Novel μ-CO-Containing Butterfly Fe/S Cluster Anions Generated from Tetrathiols, $Fe_3(CO)_{12}$, and Et_3N: Their Reactions with Electrophiles To Give Neutral Butterfly Fe/S Cluster Complexes

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Tetrathiol 1,2,4,5-$(HSCH_2)_4C_6H_2$ reacted with $Fe_3(CO)_{12}$ and Et_3N followed by treatment of the intermediate μ-CO-containing tetraanion $\{[(\mu\text{-CO})Fe_2(CO)_6]_4[1,2,4,5\text{-}(\mu\text{-SCH}_2)_4C_6H_2]\}^{4-}$ (**7**) with 2-furancarbonyl chloride to give quadruple-butterfly complex $[(\mu\text{-}\sigma,\pi\text{-}C_4H_3O)Fe_2(CO)_6]_4[1,2,4,5\text{-}(\mu\text{-SCH}_2)_4C_6H_2]$ (**9**), whereas triple-butterfly complex $[(\mu\text{-Ph}_2P)Fe_2(CO)_6]_2[Fe_2(CO)_6][1,2,4,5\text{-}(\mu\text{-SCH}_2)_4C_6H_2]$ (**11**) could be produced by reaction of Ph_2PCl with the μ-CO-containing dianion $\{[(\mu\text{-CO})Fe_2(CO)_6]_2[Fe_2(CO)_6][1,2,4,5\text{-}(\mu\text{-SCH}_2)_4C_6H_2]\}^{2-}$ (**10**) generated in situ from the initially formed tetraanion **7**. Similarly, the triple-butterfly complexes $[(\mu\text{-Ph}_2P)Fe_2(CO)_6]_2[Fe_2(CO)_6][(\mu\text{-SCH}_2)_4C]$ (**14**) and $[(\mu\text{-}\sigma,\pi\text{-}CH_2CH{=}CH_2)Fe_2(CO)_6]_2[Fe_2(CO)_6][(\mu\text{-SCH}_2)_4C]$ (**16**) were produced by reaction of Ph_2PCl or $CH_2{=}CHCH_2Br$ with the μ-CO-containing dianion $\{[(\mu\text{-CO})Fe_2(CO)_6]_2[Fe_2(CO)_6][(\mu\text{-SCH}_2)_4C]\}^{2-}$ (**13**) formed in situ from tetraanion $\{[(\mu\text{-CO})Fe_2(CO)_6]_4[(\mu\text{-SCH}_2)_4C]\}^{4-}$ (**12**) generated initially by reaction of tetrathiol $C(CH_2SH)_4$ with $Fe_3(CO)_{12}$ and Et_3N. The double-butterfly complex $[Fe_2(CO)_6]_2[(\mu\text{-SCH}_2)_4C]$ (**15**) derived in situ from dianion **13** was also isolated as a minor product along with major products **14** and **15**. All the new complexes **9**, **11**, and **14**−**16** were characterized by elemental analysis and IR and NMR spectroscopy, as well as by X-ray crystallography for **9**, **11**, **14**, and **15**.

Introduction

Butterfly Fe/S cluster complexes have attracted great interest in view of their unique structures and varied chemical reactivities,[1,2] and particularly their recent widespread uses to serve as the structural and functional models for the active site of [FeFe]-hydrogenases.[3,4] In 1985 Seyferth first prepared the single-butterfly one-μ-CO-containing Fe/S cluster monoanions $[(\mu\text{-CO})(\mu\text{-RS})Fe_2(CO)_6]^-$ (**1**) via reaction of monomercaptan RSH with $Fe_3(CO)_{12}$ in the presence of Et_3N.[5] Since then, we have prepared various butterfly μ-CO-containing Fe/S cluster anions, such as the double-butterfly two-μ-CO-containing dianions $\{[(\mu\text{-CO})Fe_2(CO)_6]_2(\mu\text{-SZS-}\mu)\}^{2-}$ (**2**: Z = $CH_2(CH_2OCH_2)_2CH_2$, $CH_2(CH_2OCH_2)_3CH_2$) produced through reaction of dithiols HSZSH with $Fe_3(CO)_{12}$ and Et_3N,[6] the triple-butterfly three-μ-CO-containing trianions $\{[(\mu\text{-CO})Fe_2(CO)_6]_3[(\mu\text{-SCH}_2CH_2)_3N]\}^{3-}$ (**3**) and $\{[(\mu\text{-CO})Fe_2(CO)_6]_3[1,3,5\text{-}(\mu\text{-SCH}_2)_3C_6H_3]\}^{3-}$ (**4**) yielded by reaction of trithiol $N(CH_2CH_2SH)_3$ or 1,3,5-$(HSCH_2)_3C_6H_3$ with $Fe_3(CO)_{12}$ and Et_3N,[7] and the triple-butterfly three-μ-CO-containing trianion $\{[(\mu\text{-CO})Fe_2(CO)_6]_3[(\mu\text{-SCH}_2)_3CMe]\}^{3-}$ (**5**) and the double-butterfly one-μ-CO-containing monoanion $\{[(\mu\text{-CO})Fe_2(CO)_6][Fe_2(CO)_6][(\mu\text{-SCH}_2)_2CMe]\}^-$ (**6**) generated by reaction of trithiol $MeC(CH_2SH)_3$, $Fe_3(CO)_{12}$, and Et_3N[8] (Scheme 1). Particularly noteworthy is that these μ-CO-containing cluster anions have been well applied to synthesize a great variety of acyclic, macrocyclic, and starlike Fe/S cluster complexes.[5−12]

Recently, as a continuation of our project regarding the μ-CO-containing Fe/S cluster anions, we carried out a study on sequential reactions of tetrathiols $C(CH_2SH)_4$ and 1,2,4,5-$(HSCH_2)_4C_6H_2$ with $Fe_3(CO)_{12}$, Et_3N, and electrophiles. Our initial objective in this study was to examine if the corresponding

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(1) For reviews, see for example: (a) Ogino, H.; Inomata, S.; Tobita, H. *Chem. Rev.* **1998**, *98*, 2093. (b) Bruce, M. I. *J. Organomet. Chem.* **1985**, *283*, 339. (c) Song, L.-C. *Acc. Chem. Res.* **2005**, *38*, 21.

(2) (a) Seyferth, D.; Henderson, R. S.; Song, L.-C. *Organometallics* **1982**, *1*, 125. (b) Seyferth, D.; Song, L.-C.; Henderson, R. S. *J. Am. Chem. Soc.* **1981**, *103*, 5103. (c) Seyferth, D.; Anderson, L. L.; Villafane, F.; Cowie, M.; Hilts, R. W. *Organometallics* **1992**, *11*, 3262. (d) Song, L.-C.; Lu, G.-L.; Hu, Q.-M.; Fan, H.-T.; Chen, Y.; Sun, J. *Organometallics* **1999**, *18*, 3258. (e) Nametkin, N. S.; Tyurin, V. D.; Kukina, M. A. *J. Organomet. Chem.* **1978**, *149*, 355. (f) de Beer, J. A.; Haines, R. J. *J. Organomet. Chem.* **1970**, *24*, 757. (g) Bose, K. S.; Sinn, E.; Averill, B. A. *Organometallics* **1984**, *3*, 1126.

(3) For reviews, see for example: (a) Darensbourg, M. Y.; Lyon, E. J.; Zhao, X.; Georgakaki, I. P. *PNAS* **2003**, *100*, 3683. (b) Liu, X.; Ibrahim, S. K.; Tard, C.; Pickett, C. J. *Coord. Chem. Rev.* **2005**, *249*, 1641.

(4) (a) Li, H.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **2002**, *124*, 726. (b) Song, L.-C.; Yang, Z.-Y.; Bian, H.-Z.; Liu, Y.; Wang, H.-T.; Liu, X.-F.; Hu, Q.-M. *Organometallics* **2005**, *24*, 6126. (c) Liu, T.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **2007**, *129*, 7008.

(5) Seyferth, D.; Womack, G. B.; Dewan, J. C. *Organometallics* **1985**, *4*, 398.

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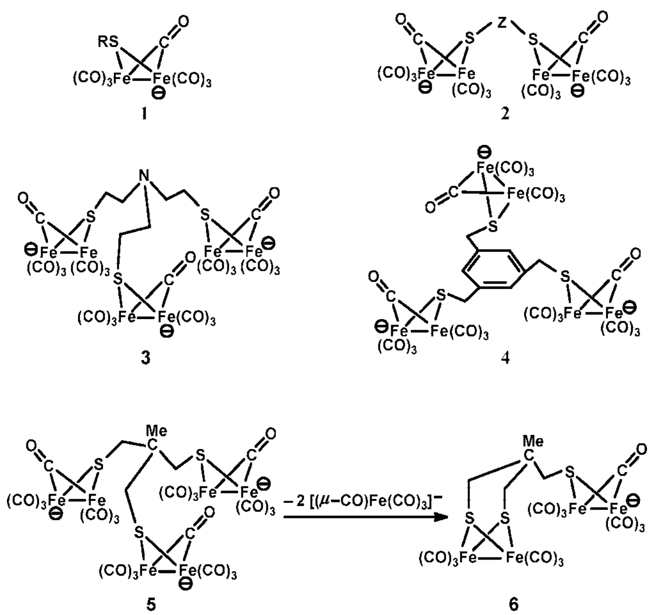
Scheme 1



four μ-CO-containing quadruple-butterfly tetraanions could be initially formed and if they could further react in situ with electrophiles to give the expected neutral butterfly Fe/S cluster complexes. Interestingly, from this study we have prepared a series of unexpected neutral butterfly Fe/S cluster complexes from the initially formed four-μ-CO-containing quadruple-butterfly tetraanions and the corresponding two-μ-CO-containing triple-butterfly dianions generated in situ from the initially formed tetraanions. Herein we report the results obtained from this study.

Results and Discussion

Reactions of Tetrathiol System 1,2,4,5-($HSCH_2$)$_4$$C_6H_2$/$Fe_3(CO)_{12}$/$Et_3N$ with Electrophiles. Synthesis and Characterization of Quadruple- and Triple-Butterfly Complexes [(μ-σ,π-C_4H_3O)$Fe_2(CO)_6$]$_4$[1,2,4,5-(μ-SCH_2)$_4$$C_6H_2$] (9) and [($\mu$-$Ph_2P$)-$Fe_2(CO)_6$]$_2$[$Fe_2(CO)_6$][1,2,4,5-($\mu$-$SCH_2$)$_4$$C_6H_2$] (11). We found that the benzene ring-centralized tetrathiol 1,2,4,5-($HSCH_2$)$_4$$C_6H_2$ could react with $Fe_3(CO)_{12}$ and Et_3N in a 1:4:4 molar ratio in THF at room temperature to give a brown-red solution that contains the [Et_3NH]$_4$ salt of tetraanion {[(μ-CO)$Fe_2(CO)_6$]$_4$[1,2,4,5-(μ-SCH_2)$_4$$C_6H_2$]}$^{4-}$ (**7**) (Scheme 2). The IR spectrum of **7** in solution displayed a medium absorption band at 1734 cm^{-1} for its μ-CO ligands, which is very similar to those reported for the other μ-CO-containing anions, such as monoanion **1** (R = Et),[5] dianion **2** (Z = $CH_2(CH_2OCH_2)_3CH_2$),[9] and trianions **3** and **4**.[11] Further treatment of the [Et_3NH]$_4$ salt of tetraanion **7** with 2-furancarbonyl chloride resulted in formation of the unexpected quadruple-butterfly complex **9** in 16% yield (Scheme 2). According to the well-known reaction manners of the μ-CO-containing Fe/S cluster anions with acyl chlorides,[5,9] as well as the easy extrusion of μ-acyl CO in the α,β-unsaturated acyl Fe/S complexes,[13] we might suggest that the formation of the starlike complex **9** is most likely via loss of the four μ-acyl carbonyls of the expected quadruple-butterfly complex **8** (generated by nucleophilic attack of the four negatively charged Fe atoms in **7** at the leaving group (Cl$^-$)-attached C atoms in four molecules of furancarbonyl chloride followed by displacement of the four μ-CO ligands in **7**) and subsequent σ,π-coordination of the four C=C double bonds in four furan rings of **8** (Scheme 2).

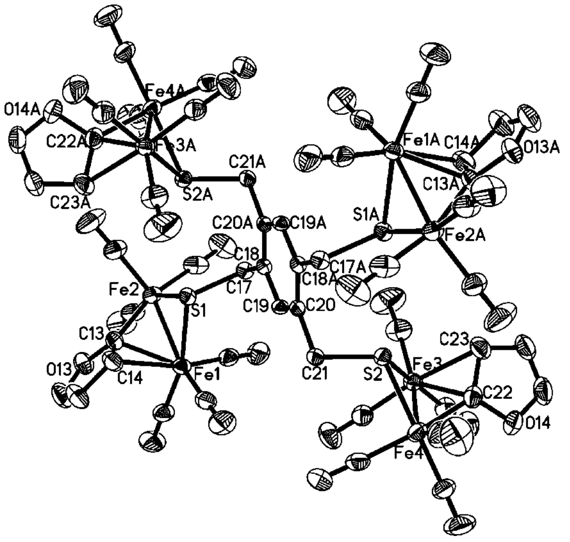


Figure 1. Molecular structure of **9** with 30% probability level ellipsoids.

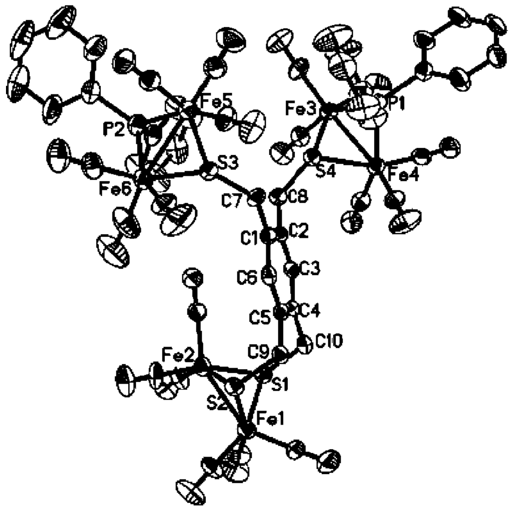


Figure 2. Molecular structure of **11** with 30% probability level ellipsoids.

It was further found that when the above-mentioned tetrathiol system 1,2,4,5-($HSCH_2$)$_4$$C_6H_2$/$Fe_3(CO)_{12}$/$Et_3N$ was treated with electrophile Ph_2PCl under the same conditions, the expected quadruple-butterfly complex was not isolated, but instead, the triple-butterfly starlike complex **11** was obtained in 20% yield (Scheme 3). At present, we are not clear about the mechanism for formation of complex **11**. However, if considering the previously reported transformation from trianion **5** to monoanion **6**,[8] we might propose a pathway to explain how product **11**was produced. The proposed pathway (Scheme 3) involves dianion **10** derived in situ from tetraanion **7** via formal loss of its two (μ-CO)$Fe(CO)_3$ units with their negative charges from the neighboring two butterfly clusters of **7** followed by dimerization of the remaining two (μ-SCH_2)$Fe(CO)_3$ units.[8,14] Then, dianion **10** reacts further with electrophile Ph_2PCl (through nucleophilic attack of the negatively charged two Fe atoms in **10** at the two

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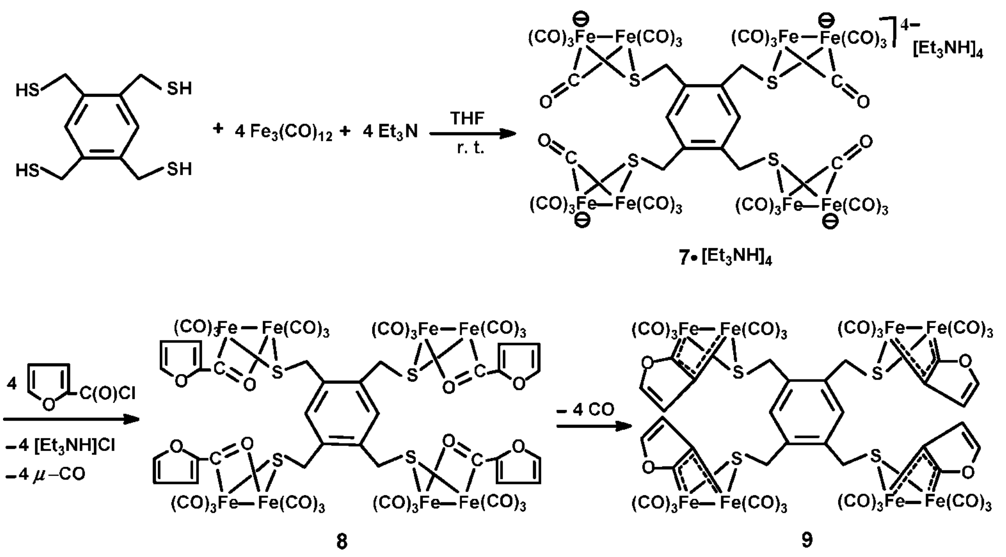
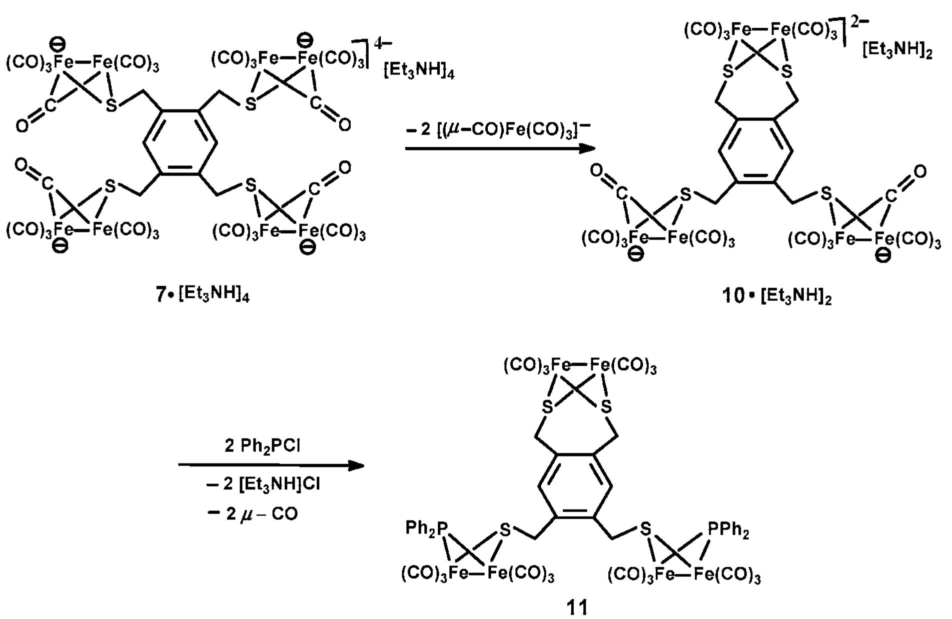
[13] (a) Song, L.-C.; Liu, J.-T.; Liu, R.-G.; Wang, J.-T. *Chem. J. Chin. Univ.* **1988**, *9*, 802. (b) Song, L.-C.; Liu, J.-T.; Wang, J.-T. *Chin. J. Org. Chem.* **1989**, *9*, 51. (c) Song, L.-C.; Wang, R.-J.; Hu, Q.-M.; Wang, H.-G. *Chin. J. Struct. Chem.* **1989**, *8*, 115. (d) Song, L.-C.; Liu, J.-T.; Wang, J.-T. *Acta Chim. Sin.* **1990**, *48*, 110.

Scheme 2



Scheme 3



P atoms in two molecules of Ph_2PCl) followed by displacement of the two μ-CO ligands in **10** to give **11**.

Starlike complexes **9** and **11** are air-stable red solids, which have been fully characterized by elemental analysis, spectroscopy, and X-ray diffraction techniques. The IR spectra of **9** and **11** showed three to four absorption bands in the range 2074−1985 cm^{-1} for their terminal carbonyls. The ^1H NMR spectrum of **9** displayed a singlet at 7.0 ppm for its benzene ring protons, a singlet at 3.65 ppm for its methylene protons, and three singlets in the region 4.96−7.86 ppm for its furan ring protons, respectively. The ^1H NMR spectrum of **11** exhibited a singlet at 6.91 ppm for its benzene ring protons, a multiplet in the range 7.20−7.58 ppm for its Ph_2P protons, and one singlet and two doublets in the region 3.08−3.79 ppm for its methylene protons, respectively. The ^{31}P NMR spectrum of **11** displayed a singlet at 141.51 ppm for P atoms in its Ph_2P groups. The molecular structures of **9** and **11** were confirmed by X-ray diffraction analysis. Their ORTEP plots are shown in Figures 1 and 2, whereas Table 1 lists their selected bond lengths and angles. As can be seen in Figure 1, complex **9** contains four identical butterfly cluster $[(\mu\text{-}C_4H_3O)Fe_2(CO)_6(\mu\text{-}S)]_4$ moieties, which are connected through their μ-S atoms to each α-C atom of the central benzene ring by equatorial bonds, in order to avoid the strong steric repulsions between these bulky cluster moieties.[2a,11] It is worthy to note that one of the C=C double bonds in each of the bridged furan rings is coordinated to two Fe atoms in a σ,π-manner. The bond lengths involved in each of the coordinated furan rings are, for example, C13−Fe1 = 2.166 Å, C14−Fe1 = 2.322 Å, C13−Fe2 = 1.969 Å, and C13−C14 = 1.423 Å, which are close to those corresponding to the reported σ,π-vinyl-coordinated diiron complexes.[15]This molecule possesses a symmetric center, i.e., the center of the benzene ring. To our knowledge, **9** is the first starlike quadruple-butterfly Fe/S cluster complex, al-

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(14) (a) Seyferth, D.; Hoke, J. B.; Womack, G. B. *Organometallics* **1990**, *9*, 2662. Similar intermolecular processes are known, by which the $[Et_3NH]$ salts of monoanions $[(\mu\text{-RE})(\mu\text{-CO})Fe_2(CO)_6]^-$ (E = S, Se) can be converted to dimers $(\mu\text{-RE})_2Fe_2(CO)_6$; see for example: (b) Song, L.-C.; Lu, G.-L.; Hu, Q.-M.; Fan, H.-T.; Chen, J.; Sun, J.; Huang, X.-Y. *J. Organomet. Chem.* **2001**, *627*, 255.

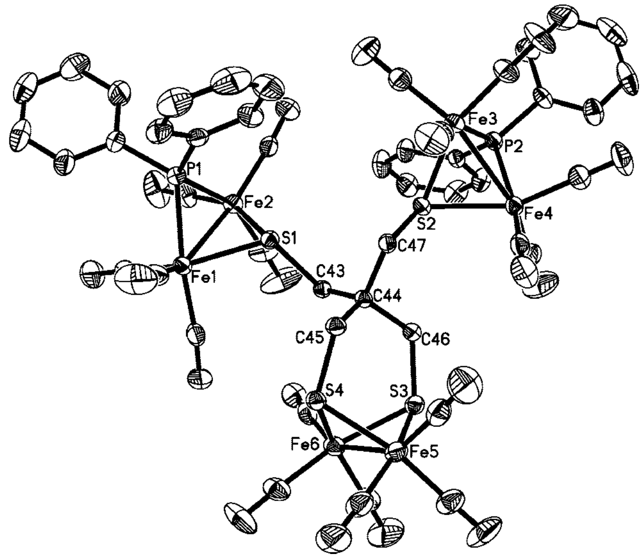

Figure 3. Molecular structure of **14** with 30% probability level ellipsoids.

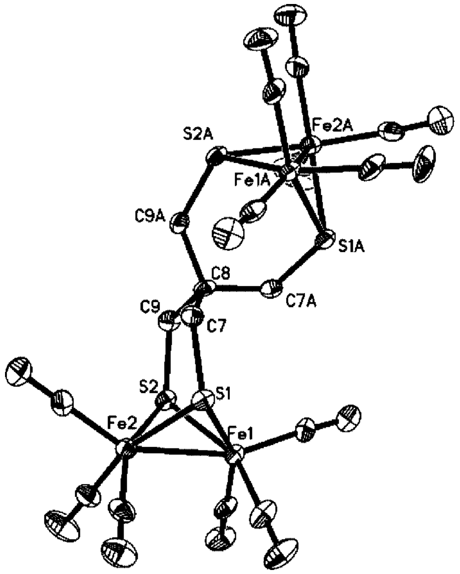

Figure 4. Molecular structure of **15** with 30% probability level ellipsoids.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 9, 11, 14, and 15

		9	
Fe(1)−S(1)	2.298(2)	Fe(4)−S(2)	2.275(2)
Fe(2)−S(1)	2.261(2)	Fe(3)−Fe(4)	2.559(2)
Fe(1)−Fe(2)	2.551(2)	Fe(1)−C(13)	2.166(6)
Fe(3)−S(2)	2.287(2)	Fe(1)−C(14)	2.322(7)
S(2)−Fe(4)−Fe(3)	56.11(5)	Fe(4)−S(2)−Fe(3)	68.24(6)
C(17)−S(1)−Fe(1)	115.5(2)	S(2)−Fe(3)−Fe(4)	55.65(4)
Fe(2)−S(1)−Fe(1)	68.04(5)	S(1)−Fe(1)−C(14)	77.9(2)
C(21)−S(2)−Fe(3)	113.6(2)	S(2)−Fe(3)−C(23)	78.6(2)
S(1)−Fe(1)−Fe(2)	55.29(4)	Fe(2)−C(13)−Fe(1)	76.0(2)
		11	
Fe(1)−S(1)	2.262(2)	Fe(3)−S(4)	2.276(2)
Fe(1)−S(2)	2.257(2)	Fe(3)−Fe(4)	2.549(2)
Fe(1)−Fe(2)	2.522(2)	Fe(4)−P(1)	2.227(2)
Fe(3)−P(1)	2.24524(2)	Fe(4)−S(4)	2.256(2)
S(2)−Fe(1)−S(1)	87.37(6)	Fe(4)−S(4)−Fe(3)	68.44(5)
S(2)−Fe(1)−Fe(2)	55.99(4)	C(35)−P(1)−C(41)	100.7(2)
S(1)−Fe(1)−Fe(2)	56.27(4)	P(1)−Fe(3)−S(4)	75.10(6)
C(10)−S(1)−Fe(1)	114.3(2)	P(1)−Fe(3)−Fe(4)	54.91(5)
Fe(1)−S(1)−Fe(2)	67.66(5)	Fe(4)−P(1)−Fe(3)	69.48(6)
		14	
Fe(1)−P(1)	2406(12)	Fe(3)−Fe(4)	2.5646(8)
Fe(1)−S(1)	2.2786(11)	Fe(5)−S(3)	2.2499(12)
Fe(2)−P(1)	2.2259(12)	Fe(5)−S(4)	2.2541(12)
Fe(1)−Fe(2)	2.5730(8)	Fe(5)−Fe(6)	2.5129(10)
P(1)−Fe(1)−S(1)	77.16(4)	S(3)−Fe(5)−S(4)	83.70(4)
P(1)−Fe(1)−Fe(2)	54.56(3)	S(3)−Fe(5)−Fe(6)	55.59(3)
S(1)−Fe(1)−Fe(2)	55.29(3)	S(4)−Fe(5)−Fe(6)	56.65(3)
Fe(2)−P(1)−Fe(1)	70.35(4)	S(3)−Fe(6)−S(4)	83.64(4)
Fe(2)−S(1)−Fe(1)	68.96(3)	C(45)−C(44)−C(46)	112.83(3)
		15	
Fe(1)−S(1)	2.319(3)	Fe(1)−Fe(2)	2.532(2)
Fe(2)−S(2)	2.283(3)	Fe(2)−S(1)	2.286(3)
S(1)−C(7)	1.847(11)	S(2)−C(9)	1.845(11)
Fe(1)−S(2)	2.270(4)	C(7)−C(8)	1.543(14)
S(1)−Fe(1)−Fe(2)	56.02(8)	S(2)−Fe(1)−Fe(2)	56.44(9)
S(2)−Fe(2)−S(1)	83.50(12)	S(1)−Fe(2)−Fe(1)	57.26(10)
S(2)−Fe(2)−Fe(1)	55.98(10)	C(7)−S(1)−Fe(1)	118.8(4)
Fe(2)−S(1)−Fe(1)	66.72(9)	Fe(1)−S(2)−Fe(2)	67.58(9)
S(2)−Fe(1)−S(1)	83.04(11)	C(7)−C(8)−C(9)	111.2(6)

though several starlike complexes terminated with three-butterfly Fe/S clusters are known.[11]

Figure 2 shows that complex **11** is different from complex **9**, which includes one butterfly cluster $[Fe_2(CO)_6(\mu\text{-}S)_2]$ unit and two identical butterfly cluster $[(\mu\text{-}Ph_2P)Fe_2(CO)_6(\mu\text{-}S)]_2$ moieties. The former moiety is connected via its two μ-S atoms to the two neighboring α-C atoms of the central benzene ring by axial bonds, whereas the latter two moieties are attached to another two neighboring α-C atoms via their μ-S atoms by equatorial bonds.[2a,11] The metal−metal bond length of Fe1−Fe2 (2.522 Å) is slightly shorter than that of Fe3−Fe4 (2.549 Å) or Fe5−Fe6 (2.544 Å), which is obviously due to the Fe1−Fe2 bond being involved in a closed and axially bridged butterfly Fe_2S_2 cluster moiety. Although the homotriple-butterfly starlike complexes were previously reported,[7,11] complex **11** is, to our knowledge, the first heterotriple-butterfly Fe/S cluster complex reported so far.

Reactions of Tetrathiol System $C(CH_2SH)_4/Fe_3(CO)_{12}/Et_3N$ with Electrophiles. Synthesis and Characterization of Triple- and Double-Butterfly Complexes $[(\mu\text{-}Ph_2P)Fe_2(CO)_6]_2[Fe_2(CO)_6][(\mu\text{-}SCH_2)_4C]$ (14), $[Fe_2(CO)_6]_2[(\mu\text{-}SCH_2)_4C]$ (15), and $[(\mu\text{-}\sigma,\pi\text{-}CH_2CH{=}CH_2)Fe_2(CO)_6]_2[Fe_2(CO)_6][(\mu\text{-}SCH_2)_4C]$ (16). The quaternary carbon atom-centralized tetrathiol $C(CH_2SH)_4$ was found to react similarly with $Fe_3(CO)_{12}$ and Et_3N in a 1:4:4 molar ratio in THF at room temperature to afford the $[Et_3NH]_4$ salt of tetraanion $\{[(\mu\text{-}CO)Fe_2(CO)_6]_4[(\mu\text{-}SCH_2)_4C]\}^{4-}$ (**12**) (Scheme 4). The IR spectrum of **12** in solution showed a medium absorption band at 1745 cm^{-1} for its μ-CO ligands, which is very similar to those corresponding to tetraanion **7** and the other μ-CO-containing Fe/S cluster anions.[5,9,11] Similar to the above-mentioned reaction of the tetrathiol system $1,2,4,5\text{-}(HSCH_2)_4C_6H_2/Fe_3(CO)_{12}/Et_3N$ with Ph_2PCl, when the tetrathiol system $C(CH_2SH)_4/Fe_3(CO)_{12}/Et_3N$ was treated with excess electrophile Ph_2PCl or $CH_2{=}CHCH_2Br$, we did not isolate the corresponding quadruple-butterfly complexes, but instead, the triple-butterfly starlike complex **14** (20%) and double-butterfly complex **15** (3%), or the corresponding complexes **16** (21%) and **15** (5%) were isolated, respectively (Scheme 5).

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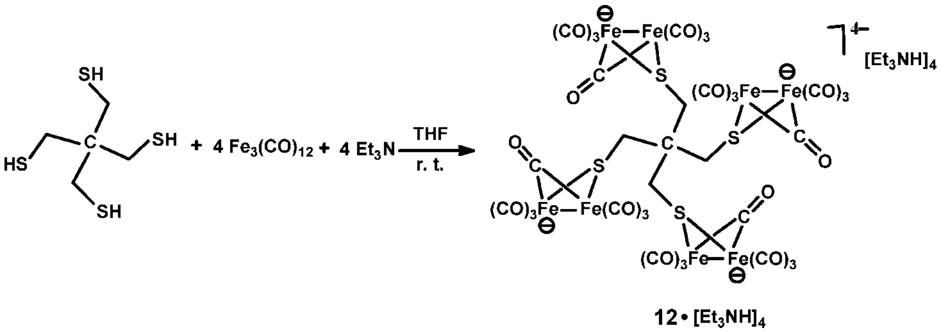
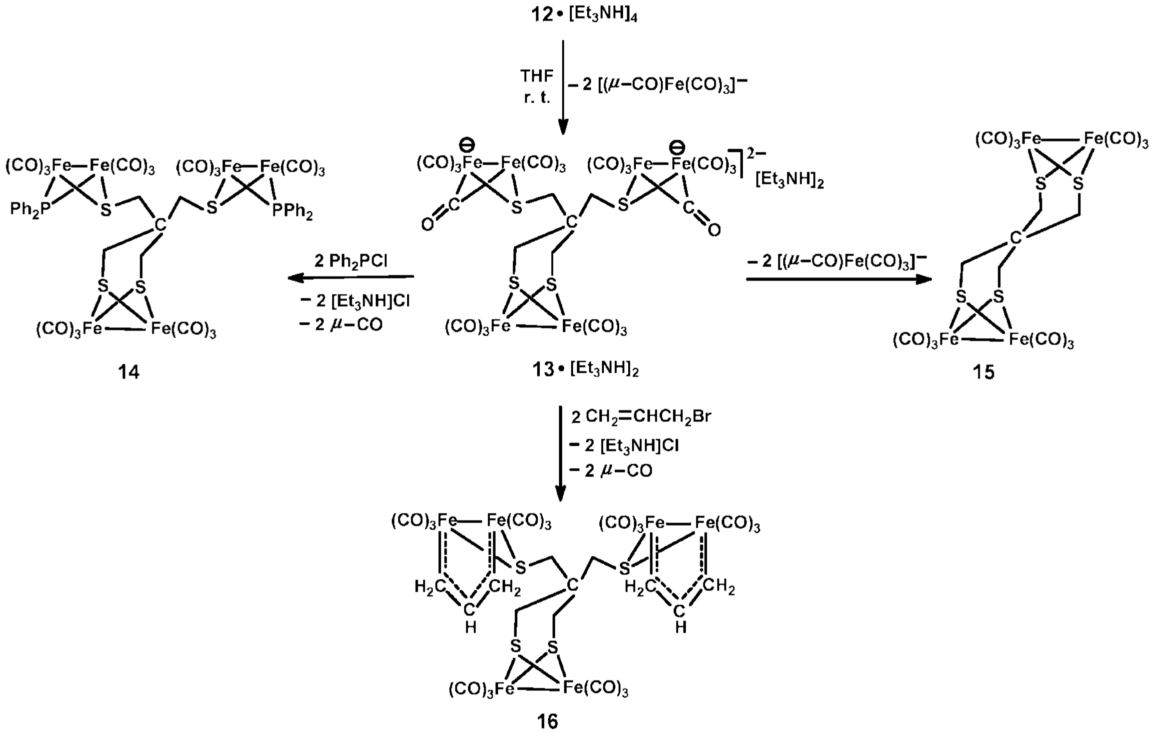
(15) (a) Song, L.-C.; Wang, R.-J.; Liu, J.-T.; Wang, H.-G.; Wang, J.-T. *Acta Chim. Sin.* **1990**, *48*, 1141. (b) Song, L.-C.; Hu, Q.-M.; Zhou, Z.-Y.; Liu, L. *Chin. J. Struct. Chem.* **1989**, *8*, 197.

Scheme 4



Scheme 5



Although the mechanisms for formation of complexes **14**−**16** are not completely understood, the possible pathways (which are similar to that suggested for formation of complex **11**) could be proposed (Scheme 5). That is, the initially formed tetraanion **12** is first converted to dianion **13** through formal loss of its two (μ-CO)Fe(CO)$_3$ units with their negative charges followed by dimerization of the remaining two (μ-SCH$_2$)$_2$Fe(CO)$_3$ moieties.[8,14] Then, the resulting dianion **13** reacts further with electrophile Ph$_2$PCl or CH$_2$=CHCH$_2$Br via the processes similar to that mentioned above for formation of **11** to give products **14** and **16**. The common double-butterfly complex **15** is produced via a process similar to that suggested for formation of dianion **13** from tetraanion **12**.[8,14]

Complexes **14**−**16** are also air-stable red solids and characterized by elemental analysis and spectroscopy. The IR spectra of **14**−**16** displayed four absorption bands in the range 2076−1980 cm^{-1} for their terminal carbonyls. The ^{1}H NMR spectra of **14**−**16** exhibited a singlet in the range 2.18−2.52 ppm for their μ-SCH$_2$ groups, and that of **16** showed two additional doublets at ca. 0.6 and ca. 2 ppm for the anti and syn protons of the CH$_2$ groups in its two allyl ligands. The ^{31}P NMR spectrum of **14** (showing a singlet at 141.29 ppm) is very similar to those spectra of complex **11** and the previously reported single-,[5,16] double-,[9] and triple[11]-butterfly Fe$_2$PS cluster complexes.

The molecular structures of **14** and **15** have been unequivocally confirmed by X-ray diffraction techniques. While their ORTEP drawings are depicted in Figures 3 and 4, the selected bond lengths and angles are given in Table 1. Figure 3 shows that starlike complex **14** consists of one butterfly Fe$_2$S$_2$ moiety [Fe$_2$(CO)$_6$(μ-S)$_2$] and two identical butterfly Fe$_2$SP units [(μ-Ph$_2$P)Fe$_2$(CO)$_6$(μ-S)]$_2$. While the former is connected via its two μ-S atoms to the two methylene C atoms of the centralized "pentaerythrityl" group by the axial bonds, the latter two moieties are bound to another two methylene C atoms through their μ-S atoms by equatorial bonds.[2a,11] The bond length of Fe5−Fe6 (2.5129 Å) in the closed cluster is shorter than those of Fe1−Fe2 (2.5730 Å) and Fe3−Fe4 (2.5646 Å) in the two open clusters. It follows that starlike complex **14** is virtually isostructural with complex **11**, except that they have different central parts, that is, for **14** a quaternary C atom-centralized organic group, but for **11** a benzene ring-centralized group. It can be seen in Figure 4 that complex **15** is centrosymmetric

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Table 2. Crystal Data and Structure Refinement Details for 9, 11, 14, and 15

	9	11	14	15
mol formula	$C_{50}H_{22}Fe_8O_{28}S_4 \cdot 2CHCl_3$	$C_{52}H_{30}Fe_6O_{18}P_2S_4$	$C_{47}H_{28}Fe_6O_{18}P_2S_4$	$C_{8.5}H_4Fe_2O_6S_2$
mol wt	1884.45	1468.04	1405.97	377.94
cryst syst	monoclinic	triclinic	monoclinic	orthorhombic
space group	*P*2(1)/*c*	$P\bar{1}$	*C*2/*c*	*Iba*2
a/Å	13.241(6)	12.876(1)	13.7796(17)	11.825(10)
b/Å	26.387(12)	14.861(2)	20.849(3)	17.627(15)
c/Å	11.576(5)	17.022(2)	40.694(5)	12.708(12)
α/deg	90	103.426(1)	90	90
β/deg	115.037(7)	94.687(1)	94.807(2)	90
γ/deg	90	108.111(1)	90	90
V/Å^3	3665(3)	2969.2(4)	11650(3)	2649(4)
Z	2	2	8	8
D_c/g cm^{-3}	1.708	1.642	1.603	1.895
abs coeff/mm^{-1}	1.945	1.690	1.719	2.519
F(000)	1868	1472	5712	1496
index ranges	$-16 \le h \le 16$ $-19 \le k \le 32$ $-14 \le l \le 13$	$-15 \le h \le 15$ $-17 \le k \le 17$ $-20 \le l \le 20$	$-17 \le h \le 17$ $-26 \le k \le 20$ $-50 \le l \le 47$	$-8 \le h \le 14$ $-19 \le k \le 20$ $-12 \le l \le 15$
no. of rflns	20 611	17 871	32 686	5949
no. of indep rflns	7456	9664	11 909	2076
$2\theta_{max}$/deg	52.90	50.00	52.76	50.02
R	0.0515	0.0482	0.0465	0.0723
R_w	0.1299	0.0707	0.0919	0.1806
goodness of fit	1.017	1.051	0.940	1.037
largest diff peak and hole/e Å^{-3}	0.990/−0.871	0.419/−0.369	0.398/−0.351	1.467/−1.016

with respect to atom C8 and consists of two identical butterfly Fe_2S_2 clusters $[Fe_2(CO)_6(\mu\text{-}S)_2]_2$ joined together through the four methylene C atoms of the "pentaerythrityl" bridge by axial bonds C7−S1, C9−S2, C7A−S1A, and C9A−S2A. The metal−metal bond lengths of Fe1−Fe2 = Fe1A−Fe2A (2.532 Å) are very close to those corresponding to the closed Fe_2S_2 butterfly clusters of starlike complexes **11** and **14**.

Conclusions

The sequential reactions of tetrathiols with $Fe_3(CO)_{12}$ and Et_3N followed by treatment with electrophiles are first investigated. It has been found that (i) tetrathiol 1,2,4,5-$(HSCH_2)_4C_6H_2$ or $C(CH_2SH)_4$ reacts with $Fe_3(CO)_{12}$ and Et_3N in a molar ratio of 1:4:4 to give the *μ*-CO-containing quadruple-butterfly tetraanions **7** and **12**, (ii) quadruple-butterfly complex **9** can be produced by direct reaction of tetraanion **7** with furancarbonyl chloride followed by CO extrusion and C═C double bond coordination of the thermodynamically unstable complex **8**, (iii) tetraanions **7** and **12** can be in situ converted to the *μ*-CO-containing triple-butterfly dianions **10** and **13**, respectively, (iv) while dianion **10** reacts with Ph_2PCl to give triple-butterfly complex **11**, reaction of dianion **13** with Ph_2PCl or $CH_2═CHCH_2Br$ affords triple-butterfly complexes **14** and **16**, respectively, and (v) double-butterfly complex **15** derived in situ from dianion **13** can be isolated as a minor product along with major products **14** and **16**. Further studies on the proposed pathways for formation of products **9**, **11**, and **14**−**16**, and particularly on the chemical reactivities of the *μ*-CO-containing anions **7**, **10**, **12**, and **13** involved in the suggested pathways, are in progress in our laboratory.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of prepurified nitrogen by using standard Schlenk and vacuum-line techniques. Tetrahydrofuran (THF) was distilled from Na/benzophenone ketyl under nitrogen. $Fe_3(CO)_{12}$,[17] 1,2,4,5-$(HSCH_2)_4C_6H_2$,[18] $C(CH_2SH)_4$,[19] and furancarbonyl chloride C_4H_3-$OC(O)Cl$[20] were prepared according to literature procedures. Et_3N, Ph_2PCl, and $CH_2═CHCH_2Br$ 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 *μ*m). IR spectra were recorded on a Bio-Rad FTS 135 infrared spectrophotometer. ^1H (^{31}P) NMR spectra were taken on a Bruker Avance 300 NMR spectrometer. Elemental analyses were performed with an Elementar Vario EL analyzer. Melting points were determined on a Yanaco MP-500 apparatus and were uncorrected.

Preparation of $[(\mu\text{-}\sigma,\pi\text{-}C_4H_3O)Fe_2(CO)_6]_4[1,2,4,5\text{-}(\mu\text{-}SCH_2)_4C_6H_2]$ (9). A mixture of 1,2,4,5-$(HSCH_2)_4C_6H_2$ (0.100 g, 0.38 mmol), $Fe_3(CO)_{12}$ (0.75 g, 1.49 mmol), Et_3N (0.21 mL, 1.50 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 $C_4H_3C(O)Cl$ (0.15 mL, 1.50 mmol), and the new mixture was stirred at room temperature for 24 h. After solvent was removed at reduced pressure, the residue was subjected to TLC using petroleum ether/CH_2Cl_2 (3:1 v/v) as eluent to develop a major red band with many tiny bands such as the purple, green, and orange bands. From the major red band, **9** (0.096 g, 16%) was obtained as a red solid, mp 171 °C (dec). Anal. Calcd for $C_{50}H_{22}Fe_8O_{28}S_4$: C, 36.49 H, 1.35. Found: 36.21; H, 1.39. IR (KBr disk) $\nu_{C≡O}$ 2073 (s), 2035 (vs), 1995 (vs) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): 3.65 (s, 8H, $4CH_2S$), 4.96 (s, 4H, 4CHFe), 6.25 (s, 4H, 4C*H*CHO), 7.01 (s, 2H, C_6H_2), 7.86 (s, 4H, 4CHO) ppm.

Preparation of $[(\mu\text{-}Ph_2P)Fe_2(CO)_6]_2[Fe_2(CO)_6][1,2,4,5\text{-}(\mu\text{-}SCH_2)_4\text{-}C_6H_2]$ (11). The same procedure was followed as for **9**, but Ph_2PCl (0.27 mL, 1.50 mmol) was used instead of $C_4H_3C(O)Cl$. From the major red band, **11** (0.110 g, 20%) was obtained as a red solid, mp 183 °C (dec). Anal. Calcd for $C_{52}H_{30}Fe_6O_{18}P_2S_4$: C, 42.54; H, 2.06. Found: 42.30; H, 2.16. IR (KBr disk): $\nu_{C≡O}$ 2074 (s), 2059 (s), 2021 (vs), 1985 (vs) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): 3.59 (s,

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4H, $2CH_2SFe_2P$), 3.08, 3.79 (2d, $J = 12.0$ Hz, 4H, $2CH_2SFe_2$), 6.91 (s, 2H, C_6H_2), 7.20−7.58 (m, 20H, $4C_6H_5$) ppm. ^{31}P NMR (121.48 MHz, $CDCl_3$, 85% H_3PO_4): 141.51 (s) ppm.

Preparation of $[(\mu\text{-}Ph_2P)Fe_2(CO)_6]_2[Fe_2(CO)_6][(\mu\text{-}SCH_2)_4C]$ (14) and $[Fe_2(CO)_6]_2[(\mu\text{-}SCH_2)_4C]$ (15). A mixture of $C(CH_2SH)_4$ (0.200 g, 1.0 mmol), $Fe_3(CO)_{12}$ (2.00 g, 4.0 mmol), Et_3N (0.55 mL, 4.0 mmol), and THF (60 mL) was stirred at room temperature for 0.5 h to give a brown-red solution. To this solution was added Ph_2PCl (1.44 mL, 8.0 mmol), and the new mixture was stirred at room temperature for 24 h. Solvent was removed at reduced pressure and the residue was subjected to TLC using petroleum ether/CH_2Cl_2 (4:1 v/v) as eluent to develop a major red band and a small orange band along with several tiny purple, yellow, orange-red, and brown bands. From the lower major red band, **14** (0.310 g, 22%) was obtained as a red solid, mp 101−103 °C. Anal. Calcd for $C_{47}H_{28}Fe_6O_{18}P_2S_4$: C, 40.15; H, 2.01. Found: 39.98; H, 2.25. IR (KBr disk): $\nu_{C\equiv O}$ 2075 (s), 2062 (s), 2024 (vs), 1984 (vs) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): 2.30 (s, 4H, $2CH_2SFe_2$), 2.51 (s, 4H, $2CH_2SFe_2P$), 7.18−7.55 (m, 20H, $4C_6H_5$) ppm. ^{31}P NMR (121.48 MHz, $CDCl_3$, 85% H_3PO_4): 141.29 (s) ppm. From the upper small orange band, **15** (0.024 g, 3%) was obtained as a red solid, mp 180 °C (dec). Anal. Calcd for $C_{17}H_8Fe_4O_{12}S_4$: C, 27.01; H, 1.07. Found: C, 27.15; H, 1.23. IR (KBr disk): $\nu_{C\equiv O}$ 2076 (vs), 2038 (vs), 1997 (vs), 1980 (vs) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): 2.18 (s, 8H, $4CH_2S$) ppm.

Preparation of $[(\mu\text{-}\sigma,\pi\text{-}CH_2CH{=}CH_2)Fe_2(CO)_6]_2[Fe_2(CO)_6][(\mu\text{-}SCH_2)_4C]$ (16) and 15. The same procedure was followed as for **14** and **15**, but $CH_2{=}CHCH_2Br$ (0.70 mL, 8.0 mmol) was utilized in place of Ph_2PCl. From the lower major red band, **16** (0.235 g, 21%) was obtained as a red solid, mp 240 °C (dec). Anal. Calcd for $C_{29}H_{18}Fe_6O_{18}S_4$: C, 31.16; H, 1.62. Found: C, 31.07; H, 1.86. IR (KBr disk): $\nu_{C\equiv O}$ 2075 (s), 2065 (s), 2028 (vs), 1981 (vs) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): 0.58 (d, $J = 13.2$ Hz, 4H, 4 anti-FeC *H*H), 2.04 (d, $J = 6.9$ Hz, 4H, 4 syn-FeCH *H*), 2.42 (s, 4H, $2CH_2SFe_2$), 2.52 [s, 4H, $2CH_2SFe_2$ (allyl)], 4.85−5.05 (m, 2H, 2CH) ppm. From the upper small orange band, **15** (0.038 g, 5%) was obtained.

X-ray Structure Determinations of 9, 14, and 15. While single crystals of **9** suitable for X-ray diffraction analysis were grown by slow evaporation of its $CHCl_3$/hexane solution at about 4 °C, those of **14** and **15** were produced by slow evaporation of their CH_2Cl_2/hexane solutions at about 4 and −20 °C, respectively. A single crystal of **9**, **14**, or **15** was mounted on a Bruker SMART 1000 automated diffractometer. Data were collected at room temperature, using a graphite monochromator with Mo Kα radiation (λ = 0.71073 Å) in the $\omega-\phi$ scanning mode. Absorption correction was performed by the SADABS program.[21] The structures were solved by direct methods using the SHELXS-97 program[22] and refined by full-matrix least-squares techniques (SHELXL-97)[23] on F^2. Hydrogen atoms were located by using the geometric method. Details of crystal data, data collections, and structure refinements of **9**, **14**, and **15** are summarized in Table 2.

X-ray Structure Determination of 11. The single crystals of **11** suitable for X-ray diffraction analysis were grown by slow evaporation of their $CHCl_3$/hexane solutions at about 4 °C and were mounted on a Bruker APEX-II CCD diffractometer. Data were collected at 296(2) K, using a graphite monochromator with Mo Kα radiation (λ = 0.71073 Å) in the $\varphi-\omega$ scanning mode. Absorption correction was performed by the SADABS program. The structure was solved by direct methods and subsequently refined by full-matrix least-squares techniques on F^2. Hydrogen atoms were located by using the geometric method, and non-hydrogen atoms were refined anisotropically. All software programs employed are from the Bruker AXS APEX2 software package.[24] Details of crystal data, data collection, and structure refinement of **11** are summarized in Table 2.

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Supporting Information Available: Full tables of crystal data, atomic coordinates and thermal parameters, and bond lengths and angles for **9**, **11**, **14**, and **15**. This material is available free of charge via the Internet at http://pubs.acs.org.

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