General Synthetic Route to Double-Butterfly Fe/S Cluster Complexes via Reactions of the Dianions $\{[(\mu\text{-CO})Fe_2(CO)_6]_2(\mu\text{-SZS-}\mu)\}^{2-}$ with Electrophiles†

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A simple and convenient route for the synthesis of linear and macrocyclic double-butterfly Fe/S cluster complexes has been developed, which involves a sequential reaction of $Fe_3(CO)_{12}$ with the dithiol HSZSH in the presence of Et_3N, followed by treatment of the intermediate $[Et_3NH]^+$ salts of dianions $\{[(\mu\text{-CO})Fe_2(CO)_6]_2(\mu\text{-SZS-}\mu)\}^{2-}$ (**4**) with electrophiles. For example, treatment of the $[Et_3NH]^+$ salts of dianions **4** with allyl bromide and PhSBr produces the linear complexes $[(\mu\text{-}CH_2{=}CHCH_2)Fe_2(CO)_6]_2(\mu\text{-SZS-}\mu)$ (**5a**, Z = $(CH_2)_4$; **5b**, Z = $CH_2(CH_2OCH_2)_2CH_2$; **5c**, Z = $CH_2(CH_2OCH_2)_3CH_2$) and $[(\mu\text{-PhS})Fe_2(CO)_6]_2(\mu\text{-SZS-}\mu)$ (**6a**, Z = $CH_2(CH_2OCH_2)_2CH_2$; **6b**, Z = $CH_2(CH_2OCH_2)_3CH_2$), whereas treatment with S_2Cl_2 and ClSZSCl yields the macrocyclic complexes $[Fe_2(CO)_6]_2(\mu\text{-S}-\text{S-}\mu)(\mu\text{-SZS-}\mu)$ (**7a**, Z = $CH_2(CH_2OCH_2)_2CH_2$; **7b**, Z = $CH_2(CH_2OCH_2)_3CH_2$) and $[Fe_2(CO)_6]_2(\mu\text{-SZS-}\mu)_2$ (**8a**, Z = $CH_2(CH_2OCH_2)_2CH_2$; **8b**, Z = $CH_2(CH_2OCH_2)_3CH_2$), respectively. In addition, while the $[Et_3NH]^+$ salts of dianions **4** react in situ with PhNCS and $SCN(CH_2)_4NCS$ to give the linear complexes $[(\mu\text{-PhNHC}{=}S)Fe_2(CO)_6]_2(\mu\text{-SZS-}\mu)$ (**9a**, Z = $CH_2CH_2OCH_2CH_2$; **9b**, Z = $CH_2(CH_2OCH_2)_2CH_2$; **9c**, Z = $CH_2(CH_2OCH_2)_3CH_2$) and macrocyclic complexes $[Fe_2(CO)_6]_2[\mu\text{-S}{=}CNH(CH_2)_4NHC{=}S\text{-}\mu](\mu\text{-SZS-}\mu)$ (**10a**, Z = $(CH_2)_4$; **10b**, Z = $CH_2(CH_2OCH_2)_2CH_2$), the in situ reactions with PhC≡CPh and PhC≡CH afford the linear complexes $[(\mu\text{-}\sigma,\pi\text{-PhCH}{=}CPh)Fe_2(CO)_6]_2(\mu\text{-SZS-}\mu)$ (**11a**, Z = $CH_2(CH_2OCH_2)_2CH_2$; **11b**, Z = $CH_2(CH_2OCH_2)_3CH_2$) and $[(\mu\text{-}\sigma,\pi\text{-PhCH}{=}CH)Fe_2(CO)_6]_2(\mu\text{-SZS-}\mu)$ (**12a**, Z = $(CH_2)_4$; **12b**, Z = $CH_2(CH_2OCH_2)_2CH_2$; **12c**, Z = $CH_2(CH_2OCH_2)_3CH_2$). The possible pathways for production of these linear and macrocyclic cluster complexes are suggested, and their structures have been characterized by elemental analysis and IR and ^1H NMR spectroscopy, as well as for **5a, 7a, 8a**, and **12a** by X-ray diffraction analysis.

Introduction

Butterfly Fe/S cluster complexes have recently attracted growing interest, because of their novel chemistry[1] and the closely related biological relevance to the active site of the Fe-only hydrogenases.[2] Among them, the double-butterfly Fe/S cluster complexes[3−11] are of particular interest. This is because that they might be expected, like double-tetrahedral MoFeCoS clusters,[12] to have new chemical reactivity patterns through the interactions between the two subcluster cores or, like double-cubane $MoFe_3S_4$ clusters,[13] to become a new class of biologically relevant molecules. Previously, Seyferth's group and we reported a series of double-butterfly Fe/S cluster complexes, for instance **1**−**3**, which were prepared by reactions of $(\mu\text{-}S_2)Fe_2(CO)_6$ with alkyllithium

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† Dedicated to Professor Dietmar Seyferth, on the occasion of his 75th birthday and in recognition of his outstanding contributions to Organometallic Chemistry.

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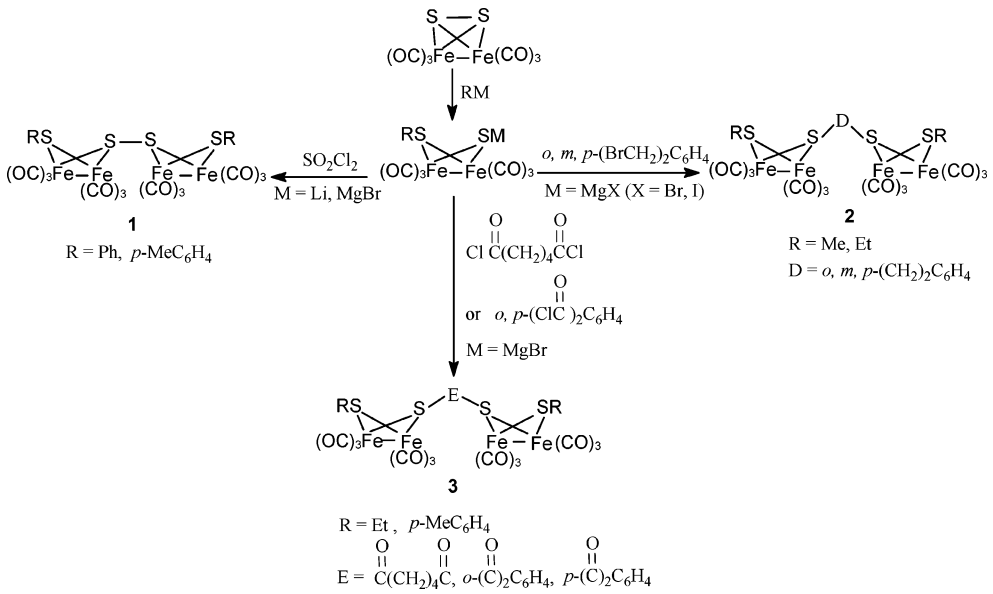
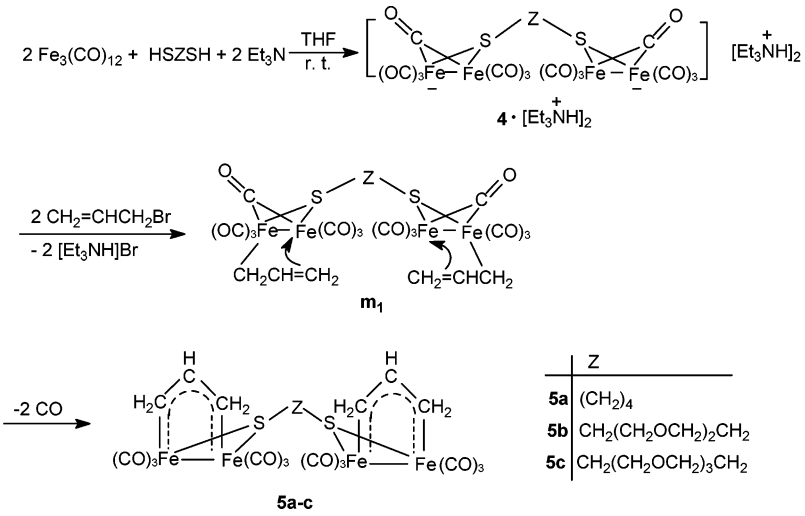
Scheme 1



Scheme 2



or Grignard reagents and subsequent treatment of the S-centered monoanions $(\mu\text{-RS})(\mu\text{-S}^-)Fe_2(CO)_6$ with organic or inorganic halides (Scheme 1). [4−7]

Another synthetic route to double-butterfly Fe/S cluster complexes has also been developed. It involves the reactions of a new type of double-butterfly, two μ-CO-containing dianions $\{[(\mu\text{-CO})Fe_2(CO)_6]_2(\mu\text{-SZS-}\mu)\}^{2-}$ (**4**) with electrophiles, such as Ph_2PCl and PhC(O)Cl.[14] To further develop the chemistry of novel dianions **4** and to see if this route has generality for the synthesis of double-butterfly Fe/S cluster compounds, we carried out the reactions of dianions **4** with other types of electrophiles, such as $CH_2{=}CHCH_2Br$, S_2Cl_2, PhN=C=S, PhC≡CH, $SCN(CH_2)_2NCS$, etc. As a result, a series of linear and cyclic double-butterfly Fe/S cluster complexes were produced. It follows that the route involving dianions **4** is indeed a general route suitable for synthesizing a wide variety of double-butterfly Fe/S cluster complexes. Now, we report the interesting results obtained from this study.

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Results and Discussion

Synthesis and Characterization of $[(\mu\text{-}CH_2{=}CHCH_2)Fe_2(CO)_6]_2(\mu\text{-SZS-}\mu)$ (5a−c). The $[Et_3NH]^+$ salts of dianions **4** (Z = $(CH_2)_4$, $CH_2(CH_2OCH_2)_{2,3}CH_2$) (generated from $Fe_3(CO)_{12}$, HSZSH, and Et_3N) reacted in situ with an excess of allyl bromide in THF at room temperature (through nucleophilic attack of the two negatively charged Fe atoms of **4** at two molecules of allyl bromide followed by displacement of the two μ-CO ligands in intermediate $\mathbf{m_1}$) to produce the series of double-butterfly cluster complexes **5a**−**c** (Scheme 2).

Products **5a**−**c** are red air-stable materials, whose elemental analysis and spectroscopic data are consistent with the structures shown in Scheme 2. The ^{1}H NMR spectra of **5a**−**c** showed the CH_2 proton signals of the allyl ligands as two doublets at ca. 0.5 ppm ($J \approx 12$ Hz) and ca. 2 ppm ($J \approx 6$ Hz), corresponding to the anti and syn hydrogens. An ORTEP drawing of **5a** is shown in Figure 1. Table 1 lists selected bond lengths and angles. Compound **5a** is a centrosymmetric double-butterfly cluster complex, in which two identical butterfly Fe_2SC_3 subcluster cores are joined together through its two

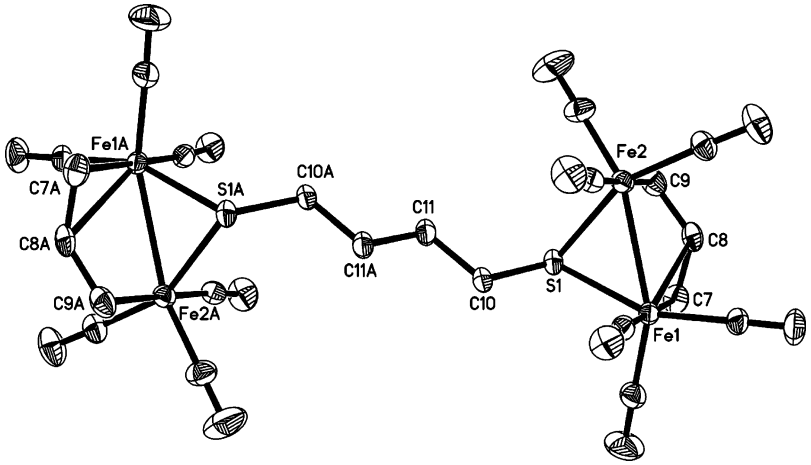

Figure 1. ORTEP drawing of **5a** with atom-labeling scheme.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 5a

Fe(1)−C(1)	1.771(5)	Fe(2)−C(9)	2.096(4)
Fe(1)−C(7)	2.110(4)	Fe(2)−S(1)	2.2181(13)
Fe(1)−S(1)	2.2232(14)	S(1)−C(10)	1.800(4)
Fe(1)−C(8)	2.429(4)	C(7)−C(8)	1.383(6)
Fe(1)−Fe(2)	2.6530(12)	C(8)−C(9)	1.403(6)
C(7)−Fe(1)−S(1)	86.96(13)	Fe(2)−S(1)−Fe(1)	73.36(5)
C(7)−Fe(1)−C(8)	34.56(14)	C(7)−C(8)−Fe(1)	60.0(2)
S(1)−Fe(1)−C(8)	82.24(11)	C(9)−C(8)−Fe(1)	114.0(3)
C(7)−Fe(1)−Fe(2)	89.34(13)	C(8)−C(9)−Fe(2)	89.7(3)
S(1)−Fe(1)−Fe(2)	53.23(3)	C(9)−Fe(2)−Fe(1)	85.92(13)
C(8)−Fe(1)−Fe(2)	59.16(11)	S(1)−Fe(2)−Fe(1)	53.41(4)

S atoms by a butylene group. The two S atoms attached to the butylene group are bound symmetrically across the two iron atoms (Fe(1)−S(1) = 2.2232(14) Å; Fe(2)−S(1) = 2.2181 (13) Å), as are the two terminal carbon atoms in each of the allyl ligands (Fe(1)−C(7) = 2.110 (4) Å; Fe(2)−C(9) = 2.096 (4) Å). The C−C bond lengths of the allyl ligands (C(7)−C(8) = 1.383(6) Å; C(8)−C(9) = 1.403(6) Å) lie between the values reported for C−C single and double bonds, indicating that the ligands are best regarded as delocalized π-allyl ligands.[15] In addition, the dihedral angle between two wings of each butterfly subcluster core is 87.4° and the butylene bridge is connected to S atoms (the angle C(10)−S(1)···C(8) = 160.9°) by an equatorial type of bond.[16] In fact, the basic geometry of the subcluster cores in this double-butterfly cluster complex is very similar to that of the single-butterfly cluster complex (μ-EtS)(μ-CH_2=$CHCH_2$)Fe_2-$(CO)_6$.[17]

Synthesis and Characterization of [(μ-PhS)Fe_2-$(CO)_6$]$_2$(μ-SZS-μ) (6a,b), [$Fe_2(CO)_6$]$_2$(μ-S−S-μ)(μ-SZS-μ) (7a,b), and [$Fe_2(CO)_6$]$_2$(μ-SZS-μ)$_2$ (8a,b). While the $[Et_3NH]^+$ salts of dianions **4** (Z = $CH_2(CH_2OCH_2)_{2,3}CH_2$) reacted with PhSBr in THF at room temperature (through nucleophilic attack of the two negatively charged Fe atoms of **4** at two molecules of PhSBr and subsequent displacement of the two μ-CO ligands in intermediate $\mathbf{m_2}$) to give the linear double-butterfly

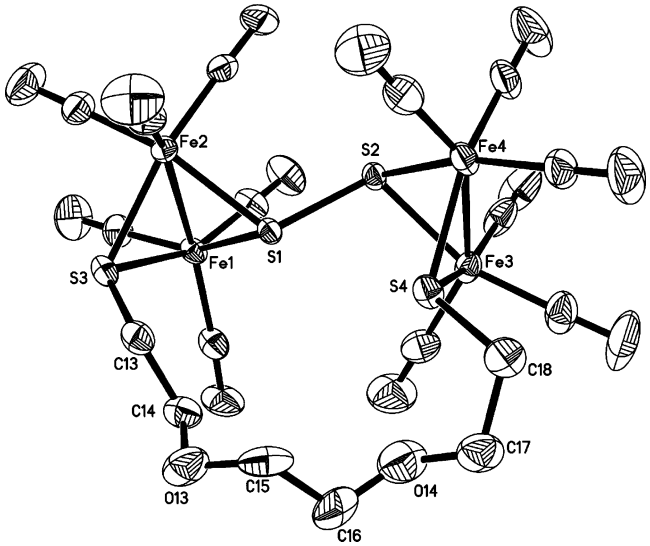

Figure 2. ORTEP drawing of **7a** with atom-labeling scheme.

complexes **6a**,**b**, they reacted with S_2Cl_2 and ClSZSCl (Z = $CH_2(CH_2OCH_2)_{2,3}CH_2$) under similar conditions (through double nucleophilic attack of the two negatively charged Fe atoms of **4** at one molecule of S_2Cl_2 or ClSZSCl followed by loss of two μ-CO ligands from intermediate $\mathbf{m_3}$ or $\mathbf{m_4}$) to afford the macrocyclic cluster complexes **7a**,**b** and **8a**,**b**, respectively (Scheme 3).

Products **6a**,**b**, **7a**,**b**, and **8a**,**b** may be regarded as new types of acyclic and cyclic cluster crown ethers, which have been characterized by elemental analyses and IR and ^{1}H NMR spectroscopy, as well as for **7a** and **8a** by X-ray diffraction analyses. While the ^{1}H NMR spectra of **6a**,**b**, **7a**,**b**, and **8a,b** displayed the corresponding H-containing organic groups, their IR spectra exhibited several absorption bands in the range 2081−1966 cm^{-1} for their terminal carbonyls and one absorption band in the region 1128−1116 cm^{-1} for their ether chain functionalities.

Figure 2 shows the molecular structure of **7a**, and Table 2 displays its bond lengths and angles. As can be seen in Figure 2, complex **7a** contains the two butterfly subcluster cores Fe(1)Fe(2)S(1)S(3) and Fe(3)Fe(4)S(2)S(4), which are connected by an S(1)−S(2) bond and the ether chain C(13)C(14)O(13)C(15)C(16)-O(14)C(17)C(18) to afford a 16-membered macrocycle.

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Scheme 3

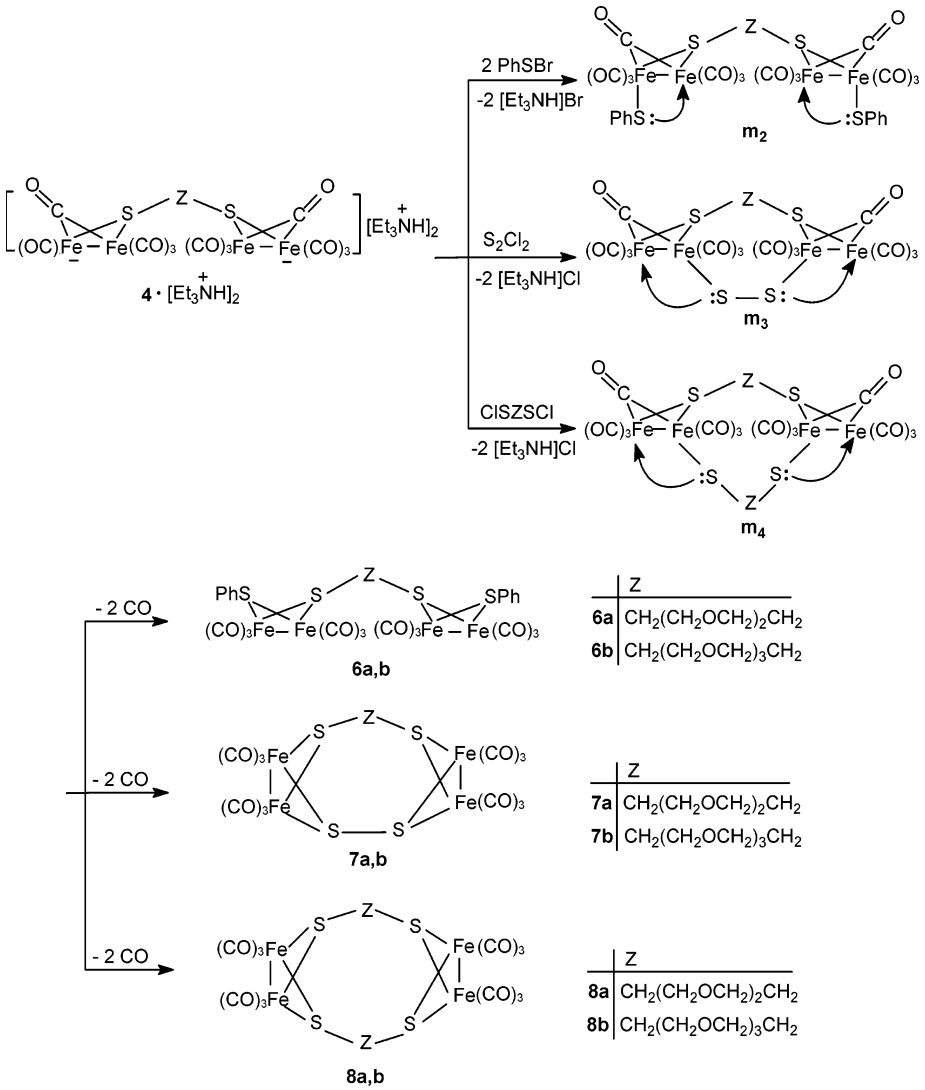

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 7a

Fe(1)−C(1)	1.808(6)	Fe(1)−S(3)	2.286(2)
Fe(1)−C(2)	1.800(7)	Fe(2)−S(3)	2.2802(18)
Fe(1)−S(1)	2.239(2)	Fe(3)−S(4)	2.2581(19)
Fe(2)−S(1)	2.2428(18)	Fe(3)−Fe(4)	2.5304(17)
Fe(1)−Fe(2)	2.5103(16)	S(1)−S(2)	2.118(2)
S(1)−Fe(1)−S(3)	78.30(5)	S(1)−Fe(2)−S(3)	78.34(7)
S(1)−Fe(1)−Fe(2)	56.01(4)	S(1)−Fe(2)−Fe(1)	55.87(6)
S(3)−Fe(1)−Fe(2)	56.55(4)	S(2)−Fe(3)−S(4)	80.89(6)
S(4)−Fe(4)−S(2)	80.86(5)	S(2)−Fe(3)−Fe(4)	55.96(6)
S(4)−Fe(4)−Fe(3)	55.95(5)	Fe(1)−S(1)−Fe(2)	68.12(5)
S(2)−S(1)−Fe(1)	111.78(7)	S(2)−S(1)−Fe(2)	113.78(7)

In addition, the ether chain is bound to S(3) by the axial bond C(13)−S(3) (the angle C(13)−S(3)···S(1) = 77.9°) and to S(4) by the equatorial bond C(18)−S(4) (the angle C(18)−S(4)···S(2) = 158.0°), whereas the subcluster core Fe(1)Fe(2)S(1)S(3) is bonded to S(2) by its equatorial bond (the angle S(2)−S(1)···S(3) = 159.1°) and the subcluster core Fe(3)Fe(4)S(2)S(4) to S(1) by its axial bond (the angle S(1)−S(2)···S(4) = 74.4°),[16] respectively. The S−S bond (2.118(2) Å) of **7a** is lengthened from the single S−S bond (2.037(5) Å) in elemental sulfur.[18] It is

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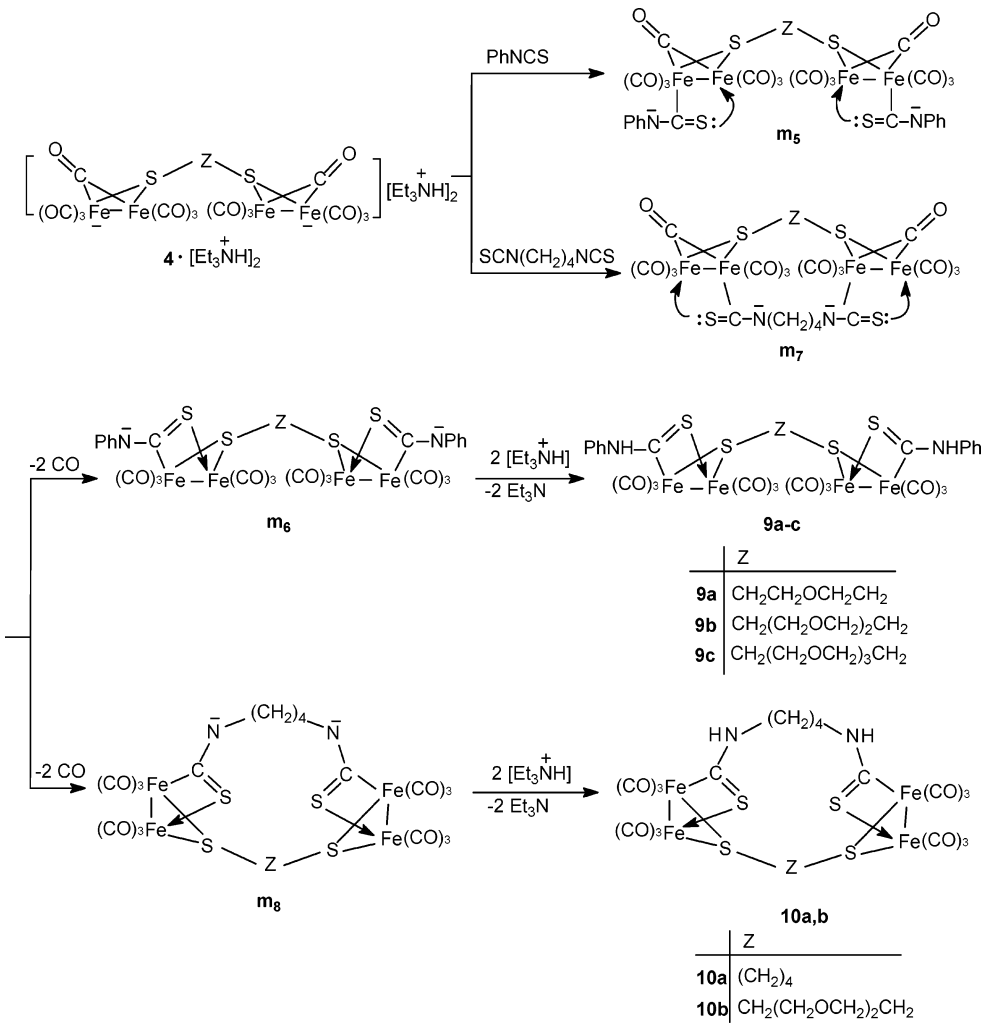
Table 3. Selected Bond Lengths (Å) and Angles (deg) for 8a

Fe(1)−C(1)	1.793(7)	Fe(2)−S(2A)	2.2592(19)
Fe(1)−S(1)	2.2468(19)	S(1)−C(7)	1.838(6)
Fe(2)−S(1)	2.2541(19)	S(2)−C(12)	1.842(6)
Fe(1)−S(2A)	2.2601(18)	Fe(2)−C(4)	1.788(7)
Fe(1)−Fe(2)	2.5130(14)	S(2)−Fe(1A)	2.2601(18)
C(1)−Fe(1)−S(1)	94.1(2)	S(1)−Fe(2)−S(2A)	80.32(7)
S(1)−Fe(1)−S(2A)	80.46(6)	S(1)−Fe(2)−Fe(1)	55.92(5)
C(1)−Fe(1)−Fe(2)	102.8(2)	S(2A)−Fe(2)−Fe(1)	56.23(5)
S(1)−Fe(1)−Fe(2)	56.20(5)	C(7)−S(1)−Fe(1)	114.6(2)
S(2A)−Fe(1)−Fe(2)	56.20(5)	Fe(1)−S(1)−Fe(2)	67.88(6)

also lengthened compared to the S−S bond (2.108(3) Å) of the linear double cluster complex [(μ-PhS)$Fe_2(CO)_6$]$_2$-(μ-S−S-μ),[3] obviously due to formation of its 16-membered ring, in which the ether chain pulls the two butterfly Fe_2S_2 cluster cores closer and thus makes the S−S bond longer.

The molecular structure of **8a** is shown in Figure 3, and its bond lengths and angles are displayed in Table 3. Similar to **7a**, product **8a** is composed of the two butterfly cluster cores Fe(1)Fe(2)S(1)S(2A) and Fe(1A)Fe(2A)S(2)S(1A) linked together by the two ether chains C(7)C(8)O(7)C(9)C(10)O(8)C(11)C(12) and C(7A)C(8A)O(7A)C(9A)C(10A)O(8A)C(11A)C(12A) to form a 24-membered macrocycle. The heteroatom distances

Scheme 4



S(1)−S(1A), S(2)−S(2A), O(7)−O(7A), and O(8)−O(8A) are in the range 7.122−8.815 Å. While one ether chain is bonded to S(1) and S(2) by the equatorial bond C(7)−S(1) (the angle C(7)−S(1)···S(2A) = 158.8°) and axial bond C(12)−S(2) (the angle C(12)−S(2)···S(1A) = 79.8°), the other ether chain is bound to S(1A) and S(2A) by the equatorial bond C(7A)−S(1A) (the angle C(7A)−S(1A)···S(2) = 158.5°) and axial bond C(12A)−S(2A) (the angle C(12A)-S(2A)···S(1) = 79.8°),[16] respectively. However, in contrast to **7a**, product **8a** has two identical ether chains, whose structure is centrosymmetric. To our knowledge, both **7a** and **8a** are so far the first crystallographically characterized cyclic double-butterfly Fe_2S_2 clusters.

Synthesis and Characterization of [(*μ*-PhNHC=S)$Fe_2(CO)_6$]$_2$(*μ*-SZS-*μ*) (9a−c), [$Fe_2(CO)_6$]$_2$[*μ*-S=CNH-$(CH_2)_4$NHC=S-*μ*](*μ*-SZS-*μ*) (10a,b), [(*μ*-*σ*,*π*-PhCH=CPh)$Fe_2(CO)_6$]$_2$(*μ*-SZS-*μ*) (11a,b), and [(*μ*-*σ*,*π*-PhCH=CH)$Fe_2(CO)_6$]$_2$(*μ*-SZS-*μ*) (12a−c). We further found that the $[Et_3NH]^+$ salts of dianions **4** not only reacted with the electrophiles having one and two leaving groups to produce the linear and cyclic double-butterfly clusters of types **5**−**8** as described above, but also they could react with the electrophiles that have no leaving group to yield the corresponding linear and cyclic double-butterfly clusters. For example, the $[Et_3NH]^+$ salts of **4** (Z = $CH_2(CH_2OCH_2)_{1-3}CH_2$) reacted with phenyl isothiocyanate in THF at room temperature to afford the double-butterfly cluster compounds **9a**−**c**, whereas the $[Et_3NH]^+$ salts of dianions **4** (Z = $(CH_2)_4$, $CH_2(CH_2OCH_2)_2CH_2$) reacted with diisothiocyanate $SCN(CH_2)_4NCS$ under similar conditions to yield the macrocyclic double-butterfly clusters **10a**,**b** (Scheme 4). Clusters **9a**−**c** might be suggested as being derived from nucleophilic attack of the two negatively charged Fe atoms of **4** at the central C atoms of two molecules of PhNCS followed by loss of two *μ*-CO ligands of dianions $\mathbf{m_5}$ and protonation of the N-centered dianions $\mathbf{m_6}$ by

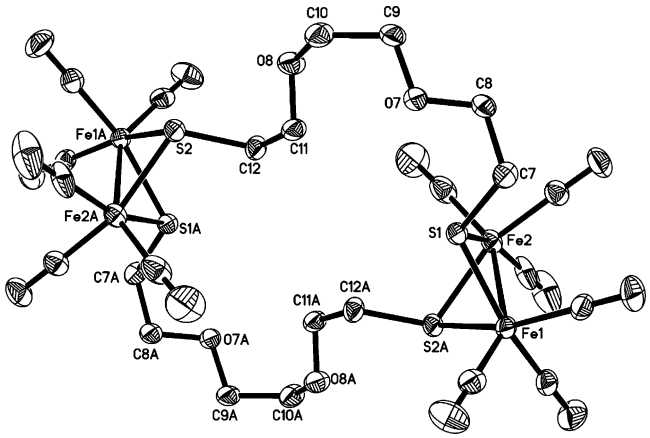
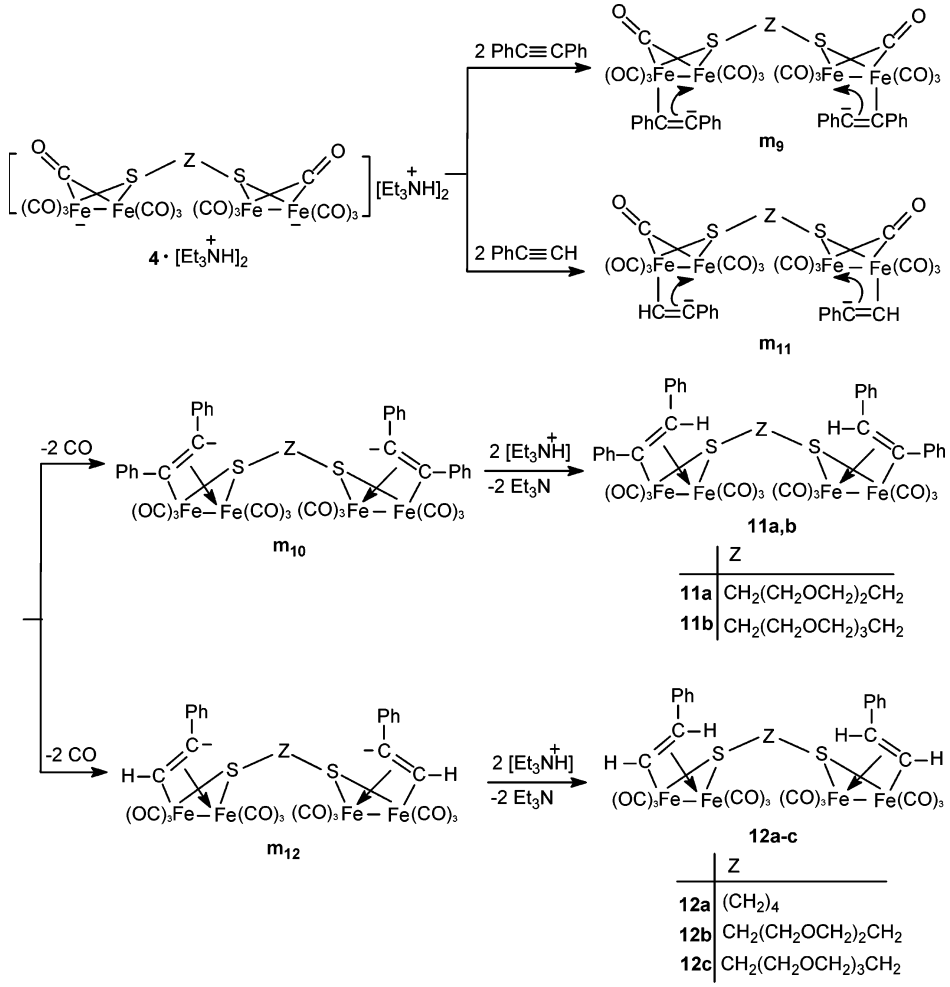


Figure 3. ORTEP drawing of **8a** with atom-labeling scheme.

Scheme 5



the counterion $[Et_3NH]^+$; similarly, clusters **10a**,**b** could be regarded as produced through nucleophilic attack of the two negatively charged Fe atoms of **4** at the central C atoms in two N═C═S functional groups of one molecule of the diisothiocyanate followed by loss of two μ-CO ligands from dianions $\mathbf{m_7}$ and protonation of the N-centered dianions $\mathbf{m_8}$ by the $[Et_3NH]^+$ cation (Scheme 4).

Clusters **9a**−**c** and **10a**,**b** have been characterized by elemental analysis and spectroscopy. For example, while their ^{1}H NMR spectra showed one singlet at about 9 ppm for **9a**−**c** and about 7 ppm for **10a**,**b** assigned to their NH groups, their IR spectra displayed one absorption bond in the range 940−1026 cm^{-1} for their coordinated thiocarbonyl C═S groups.[19] In fact, the formation of PhNHC═S and S═CHN$(CH_2)_4$NHC═S ligands in the above-mentioned reactions could be strongly supported by the crystal structure of the single-butterfly cluster (μ-*p*-MeC_6H_4Se)(μ-PhCH_2NHC═S)$Fe_2(CO)_6$, produced from reaction of the $[Et_3NH]^+$ salt of the monoanion [(μ-*p*-MeC_6H_4Se)(μ-CO)$Fe_2(CO)_6$]$^-$ with PhCH_2NCS.[20]

Similarly, the $[Et_3NH]^+$ salts of dianions **4** (Z = $(CH_2)_4$, $CH_2(CH_2OCH_2)_{2,3}CH_2$) reacted with diphenylacetylene and phenylacetylene in refluxing THF to give the double-butterfly cluster complexes **11a**,**b** and **12a**−**c**, respectively (Scheme 5).

Apparently, **11a**,**b** were presumably formed by nucleophilic attack of the two negatively charged Fe atoms in **4** at the triply bonded C atoms of two molecules of diphenylacetylene, followed by loss of two μ-CO ligands from the C-centered dianions $\mathbf{m_9}$ and protonation of another C-centered dianion $\mathbf{m_{10}}$ by the $[Et_3NH]^+$ cation; similarly, **12a**−**c** might be produced by protonation of the C-centered danions $\mathbf{m_{12}}$ by the $[Et_3NH]^+$ cation, which were formed by nucleophilic attack of the two negatively charged Fe atoms of **4** at β-C atoms of two phenylacetylene molecules (both steric considerations and the ability of the phenyl group to stabilize α-carbanions favor β-attack of the iron nucleophile), followed by loss of two μ-CO ligands from the initially formed C-centered dianions $\mathbf{m_{11}}$ (Scheme 5).

In the ^{1}H NMR spectra of complexes **11a**,**b** and **12a**−**c**, the *endo*-PhCH signals for **11a**,**b** are overlapped with their CH_2O signals as a multiplet from 3.6 to 3.7 ppm, whereas the *endo*-PhCH signals for **12a**−**c** are found as an upfield doublet ($\delta_H \sim 4.3$ ppm, $J_{trans} \approx 13$ Hz) and the *endo*-FeCH signals for **12a**−**c** appear as a low-field doublet ($\delta_H \sim 8.4$ ppm, $J_{trans} \approx 13$ Hz). These data agree with the corresponding data reported by Seyferth and King the for single-butterfly complexes (μ-σ,π-PhCH═CH)(μ-^{t}BuS)$Fe_2(CO)_6$,[21] (μ-σ,π-PhCH═CPh)(μ-^{t}BuS)Fe_2-

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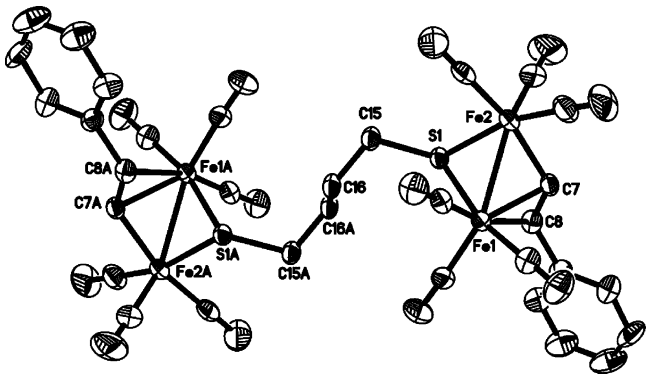

Figure 4. ORTEP drawing of **12a** with atom-labeling scheme.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 12a

Fe(1)−C(8)	2.235(6)	Fe(3)−Fe(4)	2.5517(13)
Fe(1)−S(1)	2.2737(17)	Fe(4)−S(2)	2.2563(17)
Fe(1)−Fe(2)	2.5395(14)	S(1)−C(15)	1.824(5)
Fe(2)−C(7)	1.974(6)	C(7)−C(8)	1.393(8)
Fe(3)−S(2)	2.2751(17)	C(8)−C(9)	1.502(8)
S(1)−Fe(1)−Fe(2)	55.43(5)	S(2)−Fe(4)−Fe(3)	56.08(5)
S(1)−Fe(2)−Fe(1)	56.28(5)	Fe(2)−S(1)−Fe(1)	68.28(5)
C(7)−C(8)−C(9)	126.2(6)	Fe(4)−S(2)−Fe(3)	68.54(5)
C(7)−C(8)−Fe(1)	65.5(3)	C(8)−C(7)−Fe(2)	127.9(4)
C(9)−C(8)−Fe(1)	121.3(4)	C(8)−C(7)−Fe(1)	77.1(3)
S(2)−Fe(3)−Fe(4)	55.38(5)	Fe(2)−C(7)−Fe(1)	77.4(2)

$(CO)_6$,[21] and (μ-σ,π-CH_2═CH)(μ-RS)$Fe_2(CO)_6$.[22] Thus, from the ^{1}H NMR data for the vinyl ligand in double-cluster complexes **11a**,**b** and **12a**−**c**, it was determined that overall addition of the diiron unit and the proton to the two molecules of acetylenes occurred in a cis fashion. This is completely consistent with the addition mode between the $[Et_3NH]^+$ salts of single-butterfly anions $[(\mu\text{-RS})(\mu\text{-CO})Fe_2(CO)_6]^-$ and acetylenes to form the corresponding single-butterfly complexes (μ-σ,π-R^1-CH═CR^2)(μ-RS)$Fe_2(CO)_6$.[21]

The molecular structure of **12a** is shown in Figure 4, while selected bond lengths and angles are presented in Table 4. Complex **12a**, similar to **5a**, is also a centrosymmetric double-butterfly cluster complex, which contains two butterfly Fe_2SC_2 subcluster cores coupled together by a butylene group. However, in contrast to **5a**, the two S atoms attached to the butylene group and the two C atoms of substituted vinyl ligands in **12a** are asymmetrically bonded to the two iron atoms (Fe(1)−S(1) = 2.2737(17) Å; Fe(2)−S(1) = 2.2509(17) Å; Fe(1)−C(8) = 2.235(6) Å; Fe(2)−C(7) = 1.974(6) Å). It is noteworthy that the C−C bond length of the substituted vinyl ligand (C(7)−C(8) = 1.393(8) Å) is obviously longer than the normal value for a C−C double bond, which demonstrates that the C−C double bond in each of the substituted vinyl ligands is coordinated to the two iron atoms in a σ,π-manner (Fe(2)−C(7) σ-bond length 1.974(6) Å; Fe(1)−C(7) and Fe(1)−C(8) π-bond lengths 2.087(6) and 2.235(6) Å, respectively). Finally, it is also worth noting that the dihedral angle between the two butterfly wings Fe(2)−Fe(1)−S(1) and Fe(1)−Fe(2)−C(7)−C(8) (109.5°) is much larger than the corresponding angle in **5a** (87.4°) and the subcluster cores are also linked through S atoms by an equatorial type of bond[16] (the angle C(15)−S(1)···C(7) = C(15A)−S(1A)···C(7A) = 151.4°).

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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 and bubbled for ca. 30 min before use. $Fe_3(CO)_{12}$,[23] HSZSH (Z = $(CH_2)_4$, $CH_2(CH_2OCH_2)_nCH_2$ (n = 1−3)),[24] PhSBr,[25] ClSZSCl (Z = $CH_2(CH_2OCH_2)_nCH_2$ (n = 2, 3)),[26] $SCN(CH_2)_4NCS$,[27] and PhC≡CH[28] were prepared according to literature procedures. CH_2═$CHCH_2Br$, S_2Cl_2, and PhNCS 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 Bio-Rad FTS 135 infrared spectrophotometer. ^{1}H NMR spectra were taken on a Bruker AC-P200 NMR spectrometer. C/H analyses were performed with an Elementar Vario EL analyzer. Melting points were determined on a Yanaco MP-500 apparatus and were uncorrected.

Standard in Situ Preparation of the $[Et_3NH]^+$ Salts of Dianions $\{[(\mu\text{-CO})Fe_2(CO)_6]_2(\mu\text{-SZS-}\mu)\}^{2-}$ (4·$[Et_3NH]_2$). A 100 mL three-necked flask fitted with a magnetic stir bar, a rubber septum, and a nitrogen inlet tube was charged with 1.00 g (2.0 mmol) of $Fe_3(CO)_{12}$, 30 mL of THF, 1.0 mmol of HSZSH (Z = $(CH_2)_4$, $CH_2(CH_2OCH_2)_nCH_2$ (n = 1−3)) and 0.28 mL (2.0 mmol) of Et_3N. The mixture was stirred at room temperature for 45 min to give a brown-red solution of ca. 1 mmol of the intermediate salts **4**·$[Et_3NH]_2$, which was utilized immediately in the following preparations.

Preparation of $[(\mu\text{-}CH_2$═$CHCH_2)Fe_2(CO)_6]_2[\mu\text{-}S(CH_2)_4S\text{-}\mu]$ (5a). To the above-prepared solution of **4**·$[Et_3NH]_2$ (Z = $(CH_2)_4$) was added 0.70 mL (8.0 mmol) of CH_2═$CHCH_2Br$, and the mixture was stirred at room temperature for 16 h. The solvent was removed under reduced pressure. The residue was subjected to TLC separation using CH_2Cl_2/petroleum ether (1/4 v/v) as eluent. From the main red band, 0.190 g (25%) of **5a** was obtained as a red solid, mp 125 °C dec. Anal. Calcd for $C_{22}H_{18}Fe_4O_{12}S_2$: C, 34.68; H, 2.38. Found: C, 34.45; H, 2.28. IR (KBr disk): $\nu_{C\equiv O}$ 2059 (vs), 2025 (vs), 1965 (vs) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): 0.48 (d, J = 11.9 Hz, 4H, 4 anti-FeC*H*H), 1.69 (s, 4H, $CH_2CH_2CH_2CH_2$), 1.98 (d, J = 5.6 Hz, 4H, 4 syn-FeCH*H*), 2.44 (s, 4H, $2CH_2S$), 4.70−4.85 (m, 2H, 2 allylic CH) ppm.

Preparation of $[(\mu\text{-}CH_2$═$CHCH_2)Fe_2(CO)_6]_2[\mu\text{-}SCH_2\text{-}(CH_2OCH_2)_2CH_2S\text{-}\mu]$ (5b). The same procedure was followed as for **5a**, but **4**·$[Et_3NH]_2$ (Z = $CH_2(CH_2OCH_2)_2CH_2$) was used. From the main red band, 0.259 g (32%) of **5b** was obtained as a red oil. Anal. Calcd for $C_{24}H_{22}Fe_4O_{14}S_2$: C, 35.07; H, 2.70. Found: C, 34.48; H, 2.96. IR (KBr disk): $\nu_{C\equiv O}$ 2061 (s), 2020 (vs), 1950 (vs); ν_{C-O-C} 1110 (m) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): 0.51 (d, J = 10.2 Hz, 4H, 4 anti-FeC*H*H), 1.97 (d, J = 6.1 Hz, 4H, 4 syn-FeCH*H*), 2.65 (s, 4H, $2CH_2S$), 3.62 (s, 8H, $4CH_2O$), 4.60−5.05 (m, 2H, 2 allylic CH) ppm.

Preparation of $[(\mu\text{-}CH_2$═$CHCH)Fe_2(CO)_6]_2[\mu\text{-}SCH_2\text{-}(CH_2OCH_2)_3CH_2S\text{-}\mu]$ (5c). The same procedure was followed as for **5a**, but **4**·$[Et_3NH]_2$ (Z = $CH_2(CH_2OCH_2)_3CH_2$) was utilized. From the main red band, 0.208 g (24%) of **5c** was

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obtained as a red oil. Anal. Calcd for $C_{26}H_{26}Fe_4O_{15}S_2$: C, 36.06; H, 3.02. Found: C, 36.00; H, 2.95. IR (KBr disk): $\nu_{C\equiv O}$ 2061 (s), 2016 (vs), 1955 (vs); ν_{C-O-C} 1108 (m) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): 0.49 (d, J = 12.5 Hz, 4H, 4 anti-FeC*H*H), 1.98 (d, J = 5.6 Hz, 4H, 4 syn-FeCH*H*), 2.62−2.67 (m, 4H, $2CH_2S$), 3.63 (s, 12H, $6CH_2O$), 4.70−4.85 (m, 2H, 2 allylic CH) ppm.

Preparation of [(μ-PhS)Fe$_2$(CO)$_6$]$_2$[μ-SCH$_2$(CH$_2$OCH$_2$)$_2$-CH$_2$S-μ] (6a). To the above-prepared solution of **4**·[Et_3NH]$_2$ (Z = $CH_2(CH_2OCH_2)_2CH_2$) was added 0.378 g (2.0 mmol) of PhSBr, and the mixture was stirred at room temperature for 12 h. Solvent was removed under reduced pressure. The residue was subjected to TLC separation using CH_2Cl_2/petroleum ether (1/1 v/v) as eluent. From the main red band, 0.342 g (36%) of **6a** was obtained as a red solid, mp 146 °C dec. Anal. Calcd for $C_{30}H_{22}Fe_4O_{14}S_4$: C, 37.61; H, 2.31. Found: C, 37.53; H, 2.25. IR (KBr disk): $\nu_{C\equiv O}$ 2070 (s), 2032 (vs), 1990 (vs), 1968 (vs); ν_{C-O-C} 1125 (s) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): 2.52 (t, J = 6.4 Hz, 4H, $2CH_2S$), 3.50−3.62 (m, 8H, $4CH_2O$), 7.13−7.24 (m, 10H, $2C_6H_5$) ppm.

Preparation of [(μ-PhS)Fe$_2$(CO)$_6$]$_2$[μ-SCH$_2$(CH$_2$OCH$_2$)$_3$-CH$_2$S-μ] (6b). The same procedure was followed as for **6a**, but **4**·[Et_3NH]$_2$ (Z = $CH_2(CH_2OCH_2)_3CH_2$) was used. From the main red band, 0.410 g (41%) of **6b** was obtained as a red oil. Anal. Calcd for $C_{32}H_{26}Fe_4O_{15}S_4$: C, 38.35; H, 2.61. Found: C, 38.22; H, 2.55. IR (KBr disk): $\nu_{C\equiv O}$ 2071 (s), 2033 (vs), 1993 (vs); ν_{C-O-C} 1116 (m) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): 2.56 (s, 4H, 2 CH_2S), 3.58 (s, 12H, $6CH_2O$), 7.24 (s, 10H, $2C_6H_5$) ppm.

Preparation of [Fe$_2$(CO)$_6$]$_2$(μ-S−S-μ)[μ-SCH$_2$(CH$_2$OCH$_2$)$_2$-CH$_2$S-μ] (7a). To the above-prepared solution of **4**·[Et_3NH]$_2$ (Z = $CH_2(CH_2OCH_2)_2CH_2$) was added 0.16 mL (2.0 mmol) of S_2Cl_2, and the mixture was stirred at room temperature for 4 h. Solvent was removed under reduced pressure. The residue was subjected to TLC separation using acetone/petroleum ether (1/10 v/v) as eluent. From the main red band, 0.103 (13% yield) of **7a** was obtained as a red solid, mp 155 °C dec. Anal. Calcd for $C_{18}H_{12}Fe_4O_{14}S_4$: C, 26.89; H, 1.50. Found: C, 26.85; H, 1.45. IR (KBr disk): $\nu_{C\equiv O}$ 2080 (s), 2067 (s), 2045 (vs), 2022 (vs), 1998 (vs), 1980 (vs); ν_{C-O-C} 1127 (m) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): 2.24−2.30, 2.70−2.75 (m, m, 4H, $2CH_2S$), 3.27−3.78 (m, 8H, $4CH_2O$) ppm.

Preparation of [Fe$_2$(CO)$_6$]$_2$(μ-S−S-μ)[μ-SCH$_2$(CH$_2$OCH$_2$)$_3$-CH$_2$S-μ] (7b). The same procedure was followed as for **7a**, but **4**·[Et_3NH]$_2$ (Z = $CH_2(CH_2OCH_2)_3CH_2$) was employed. From the main red band, 0.149 g (18% yield) of **7b** was obtained as a red solid, mp 148 °C dec. Anal. Calcd for $C_{20}H_{16}Fe_4O_{15}S_4$: C, 28.33; H, 1.90. Found: C, 28.20; H, 1.91. IR (KBr disk): $\nu_{C\equiv O}$ 2081 (s), 2069 (s), 2046 (vs), 2022 (vs), 1999 (vs), 1980 (vs); ν_{C-O-C} 1128 (m) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): 2.13−2.20, 2.70−2.79 (m, m, 4H, $2CH_2S$), 3.26−3.83 (m, 12H, $6CH_2O$) ppm.

Preparation of [Fe$_2$(CO)$_6$]$_2$[(μ-SCH$_2$(CH$_2$OCH$_2$)$_2$CH$_2$S-μ)]$_2$ (8a). After the above-prepared solution of **4**·[Et_3NH]$_2$ (Z = $CH_2(CH_2OCH_2)_2CH_2$) was cooled to −10 °C, 0.252 g (1.0 mmol) of $ClCH_2(CH_2OCH_2)_2CH_2SCl$ was added. The mixture was stirred at room temperature for 12 h. Solvent was removed under reduced pressure. The residue was subjected to TLC separation using acetone/petroleum ether (1/3 v/v) as eluent. From the main red band, 0.132 g (14%) of **8a** was obtained as a red solid, mp 146−148 °C. Anal. Calcd for $C_{24}H_{24}Fe_4O_{16}S_4$: C, 31.33; H, 2.63. Found: C, 31.19; H, 2.89. IR (KBr disk): $\nu_{C\equiv O}$ 2071 (s), 2036 (vs), 1995 (vs), 1966 (vs); ν_{C-O-C} 1119 (s) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): 2.27−2.71 (m, 8H, $4CH_2S$), 3.44−3.96 (m, 16H, $8CH_2O$) ppm.

Preparation of [Fe$_2$(CO)$_6$]$_2$[(μ-SCH$_2$(CH$_2$OCH$_2$)$_3$CH$_2$S-μ)]$_2$ (8b). The same procedure was followed as for **8a**, but **4**·[Et_3NH]$_2$ (Z = $CH_2(CH_2OCH_2)_3CH_2$) was employed. From the main red band, 0.148 g (15%) of **8b** was obtained as a red solid, mp 148 °C dec. Anal. Calcd for $C_{28}H_{32}Fe_4O_{18}S_4$: C, 33.36; H, 3.20. Found: C, 33.30; H, 3.15. IR (KBr disk): $\nu_{C\equiv O}$ 2068 (s), 2031 (vs), 1994 (vs), 1975 (s); ν_{C-O-C} 1127 (s) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): 2.32−2.68 (m, 8H, $4CH_2S$), 3.38−3.87 (m, 24H, $12CH_2O$) ppm.

Preparation of [(μ-PhNHC=S)Fe$_2$(CO)$_6$]$_2$(μ-SCH$_2$CH$_2$-OCH$_2$CH$_2$S-μ) (9a). To the above-prepared solution of **4**·[Et_3NH]$_2$ (Z = $CH_2CH_2OCH_2CH_2$) was added 0.24 mL (2.0 mmol) of PhN=C=S, and the mixture was stirred at room temperature for 12 h. Solvent was removed under reduced pressure. The residue was subjected to TLC separation. Acetone/petroleum ether (1/4 v/v) eluted the first main red band, which gave 0.387 g (40%) of **9a** as an orange solid, mp 68−70 °C. Anal. Calcd for $C_{30}H_{20}Fe_4N_2O_{13}S_4$: C, 37.22; H, 2.08; N, 2.89. Found: C, 37.21; H, 2.11; N, 2.85. IR (KBr disk): $\nu_{C\equiv O}$ 2065 (vs), 2024 (vs), 1989 (vs); ν_{N-H} 3380 (m); ν_{C-O-C} 1107 (m); $\nu_{C=S}$ 943 (w) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): 2.86−2.94 (m, 4H, $2CH_2S$), 3.93 (t, J = 6.4 Hz, 4H, $2CH_2O$), 7.24−7.31 (m, 10H, $2C_6H_5$), 8.73 (s, 2H, 2NH) ppm.

Preparation of [(μ-PhNHC=S)Fe$_2$(CO)$_6$]$_2$[μ-SCH$_2$-(CH$_2$OCH$_2$)$_2$CH$_2$S-μ] (9b). The same procedure was followed as for **9a**, but **4**·[Et_3NH]$_2$ (Z = $CH_2(CH_2OCH_2)_2CH_2$) was utilized. The residue was subjected to TLC separation using acetone/petroleum ether (1/10 v/v) as eluent. From the main red band, 0.705 g (70%) of **9b** was obtained as an orange solid, mp 68−71 °C. Anal. Calcd for $C_{32}H_{24}Fe_4N_2O_{14}S_4$: C, 37.97; H, 2.39; N, 2.77. Found: C, 37.85; H, 2.48; N, 3.04. IR (KBr disk): $\nu_{C\equiv O}$ 2064 (vs), 2024 (vs), 1989 (vs); ν_{N-H} 3379 (m); ν_{C-O-C} 1113 (m); $\nu_{C=S}$ 940 (w) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): 2.80 (s, 4H, $2CH_2S$), 3.63−3.85 (m, 8H, $4CH_2O$), 7.26 (s, 10H, $2C_6H_5$), 8.69 (s, 2H, 2NH) ppm.

Preparation of [(μ-PhNHC=S)Fe$_2$(CO)$_6$]$_2$[μ-SCH$_2$-(CH$_2$OCH$_2$)$_3$CH$_2$S-μ] (9c). The same procedure was followed as for **9a**, but **4**·[Et_3NH]$_2$ (Z = $CH_2(CH_2OCH_2)_3CH_2$) was employed. From the main red band, 0.698 g (66%) of **9c** was obtained as an orange solid, mp 55−57 °C. Anal. Calcd for $C_{34}H_{28}Fe_4N_2O_{15}S_4$: C, 38.66; H, 2.67; N, 2.65. Found: C, 38.74; H, 2.78; N, 3.04. IR (KBr disk): $\nu_{C\equiv O}$ 2064 (vs), 2024 (vs), 1988 (vs); ν_{N-H} 3379 (m); ν_{C-O-C} 1111 (m); $\nu_{C=S}$ 941 (w) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): 2.84 (s, 4H, $2CH_2S$), 3.65−3.95 (m, 12H, $6CH_2O$), 7.30 (s, 10H, $2C_6H_5$), 8.74 (s, 2H, 2NH) ppm.

Preparation of [Fe$_2$(CO)$_6$]$_2$[μ-S=CNH(CH$_2$)$_4$NHC=S-μ]-(μ-S(CH$_2$)$_4$S-μ) (10a). To the above-prepared solution of **4**·[Et_3NH]$_2$ (Z = $(CH_2)_4$) was added 0.172 g (1.0 mmol) of $SCN(CH_2)_4NCS$, and the mixture was stirred at room temperature for 12 h. Solvent was removed under reduced pressure. The residue was subjected to TLC separation using acetone/petroleum ether (1/1 v/v) as eluent. From the main red band, 0.146 g (17%) of **10a** was obtained as a red oil. Anal. Calcd for $C_{22}H_{18}Fe_4N_2O_{12}S_4$: C, 30.94; H, 2.12; N, 3.28. Found: C, 31.11; H, 2.19; N, 3.39. IR (KBr disk): $\nu_{C\equiv O}$ 2069 (v), 2025 (vs), 1963 (vs); $\nu_{C=S}$ 1026 (m) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): 1.35−2.10 (m, 8H, $2CH_2CH_2CH_2CH_2$), 2.40−2.65 (m, 4H, $2CH_2S$), 2.80−2.95 (m, 4H, $2CH_2N$), 6.56 (s, 2H, 2HN) ppm.

Preparation of [Fe$_2$(CO)$_6$]$_2$[μ-S=CNH(CH$_2$)$_4$NHC=S-μ]-(μ-SCH$_2$(CH$_2$OCH$_2$)$_2$CH$_2$S-μ) (10b). The same procedure was followed as for **10a**, but **4**·[Et_3NH]$_2$ (Z = $CH_2(CH_2OCH_2)_2CH_2$) was utilized. From the main red band, 0.118 g (13%) of **10b** was obtained as a red oil. Anal. Calcd for $C_{24}H_{22}Fe_4N_2O_{12}S_4$: C, 31.54; H, 2.43; N, 3.06. Found: C, 31.70; H, 2.22; N, 3.25. IR (KBr disk): $\nu_{C\equiv O}$ 2063 (s), 2017 (vs), 1944 (vs); ν_{C-O-C} 1093 (m); $\nu_{C=S}$ 1025 (m) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): 1.35−2.12 (m, 4H, $CH_2CH_2CH_2CH_2$), 2.24−2.80 (m, 4H, $2CH_2S$), 2.75−3.18 (m, 4H, $2CH_2N$), 3.71 (br.s, 8H, $4CH_2O$), 6.62 (s, 2H, 2HN) ppm.

Preparation of [(μ-σ,π-PhCH=CPh)Fe$_2$(CO)$_6$]$_2$[μ-SCH$_2$-(CH$_2$OCH$_2$)$_2$CH$_2$S-μ] (11a). To the above-prepared solution of **4**·[Et_3NH]$_2$ (Z = $CH_2(CH_2OCH_2)_2CH_2$) was added 0.356 g (2.0 mmol) of PhC≡CPh. The mixture was refluxed for 45 min. Solvent was removed under reduced pressure. The residue was subjected to TLC separation using acetone/petroleum ether (1/10 v/v) as eluent. From the main red band, 0.200 g (18%) of **11a** was obtained as a red solid, mp 67−69 °C. Anal. Calcd for $C_{46}H_{32}Fe_4O_{14}S_2$: C, 50.40; H, 2.94. Found: C, 50.08; H, 3.13.

Table 5. Crystal Data and Structural Refinement Details for 5a, 7a, 8a, and 12a

	5a	7a	8a	12a
mol formula	$C_{22}H_{18}Fe_4O_{12}S_2$	$C_{18}H_{12}Fe_4O_{14}S_4$	$C_{24}H_{24}Fe_4O_{16}S_4$	$C_{32}H_{22}Fe_4O_{12}S_2$
mol wt	761.8	803.92	920.07	886.02
temp/K	293(2)	293(2)	293(2)	293(2)
cryst syst	triclinic	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	7.949(4)	9.301(6)	8.224(3)	7.689(2)
b/Å	8.814(4)	11.760(8)	9.766(3)	13.441(4)
c/Å	11.157(5)	14.532(10)	11.153(4)	19.125(6)
α/deg	98.568(8)	103.889(11)	88.962(6)	75.116(5)
β/deg	98.011(8)	97.842(11)	81.064(6)	87.337(5)
γ/deg	110.770(8)	104.773(10)	88.230(6)	74.286(6)
V/Å^3	706.9(6)	1458.5(17)	884.4(5)	1838.3(9)
Z	1	2	1	2
D_c/g cm^{-3}	1.790	1.831	1.728	1.601
abs coeff/mm^{-1}	2.218	2.298	1.911	1.719
F(000)	382	800	464	892
limiting indices	$-7 \le h \le 9$	$-11 \le h \le 10$	$-10 \le h \le 10$	$-9 \le h \le 8$
	$-10 \le k \le 11$	$-9 \le k \le 13$	$-12 \le k \le 6$	$-11 \le k \le 15$
	$-10 \le l \le 13$	$-17 \le l \le 10$	$-13 \le l \le 13$	$-18 \le l \le 22$
scan type	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
no. of rflns	3350	7291	5103	7198
no. of indep rflns	2643	5041	3574	6370
R_{int}	0.0243	0.0204	0.0331	0.0324
$2\theta_{max}$/deg	52.88	50.00	52.86	50.06
no. of data/restraints/params	2643/0/181	5041/304/399	3574/0/217	6370/0/451
R	0.0392	0.0434	0.0504	0.0516
R_w	0.0706	0.1437	0.1161	0.1025
goodness of fit	0.931	1.087	1.065	1.014
largest diff peak and hole/e Å^{-3}	0.501 and −0.323	0.816 and −0.783	0.515 and −0.411	0.381 and −0.320

IR (KBr disk): $\nu_{C\equiv O}$ 2066 (s), 2036 (vs), 1990 (vs); ν_{C-O-C} 1125 (m); $\nu_{C=C}$ 1001 (w) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): 2.63 (s, 4H, $2CH_2S$), 3.66−3.77 (m, 10H, $4CH_2O$, 2PhCH), 6.69−7.24 (m, 20H, $4C_6H_5$) ppm.

Preparation of [(*μ*-*σ*,*π*-PhCH═CPh)Fe$_2$(CO)$_6$]$_2$[*μ*-SCH$_2$(CH$_2$OCH$_2$)$_3$CH$_2$S-*μ*] (11b). The same procedure was followed as for **11a**, but **4**·$[Et_3NH]_2$ ($Z = CH_2(CH_2OCH_2)_3CH_2$) was used. From the main red band, 0.182 g (16%) of **11b** was obtained as a red solid, mp 54−55 °C. Anal. Calcd for $C_{48}H_{36}Fe_4O_{15}S_2$: C, 50.56; H, 3.18. Found: C, 50.54; H, 3.38. IR (KBr disk): $\nu_{C\equiv O}$ 2064 (s), 2033 (vs), 1990 (vs); ν_{C-O-C} 1116 (m); $\nu_{C=C}$ 992 (w) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): 2.62 (s, 4H, $2CH_2S$), 3.64−3.75 (m, 14H, $6CH_2O$, 2PhCH), 6.69−7.24 (m, 20H, $4C_6H_5$) ppm.

Preparation of [(*μ*-*σ*,*π*-PhCH═CH)Fe$_2$(CO)$_6$]$_2$(*μ*-S(CH$_2$)$_4$S-*μ*) (12a). To the above-prepared solution of **4**·$[Et_3NH]_2$ ($Z = (CH_2)_4$) was added 0.408 g (4.0 mmol) of PhC≡CH. The mixture was refluxed for 1 h and stirred at room temperature for 3 h. Solvent was removed under reduced pressure. The residue was subjected to TLC separation using CH_2Cl_2/petroleum ether (1/1 v/v) as eluent. From the main red band, 0.450 g (51%) of **12a** was obtained as a red solid, mp 167 °C dec. Anal. Calcd for $C_{32}H_{22}Fe_4O_{12}S_2$: C, 43.38; H, 2.50. Found: C, 43.42; H, 2.49. IR (KBr disk): $\nu_{C\equiv O}$ 2068 (vs), 2036 (vs), 1985 (vs); $\nu_{C=C}$ 1597 (w) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): 1.82 (s, 4H, $SCH_2CH_2CH_2CH_2S$), 2.38 (s, 4H, $2CH_2S$), 4.35 (d, J = 13.8 Hz, 2H, 2 endo-PhCH), 7.27 (s, 10H, $2C_6H_5$), 8.46 (d, 2H, J = 13.8 Hz, 2 exo-FeCH) ppm.

Preparation of [(*μ*-*σ*,*π*-PhCH═CH)Fe$_2$(CO)$_6$]$_2$[*μ*-SCH$_2$(CH$_2$OCH$_2$)$_2$CH$_2$S-*μ*] (12b). The same procedure was followed as for **12a**, but **4**·$[Et_3NH]_2$ ($Z = CH_2(CH_2OCH_2)_2CH_2$) was used. From the main red band, 0.374 g (40%) of **12b** was obtained as a red solid, mp 121 °C dec. Anal. Calcd for $C_{34}H_{26}Fe_4O_{14}S_2$: C, 43.16; H, 2.77. Found: C, 42.97; H, 3.01. IR (KBr disk): $\nu_{C\equiv O}$ 2069 (vs), 2038 (vs), 1988 (vs); $\nu_{C=C}$ 1597 (w); ν_{C-O-C} 1126 (s) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): 2.57 (t, J = 6.0 Hz, 4H, $2CH_2S$), 3.70(s, 4H, $4CH_2O$), 4.33 (d, J = 13.8 Hz, 2H, 2 endo-PhCH), 7.26 (s, 10H, $2C_6H_5$), 8.45 (d, J = 13.8 Hz, 2H, 2 exo-FeCH) ppm.

Preparation of [(*μ*-*σ*,*π*-PhCH═CH)Fe$_2$(CO)$_6$]$_2$[*μ*-SCH$_2$(CH$_2$OCH$_2$)$_3$CH$_2$S-*μ*] (12c). The same procedure was followed as for **12a**, but **4**·$[Et_3NH]_2$ ($Z = CH_2(CH_2OCH_2)_3CH_2$) was utilized. From the main red band, 0.444 g (45%) of **12c** was obtained as a red solid, mp 135 °C dec. Anal. Calcd for $C_{36}H_{30}Fe_4O_{15}S_2$: C, 43.67; H, 3.05. Found: C, 43.60; H, 3.06. IR (KBr disk): $\nu_{C\equiv O}$ 2068 (vs), 2036 (vs), 1988 (vs); $\nu_{C=C}$ 1596 (w); ν_{C-O-C} 1124 (s) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): 2.57 (s, 4H, $2CH_2S$), 3.69 (s, 12H, $6CH_2O$), 4.32 (d, J = 13.8 Hz, 2H, 2 endo-PhCH), 7.24 (s, 10H, $2C_6H_5$), 8.44 (d, J = 13.8 Hz, 2H, 2 exo-FeCH) ppm.

X-ray Structure Determinations of 5a, 7a, 8a, and 12a. Single crystals of **5a**, **7a**, **8a**, and **12a** suitable for X-ray diffraction analyses were grown by slow evaporation of their CH_2Cl_2/petroleum ether solutions at −20 °C for **7a** and at about 4 °C for **5a, 8a**, and **12a**. Each crystal was mounted on a Bruker SMART 1000 automated diffractometer with a graphite monochromator with Mo Kα radiation (λ = 0.710 73 Å). 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 SHELXTL-97 program. Details of the crystal data, data collections, and structure refinements are summarized in Table 5.

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Supporting Information Available: All crystal data, atomic coordinates and thermal parameters and bond lengths and angles for **5a**, **7a**, **8a**, and **12a** as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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