4** (R = Me, *p*-MeC_6H_4, $PhCH_2$) could react with μ-$S_2Fe_2(CO)_6$ to give the triple-butterfly Fe/S cluster anions **5** (R = Me, *p*-MeC_6H_4, $PhCH_2$), higher homologues of anions **3**, as their $[MgX]^+$ (X = I, Br) salts. Treatment of this type of anion in situ with MeI, EtBr, or $PhCH_2Br$ afforded not only symmetrical neutral triple-butterfly Fe/S cluster complexes **13** and **16** but also the unsymmetrical complexes **14** and **15**, as shown in Scheme 3.

Products **13**−**16** generated from anions **5** have been fully characterized by elemental analysis and IR and ^1H NMR spectroscopy, as well as by X-ray diffraction of **16**. The IR spectra of **13**−**16** exhibited two or four absorption bands in the range 2056−1986 cm^{-1} for their terminal carbonyls.[28] In addition, the ^1H NMR spectra of **13**−**16** displayed only one signal or one set of signals for their Me, Et, $PhCH_2$, and *p*-MeC_6H_4 groups. For example, in the ^1H NMR spectrum of **13** there is only one singlet at 2.20 ppm for the magnetically equivalent three protons in each of its two identical Me groups, whereas in that of **16** there is only one quartet at 3.66 ppm for the magnetically nonequivalent two protons in each of its two methylenes in benzyl groups. This observation is completely consistent with the fact that the μ_4-S-containing butterfly Fe/S clusters have only one isomer in which the substituents are attached to bridged S atoms by an equatorial type of bond.[22,31]

Figure 3 shows the ORTEP drawing of the structure of **16**. Table 3 lists its selected bond lengths and angles.

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[32] Butler, I. S.; Fenster, A. E. *J. Organomet. Chem.* **1974**, *66*, 161.

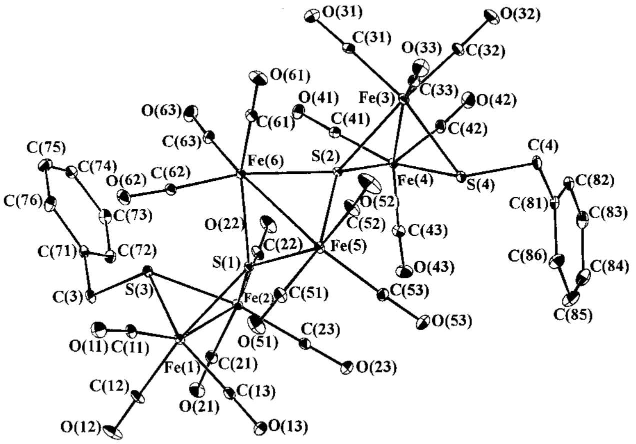

Figure 3. ORTEP drawing of **16** with atom-labeling scheme.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 16

Fe(1)−Fe(2)	2.516(2)	Fe(1)−S(3)	2.264(2)
Fe(1)−S(1)	2.276(2)	Fe(2)−S(3)	2.266(2)
Fe(2)−S(1)	2.270(2)	Fe(3)−S(4)	2.272(3)
Fe(3)−S(2)	2.275(2)	Fe(4)−S(4)	2.263(2)
Fe(4)−S(2)	2.270(2)	Fe(5)−S(1)	2.253(2)
Fe(5)−S(2)	2.264(2)	Fe(5)−Fe(6)	2.575(2)
Fe(6)−S(1)	2.258(2)	Fe(6)−S(2)	2.260(2)
S(3)−Fe(1)−Fe(2)	56.29(6)	S(4)−Fe(3)−S(2)	76.64(8)
S(1)−Fe(1)−Fe(2)	56.29(6)	S(2)−Fe(3)−Fe(4)	56.41(6)
S(4)−Fe(4)−S(2)	76.91(8)	S(1)−Fe(6)−S(2)	82.56(7)
S(1)−Fe(5)−S(2)	82.58(7)	S(2)−Fe(6)−Fe(5)	55.39(6)
S(2)−Fe(5)−Fe(6)	55.24(6)	Fe(5)−S(1)−Fe(6)	69.60(7)
Fe(1)−S(3)−Fe(2)	67.48(7)	Fe(2)−S(1)−Fe(1)	67.22(6)
Fe(4)−S(4)−Fe(3)	67.14(7)	Fe(6)−S(2)−Fe(5)	69.36(6)

It can be seen in Figure 3 that **16** comprises, indeed, the three butterfly Fe_2S_2 subcluster cores Fe(1)Fe(2)-S(1)S(3), Fe(5)Fe(6)S(1)S(2), and Fe(3)Fe(4)S(2)S(4) joined together by two μ_4-S (S(1) and S(2)) atoms. In addition, each Fe atom has three terminal CO ligands, and each benzyl group is bonded to S(3) and S(4) atoms by an equatorial bond, respectively. This molecule is chiral and has a C_2 axis passing through the two midpoints of Fe(5)−Fe(6) and S(1)···S(2). It is noteworthy that the geometric parameters of the middle subcluster core are somewhat different from those of the two side subcluster cores. For example, the bond length of Fe(1)−Fe(2) (2.516(2) Å) or Fe(3)−Fe(4) (2.508(2) Å) is shorter than that of Fe(5)−Fe(6) (2.575(2) Å). The dihedral angles between Fe(1)−Fe(2)−S(1) and Fe(1)−Fe(2)−S(3) (95.64°) and between Fe(3)−Fe(4)−S(2) and Fe(3)−Fe(4)−S(4) (88.22°) are larger than that between Fe(5)−Fe(6)−S(1) and Fe(5)−Fe(6)−S(2) (73.23°). In fact, the basic geometric parameters of **16** are comparable with those of butterfly Fe/S cluster complexes, such as (μ-EtS)(μ-PhS)-$[Fe_2(CO)_6]_2(\mu_4\text{-}S)$[33] and ($\mu$-*t*-BuS)$_2[Fe_2(CO)_6]_3(\mu_4\text{-}S)_2$.[24]

Conclusions

We have successfully synthesized two novel types of butterfly Fe/S cluster anions, $\{(\mu\text{-RS})(\mu\text{-CO})[Fe_2(CO)_6]_2(\mu_4\text{-S})\}^-$ (**4**) and $(\mu\text{-RS})(\mu\text{-S}^-)[Fe_2(CO)_6]_3(\mu_4\text{-S})_2$ (**5**), through two new reactions of the anions $(\mu\text{-RS})(\mu\text{-S}^-)Fe_2(CO)_6$ (**1**) with $Fe_3(CO)_{12}$ and anions **4** with $\mu\text{-}S_2Fe_2(CO)_6$, respectively. Anions **4** and **5** have proved to be very useful in the synthesis of neutral double- and triple-butterfly Fe/S cluster complexes **6**−**16**, which were fully characterized by spectroscopy and X-ray diffraction. Considering that the double- and triple-butterfly anions **4** and **5** are produced by reaction of the single-butterfly anions $(\mu\text{-RS})(\mu\text{-S}^-)Fe_2(CO)_6$ (**1**) with $Fe_3(CO)_{12}$ and the double-butterfly anions **4** with $\mu\text{-}S_2Fe_2(CO)_6$, respectively, we might imagine that the higher homologues of **4** and **5** could be also produced by reaction of **3** with $Fe_3(CO)_{12}$ and by further reaction with $\mu\text{-}S_2Fe_2(CO)_6$. In addition, considering that **6**−**16** can be yielded from **4** and **5**, the higher homologues of **6**−**16** could be similarly produced by subsequent reactions of the higher homologues of **4** and **5** with corresponding electrophiles. Therefore, these two novel types of anions **4** and **5**, as well as the two new reactions of anions **1** with $Fe_3(CO)_{12}$ and anions **4** with $\mu\text{-}S_2Fe_2(CO)_6$, are very important for further development of Fe/S cluster chemistry.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of prepurified nitrogen using standard Schlenk and vacuum-line techniques. Tetrahydrofuran (THF) was distilled from Na/benzophenone ketyl under nitrogen. $Fe_3(CO)_{12}$,[34] $\mu\text{-}S_2Fe_2(CO)_6$,[35] and Grignard reagents RMgX[36] were prepared according to literature procedures. PhNCS, CF_3CO_2H, CS_2, MeI, EtBr, PhBr, $PhCH_2Br$, and *p*-MeC_6H_4Br were of commercial origin and used without further purification. Preparative TLC was carried out on glass plates (26 × 20 × 0.25 cm) coated with silica gel H (10−40 μm). IR spectra were recorded on a Nicolet FT-IR infrared spectrophotometer. ^1H NMR spectra were recorded on a Bruker AC-P200 NMR spectrometer. C/H analyses were performed on a Yanaco CHN Corder MT-3 analyzer. Melting points were determined on a Yanaco MP-500 apparatus and were uncorrected.

Preparation of (μ-MeS)(μ-PhNHC═S)$[Fe_2(CO)_6]_2(\mu_4\text{-S})$ (6). A 100 mL two-necked flask equipped with a stir bar, an N_2 inlet tube, and a serum cap was charged with 0.172 g (0.5 mmol) of $\mu\text{-}S_2Fe_2(CO)_6$ and 10 mL of THF. The resulting red solution was stirred and cooled to −78 °C using a dry ice/acetone bath. Into this solution was injected a solution of $MeMgI/Et_2O$ by a syringe until the mixture turned to emerald green. The mixture was stirred for an additional 20 min, and 0.252 g (0.5 mmol) of $Fe_3(CO)_{12}$ was added. After the bath was removed, the mixture was naturally warmed to room temperature and then was stirred at this temperature for 2 h to give a red-brown solution of the $[MgI]^+$ salt of the anion $\{(\mu\text{-MeS})(\mu\text{-CO})[Fe_2(CO)_6]_2(\mu_4\text{-S})\}^-$. To this solution was added 0.12 mL (1.0 mmol) of PhNCS, and the mixture was stirred for 2 h. Then, 0.08 mL (1.0 mmol) of CF_3CO_2H was added and the mixture was stirred for an additional 2 h. Solvent was removed under reduced pressure. The residue was subjected to TLC separation using CH_2Cl_2/petroleum ether (v/v, 1/4) as eluent. From the main orange-red band 0.100 g (26%) of **6** was obtained as an orange-red solid. Mp: 146 °C dec. Anal. Calcd for $C_{20}H_9Fe_4NO_{12}S_3$: C, 31.00; H, 1.17; N, 1.81. Found: C, 30.96; H, 1.20; N, 1.86. IR (KBr disk): $\nu_{C\equiv O}$ 2079 (s), 2054 (vs), 2030 (vs), 1986 (vs), 1953 (s); $\nu_{C=S}$ 944 (w) cm^{-1}. ^1H NMR ($CDCl_3$): 2.25 (s, 3H, CH_3), 7.37 (s, 5H, C_6H_5), 8.70 (s, 1H, NH) ppm.

Preparation of (μ-EtS)(μ-PhNHC═S)$[Fe_2(CO)_6]_2(\mu_4\text{-S})$ (7). The same procedure as that for **6** was followed, but

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[34] King, R. B. *Organometallic Syntheses; Transition-Metal Compounds*; Academic Press: New York, 1965; Vol. 1, p 95.

[35] Seyferth, D.; Henderson, R. S.; Song, L.-C. *Organometallics* **1982**, *1*, 125.

[36] Gilman, H.; Zoellner, E. A.; Dickey, J. B. *J. Am. Chem. Soc.* **1929**, *51*, 1576.

$\text{EtMgBr/Et}_2\text{O}$ was used instead of $\text{MeMgI/Et}_2\text{O}$ to prepare the $[\text{MgBr}]^+$ salt of the anion $\{(\mu\text{-EtS})(\mu\text{-CO})[\text{Fe}_2(\text{CO})_6]_2(\mu_4\text{-S})\}^-$. From the main orange-red band 0.083 g (21%) of **7** was obtained as a orange-red solid. Mp: 140 °C dec. Anal. Calcd for $\text{C}_{21}\text{H}_{11}\text{Fe}_4\text{NO}_{12}\text{S}_3$: C, 31.97; H, 1.41; N, 1.78. Found: C, 32.09; H, 1.41; N, 1.79. IR (KBr disk): $\nu_{\text{C}\equiv\text{O}}$ 2081 (s), 2052 (vs), 2029 (vs), 2008 (s), 1993 (vs) 1975 (s); $\nu_{\text{C=S}}$ 948 (w) cm^{-1}. ^1H NMR (CDCl_3): 1.43 (t, J = 7.2 Hz, 3H, CH_3). 2.55 (q, J = 7.2 Hz, 2H, CH_2), 7.24−7.37 (m, 5H, C_6H_5), 8.63 (s, 1H, NH) ppm.

Preparation of $(\mu\text{-MeS})(\mu\text{-MeSC=S})[\text{Fe}_2(\text{CO})_6]_2(\mu_4\text{-S})$ (8). To the $[\text{MgI}]^+$ salt of the anion $\{(\mu\text{-MeS})(\mu\text{-CO})[\text{Fe}_2(\text{CO})_6]_2(\mu_4\text{-S})\}^-$, prepared as described above, was added 0.10 mL (1.8 mmol) of CS_2. The mixture was stirred at room temperature for 1 h, and then 0.10 mL (1.6 mmol) of MeI was added. The mixture was stirred for an additional 12 h. Solvent was removed under reduced pressure. The residue was subjected to TLC separation using petroleum ether as eluent. From the main orange-red band 0.170 g (47%) of **8** was obtained as an orange-red solid. Mp: 37−38 °C. Anal. Calcd for $\text{C}_{15}\text{H}_6\text{Fe}_4\text{O}_{12}\text{S}_4$: C, 24.68; H, 0.83. Found: C, 24.54; H, 0.91. IR (KBr disk): $\nu_{\text{C}\equiv\text{O}}$ 2084 (s), 2055 (vs), 2033 (vs), 1991 (vs); $\nu_{\text{C=S}}$ 1019 (m) cm^{-1}. ^1H NMR (CDCl_3): 2.21, 2.24 (s, s, 3H, SCH_3), 2.57, 2.65 (s, s, 3H, S=CSCH_3) ppm.

Preparation of $(\mu\text{-MeS})(\mu\text{-PhCH}_2\text{SC=S})[\text{Fe}_2(\text{CO})_6]_2(\mu_4\text{-S})$ (9). To the $[\text{MgI}]^+$ salt of the anion $\{(\mu\text{-MeS})(\mu\text{-CO})[\text{Fe}_2(\text{CO})_6]_2(\mu_4\text{-S})\}^-$, prepared as described above, was added 0.10 mL (1.8 mmol) of CS_2. The mixture was stirred at room temperature for 1 h, and then 0.18 mL (1.5 mmol) of PhCH_2Br was added. The mixture was stirred for an additional 12 h. The solvent was removed under reduced pressure. The residue was subjected to TLC separation using petroleum ether as eluent. From the main orange-red band 0.180 g (45%) of **9** was obtained as an orange-red solid. Mp: 128 °C dec. Anal. Calcd for $\text{C}_{21}\text{H}_{10}\text{Fe}_4\text{O}_{12}\text{S}_4$: C, 31.29; H, 1.25. Found: C, 31.24; H, 1.36. IR (KBr disk): $\nu_{\text{C}\equiv\text{O}}$ 2081 (s), 2054 (vs), 2036 (vs), 2013 (s), 1983 (vs); $\nu_{\text{C=S}}$ 1009 (m) cm^{-1}. ^1H NMR (CDCl_3): 2.25 (s, 3H, CH_3), 4.35 (q, AB pattern, 2H, CH_2), 7.24−7.30 (m, 5H, C_6H_5) ppm.

Preparation of $(\mu\text{-}p\text{-MeC}_6\text{H}_4\text{S})(\mu\text{-MeSC=S})[\text{Fe}_2(\text{CO})_6]_2(\mu_4\text{-S})$ (10). To the $[\text{MgBr}]^+$ salt of the anion $\{(\mu\text{-}p\text{-MeC}_6\text{H}_4\text{S})(\mu\text{-CO})[\text{Fe}_2(\text{CO})_6]_2(\mu_4\text{-S})\}^-$, prepared similarly from $(p\text{-MeC}_6\text{H}_4)\text{MgBr/Et}_2\text{O}$, $\mu\text{-S}_2\text{Fe}_2(\text{CO})_6$, and $\text{Fe}_3(\text{CO})_{12}$, was added 0.10 mL (1.8 mmol) of CS_2. The mixture was stirred at room temperature for 1 h, and then 0.10 mL (1.6 mmol) of MeI was added. The mixture was stirred for an additional 12 h. Solvent was removed under reduced pressure. The residue was subjected to TLC separation using petroleum ether as eluent. From the main orange-red band 0.208 g (52%) of **10** was obtained as an orange-red solid. Mp: 153 °C dec. Anal. Calcd for $\text{C}_{21}\text{H}_{10}\text{Fe}_4\text{O}_{12}\text{S}_4$: C, 31.29; H, 1.25. Found: C, 31.09; H, 1.11. IR (KBr disk): $\nu_{\text{C}\equiv\text{O}}$ 2084 (s), 2057 (vs), 2034 (vs), 1992 (vs); $\nu_{\text{C=S}}$ 1017 (m) cm^{-1}. ^1H NMR (CDCl_3): 2.29 (s, 3H, CH_3), 2.62, 2.69 (s, s, 3H, S=CSCH_3), 7.01−7.24 (m, 4H, C_6H_4) ppm.

Preparation of $(\mu\text{-}p\text{-MeC}_6\text{H}_4\text{S})(\mu\text{-PhCH}_2\text{SC=S})[\text{Fe}_2(\text{CO})_6]_2(\mu_4\text{-S})$ (11). To the $[\text{MgBr}]^+$ salt of the anion $\{(\mu\text{-}p\text{-MeC}_6\text{H}_4\text{S})(\mu\text{-CO})[\text{Fe}_2(\text{CO})_6]_2(\mu_4\text{-S})\}^-$ was added 0.10 mL (1.8 mmol) of CS_2. The mixture was stirred at room temperature for 1 h, and then 0.18 mL (1.5 mmol) of PhCH_2Br was added. The mixture was stirred for an additional 12 h. Solvent was removed under reduced pressure. The residue was subjected to TLC separation using petroleum ether as eluent. From the main orange-red band 0.221 g (50%) of **11** was obtained as an orange-red solid. Mp: 78−79 °C. Anal. Calcd for $\text{C}_{27}\text{H}_{14}\text{Fe}_4\text{O}_{12}\text{S}_4$: C, 36.76; H, 1.60. Found: C, 37.02; H, 1.69. IR (KBr disk): $\nu_{\text{C}\equiv\text{O}}$ 2082 (s), 2057 (vs), 2033 (vs), 1992 (vs); $\nu_{\text{C=S}}$ 1014 (m) cm^{-1}. ^1H NMR (CDCl_3): 2.29 (s, 3H, CH_3), 4.41 (q, AB pattern, 2H, CH_2), 7.01−7.33 (m, 9H, C_6H_5, C_6H_4) ppm.

Preparation of $(\mu\text{-PhS})(\mu\text{-MeSC=S})[\text{Fe}_2(\text{CO})_6]_2(\mu_4\text{-S})$ (12). To the $[\text{MgBr}]^+$ salt of the anion $\{(\mu\text{-PhS})(\mu\text{-CO})[\text{Fe}_2(\text{CO})_6]_2(\mu_4\text{-S})\}^-$, prepared similarly from $\text{PhMgBr/Et}_2\text{O}$, $\mu\text{-S}_2\text{Fe}_2(\text{CO})_6$, and $\text{Fe}_3(\text{CO})_{12}$, was added 0.10 mL (1.8 mmol) of CS_2. The mixture was stirred at room temperature for 1 h, and then 0.10 mL (1.6 mmol) of MeI was added. The mixture was stirred for an additional 12 h. Solvent was removed under reduced pressure. The residue was subjected to TLC separation using petroleum ether as eluent. From the main orange-red band 0.188 g (48%) of **12** was obtained as an orange-red solid. Mp: 164 °C dec. Anal. Calcd for $\text{C}_{20}\text{H}_8\text{Fe}_4\text{O}_{12}\text{S}_4$: C, 30.33; H, 1.02. Found: C, 30.04; H, 0.88. IR (KBr disk): $\nu_{\text{C}\equiv\text{O}}$ 2084 (m), 2058 (vs), 2036 (vs), 1998 (vs), 1997 (s); $\nu_{\text{C=S}}$ 1020 (m) cm^{-1}. ^1H NMR (CDCl_3): 2.62, 2.69 (s, s, 3H, CH_3), 7.24−7.37 (m, 5H, C_6H_5) ppm.

Table 4. Crystal Data and Structural Refinement Details for 6, 8, and 16

	6	**8**	**16**
formula	$\text{C}_{20}\text{H}_9\text{Fe}_4\text{NO}_{12}\text{S}_3$	$\text{C}_{15}\text{H}_6\text{Fe}_4\text{O}_{12}\text{S}_4$	$\text{C}_{32}\text{H}_{14}\text{Fe}_6\text{O}_{18}\text{S}_4$
fw	774.86	729.84	1149.77
cryst dimens, mm	0.60 × 0.50 × 0.30	0.20 × 0.25 × 0.30	1.00 × 0.30 × 0.10
cryst syst	monoclinic	triclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
a, Å	10.816(4)	9.3683(9)	10.281(4)
b, Å	15.820(3)	9.5511(9)	29.454(7)
c, Å	16.541(3)	15.6898(15)	13.971(4)
α, deg		75.976(2)	
β, deg	95.94(2)	80.678(2)	92.24(2)
γ, deg		71.735(2)	
V, Å^3	2815(1)	1287.8(2)	4227(2)
Z	4	2	4
D_{calcd}, g cm^{-3}	1.83	1.882	1.81
$F(000)$	1536	720	2280
μ(Mo Kα), cm^{-1}	22.93	25.87	22.66
temp, K	296	298	296
wavelength, Å	0.710 69	0.710 73	0.710 69
scan type	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
$2\theta_{\text{max}}$, deg	52.0	50.06	52.0
no. of observns, n	4025	4535	5041
no. of variables, p	361	316	541
R	0.039	0.0342	0.050
R_w	0.060	0.0788	0.075
goodness of fit	1.76	0.985	1.81
largest diff peak, e Å^{-3}	0.94	0.324	0.76

Preparation of $(\mu\text{-MeS})_2[\text{Fe}_2(\text{CO})_6]_3(\mu_4\text{-S})_2$ (13). The $[\text{MgI}]^+$ salt of the anion $\{(\mu\text{-MeS})(\mu\text{-CO})[\text{Fe}_2(\text{CO})_6]_2(\mu_4\text{-S})\}^-$ as described above was cooled to −78 °C using a dry ice/acetone bath, and then 0.172 g (0.5 mmol) of $\mu\text{-S}_2\text{Fe}_2(\text{CO})_6$ was added. The mixture was stirred for 2 h at this temperature to give the $[\text{MgI}]^+$ salt of the anion $(\mu\text{-MeS})(\mu\text{-S}^-)[\text{Fe}_2(\text{CO})_6]_3(\mu_4\text{-S})_2$ and then was warmed to room temperature. To this mixture was added 0.10 mL (1.6 mmol) of MeI, and the new mixture was stirred for 14 h. Solvent was removed under reduced pressure. The residue was subjected to TLC separation using petroleum ether as eluent. From the main red band 0.150 g (30%) of **13** was obtained as a red solid. Mp: 153 °C dec. Anal. Calcd for $\text{C}_{20}\text{H}_6\text{Fe}_6\text{O}_{18}\text{S}_4$: C, 24.08; H, 0.61. Found: C, 23.87; H, 0.86. IR (KBr disk): $\nu_{\text{C}\equiv\text{O}}$ 2056 (vs), 2037 (vs), 2018 (s), 1986 (vs) cm^{-1}. ^1H NMR (CDCl_3): 2.20 (s, 6H, 2CH_3) ppm.

Preparation of $(\mu\text{-}p\text{-MeC}_6\text{H}_4\text{S})(\mu\text{-MeS})[\text{Fe}_2(\text{CO})_6]_3(\mu_4\text{-S})_2$(14). To the $[\text{MgBr}]^+$ salt of the anion $(\mu\text{-}p\text{-MeC}_6\text{H}_4\text{S})(\mu\text{-S}^-)[\text{Fe}_2(\text{CO})_6]_3(\mu_4\text{-S})_2$, prepared similarly from the $[\text{MgBr}]^+$ salt of the anion $\{(\mu\text{-}p\text{-MeC}_6\text{H}_4\text{S})(\mu\text{-CO})[\text{Fe}_2(\text{CO})_6]_2(\mu_4\text{-S})\}^-$ and $\mu\text{-S}_2\text{Fe}_2(\text{CO})_6$, was added 0.10 mL (1.6 mmol) of MeI at room temperature, and the new mixture was stirred for 14 h. Through the same workup as for **13**, 0.252 g (47%) of **14** was obtained as a red solid. Mp: 171 °C dec. Anal. Calcd for $\text{C}_{26}\text{H}_{10}\text{Fe}_6\text{O}_{18}\text{S}_4$: C, 29.09; H, 0.94. Found: C, 29.10; H, 0.90. IR (KBr disk): $\nu_{\text{C}\equiv\text{O}}$ 2041 (vs), 1987 (vs) cm^{-1}. ^1H NMR (CDCl_3): 2.21 (s, 3H, CH_3), 2.28 (s, 3H, SCH_3), 7.02−7.24 (m, 4H, C_6H_4) ppm.

Preparation of $(\mu\text{-}p\text{-MeC}_6\text{H}_4\text{S})(\mu\text{-EtS})[\text{Fe}_2(\text{CO})_6]_3(\mu_4\text{-S})_2$ (15). To the $[\text{MgBr}]^+$ salt of the anion $(\mu\text{-}p\text{-MeC}_6\text{H}_4\text{S})(\mu\text{-S}^-)[\text{Fe}_2(\text{CO})_6]_3(\mu_4\text{-S})_2$, prepared similarly as described above, was added 0.12 mL (1.5 mmol) of EtBr at room temperature, and the new mixture was stirred for 14 h. Through the same workup as for **13**, 0.164 g (30%) of **15** was obtained as a red solid. Mp: 118−120 °C. Anal. Calcd for $C_{27}H_{12}Fe_6O_{18}S_4$: C, 29.81; H, 1.11. Found: C, 29.94; H, 0.96. IR (KBr disk): $\nu_{C\equiv O}$ 2043 (vs), 1993 (vs) cm^{-1}. ^{1}H NMR ($CDCl_3$): 1.42 (t, $J = 7.0$ Hz, 3H, CH_3), 2.28 (s, 3H, p-CH_3), 2.53 (q, $J = 7.0$ Hz, 2H, CH_2), 7.02, 7.06, 7.21, 7.24 (q, A_2B_2 pattern, 4H, C_6H_4) ppm.

Preparation of (μ-PhCH$_2$S)$_2$[Fe$_2$(CO)$_6$]$_3$(μ_4-S)$_2$ (16). The solution of the [MgBr]$^+$ salt of the anion {(μ-PhCH$_2$S)(μ-CO)[Fe$_2$(CO)$_6$]$_2$(μ_4-S)}$^-$ was prepared from PhCH$_2$MgBr/Et$_2$O, μ-S$_2$Fe$_2$(CO)$_6$, and Fe$_3$(CO)$_{12}$, according to a procedure similar to that for the [MgI]$^+$ salt of {(μ-MeS)(μ-CO)[Fe$_2$(CO)$_6$]$_2$(μ_4-S)}$^-$ described above, and then was cooled to −78 °C using a dry ice/acetone bath. To this solution was added 0.172 g (0.5 mmol) of μ-S$_2$Fe$_2$(CO)$_6$, and then the mixture was stirred for 2 h at this temperature to give the [MgBr]$^+$ salt of the anion (μ-PhCH$_2$S)(μ-S$^-$)[Fe$_2$(CO)$_6$]$_3$(μ_4-S)$_2$. After the mixture was warmed to room temperature, 0.18 mL (1.5 mmol) of PhCH$_2$Br was added and the new mixture was stirred for 14 h. Solvent was removed under reduced pressure. The residue was subjected to TLC separation using petroleum ether as eluent. From the main red band 0.328 g (57%) of **16** was obtained as a red solid. Mp: 175 °C dec. Anal. Calcd for $C_{32}H_{14}Fe_6O_{18}S_4$: C, 33.43; H, 1.23. Found: C, 33.12; H, 1.23. IR (KBr disk): $\nu_{C\equiv O}$ 2041 (vs), 1988 (vs) cm^{-1}. ^{1}H NMR ($CDCl_3$): 3.66 (q, AB pattern, 4H, 2CH_2), 7.33 (s, 10H, 2C_6H_5) ppm.

X-ray Structure Determinations of 6, 8, and 16. Single crystals of **6**, **8**, and **16** suitable for X-ray diffraction analyses were grown by slow evaporation of their CH_2Cl_2/hexane solutions at about 4 °C. Each crystal was mounted on a Rigaku AFC5R or a Bruker SMART 1000 automated diffractometer equipped with a graphite monochromator with Mo Kα radiation ($\lambda = 0.710\ 69$ or 0.710 73 Å). Details of the crystal data, data collection, and structure refinements are summarized in Table 4.

The structures were solved by direct methods and expanded by Fourier techniques. The final refinements were accomplished by the full-matrix least-squares method with anisotropic thermal parameters for non-hydrogen atoms. The calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corp. for **6** and **16** and using the SHELXTL-97 program for **8**.

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Supporting Information Available: Full tables of crystal data, atomic coordinates and thermal parameters, and bond lengths and angles, in CIF format, for **6**, **8** and **16**. This material is available free of charge via the Internet at http://pubs. acs.org.

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