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Synthesis of Double and Quadruple Butterfly Fe/E Cluster Complexes via a New Type of Selenium-Centered Anions (μ-RE)(μ-Se^-)[$Fe_2(CO)_6$]$_2$(μ_4-Se) (E = S, Se, Te) Derived from Novel Reaction of [(μ-RE)(μ-CO)[$Fe_2(CO)_6$]$^-$ with (μ-Se_2)$Fe_2(CO)_6$. Crystal Structures of μ_4-Se-Containing Double Clusters (μ-EtS)(μ-$PhCH_2Se$)[$Fe_2(CO)_6$]$_2$(μ_4-Se), (μ-*p*-MeC_6H_4Se)(μ-MeSe)[$Fe_2(CO)_6$]$_2$(μ_4-Se), and (μ-*p*-MeC_6H_4Te)(μ-MeSe)[$Fe_2(CO)_6$]$_2$(μ_4-Se)

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The [Et_3NH]$^+$ or [MgBr]$^+$ salts of anions [(μ-RE)(μ-CO)$Fe_2(CO)_6$]$^-$ (**1**, E = S, Se, Te) reacted with (μ-Se_2)$Fe_2(CO)_6$ followed by treatment of the [Et_3NH]$^+$ or [MgBr]$^+$ salts of the intermediate selenium-centered anions (μ-RE)(μ-Se^-)[$Fe_2(CO)_6$]$_2$(μ_4-Se) (**3**) with monohalide $PhCH_2Br$ or MeI to give a series of double butterfly Fe/E cluster complexes (μ-RE)(μ-R^1Se)-[$Fe_2(CO)_6$]$_2$(μ_4-Se) (**4**, RE = EtS, R^1 = $PhCH_2$; **5**, *t*-BuS, $PhCH_2$; **6**, *p*-MeC_6H_4Se, $PhCH_2$; **7**, *p*-MeC_6H_4Se, Me; **8**, *p*-MeC_6H_4Te, $PhCH_2$; **9**, *p*-MeC_6H_4Te, Me). Similarly, reaction of the in situ prepared [Et_3NH]$^+$ salt of the intermediate selenium-centered anion (μ-*t*-BuS)(μ-Se^-)-[$Fe_2(CO)_6$]$_2$(μ_4-Se) with dihalide 1,2-($BrCH_2$)$_2C_6H_4$ or 1,3-($BrCH_2$)$_2$-5-MeC_6H_3 afforded quadruple butterfly Fe/E cluster {(μ-*t*-BuS)[$Fe_2(CO)_6$]$_2$(μ_4-Se)}$_2$(μ-1-$SeCH_2C_6H_4CH_2Se$-2-μ) (**10**) or double butterfly Fe/E cluster (μ-*t*-BuS)[(μ-1-$SeCH_2$-3-$BrCH_2$-5-MeC_6H_3)[$Fe_2(CO)_6$]$_2$ (μ_4-Se) (**11**) and quadruple butterfly Fe/E cluster {(μ-*t*-BuS)[$Fe_2(CO)_6$]$_2$(μ_4-Se)}$_2$(μ-1-$SeCH_2$-5-$MeC_6H_3CH_2Se$-3-μ) (**12**), respectively. All the new products **4**−**11** have been characterized by elemental analysis, IR, ^1H and ^{77}Se NMR spectroscopy, and for **4**, **7**, and **9** single-crystal X-ray diffraction techniques.

Introduction

The μ-CO-bridged anions of type [(μ-RE)(μ-CO)$Fe_2(CO)_6$]$^-$ (**1**, E = S, Se, Te) are rich in chemical reactivities and have been extensively used as an important class of synthon to synthesize a variety of novel cluster complexes.[1−23] In previous papers[18−20] we reported that anions **1** reacted with (μ-S_2)$Fe_2(CO)_6$ in THF at room temperature (for E = S) or from −78 °C to room temperature (for E = Se, Te) to give a new type of

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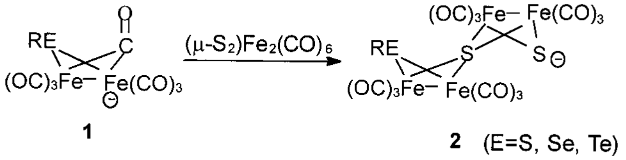
Scheme 1



butterfly Fe/E cluster sulfur-centered anions (μ-RE)(μ-S$^-$)[Fe$_2$(CO)$_6$]$_2$(μ_4-S) (**2**) (Scheme 1).

In view of the similarity of (μ-S$_2$)Fe$_2$(CO)$_6$[24] with its selenium analogue (μ-Se$_2$)Fe$_2$(CO)$_6$[25] in structure and reactivity, it might be expected that anions **1** would react with (μ-Se$_2$)Fe$_2$(CO)$_6$ through a similar process,[18] which involves an initially nucleophilic attack of the negatively charged Fe atom of **1** at the Se atom of (μ-Se$_2$)Fe$_2$(CO)$_6$ followed by coordination of the μ_3-Se atom of the intermediate m$_1$ to another Fe atom and concomitant loss of the μ-CO ligand, to give another new type of butterfly Fe/E cluster selenium-centered anions (μ-RE)(μ-Se$^-$)[Fe$_2$(CO)$_6$]$_2$(μ_4-Se) (**3**) (Scheme 2).

In this paper we describe the formation of such a new type of selenium-centered anions **3** and their in situ reactions with organic mono- and dihalides, as well as the structural characterization of the products by means of spectroscopic and X-ray diffraction techniques.

Results and Discussion

Formation of Anions 3 and Their Reactions with Organic Halides. Synthesis and Spectroscopic Characterization of 4−12. As the expectation mentioned above, the [Et$_3$NH]$^+$ salts of anions [(μ-RE)(μ-CO)Fe$_2$(CO)$_6$]$^-$ (E = S, Se) (**1**) (prepared from Fe$_3$(CO)$_{12}$, REH (E = S, Se), and Et$_3$N) or the [MgBr]$^+$ salts of anions [(μ-RE)(μ-CO)Fe$_2$(CO)$_6$]$^-$ (E = Te) (**1**) (prepared from RMgBr, elemental Te, and Fe$_3$(CO)$_{12}$) reacted with (μ-Se$_2$)Fe$_2$(CO)$_6$ in THF at −78 °C to give the corresponding salts of the selenium-centered anions (μ-RE)(μ-Se$^-$)[Fe$_2$(CO)$_6$]$_2$(μ_4-Se) (E = S, Se, Te) (**3**) (Scheme 2), which reacted further with an excess amount of organic monohalides MeI and PhCH$_2$Br to produce a series of double butterfly Fe/E cluster complexes (μ-RE)(μ-R^{1}Se)[Fe$_2$(CO)$_6$]$_2$(μ_4-Se) (**4−9**) (Scheme 3).

Similarly, if the [Et$_3$NH]$^+$ salt of the anion **3** (RE = *t*-BuS) reacted in situ with an excess quantity of dihalides 1,2-(BrCH$_2$)$_2$C$_6$H$_4$ or 1,3,5-(BrCH$_2$)$_2$MeC$_6$H$_3$, the corresponding quadruple butterfly Fe/E cluster complex {(μ-*t*-BuS)[Fe$_2$(CO)$_6$]$_2$(μ_4-Se)}$_2$(μ-1-SeCH$_2$C$_6$H$_4$-CH$_2$Se-2-μ) (**10**) or the corresponding double butterfly Fe/E cluster complex (μ-*t*-BuS)[(μ-1-SeCH$_2$-3-BrCH$_2$-5-MeC$_6$H$_3$)[Fe$_2$(CO)$_6$]$_2$(μ_4-Se) (**11**) and quadruple butterfly Fe/E cluster complex {(μ-*t*-BuS)[Fe$_2$(CO)$_6$]$_2$(μ_4-Se)}$_2$(μ-1-SeCH$_2$-5-MeC$_6$H$_3$CH$_2$Se-3-μ) (**12**) were obtained, respectively (Scheme 4).

The butterfly clusters **4−12** are air-stable, red solids, which have been characterized by elemental analysis and spectroscopy. The IR spectra of **4−12** showed several strong and very strong absorption bands in the range 2082−1962 cm^{-1} for their Fe(CO)$_3$ structural units, whereas the ^{1}H NMR spectra of **4−12** exhibited several resonance signals for their respective organic groups. For example, while product **5** showed one singlet at 1.47 ppm for *t*-Bu, one singlet at 4.03 ppm for CH$_2$, and one multiplet in the range 7.40−7.34 ppm for the Ph group, product **12** displayed one singlet at 1.43 ppm for *t*-Bu, one singlet at 2.35 ppm for Me attached to the benzene ring, one singlet at 3.76 ppm for CH$_2$ attached to the Se atom, and one multiplet in the range 7.15−7.00 ppm for the three protons of the benzene ring. It is worth noting that although the two protons of each CH$_2$ group attached to the benzene ring in clusters **4−6**, **8**, and **10−12** are diastereotopic, they showed only one singlet, but not an AB quartet. This observation could be possibly attributed to the negligible influence of the chiral cluster moiety on the attached CH$_2$ group. Since ^{77}Se NMR spectroscopy is a powerful tool for characterization of organometallic selenium complexes,[26] we determined the ^{77}Se NMR spectra of clusters **4−12**. It is interesting to note that the ^{77}Se NMR spectra of these clusters all showed one singlet for the μ_4-Se atoms (each attached to four Fe(CO)$_3$ electron-withdrawing groups) in the range of lower field 278.92−346.38 ppm and one singlet for the μ_2-Se atoms (each attached to two Fe(CO)$_3$ electron-withdrawing groups and one corresponding organic group) in the range of higher field 83.44−272.04 ppm, respectively. Although the ^{77}Se NMR data of μ_2-Se in some similar compounds were reported,[17,18] such μ_4-Se ^{77}Se NMR data are reported here for the first time. In addition, it is worthy of note that clusters **6** and **7** exhibited three singlets for their three different Se atoms and the others displayed two singlets for their two different Se atoms. This can be clearly seen from Figure 1, as examplified by clusters **5** and **6**.

Finally, it should be pointed out that since clusters **4−12** are μ_4-Se-containing complexes, the R, R^1, 1,2-(CH$_2$)$_2$C$_6$H$_4$ or 1-CH$_2$-3-BrCH$_2$-5-MeC$_6$H$_3$, and 1,3-(CH$_2$)$_2$-5-MeC$_6$H$_3$ organic groups are all attached to the bridged S, Se, and Te atoms by an equatorial (but not axial) type of bond, to avoid the strong steric repulsions of the axially bonded structural unit at μ_4-Se with the corresponding organic group.[9,14,24b] This is completely consistent with the ^{1}H and ^{77}Se NMR data discussed above and has been further confirmed by X-ray crystal diffraction analyses for clusters **4**, **7**, and **9**.

Crystal Molecular Structures of 4, 7, and 9. To further confirm the structures of clusters **4−12**, single-crystal X-ray diffraction analyses for **4**, **7**, and **9** were carried out. Tables 1−3 list the selected bond lengths and angles. Figures 2−4 show their molecular structures.

As can be seen from Figures 2−4, the molecules of **4**, **7**, and **9** indeed consist of two different structural units, (μ-EtS)Fe$_2$(CO)$_6$ and (μ-PhCH$_2$Se)Fe$_2$(CO)$_6$ for **4**, (μ-*p*-MeC$_6$H$_4$Se)Fe$_2$(CO)$_6$ and (μ-MeSe)Fe$_2$(CO)$_6$ for **7**, and (μ-*p*-MeC$_6$H$_4$Te)Fe$_2$(CO)$_6$ and (μ-MeSe)Fe$_2$(CO)$_6$ for **9**, joined together by a spiro-type four-coordinate Se atom, μ_4-Se. In each molecule of **4**, **7**, and **9** this μ_4-Se is situated on the center of a distorted tetrahedron constructed by

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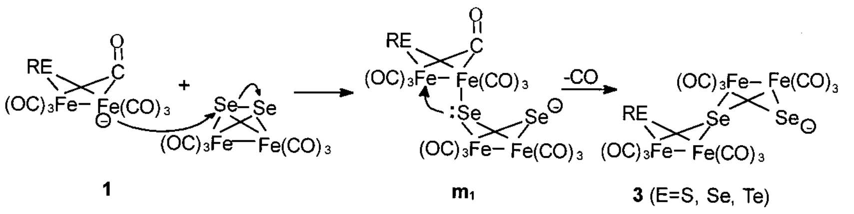
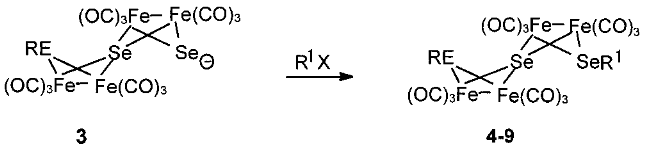
Scheme 2

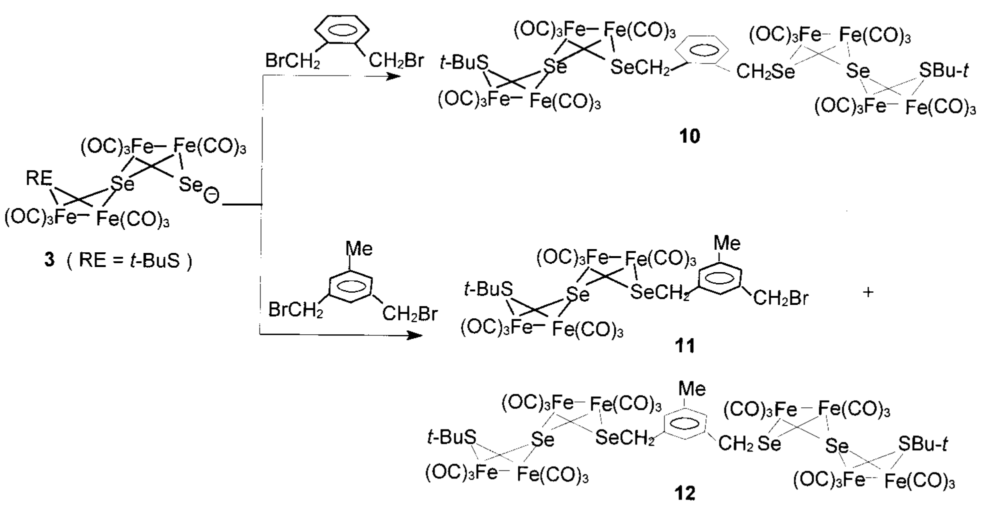


Scheme 3



	4	5	6	7	8	9
RE	EtS	*t*-BuS	*p*-MeC_6H_4Se	*p*-MeC_6H_4Se	*p*-MeC_6H_4Te	*p*-MeC_6H_4Te
R^1	$PhCH_2$	$PhCH_2$	$PhCH_2$	Me	$PhCH_2$	Me

Scheme 4



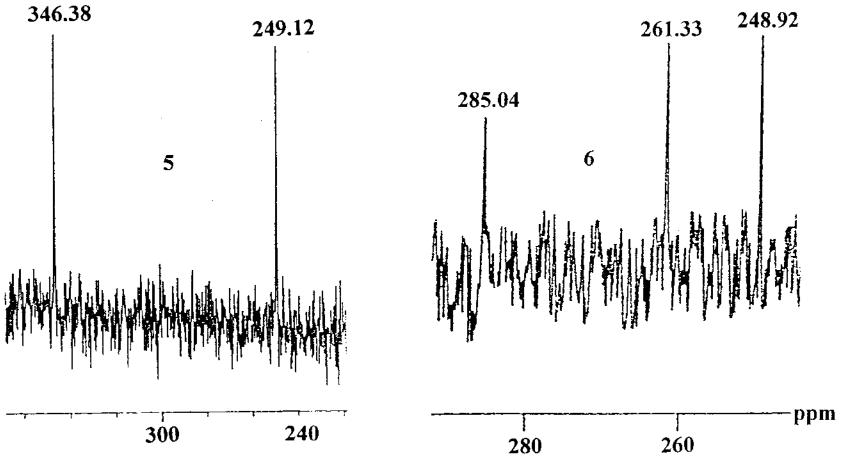


Figure 1. ^{77}Se NMR spectra of compounds **5** and **6**.

four Fe atoms, and the two different alkylchalcogenido ligands bridge the four Fe atoms to form a double butterfly Fe/E (E = S, Se, Te) cluster complex.

Although the two μ_4-Se-containing analogues with identical alkylchalcogenido ligands μ_4-selenidobis[(μ-ethylsulfido)hexacarbonyldiiron] (abbreviated as SESU, hereafter), $[(\mu\text{-EtS})Fe_2(CO)_6]_2(\mu_4\text{-Se})$,[14] and μ_4-selenidobis[(μ-4-tolylselenido)hexacarbonyldiiron] (abbreviated as STSE, hereafter), $[(\mu\text{-}p\text{-}MeC_6H_4Se)Fe_2(CO)_6]_2(\mu_4\text{-}Se)$,[27] are known to be structurally characterized, clusters **4**, **7**, and **9** are so far the first examples of μ_4-Se double butterfly Fe/E clusters with different alkylchalcogenido

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 4

Se(1)−Fe(4)	2.3462(12)	Se(1)−Fe(3)	2.3500(12)
Se(1)−Fe(1)	2.3619(13)	Se(1)−Fe(2)	2.3629(12)
Se(2)−C(13)	2.004(7)	Se(2)−Fe(3)	2.3856(14)
Se(2)−Fe(4)	2.3896(13)	Fe(1)−S(1)	2.269(2)
Fe(1)−Fe(2)	2.5646(17)	Fe(2)−S(1)	2.260(3)
Fe(3)−Fe(4)	2.5938(14)	S(1)−C(20)	1.838(10)
Fe(4)−Se(1)−Fe(3)	67.05(4)	Fe(3)−Se(1)−Fe(1)	129.27(5)
Fe(4)−Se(1)−Fe(2)	135.63(5)	Fe(3)−Se(1)−Fe(2)	131.94(5)
Fe(1)−Se(1)−Fe(2)	65.75(4)	Fe(3)−Se(2)−Fe(4)	65.80(4)
S(1)−Fe(1)−Se(1)	76.58(7)	Se(1)−Fe(1)−Fe(2)	57.14(4)
S(1)−Fe(1)−Fe(2)	55.33(8)	Se(1)−Fe(3)−Se(2)	79.01(4)
Se(1)−Fe(3)−Fe(4)	56.40(3)	Se(2)−Fe(3)−Fe(4)	57.17(4)

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

Se(2)−Fe(1)	2.3499(14)	Se(1)−Fe(1)	2.3908(17)
Fe(1)−Fe(2)	2.6005(18)	Fe(2)−Se(2)	2.3520(15)
Fe(2)−Se(1)	2.3816(17)	Fe(3)−Se(2)	2.3628(15)
Fe(3)−Se(3)	2.4021(16)	Fe(3)−Fe(4)	2.594(2)
Fe(4)−Se(2)	2.3467(15)	Fe(4)−Se(3)	2.3974(16)
Se(1)−C(13)	1.960(11)	Se(3)−C(14)	1.944(9)
Se(2)−Fe(1)−Se(1)	78.60(5)	Se(2)−Fe(1)−Fe(2)	56.46(4)
Se(1)−Fe(1)−Fe(2)	56.81(5)	Se(2)−Fe(2)−Se(1)	78.74(5)
Se(2)−Fe(3)−Fe(4)	56.28(5)	Se(3)−Fe(3)−Fe(4)	57.19(5)
Fe(2)−Se(1)−Fe(1)	66.04(5)	Fe(4)−Se(2)−Fe(1)	135.60(6)
Fe(4)−Se(2)−Fe(2)	133.97(6)	Fe(1)−Se(2)−Fe(2)	67.16(5)
Fe(4)−Se(2)−Fe(3)	66.85(5)	Fe(3)−Se(3)−Fe(4)	65.44(5)

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

Te(1)−Fe(2)	2.5663(16)	Te(1)−Fe(1)	2.5673(17)
Fe(1)−Se(1)	2.3458(19)	Fe(1)−Fe(2)	2.608(2)
Fe(2)−Se(1)	2.3669(17)	Fe(3)−Se(1)	2.3614(19)
Fe(3)−Se(2)	2.3938(18)	Fe(3)−Fe(4)	2.575(2)
Fe(4)−Se(1)	2.3569(17)	Fe(4)−Se(2)	2.3980(19)
Fe(2)−Te(1)−Fe(1)	61.06(5)	Se(1)−Fe(1)−Te(1)	79.34(6)
Se(1)−Fe(1)−Fe(2)	56.79(5)	Te(1)−Fe(1)−Fe(2)	59.45(5)
Se(1)−Fe(2)−Te(1)	78.98(5)	Se(1)−Fe(2)−Fe(1)	56.02(5)
Te(1)−Fe(2)−Fe(1)	59.49(5)	Se(1)−Fe(3)−Se(2)	78.14(6)
Se(1)−Fe(3)−Fe(4)	56.83(5)	Se(2)−Fe(3)−Fe(4)	57.57(5)
Se(1)−Fe(4)−Fe(3)	57.00(5)	Se(2)−Fe(4)−Fe(3)	57.41(5)
Fe(1)−Se(1)−Fe(4)	133.71(7)	Se(1)−Fe(4)−Se(2)	78.14(6)
Fe(1)−Se(1)−Fe(2)	67.19(6)	Fe(3)−Se(1)−Fe(4)	66.16(6)

ligands prepared and characterized by crystal X-ray diffraction.

In fact, **4**, **7**, and **9** are structurally similar to those of their analogues SESU and STSE. It can be seen intuitively from Figures 2−4 that the two different organic groups (Et and $PhCH_2$ for **4**; p-MeC_6H_4 and Me for **7** and **9**), just like the two identical groups (Et in SESU; p-MeC_6H_4 in STSE), are attached to μ_2-chalcogen atoms by an equatorial type of bond.

Conclusions

The reductive cleavage of the Se−Se bond of (μ-Se_2)$Fe_2(CO)_6$ by the Fe-centered anionic nucleophiles $[(\mu\text{-RE})(\mu\text{-CO})Fe_2(CO)_6]^-$ (**1**, E = S, Se, Te) is first demonstrated to give a new type of selenium-centered anions (μ-RE)(μ-Se^-)$[Fe_2(CO)_6]_2$(μ_4-Se) (**3**). More interestingly, the in situ reactions of anions **3** with mono- and dihalides can afford a series of new Fe/E cluster complexes containing one or two double butterfly structural units (μ-RE)(μ-Se)$[Fe_2(CO)_6]_2$(μ_4-Se) (E = S, Se, Te). Apparently, these results highlight the possibility of practical applications in the synthesis of a new class of mixed transition metal/chalcogen butterfly cluster complexes.

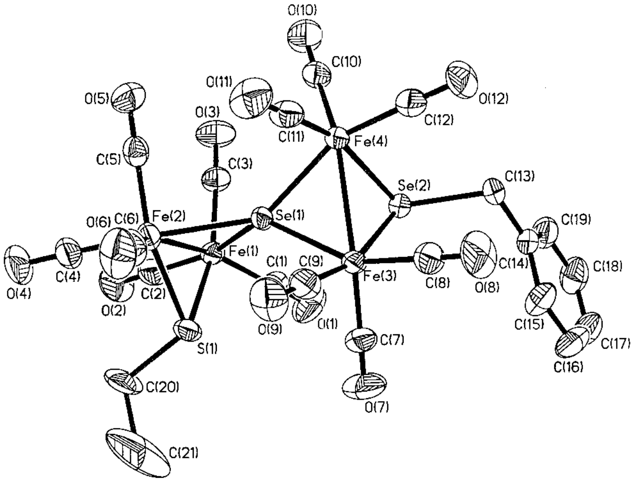


Figure 2. ORTEP drawing of **4** with atom-labeling scheme.

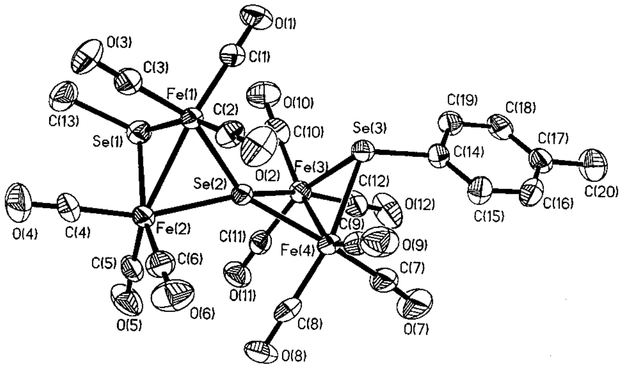


Figure 3. ORTEP drawing of **7** with atom-labeling scheme.

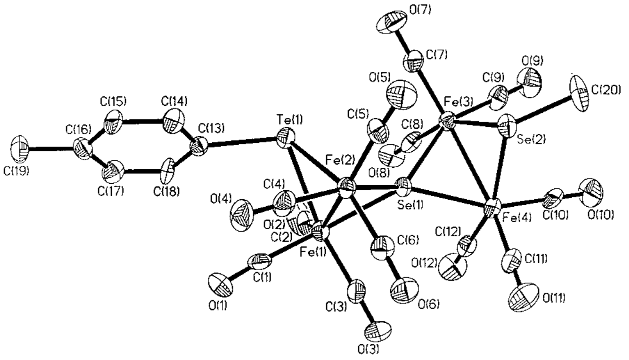


Figure 4. ORTEP drawing of **9** with atom-labeling scheme.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of highly purified nitrogen using standard Schlenk and vacuum-line techniques. Tetrahydrofuran (THF) was distilled under nitrogen from sodium/benzophenone ketyl, and triethylamine from potassium hydroxide. MeI, $PhCH_2Br$, EtSH, and t-BuSH were commercially available and used without further purification. $Fe_3(CO)_{12}$,[28] p-MeC_6H_4SeH,[29] (μ-Se)$_2Fe_2(CO)_6$,[30] 1,2-$(BrCH_2)_2C_6H_4$,[31] and 1,3,5-$(BrCH_2)_2$-MeC_6H_3[32] were prepared according to the literature. The

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Table 4. Crystal Data and Structural Refinements Details for 4, 7, and 9

	4	7	9
mol formula	$C_{21}H_{12}Fe_4O_{12}SSe_2$	$C_{20}H_{10}Fe_4O_{12}Se_3$	$C_{20}H_{10}Fe_4O_{12}Se_2Te$
mol wt	869.69	902.56	951.20
cryst syst	orthorhombic	monoclinic	triclinic
space group	*Pbca*	*P*2(1)/*c*	$P\bar{1}$
a/Å	9.3240(6)	19.1272(11)	9.217(3)
b/Å	17.5418(12)	9.1357(5)	10.060(3)
c/Å	36.729(3)	16.5772(9)	16.890(5)
α/deg	90	90	106.742(6)
β/deg	90	93.4400(10)	104.268(5)
γ/deg	90	90	90.759(6)
V/Å^3	6007.3(7)	2891.5(3)	1447.5(8)
Z	8	4	2
D_c/g cm^{-3}	1.923	2.073	2.182
F(000)	3376	1728	900
abs coeff/mm^{-1}	4.441	5.799	5.522
temp/K	293	293	293
wavelength/Å	0.71073	0.71073	0.71073
scan type	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
$2\theta_{max}$/deg	50.06	50.02	50.04
no. of observns, n	5306	5077	5084
no. of variables, p	370	352	352
R	0.0548	0.0552	0.0511
R_w	0.1330	0.1138	0.0930
goodness of fit	1.124	1.290	0.853
largest diff peak and hole/e Å^{-3}	0.968 and −0.496	0.882 and −0.496	0.837 and −1.084

products were separated by TLC (20 × 25 × 0.25 cm, silica gel G) and further purified by recrystallization from mixed CH_2Cl_2/hexane solvent. IR spectra were recorded on a Nicolet 170 SX FT IR spectrophotometer, and ^{1}H NMR and ^{77}Se NMR spectra on a Bruker AC-P200 NMR spectrometer. Ph_2Se_2 was used as an external standard, and the chemical shifts were referenced to Me_2Se (δ 0) for ^{77}Se NMR spectra. C/H analyses were performed on an Elementa Vario EL analyzer. Melting points were determined on a Yanaco MP-500 apparatus.

Preparation of (μ-EtS)(μ-PhCH$_2$Se)[Fe$_2$(CO)$_6$]$_2$(μ_4-Se) (4). A 100 mL three-necked flask equipped with a magnetic stir-bar, a N_2 inlet tube, and a serum cap was charged with 0.275 g (0.55 mmol) of $Fe_3(CO)_{12}$, 15 mL of THF, 0.04 mL (0.54 mmol) of EtSH, and 0.08 mL (0.57 mmol) of Et_3N. The mixture was stirred at room temperature for 0.5 h to give a yellow-brown solution, which was cooled to −78 °C. To this solution was slowly added 0.218 g (0.50 mmol) of (μ-Se)$_2$Fe$_2$(CO)$_6$ in 10 mL of THF. The mixture was stirred at −78 °C for 1.5 h, and then 0.12 mL (1.00 mmol) of $PhCH_2Br$ was added. The mixture was warmed naturally to room temperature and was stirred for an additional 12 h. The resulting mixture was filtered, and the filtrate was condensed under reduced pressure. The residue was subjected to TLC separation using petroleum ether as eluent. The first major red band afforded 0.110 g (51%) of (μ-EtS)$_2$Fe$_2$(CO)$_6$, which was identified by comparison of its melting point and ^{1}H NMR spectrum with those of an authentic sample.[33] The second major red band gave 0.100 g (23%) of **4** as a red solid, mp 125 °C dec. Anal. Calcd for $C_{21}H_{12}Fe_4O_{12}SSe_2$: C, 29.00; H, 1.39. Found: C, 29.11; H, 1.23. IR (KBr disk): $\nu_{C\equiv O}$, 2082(s), 2056(vs), 2032(vs), 1986(vs) cm^{-1}. ^{1}H NMR (acetone-d_6): 1.38(t, J = 10.8 Hz, 3H, CH_3), 2.59(q, J = 10.8 Hz, 2H, CH_2), 4.03(s, 2H, CH_2Ph), 7.33−7.41(m, 5H, C_6H_5) ppm. ^{77}Se NMR ($CDCl_3$, Me_2Se): 247.97(s, $SeCH_2Ph$), 310.07(s, μ_4-*Se*) ppm.

Preparation of (μ-*t*-BuS)(μ-PhCH$_2$Se)[Fe$_2$(CO)$_6$]$_2$(μ_4-Se) (5). The procedure for preparation of **5** is similar to that of **4**, but using 0.05 mL (0.47 mmol) of *t*-BuSH instead of EtSH. The major band gave 0.313 g (70%) of **5** as a red solid, mp 146 °C dec. Anal. Calcd for $C_{23}H_{16}Fe_4O_{12}SSe_2$: C, 30.77; H, 1.80. Found: C, 30.49; H, 1.73. IR (KBr disk): $\nu_{C\equiv O}$, 2078(s), 2032(vs), 2014(s), 1995(vs), 1980(vs) cm^{-1}. ^{1}H NMR (acetone-d_6): 1.47(s, 9H, $C(CH_3)_3$), 4.03(s, 2H, CH_2), 7.34−7.40(m, 5H, C_6H_5) ppm. ^{77}Se NMR ($CDCl_3$, Me_2Se): 249.12(s, $SeCH_2Ph$), 346.38(s, μ_4-*Se*) ppm.

Preparation of (μ-*p*-MeC$_6$H$_4$Se)(μ-PhCH$_2$Se)[Fe$_2$(CO)$_6$]$_2$(μ_4-Se) (6). The flask described above was charged with 0.275 g (0.55 mmol) of $Fe_3(CO)_{12}$, 15 mL of THF, 0.085 g (0.50 mmol) of *p*-MeC_6H_4SeH, and 0.08 mL (0.57 mmol) of Et_3N. The mixture was stirred at room temperature for 0.5 h to give a brown-red solution, which was cooled to −78 °C. To this solution was slowly added 0.218 g (0.5 mmol) of (μ-Se)$_2$Fe$_2$(CO)$_6$ in 10 mL of THF. The mixture was stirred for 2 h at −78 °C, and then 0.12 mL (1.00 mmol) of $PhCH_2Br$ was added. The mixture was warmed naturally to room temperature and was stirred for an additional 16 h. The resulting mixture was filtered, and the filtrate was condensed under reduced pressure. The residue was subjected to TLC separation using CH_2Cl_2/petroleum ether (v/v = 1:20) as eluent. From the first brown-red band was obtained 0.060 g (19%) of (μ-*p*-MeC$_6$H$_4$Se)$_2$Fe$_2$(CO)$_6$, which was identified by comparison of its melting point and ^{1}H NMR spectrum with those of an authentic sample.[11] From the second red band was obtained 0.098 g (20%) of **6** as a red solid, mp 178 °C dec. Anal. Calcd for $C_{26}H_{14}Fe_4O_{12}Se_3$: C, 31.91; H, 1.44. Found: C, 31.87; H, 1.42. IR (KBr disk): $\nu_{C\equiv O}$, 2078(s), 2031(vs), 2007(s), 1997(vs), 1988(vs), 1978(s) cm^{-1}. ^{1}H NMR (acetone-d_6): 2.26(s, 3H, CH_3), 4.06(s, 2H, CH_2Ph), 7.10−7.42(m, 9H, C_6H_5, C_6H_4) ppm. ^{77}Se NMR ($CDCl_3$, Me_2Se): 248.92(s, $SeCH_2Ph$), 261.33(s, Se-Tol), 285.04(s, μ_4-*Se*) ppm.

Preparation of (μ-*p*-MeC$_6$H$_4$Se)(μ-MeSe)[Fe$_2$(CO)$_6$]$_2$(μ_4-Se) (7). The procedure for preparation of **7** is similar to that of **6**, but using 0.06 mL (0.97 mmol) of MeI instead of $PhCH_2Br$. From the first brown-red band was obtained 0.078 g (25%) of (μ-*p*-MeC$_6$H$_4$Se)$_2$Fe$_2$(CO)$_6$, which was identified by comparison of its melting point and ^{1}H NMR spectrum with those of an authentic sample.[11] From the second red band was obtained 0.081 g (18%) of **7** as a red solid, mp 152 °C dec. Anal. Calcd for $C_{20}H_{10}Fe_4O_{12}Se_3$: C, 26.62; H, 1.12. Found: C, 26.69; H, 1.15. IR (KBr disk): $\nu_{C\equiv O}$, 2066(s), 2034(vs), 2004(s), 1989(vs), 1966(s) cm^{-1}. ^{1}H NMR ($CDCl_3$): 2.15(s, 3H, CH_3), 2.29(s, 3H,

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$ArCH_3$), 7.00−7.33(m, 4H, C_6H_4) ppm. ^{77}Se NMR ($CDCl_3$, Me_2Se): 83.44(s, $SeCH_3$), 260.70(s, $SeCH_2Ph$), 288.53(s, μ_4-*Se*) ppm.

Preparation of (μ-*p*-MeC_6H_4Te)(μ-$PhCH_2Se$)[$Fe_2(CO)_6$]$_2$(μ_4-Se) (8). The flask described above was charged with 0.383 g (3. 0 mmol) of Te powder, 20 mL of THF, and 3.0 mmol of *p*-MeC_6H_4MgBr in THF. The mixture was refluxed for 2.5 h to give a brown-yellow solution. Upon cooling the solution to room temperature, 1.50 g (3.0 mmol) of $Fe_3(CO)_{12}$ was added, and the reaction mixture was stirred for 2 h. After cooling this mixture to −78 °C, 0.874 g (2.0 mmol) of (μ-Se_2)$Fe_2(CO)_6$ was added, the mixture was stirred for 1 h at this temperature, and 0.48 mL (4.0 mmol) of $PhCH_2Br$ was added. The mixture was warmed naturally to room temperature and was stirred for an additional 18 h. The resulting mixture was filtered, and the filtrate was condensed under reduced pressure. The residue was subjected to TLC separation using CH_2Cl_2/petroleum ether (v/v = 1:20) as eluent. From the first major red band was obtained 0.270 g (25%) of (μ-*p*-MeC_6H_4Te)$_2Fe_2(CO)_6$, which was identified by comparison of its melting point and ^{1}H NMR spectrum with those of an authentic sample.[9] From the second major orange-red band was obtained 0.237 g (12%) of **8** as a red solid, mp 185 °C dec. Anal. Calcd for $C_{26}H_{14}Fe_4O_{12}Se_2Te$: C, 30.40; H, 1.37. Found: C, 30.45; H, 1.40. IR (KBr disk): $\nu_{C\equiv O}$, 2082(s), 2034(vs), 2001(vs), 1985(vs), 1969(vs) cm^{-1}. ^{1}H NMR ($CDCl_3$): 2.32(s, 3H, CH_3), 3.84(s, 2H, CH_2), 7.03−7.42(m, 9H, C_6H_5, C_6H_4) ppm. ^{77}Se NMR ($CDCl_3$, Me_2Se): 250.89(s, $SeCH_2Ph$), 275.15(s, μ_4-Se) ppm.

Preparation of (μ-*p*-MeC_6H_4Te)(μ-MeSe)[$Fe_2(CO)_6$]$_2$(μ_4-Se) (9). The procedure for preparation of **9** is similar to that of **8**, but using 0.24 mL (4.0 mmol) of MeI instead of $PhCH_2Br$. From the first major red band was obtained 0.290 g (27%) of (μ-*p*-MeC_6H_4Te)$_2Fe_2(CO)_6$, which was identified by comparison of its melting point and ^{1}H NMR spectrum with those of an authentic sample.[9] From the second major orange-red band was obtained 0.190 g (10%) of **9** as a red solid, mp 128 °C dec. Anal. Calcd for $C_{20}H_{10}Fe_4O_{12}Se_2Te$: C, 25.25; H, 1.06. Found: C, 25.27; H, 1.20. IR (KBr disk): $\nu_{C\equiv O}$, 2082(s), 2040(s), 2026(vs), 1985(vs), 1971(s) cm^{-1}. ^{1}H NMR ($CDCl_3$): 2.13(s, 3H, CH_3), 2.31(s, 3H, $ArCH_3$), 7.00−7.30(m, 4H, C_6H_4) ppm. ^{77}Se NMR ($CDCl_3$, Me_2Se): 85.03(s, $SeCH_3$), 278.92(s, μ_4-Se) ppm.

Preparation of {(μ-*t*-BuS)[$Fe_2(CO)_6$]$_2$(μ_4-Se)}$_2$(μ-1-$SeCH_2C_6H_4CH_2Se$-2-μ] (10). The flask described above was charged with 0.755 g (1.5 mmol) of $Fe_3(CO)_{12}$, 15 mL of THF, 0.17 mL (1.5 mmol) of *t*-BuSH, and 0.24 mL (1.7 mmol) of Et_3N. The mixture was stirred at room temperature for 0.5 h to give a brown-red solution, which was cooled to −78 °C. To this solution was slowly added 0.437 g (1.0 mmol) of (μ-Se)$_2Fe_2(CO)_6$ in 10 mL of THF. The mixture was stirred for 2 h at −78 °C, and then 0.105 g (0.4 mmol) of 1,2-$(BrCH_2)_2C_6H_4$ was added. The mixture was warmed naturally to room temperature and was stirred for an additional 18 h. The resulting mixture was filtered, and the filtrate was condensed under reduced pressure. The residue was subjected to TLC separation using petroleum ether as eluent. From the first brown-red band was obtained 0.075 g (11%) of (*t*-BuS)$_2Fe_2(CO)_6$, which was identified by comparison of its melting point and ^{1}H NMR spectrum with those of an authentic sample.[33] The second major band gave 0.197 g (29%) of **10** as a red solid, mp 76 °C dec. Anal. Calcd for $C_{40}H_{26}Fe_8O_{24}S_2Se_4$: C, 27.98; H, 1.52. Found: C, 27.83; H, 1.59. IR (KBr disk): $\nu_{C\equiv O}$, 2080(s), 2063(vs), 2031(vs), 1983(vs) cm^{-1}. ^{1}H NMR (acetone-d_6): 1.46(s, 18H, 2C$(CH_3)_3$), 4.16(s, 4H, $2CH_2$), 7.12−7.50(m, 4H, C_6H_4) ppm. ^{77}Se NMR ($CDCl_3$, Me_2Se): 226.64(s, $SeCH_2Ph$), 339.80(s, μ_4-Se) ppm.

Preparation of (μ-*t*-BuS)(μ-1-$SeCH_2$-3-$BrCH_2$-5-MeC_6H_3)[$Fe_2(CO)_6$]$_2$(μ_4-Se) (11) and {(μ-*t*-BuS)[$Fe_2(CO)_6$]$_2$(μ_4-Se)}$_2$(μ-1-$SeCH_2$-5-$MeC_6H_3CH_2Se$-3-μ) (12). The procedure for preparation of **11** and **12** is similar to that of **10**, but using 0.139 g (0.5 mmol) of 1,3,5-$(BrCH_2)_2MeC_6H_3$ instead of 1,2-$(BrCH_2)_2C_6H_4$. The first major band afforded 0.124 g (25%) of **11** as a red solid, mp 121 °C dec. Anal. Calcd for $C_{25}H_{19}BrFe_4O_{12}SSe_2$: C, 29.89; H, 1.91. Found: C, 29.80; H, 1.95. IR (KBr disk): $\nu_{C\equiv O}$, 2082(s), 2034(vs), 1989(vs), 1962(vs) cm^{-1}. ^{1}H NMR ($CDCl_3$): 1.43(s, 9H, C$(CH_3)_3$), 2.35(s, 3H, CH_3), 3.76(s, 2H, $SeCH_2$), 4.44(s, 2H, $BrCH_2$), 7.00−7.13(m, 3H, C_6H_3) ppm. ^{77}Se NMR ($CDCl_3$, Me_2Se): 248.24(s, $SeCH_2Ar$), 344.88(s, μ_4-Se) ppm. The second major band gave 0.143 g (17%) of **12** as a red solid, mp 116 °C dec. Anal. Calcd for $C_{41}H_{28}Fe_8O_{24}S_2Se_4$: C, 28.44; H, 1.63. Found: C, 28.55; H, 1.92. IR (KBr disk): $\nu_{C\equiv O}$, 2082(s), 2034(vs), 2007(s), 1981(vs), 1966(s) cm^{-1}. ^{1}H NMR ($CDCl_3$): 1.43(s, 18H, 2C$(CH_3)_3$), 2.35(s, 3H, CH_3), 3.76(s, 4H, $2CH_2$), 7.00−7.15(m, 3H, C_6H_3) ppm. ^{77}Se NMR ($CDCl_3$, Me_2Se): 248.54(s, $SeCH_2Ar$), 344.27(s, μ_4-Se) ppm.

Single-Crystal Structure Determinations of 4, 7, and 9. Single crystals of **4**, **7**, and **9** suitable for X-ray diffraction analyses were grown by slow evaporation of their CH_2Cl_2/hexane solutions at about 5 °C. The single crystals of **4** (0.20 × 0.35 × 0.40), **7** (0.42 × 0.18 × 0.18), and **9** (0.35 × 0.20 × 0.10) were glued to a glass fiber and mounted on a Bruker SMART 1000 or a SMART CCD automated diffractometer. Details of the crystal data, data collections, 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 for **4**, **7**, and **9** were performed using the TEXSAN crystallographic software package of the Molecular Structure Corporation.

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Supporting Information Available: Full tables of crystal data, atomic coordinates and thermal parameters, and bond lengths and angles for **4**, **7**, and **9**. This material is available free of charge via the Internet at http://pubs. acs.org.

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