Articles

Formation of (μ-RE)(μ-S$^-$)Fe$_2$(CO)$_6$ and (μ-RE)(μ-Se$^-$)Fe$_2$(CO)$_6$ (E = S, Se) Anions and a Comparative Study of Their Reactions with SO$_2$Cl$_2$, ClC(O)ZC(O)Cl (Z = (CH$_2$)$_2$, C$_6$H$_4$), or *p*-MeC$_6$H$_4$SO$_2$Cl. Single-Crystal Structures of [(μ-EtS)Fe$_2$(CO)$_6$]$_2$(μ_4-Se) and (μ-EtS)(μ-*p*-MeC$_6$H$_4$SO$_2$)Fe$_2$(CO)$_6$

Li-Cheng Song,* Chao-Guo Yan, and Qing-Mei Hu

Department of Chemistry, Nankai University, Tianjin 300071, China

Ru-Ji Wang

Department of Chemistry, Tsinghua University, Beijing 100084, China

Thomas C. W. Mak

Department of Chemistry, The Chinese University of Hong Kong, Shatin,
New Territories, Hong Kong

Xiao-Ying Huang

State Key Laboratory of Structural Chemistry, Fuzhou, Fujian 350002, China

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The CO-bridged anions [(μ-RE)(μ-CO)Fe$_2$(CO)$_6$]$^-$ reacted with S$_8$ to form the sulfur-centered anions (μ-RE)(μ-S$^-$)Fe$_2$(CO)$_6$ (*4*; E = S, Se), whereas reaction of the anions with Se$_8$ yielded the selenium-centered anions (μ-RE)(μ-Se$^-$)Fe$_2$(CO)$_6$ (*6*; E = S, Se). Interestingly, reaction of **4** with SO$_2$Cl$_2$ afforded the S−S-bonded clusters [(μ-RE)Fe$_2$(CO)$_6$]$_2$(μ-S−S) (**5**), whereas reaction of **6** with SO$_2$Cl$_2$ produced the μ_4-Se clusters [(μ-RE)Fe$_2$(CO)$_6$]$_2$(μ_4-Se) (**8**); clusters **8** could also be produced by the action of anions **6** on succinoyl chloride or *p*-phthaloyl chloride, while the μ_4-S clusters [(μ-RE)Fe$_2$(CO)$_6$]$_2$(μ_4-S) (**9**) were generated by reaction of anions **4** with the above organic bis acid chlorides under similar conditions. Also, reaction of **4** (E = S) with *p*-MeC$_6$H$_4$SO$_2$Cl gave the μ_4-S clusters [(μ-RE)Fe$_2$(CO)$_6$]$_2$(μ_4-S) (**9**; E = S) and the expected Fe$_2$S$_2$ butterfly clusters (μ-RE)(μ-*p*-MeC$_6$H$_4$SO$_2$S)Fe$_2$(CO)$_6$ (**10**), whereas anion **6** reacted with *p*-MeC$_6$H$_4$SO$_2$Cl to afford the unexpected S═O-bridged complexes (μ-RE)(μ-*p*-MeC$_6$H$_4$SO$_2$)Fe$_2$(CO)$_6$ (**11**) and μ_4-Se clusters **8**. Clusters **11** could be also prepared through direct reaction of the precursor of **6**, *i.e.* [(μ-RE)(μ-CO)Fe$_2$(CO)$_6$]$^-$, with *p*-MeC$_6$H$_4$SO$_2$Cl. For some of these reactions the mechanisms were preliminarily proposed. The structures of 15 new cluster compounds have been characterized by C/H analysis and IR, ^{1}H NMR, and MS spectroscopy; those of [(μ-EtS)Fe$_2$(CO)$_6$]$_2$(μ_4-Se) (**8a**) and (μ-EtS)(μ-*p*-MeC$_6$H$_4$SO$_2$)Fe$_2$(CO)$_6$ (**11a**) have been confirmed by X-ray diffraction analyses.

Introduction

Previously it was reported that the sulfur-centered anions (μ-RS)(μ-S$^-$)Fe$_2$(CO)$_6$, derived from (μ-S)$_2$Fe$_2$(CO)$_6$ and RMgX or RLi, reacted with SO$_2$Cl$_2$ to give the S−S-bonded cluster complexes[1] **1**, while they reacted with ClC(O)ZC(O)Cl (Z = (CH$_2$)$_2$, C$_6$H$_4$) to give the bridged cluster complexes[2] **2** and μ_4-S cluster complexes **3**, depending upon the reaction temperature employed[3] (Scheme 1).

In addition, although the formation and reactivity of the anionic analogs of the above anions (μ-RS)(μ-Se$^-$)-Fe$_2$(CO)$_6$ have been briefly reported recently,[4] those of other anionic analogs (μ-RSe)(μ-E$^-$)Fe$_2$(CO)$_6$ (E = S, Se) have not been reported up to now. In this paper we describe a detailed synthetic method for such anions and their reactions with sulfuryl chloride, succinoyl chloride, *p*-phthaloyl chloride, and *p*-toluenesulfonyl chloride. This study not only led to various novel selenium-containing cluster complexes but also revealed some interesting differences in reactivity between the sulfur-

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$^{\otimes}$ Abstract published in *Advance ACS Abstracts*, February 15, 1996.

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[2] Seyferth, D.; Kiwan, A. M. *J. Organomet. Chem.* **1985**, *286*, 219.

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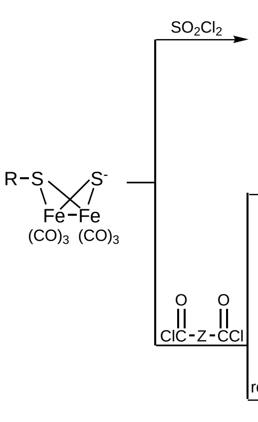
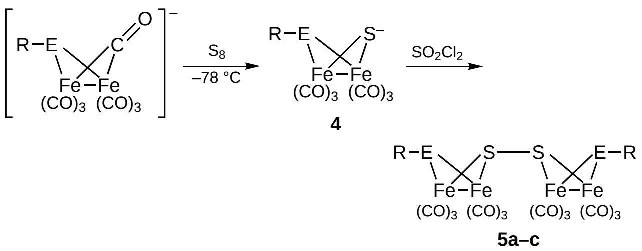
Scheme 1



Scheme 2



cluster	5a	5b	5c
RE	PhSe	*p*-MeC$_6$H$_4$Se	*t*-BuS

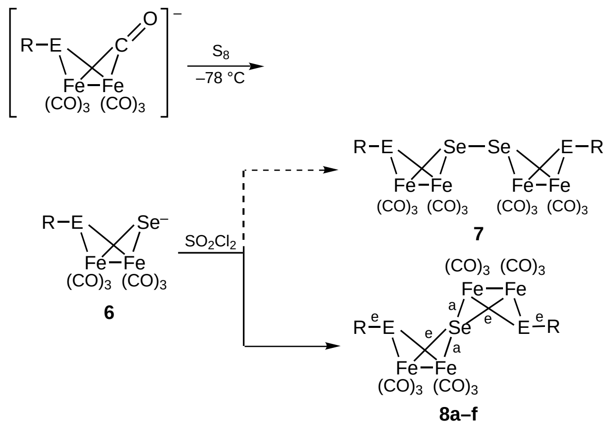
centered anions (μ-RE)(μ-S$^-$)Fe$_2$(CO)$_6$ (**4**) and the selenium-centered anions (μ-RE)(μ-Se$^-$)Fe$_2$(CO)$_6$ (**6**; E = S, Se).

Results and Discussion

1. Formation of the S-Centered Anions (μ-RE)(μ-S$^-$)Fe$_2$(CO)$_6$ (4; E = S, Se) and Their Reaction with SO$_2$Cl$_2$. Synthesis and Identification of [(μ-RE)Fe$_2$(CO)$_6$]$_2$(μ-S-S-μ) (5; E = S, Se). Similar to the preparation of the RS-bridged sulfur-centered anions (μ-RS)(μ-S$^-$)Fe$_2$(CO)$_6$ from [(μ-RS)(μ-CO)Fe$_2$(CO)$_6$]$^-$ and elemental sulfur by Seyferth group,[5] the RSe-bridged anionic analogs (μ-RSe)(μ-S$^-$)Fe$_2$(CO)$_6$ could be produced by reaction of [(μ-RSe)(μ-CO)Fe$_2$(CO)$_6$]$^-$ (derived from Fe$_3$(CO)$_{12}$/RSeH/Et$_3$N) with elemental sulfur in THF at −78 °C. The evolution of CO gas and color change of the solution from brown-red to yellow-green indicated that the μ-CO ligand in the starting anions had been replaced by elemental sulfur and the new RSe-bridged sulfur-centered anions (μ-RSe)(μ-S$^-$)Fe$_2$(CO)$_6$ had been formed. It was found that such anions (μ-RE)(μ-S$^-$)Fe$_2$(CO)$_6$ (**4**; E = S, Se) derived from [(μ-RE)(μ-CO)Fe$_2$(CO)$_6$]$^-$/S$_8$, just like (μ-RS)(μ-S$^-$)Fe$_2$(CO)$_6$ derived from μ-S$_2$Fe$_2$(CO)$_6$/RMgX or RLi,[1] reacted with SO$_2$Cl$_2$ to give the corresponding S−S-bonded cluster complexes **5**, regardless of the nature of the cationic counterion and the atom E in the μ-RE group (Scheme 2).

Compounds **5a**−**c** are all known and have been identified by comparison of their IR and ^{1}H NMR spectra with those of authentic samples, which were prepared by direct reaction of [(μ-RE)(μ-CO)Fe$_2$(CO)$_6$]$^-$ with S$_2$Cl$_2$.[6] However, the yield of **5c** (43%) is much higher than those of **5a**,**b** (15% and 14%, respectively). This may reflect the significant influences of the different bridges μ-RS and μ-RSe upon the series of reactions shown in Scheme 2.

Scheme 3



cluster	8a	8b	8c	8d	8e	8f
RE	EtS	*n*-PrS	*t*-BuS	PhS	PhSe	*p*-MeC$_6$H$_4$Se

2. Formation of the Se-Centered Anions (μ-RE)(μ-Se$^-$)Fe$_2$(CO)$_6$ (6; E = S, Se) and Their Reaction with SO$_2$Cl$_2$. Synthesis and Characterization of [(μ-RE)Fe$_2$(CO)$_6$]$_2$(μ_4-Se) (8; E = S, Se). Since selenium exhibits chemical behavior similar to sulfur,[7] we imagined that it would also react with [(μ-RE)(μ-CO)Fe$_2$(CO)$_6$]$^-$ (E = S, Se) in a way similar to that of sulfur described above. In fact, this was the case when selenium was added to a THF solution of the anions at −78 °C; an immediate evolution of CO gas accompanied by color change from brown-red to yellow-green was observed, and finally the selenium-centered anions (μ-RE)(μ-Se$^-$)Fe$_2$(CO)$_6$ (**6**) were generated. In order to compare the reactivity between sulfur-centered anions **4** and selenium-centered anions **6** and to prepare Se−Se-bonded cluster complexes **7**, we carried out the reaction of **6** with SO$_2$Cl$_2$. Surprisingly, the complexes **7**, however, were not produced and, instead, the novel cluster complexes **8** containing a μ_4-Se atom were obtained, as shown in Scheme 3.

The new cluster complexes **8a**−**f** have been characterized by C/H analysis and IR, ^{1}H NMR, and MS spectroscopy. Their IR spectra showed four to five terminal carbonyl absorption bands in the range of 2082−1975 cm^{-1}, and their ^{1}H NMR spectra all exhibited respective R resonance signals. It is worthy of note that the two R groups in **8a**−**f** cannot be attached to an E atom by an axial bond but could attach to an E atom by an equatorial bond; that is, **8a**−**f** would not exist as an a(R)e(R) or a(R)a(R) isomer but might exist as an e(R)e(R) isomer.[8a] This is because the μ_4-Se atom of **8a**−**f** utilizes two axial bonds to attach two subcluster cores (μ-RE)Fe$_2$(CO)$_6$ and because there are larger nonbonded repulsions between a(R) and a(subcluster).[8b] This deduction might be verified by some of their ^{1}H

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(8) (a) The abbreviations a = axial and e = equatorial follow the nomenclature of: Shaver, A.; Fitzpatrick, D. J.; Steliou, K.; Butler, I. S. *J. Am. Chem. Soc.* **1979**, *101*, 1313. (b) Seyferth, D.; Henderson, R. S.; Song, L.-C. *Organometallics* **1982**, *1*, 125.

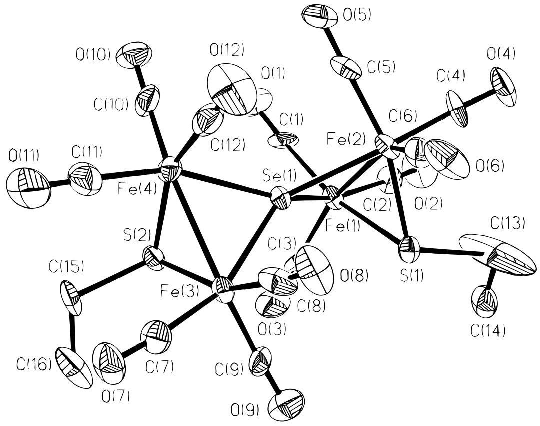


Figure 1. ORTEP view of **8a**, drawn with 35% probability ellipsoids.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for 8a

Fe(1)–Fe(2)	2.576(4)	Fe(1)–Se(1)	2.359(3)
Fe(1)–S(1)	2.288(6)	Fe(1)–C(1)	1.74(2)
Fe(1)–C(2)	1.79(2)	Fe(1)–C(3)	1.79(2)
Fe(2)–Se(1)	2.355(3)	Fe(2)–S(1)	2.265(6)
Fe(2)–C(4)	1.77(2)	Fe(2)–C(5)	1.77(2)
Fe(2)–C(6)	1.80(2)	Fe(3)–Fe(4)	2.566(4)
Fe(3)–Se(1)	2.356(3)	Fe(3)–S(2)	2.263(6)
Fe(3)–C(7)	1.78(2)	Fe(3)–C(8)	1.83(2)
Fe(3)–C(9)	1.77(2)	Fe(4)–Se(1)	2.357(3)
Fe(4)–S(2)	2.260(6)	Fe(4)–C(10)	1.79(2)
Fe(4)–C(11)	1.82(2)	Fe(4)–C(12)	1.79(2)

Fe(2)–Fe(1)–Se(1)	56.8(1)	Fe(2)–Fe(1)–S(1)	55.1(2)
Se(1)–Fe(1)–S(1)	77.5(2)	Se(1)–Fe(1)–C(1)	91.4(6)
S(1)–Fe(1)–C(1)	159.6(6)	Se(1)–Fe(1)–C(2)	157.5(7)
Fe(1)–Fe(2)–Se(1)	56.9(1)	Fe(1)–Fe(2)–S(1)	56.0(2)
Se(1)–Fe(2)–S(1)	78.0(2)	Fe(1)–Fe(2)–C(4)	100.5(6)
Se(1)–Fe(2)–C(4)	156.4(7)	S(1)–Fe(2)–C(5)	156.0(6)
Fe(4)–Fe(3)–Se(1)	57.0(1)	Fe(4)–Fe(3)–S(2)	55.4(2)
Se(1)–Fe(3)–S(2)	77.2(2)	Fe(4)–Fe(3)–C(7)	101.9(7)
Se(1)–Fe(3)–C(7)	158.4(7)	S(2)–Fe(3)–C(8)	157.7(7)
Fe(3)–Fe(4)–Se(1)	57.0(1)	Fe(3)–Fe(4)–S(2)	55.5(2)
Se(1)–Fe(4)–S(2)	77.3(2)	S(2)–Fe(4)–C(10)	103.5(7)
Fe(3)–Fe(4)–C(10)	153.0(7)	Se(1)–Fe(4)–C(11)	156.8(8)

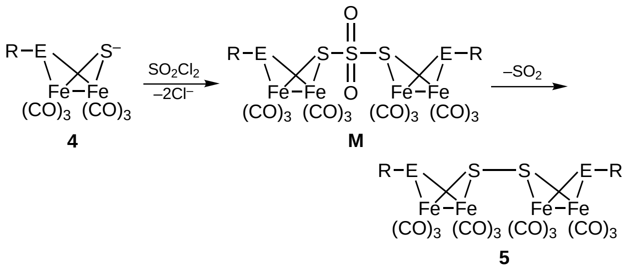
NMR spectra. For example, the ^{1}H NMR of CH$_2$ for **8a** showed one quartet at δ 2.48 ppm, the C(CH$_3$)$_3$ group of **8c** showed one singlet at δ 1.46 ppm, and the *p*-Me group of **8f** showed one singlet at δ 2.34 ppm. In the mass spectra of **8a–f**, there existed some peaks corresponding to their respective fragment ions, such as $M^+ - n$CO ($n = 2-12$), Fe$_4$SeS$_2$$^+$, and Fe$_4Se_3$$^+$.

3. Crystal Structure of [(μ-EtS)Fe$_2$(CO)$_6$]$_2$(μ_4-Se) (8a). In order to further confirm the type of structure of complexes **8a–f** mentioned above, an X-ray diffraction analysis for one representative compound, **8a**, was undertaken. Table 1 lists the bond lengths and angles. Figure 1 shows its molecular structure.

As seen from Figure 1, the molecule indeed consists of two identical subcluster units (μ-EtS)Fe$_2$(CO)$_6$ joined together through a μ_4-Se atom, which is very similar to the case for μ_4-S clusters such as [(μ-EtS)Fe$_2$(CO)$_6$]$_2$(μ_4-S)[3] and [(μ-EtS)Fe$_2$(CO)$_6$][(μ-PhS)Fe$_2$(CO)$_6$](μ_4-S).[9] Table 2 lists some bond lengths of such clusters. As seen from Table 2, the Fe–Fe and Fe–S bond lengths of **8a** are slightly longer than those of two μ_4-S analogs.

In addition, the four Fe–Se bond lengths of **8a** are basically the same (average 2.357 Å) but slightly shorter than the average Fe–Se bond length (2.428 Å) of the complex Fe$_4$(CO)$_{10}$(μ-CO)(μ_4-Se)$_2$;[10] the two ethyl groups of **8a** are both attached to bridging sulfur atoms by an e-type of bond, as seen intuitively from Figure 1. Thus, **8a** belongs to an e/e isomer, which is in good agreement with the assignment acording to its ^{1}H NMR data.

Scheme 4



It is interesting to note that clusters **8a–f** are chiral molecules. **8a** crystallizes in the space group $P2_12_12_1$, which is a chiral space group, and this means that a natural resolution of the isomers has occurred. Complexes **8a–f** are clusters containing a μ_4-Se atom coordinated to four iron atoms. Other examples involving a μ_4 main-group element coordinated to four iron atoms are known, such as [(μ-MeS)Fe$_2$(CO)$_6$]$_2$(μ_4-S),[11] {-[Fe(CO)$_4$}$_4$(μ_4-Bi)}$^{3-}$,[12] [(CO)$_8$Fe$_2$(μ_4-Sb)]$_2$Fe$_2$(CO)$_6$,[13] [(μ-Cl)(CO)$_8$Fe$_2$(μ_4-E)[Fe$_2$(CO)$_8$] (E = P, As),[14] and [(CO)$_4$-Fe]$_4$(μ_4-E) (E = Ge,[15] Sn,[16] Pb[17]).

4. Mechanistic Considerations for the Reactions of 4 or 6 with SO$_2$Cl$_2$. In the reaction of (μ-RE)(μ-S$^-$)Fe$_2$(CO)$_6$ (**4**) with SO$_2$Cl$_2$ we postulate that the negatively charged sulfur atom of nucleophile **4** first attacks at the sulfur atom of the electrophile SO$_2$Cl$_2$ to give the intermediate **M**. Then, an extrusion of SO$_2$ from **M** would give rise to the cluster complexes **5**, as shown in Scheme 4.

It is noteworthy that the extrusion of SO$_2$ is not unprecedented in similar reaction systems, such as in the preparation of organic disulfides RSSR from the oxidative coupling reaction of alkanethiolates with SO$_2$Cl$_2$[18] and in the reaction of (μ-S$^-$)$_2$Fe$_2$(CO)$_6$ with SO$_2$Cl$_2$ to give (μ-S)$_2$Fe$_2$(CO)$_6$.[8b]

By a process different from those described in Scheme 4, in the reaction of anion **6** with SO$_2$Cl$_2$ the iron atom of the intermediate **M1**, which is formed through the initial nucleophilic attack of **6** at the sulfur atom of SO$_2$Cl$_2$, would be preferentially attacked by excess anion **6**, followed by loss of the anion SeSO$_2$Cl$^-$ to give cluster complexes **8**, as shown in Scheme 5. A similar process, in which the iron atom of (μ-RS)[μ-PhC(O)S]Fe$_2$(CO)$_6$ is attacked by (μ-S$^-$)(μ-R^{1}S)Fe$_2$(CO)$_6$ to produce μ_4-S clusters, was also observed.[9,19]

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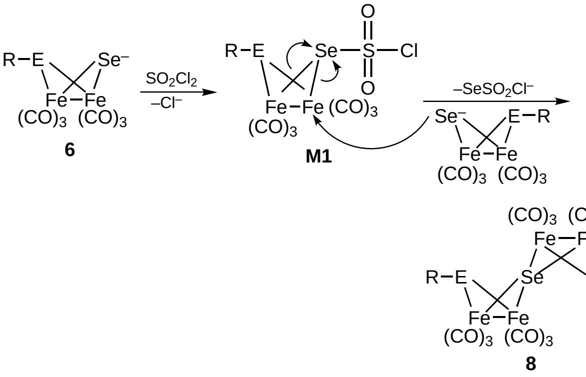
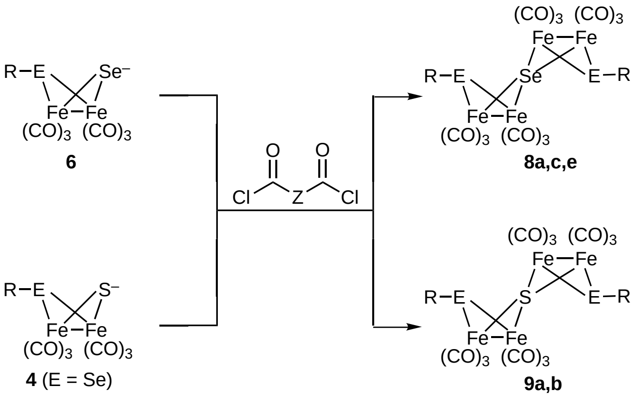
Table 2. Bond Lengths (Å) in 8a and Two μ_4-S Clusters

	8a	[(μ-EtS)$Fe_2(CO)_6$]$_2$(μ_4-S)	(μ-EtS)(μ-PhS))[$Fe_2(CO)_6$]$_2$(μ_4-S)
Fe(1)−Fe(2)	2.576(4)	2.542(2)	2.518(3)
Fe(3)−Fe(4)	2.566(4)	2.538(2)	2.526(3)
Fe(1)−S(1)	2.288(6)	2.245(2)	2.251(4)
Fe(1)−S(2)		2.275(2)	2.247(5)
Fe(2)−S(1)	2.265(6)	2.240(2)	2.233(3)
Fe(2)−S(2)		2.259(3)	2.232(4)

Scheme 5



Scheme 6



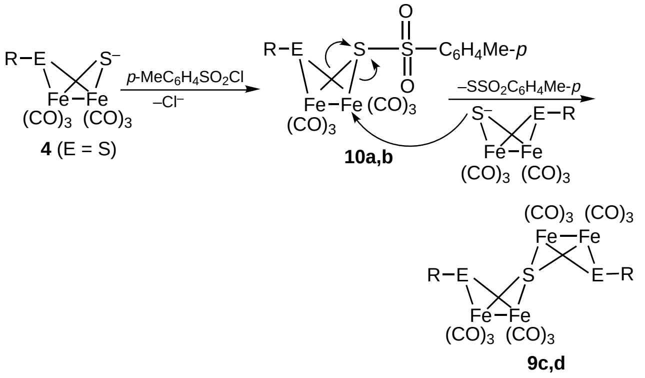
cluster	8a	8c	8e	9a	9b
RE	EtS	*t*-BuS	PhSe	PhSe	*p*-MeC$_6$H$_4$Se

It is worth pointing out that the two pathways shown in Schemes 4 and 5 reveal the different reactivities of sulfur-centered anion **4** and selenium-centered anion **6** and are proposed mainly on the basis of the strong nuclephilicity of the anions.[8b,20] Thus, the other possible pathways, such as free radical and electron-transfer processes, should not be completely ruled out.

5. Reaction of 4 or 6 with Organic Bis Acid Chlorides ClC(O)ZC(O)Cl (Z = $(CH_2)_2$, C_6H_4). Synthesis and Identification of [(μ-RE)$Fe_2(CO)_6$]$_2$(μ_4-Se) (8; E = S, Se). Synthesis and Characterization of [(μ-RSe)$Fe_2(CO)_6$]$_2$(μ_4-S) (9). In order to further compare the chemical reactivity between anions **4** and **6**, we carried out the reaction of **4** (E = Se) or **6** (E = S, Se) with some organic bis acid chlorides under conditions similar to those used in the reported corresponding reaction of **4** (E = S).[3] However, we found that the reactions, in contrast to that of **4** (E = S),[3] always gave the μ_4-E (E = S, Se) type of cluster complexes **8** and **9** without any corresponding C(O)ZC(O)-bridged clusters, even at low temperature, as shown in Scheme 6.

All characterization data for **8a**,**c**,**e** obtained from **6** and organic bis acid chlorides are completely the same as for those prepared by the reaction of **6** with SO_2Cl_2 mentioned above. The cluster complexes **9a**,**b** were fully characterized by combustion analysis and IR, ^{1}H NMR, and MS spectroscopy, whose data are in good agreement with the structures shown in Scheme 6.

Scheme 7



cluster	10a	9c	10b	9d
RE	EtS	EtS	*t*-BuS	*t*-BuS

6. Reaction of 4 (E = S) with the Organic Mono Acid Chloride *p*-MeC$_6$H$_4$SO$_2$Cl. Synthesis and Identification of [(μ-RE)$Fe_2(CO)_6$]$_2$(μ_4-S) (9; E = S). Synthesis and Characterization of [(μ-RE)(μ-*p*-MeC$_6$H$_4$SO$_2$S)$Fe_2(CO)_6$ (10; E = S). Reaction of the sulfur-centered anion **4** (E = S) with *p*-MeC$_6$H$_4$SO$_2$Cl, through a pathway similar to that shown in Scheme 5, gave rise to cluster complexes of both types of **9** and of **10**, as shown in Scheme 7.

However, the experiments showed that higher temperature favored the formation of the μ_4-S type of complexes **9**. For instance, yields of **10b** and **9d** were 36% and 4%, respectively, when the reaction was run at −78 °C for 0.5 h and then at room temperature for 2 h, while being 11% and 66% when it was run for 2 h at room temperature. Complexes **9c**,**d** were identified by comparison of their IR and ^{1}H NMR data with those of authentic samples prepared by another route,[3,21] while complexes **10a**,**b** were well characterized by elemental analysis and IR, ^{1}H NMR, and MS spectroscopy. In principle, complexes **10**, just like (μ-R^{1}S)(μ-R^{2}S)$Fe_2(CO)_6$, could exist as ae, ee, and ea isomers.[8] However, since CH_3 of the ethyl group in **10a** showed two triplets at δ 1.02 and 1.44 ppm, it should exist as a mixture of the two isomers a(Et)e($SO_2C_6H_4Me$) and e(Et)e($SO_2C_6H_4Me$) or e(Et)a($SO_2C_6H_4Me$). Likewise, since *t*-Bu of **10b** showed two singlets at δ 1.60 and 1.72 ppm, it should exist also as a mixture of the two isomers a(Bu)e($SO_2C_6H_4Me$) and e(Bu)e(SO_2-C_6H_4Me) or e(Bu)a($SO_2C_6H_4Me$).

7. Reaction of 6 with *p*-MeC$_6$H$_4$SO$_2$Cl. Synthesis and Identification of [(μ-RE)$Fe_2(CO)_6$]$_2$(μ_4-Se) (8; E = S, Se). Synthesis and Characterization of (μ-

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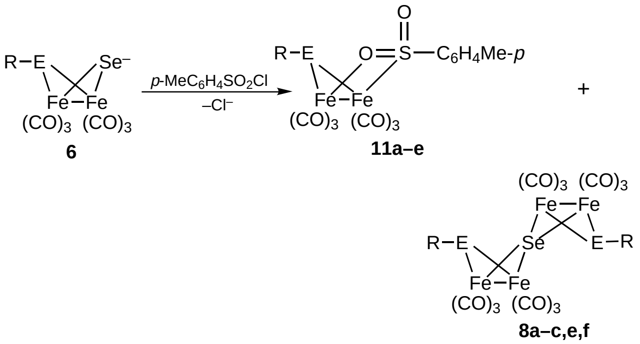
Scheme 8

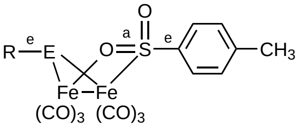


cluster	**8a**	**8b**	**8c**	**8e**	**8f**
RE	EtS	*n*-PrS	*t*-BuS	PhSe	*p*-MeC$_6$H$_4$Se
cluster	**11a**	**11b**	**11c**	**11d**	**11e**
RE	EtS	*n*-PrS	*t*-BuS	PhSe	*p*-MeC$_6$H$_4$Se

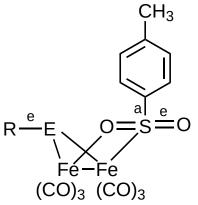
RE)(μ-*p*-MeC$_6$H$_4$SO$_2$)Fe$_2$(CO)$_6$ (11; E = S, Se). Differing from the sulfur-centered anion **4** (E = S), the selenium-centered anion **6** reacted with *p*-MeC$_6$H$_4$SO$_2$Cl to give both SO$_2$C$_6$H$_4$Me-*p* ligand-bridged complexes **11** and the μ_4-Se cluster complexes **8**, as shown in Scheme 8.

Cluster complexes of type **11** are unusual in that S=O of the SO$_2$C$_6$H$_4$Me-*p* group is bridged to two iron atoms, although there are a number of RSO$_2$-coordinated transition-metal complexes.[22] Structures of **11a**−**e** have been characterized by combustion analysis and IR, ^{1}H NMR, and MS spectroscopic methods. In the IR spectra there are two absorption bands characteristic of the coordinated S=O at around 1080−1089 cm^{-1} with medium intensity, and uncoordinated S=O appears at about 1080−1180 cm^{-1} with strong intensity. In addition, there are three to four strong to very strong bands characteristic of terminal carbonyls.

For butterfly complexes of type **11**, the two isomers **A** and **B** are possible. **A** and **B** both have e(R), since an isomer with R in the axial position would possess too strong a steric repulsion between an axial R and an axial oxygen atom or an axial *p*-MeC$_6$H$_4$ group. Fortunately, their ^{1}H NMR spectra could provide the information about the existence for such isomers. For instance, **11a**,**b** each exhibited only one triplet for the methyl group of R at δ 1.62 and 1.08 ppm; thus, they exist as only one isomer, **A** or **B**. **11c** showed two singlets at δ 1.58 and 1.70 ppm for the *tert*-butyl group and two singlets at δ 2.36 and 2.40 ppm for the methyl group of *p*-MeC$_6$H$_4$; therefore, it exists as the two isomers **A** ($\delta_{t\text{-Bu}}$ 1.70 ppm, $\delta_{p\text{-Me}}$ 2.40 ppm) and **B** ($\delta_{t\text{-Bu}}$ 1.58 ppm, $\delta_{p\text{-Me}}$ 2.36 ppm). The ratio **A**/**B** is 1/6, calculated from the integrations of ^{1}H NMR signals of *tert*-butyl or *p*-Me groups for **A** and **B**. **11d** exhibited two singlets for *p*-Me of axial *p*-MeC$_6$H$_4$ at δ 2.38 ppm and for *p*-Me of equatorial *p*-MeC$_6$H$_4$ at δ 2.50 ppm, respectively; thus it exists as two isomers and the ratio of **A**/**B** equals 10/13. The mass spectra of **11a**−**e** showed further evidence for their composition and structures. The largest fragment ion was MeC$_6$H$_4$SO$_2$Fe$_2$SH$^+$ for **11a**, M$^+$ − CO for **11b**, M$^+$ − 2CO for **11c**, M$^+$ for **11d**, and M$^+$ − 2CO for **11e**, respectively.



A



B

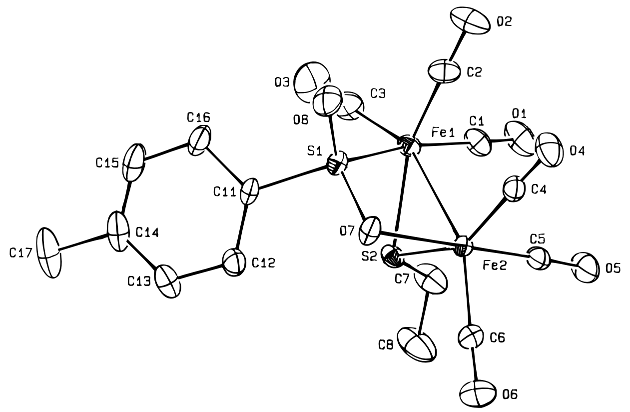


Figure 2. ORTEP view of **11a**, drawn with 30% probability ellipsoids.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for 11a

Fe(1)−Fe(2)	2.568(1)	Fe(2)−C(4)	1.808(5)
Fe(1)−C(2)	1.778(6)	Fe(2)−C(6)	1.822(6)
Fe(1)−C(3)	1.803(7)	Fe(2)−O(7)	2.008(3)
Fe(1)−C(1)	1.806(6)	Fe(2)−S(2)	2.248(2)
Fe(1)−S(1)	2.224(1)	S(1)−O(8)	1.454(4)
Fe(1)−S(2)	2.241(2)	S(1)−O(7)	1.516(3)
Fe(2)−C(5)	1.755(6)	S(1)−C(11)	1.784(5)
C(2)−Fe(1)−S(1)	88.0(2)	S(2)−Fe(2)−Fe(1)	54.96(4)
C(2)−Fe(1)−S(2)	155.2(2)	O(8)−S(1)−O(7)	113.7(2)
C(2)−Fe(1)−Fe(2)	99.9(2)	O(8)−S(1)−C(11)	106.0(2)
S(1)−Fe(1)−S(2)	84.16(5)	O(8)−S(1)−Fe(1)	116.0(2)
S(1)−Fe(1)−Fe(2)	72.27(4)	C(4)−Fe(2)−Fe(1)	94.9(2)
S(2)−Fe(1)−Fe(2)	55.24(4)	C(6)−Fe(2)−O(7)	89.0(2)
C(7)−S(2)−Fe(1)	112.0(2)	C(6)−Fe(2)−S(2)	106.8(2)
C(7)−S(2)−Fe(2)	117.8(2)	C(6)−Fe(2)−Fe(1)	158.7(2)
Fe(1)−S(2)−Fe(2)	69.80(4)	O(7)−Fe(2)−S(2)	83.7(1)

8. Crystal Structure of (μ-EtS)(μ-MeC$_6$H$_4$SO$_2$)Fe$_2$(CO)$_6$ (11a). In order to confirm the types of structures of complexes **11a**−**e** obtained by the reaction discussed above and to further establish which isomer exists for **11a** (**A** or **B**), an X-ray diffraction analysis for **11a** was undertaken. Table 3 lists bond lengths and angles. Figure 2 shows its molecular structure.

As seen from Figure 2, **11a** contains no bridged Se atom attached to the functional ligand *p*-MeC$_6$H$_4$SO$_2$, and it has a *p*-MeC$_6$H$_4$SO$_2$ ligand bridged between two iron atoms through a S=O unit. The butterfly core consists of two planar wings of Fe$_2$SO and Fe$_2$S, whose dihedral angle is 85.33°. Thus, the structure of this molecule is very similar to that of the μ-acyl complex (μ-EtS)[μ-COC(CH$_3$)=CH$_2$)]Fe$_2$(CO)$_6$.[23] The bond length of S(1)−O(7) (1.516(3) Å), due to coordination, is significantly longer than the uncoordinated bond length of S(1)−O(8) (1.454 (4) Å). The thiolate ligand of **11a** bridges between Fe(1) and Fe(2) symmetrically and gives two equivalent Fe−S bonds (2.241(1) and 2.248(2) Å), while the Fe(1)−S(1) bond (2.248(2) Å) is much longer than the Fe(2)−O(7) bond (2.008(3) Å). In this

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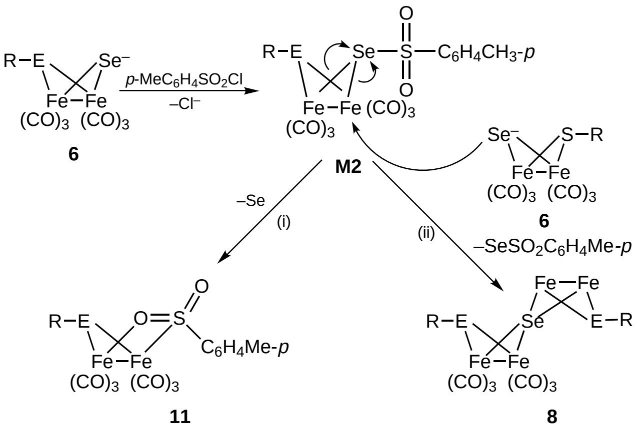
(22) Vitzthum, G.; Lindner, E. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 315.

(23) Song, L.-C.; Wang, R.-J.; Hu, Q.-M.; Wang, H.-G. *Jiegou Huaxue* **1989**, *8*, 115.

Scheme 9



molecule, each iron may be regarded as Fe^I and, therefore, possesses seven electrons in its d orbital. The stable 18-electron configuration for each iron atom is achieved by the donation of three pairs of electrons from the coordinated carbonyl groups, one pair of electrons from the bridged EtS, one pair from p-$MeC_6H_4S(O){=}O$, and one electron from the Fe−Fe single bond. An Fe−Fe single bond of 2.568(1) Å in **11a** is approximately equal to those of similar complexes, such as the bond length of Fe−Fe = 2.552(1) Å in (μ-EtS)[μ-COC-$(CH_3){=}CH_2]Fe_2(CO)_6$.[23]

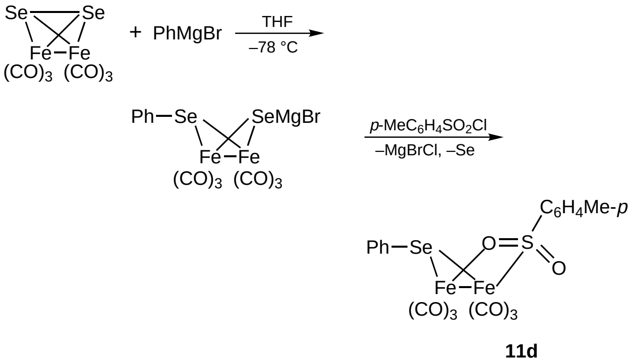
Finally, it is worthy of note that, as seen intuitively from Figure 2, the ethyl group is attached to S(2) by an e-type of bond, while the tolyl group is attached to S(1) by an a-type of bond and the uncoordinated O(8) atom is attached to S(1) by an e-type of bond; *i.e.*, **11a** exists as the isomer **B**. This result from X-ray diffraction analysis is in good agreement with its ^1H NMR spectral data.

9. Mechanistic Considerations about the Reaction of 6 with p-$MeC_6H_4SO_2Cl$. For the formation of **8** and **11** a reasonable mechanism as shown in Scheme 9 might be proposed. First, the intermediate **M2** would be generated through nucleophilic substitution of selenium-centered anion **6** by p-$MeC_6H_4SO_2Cl$. Then, **M2** might undergo two changes: one involves the extrusion of the selenium atom attached to the $SO_2C_6H_4Me$ group to afford complexes of type **11**; the other involves an attack of its one of the iron atoms by the bridged selenium atom of excess **6**, followed by loss of a p-$MeC_6H_4SO_2Se$ group to give the complexes of type **8**.

It is worth pointing out that the suggested pathway for producing complexes **8** in Scheme 9 is basically the same as the pathway proposed in Scheme 5. However, the extrusion of a selenium atom from **M2** suggested in the course of formation of **11** is unprecedented, although the extrusions of Hg[24] and CO[25] in similar systems are well-known processes.

To exclude the possibility for production of **11** directly from $[(\mu\text{-RE})(\mu\text{-CO})Fe_2(CO)_6]^-$ (for example, 42% of **11c** might be obtained by reaction of $[(\mu\text{-}t\text{-BuS})(\mu\text{-CO})Fe_2(CO)_6]^-$ with p-$MeC_6H_4SO_2Cl$) and to further confirm the extrusion process of Se from **M2**, we first prepared one selenium-centered anion, $(\mu\text{-PhSe})(\mu\text{-Se}^-)Fe_2(CO)_6$, by an old route, which involved the reaction of μ-$Se_2Fe_2(CO)_6$ with PhMgBr[26] (in ref 26 PhLi was used, actually) and then carried out an *in situ* reaction of this anion with p-$MeC_6H_4SO_2Cl$ under corresponding conditions to give **11a** in 47% yield (Scheme 10).

Scheme 10



Experimental Section

All reactions were carried out under prepurified tank nitrogen using standard Schlenk or vacuum line techniques. THF and diethyl ether were distilled from sodium−benzophenone ketyl, while triethylamine was distilled from potassium hydroxide under nitrogen. Elemental sulfur and selenium, mercaptans RSH (R = Et, n-Pr, t-Bu), thiophenol, sulfuryl chloride, and toluene-4-sulfonyl chloride were all chemically pure reagents. Triiron dodecacarbonyl,[27] $(\mu\text{-Se})_2Fe_2(CO)_6$,[28] benzeneselenol,[29] 4-methylbenzeneselenol,[29] succinoyl chloride,[30] and p-phthaloyl chloride[31] were all prepared according to the literature. Column chromatography and TLC were carried out by using 300−400 mesh silica gel and silica gel G (10−40 μm), respectively.

All new compounds were recrystallized from CH_2Cl_2/hexane and characterized by elemental analysis and IR, ^1H NMR, and MS spectroscopy. The known compounds were identified by comparison of their IR and ^1H NMR spectral data. IR spectra were recorded on a Nicolet FT-IR 5DX infrared spectrophotometer and ^1H NMR spectra on a JEOL FX 90Q NMR spectrometer. C/H analyses and MS determinations were performed by a 240C analyzer and HP 5988A spectrometer, respectively. Melting points were determined on a Yanaco micromelting point apparatus (MP-500).

Standard *in Situ* Preparation of Et_3NH^+ Salts of the Anions $(\mu\text{-RE})(\mu\text{-S}^-)Fe_2(CO)_6$ (4; E = S, Se). A 100 mL three-necked flask equipped with a magnetic stirbar, a rubber septum, and a nitrogen inlet tube was charged with 1.50 g (2.98 mmol) of $Fe_3(CO)_{12}$ and 40 mL of THF. To the resulting green solution was added successively 3.03 mmol of an appropriate thiol or selenol and 0.50 mL (3.58 mmol) of triethylamine. The mixture was stirred at room temperature for 30 min in the case of thiol and 10 min for selenol. The resulting brown solution of $[Et_3NH][(\mu\text{-RE})(\mu\text{-CO})Fe_2(CO)_6]$ (E = S, Se) was cooled to −78 °C with a dry ice/acetone bath. To this solution was added 0.196 g (6.0 mmol) of elemental sulfur. The reaction mixture was stirred at −78 °C for 30 min to give a THF solution of Et_3NH^+ salts of the anions $(\mu\text{-RE})(\mu\text{-S}^-)Fe_2(CO)_6$ (**4**; E = S, Se), utilized *in situ* in the following preparations.

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[24] Seyferth, D.; Archer, C. M. *Organometallics* **1986**, *5*, 2572.

[25] Song, L.-C.; Liu, J.-T.; Wang. J.-T. *Acta Chim. Sin.* **1990**, *48*, 110.

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[30] Ruggli, P.; Maeder, A. *Helv. Chim. Acta* **1943**, *26*, 1476.

[31] Ott, E. *Organic Syntheses*; Wiley: New York, 1955; Collect. Vol. 2, p 528.

Preparations of 5a−c by Reaction of 4 with SO$_2$Cl$_2$. To the solution of [Et$_3$NH][(μ-PhSe)(μ-S)Fe$_2$(CO)$_6$] prepared above was added 0.16 mL (2.0 mmol) of SO$_2$Cl$_2$, and stirring was continued for 10 min at −78 °C and for 2 h at room temperature. TLC indicated formation of two main products. Solvent was removed under vacuum to leave a solid residue, which was purified by column chromatography and TLC with 1:10 (v/v) CH$_2$Cl$_2$/petroleum ether as eluant. The first red band gave 0.405 g (23%) of (μ-PhSe)$_2$Fe$_2$(CO)$_6$.[32] The second red band gave 0.212 g (15%) of [(μ-PhSe)Fe$_2$(CO)$_6$]$_2$(μ-S−S) (**5a**).[6]

Compound 5b. The same procedure as for **5a** was followed, but [Et$_3$NH][(μ-p-MeC$_6$H$_4$Se)(μ-S)Fe$_2$(CO)$_6$] was used instead of [Et$_3$NH][(μ-PhSe)(μ-S)Fe$_2$(CO)$_6$]. The first red band gave 0.404 g (22%) of (μ-p-MeC$_6$H$_4$Se)$_2$Fe$_2$(CO)$_6$,[6] and the second red band gave 0.200 g (14%) of [(μ-p-MeC$_6$H$_4$Se)Fe$_2$(CO)$_6$]$_2$(μ-S−S) (**5b**).[6]

Compound 5c. The same procedure as for **5a** was followed, but [Et$_3$NH][(μ-t-BuS)(μ-S)Fe$_2$(CO)$_6$] was used instead of [Et$_3$NH]p(μ-PhSe)(μ-S)Fe$_2$(CO)$_6$]. The first band gave 0.089 g (7%) of (μ-t-BuS)$_2$Fe$_2$(CO)$_6$,[21] and the second band gave 0.512 g (43%) of [(μ-t-BuS)Fe$_2$(CO)$_6$]$_2$(μ-S−S) (**5c**).[6]

Preparation of 9a,b by Reaction of 4 with ClC(O)(CH$_2$)$_2$C(O)Cl. To a solution of [Et$_3$NH][μ-PhSe)(μ-S)Fe$_2$(CO)$_6$] was added 0.16 mL (1.40 mmol) of succinoyl chloride, and stirring was continued for 2 h at −78 °C. The same workup as for the reaction with SO$_2$Cl$_2$ gave 0.463 g (26%) of (μ-PhSe)$_2$Fe$_2$(CO)$_6$[32] and 0.069 g (5%) of [(μ-PhSe)Fe$_2$(CO)$_6$]$_2$(μ_4-S) (**9a**) as a red solid. **9a**: mp 135 °C dec. Anal. Calcd for C$_{24}$H$_{10}$Fe$_4$O$_{12}$SSe$_2$: C, 31.90; H, 1.12. Found: C, 32.41; H, 1.05. IR (KBr, disk): $\nu_{C\equiv O}$ 2057.0 (s), 2032.4 (vs), 1991.4 (s), 1966.8 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.12−7.64 (m, 10H, 2C$_6$H$_5$) ppm. MS (EI, ^{80}Se), m/z (relative intensity): 654 (M$^+$ − 9CO, 5.0), 598 (M$^+$ − 11CO, 3.8), 570 (M$^+$ − 12CO, 13.9), 416 (Fe$_4$Se$_2$S$^+$, 99.5), 224 (Fe$_2$SeS$^+$, 8.7), 192 (Fe$_2$Se$^+$, 4.2), 144 (Fe$_2$S$^+$, 3.4), 77 (C$_6$H$_5^+$, 15.1), 56 (Fe$^+$, 22.7).

Compound 9b. The same procedure as for **9a** was followed, but [Et$_3$NH][(μ-p-MeC$_6$H$_4$Se)(μ-S)Fe$_2$(CO)$_6$] was used instead of [Et$_3$NH][(μ-PhSe)(μ-S)Fe$_2$(CO)$_6$]. A 0.536 g (29%) amount of (μ-p-MeC$_6$H$_4$Se)$_2$Fe$_2$(CO)$_6$[6] and 0.135 g (10%) of [(μ-p-MeC$_6$H$_4$Se)Fe$_2$(CO)$_6$]$_2$(μ_4-S)) (**9b**) as a red solid were obtained. **9b**: mp 124 °C dec. Anal. Calcd for C$_{26}$H$_{14}$Fe$_4$O$_{12}$SSe$_2$: C, 33.52; H, 1.51. Found: C, 33.67; H, 1.48. IR (KBr, disk): $\nu_{C\equiv O}$ 2081.6 (s), 2051.6 (vs), 2032.4 (vs), 1983.2 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 2.26 (s, 6H, 2CH$_3$), 6.92−7.56 (m, 8H, 2C$_6$H$_4$) ppm. MS (EI, ^{80}Se), m/z (relative intensity): 878 (M$^+$ − 2CO, 0.9), 850 (M$^+$ − 3CO, 1.4), 766 (M$^+$ − 6CO, 1.8), 738 (M$^+$ − 7CO, 3.3), 710 (M$^+$ − 8CO, 3.3), 682 (M$^+$ − 9CO, 9.0), 654 (M$^+$ − 10CO, 2.1), 626 (M$^+$ − 11CO, 5.5), 598 (M$^+$, 12CO, 20.3), 416 (Fe$_4$Se$_2$S$^+$, 100), 224 (Fe$_2$SeS$^+$, 5.5), 192 (Fe$_2$Se$^+$, 3.7), 144 (Fe$_2$S$^+$, 3.1), 91 (CH$_3$C$_6$H$_4^+$, 77.3), 56 (Fe$^+$, 16.1).

Standard *in Situ* Preparation of Et$_3$NH$^+$ Salts of the Anion (μ-RE)(μ-Se$^-$)Fe$_2$(CO)$_6$ (6; E = S, Se). To the brown solution of [Et$_3$NH][(μ-RE)(μ-CO)Fe$_2$(CO)$_6$], obtained as described above in the preparation of [Et$_3$NH][(μ-RE)(μ-S$^-$)Fe$_2$(CO)$_6$], was added, with stirring at −78 °C, 0.474 g (6.0 mmol) of elemental selenium. The reaction mixture was stirred at −78 °C for 40 min to give a THF solution of the Et$_3$NH$^+$ salts of anions (μ-RE)(μ-Se$^-$)Fe$_2$(CO)$_6$ (**6**; E = S, Se) utilized in the following preparations.

Preparation of 8a−f by Reaction of 6 with SO$_2$Cl$_2$ or with Organic Bis Acid Chlorides. To the solution of [Et$_3$NH][(μ-EtS)(μ-Se)Fe$_2$(CO)$_6$] prepared above was added 0.16 mL (2.0 mmol) of SO$_2$Cl$_2$, and stirring was continued for 10 min at −78 °C and for 2 h at room temperature. TLC indicated that two main red products were formed. Solvent was removed under vacuum to leave a red residue, which was purified by column chromatography and TLC with petroleum ether as eluant. The first red band gave 0.168 g (14%) of (μ-EtS)$_2$Fe$_2$(CO)$_6$.[21] The second red band gave 0.655 g (58%) of [(μ-EtS)Fe$_2$(CO)$_6$]$_2$(μ_4-Se) (**8a**) as a dark red solid. **8a**: mp 129−130 °C. Anal. Calcd for C$_{16}$H$_{10}$Fe$_4$O$_{12}$S$_2$Se: C, 25.26; H, 1.33. Found: C, 25.09; H, 1.33. IR (KBr, disk): $\nu_{C\equiv O}$ 2081.6 (m), 2040.6 (vs), 1991.4 (s), 1966.8 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.43 (t, J = 7.2 Hz, 6H, 2CH$_3$), 2.48 (q, J = 7.2 Hz, 4H, 2CH$_2$) ppm. MS (EI, ^{80}Se), m/z (relative intensity): 706 (M$^+$ − 2CO, 2.7), 678 (M$^+$ − 3CO, 1.2), 650 (M$^+$ − 4CO, 3.1), 622 (M$^+$ − 5CO, 1.6), 594 (M$^+$ − 6CO, 3.5), 566 (M$^+$ − 7CO, 8.3), 538 (M$^+$ − 8CO, 13.6), 510 (M$^+$ − 9CO, 19.0), 482 (M$^+$ − 10CO, 3.1), 454 (M$^+$ − 11CO, 15.4), 426 (M$^+$ − 12CO, 1.5), 368 (Fe$_4$SeS$_2^+$, 100), 253 (Fe$_2$SeSEt$^+$, 3.0), 224 (Fe$_2$SeS$^+$, 17.9), 192 (Fe$_2$Se$^+$, 5.5), 144 (Fe$_2$S$^+$, 25.7), 56 (Fe$^+$, 15.8), 29 (Et$^+$, 35.7).

Preparation of 8a through Reaction with ClC(O)(CH$_2$)$_2$C(O)Cl. (i) Similarly to the SO$_2$Cl$_2$ method described above, to the solution of [Et$_3$NH][(μ-EtS)(μ-Se)Fe$_2$(CO)$_6$] was added 0.16 mL (1.4 mmol) of succinoyl chloride instead of SO$_2$Cl$_2$ and the reaction mixture was stirred for 30 min at −78 °C and for 3 h at room temperature. After the same workup as described above, 0.172 g (16%) of (μ-EtS)$_2$Fe$_2$(CO)$_6$ and 0.243 g (24%) of **8a** were obtained.

(ii) To the solution of [Et$_3$NH][(μ-EtS)(μ-Se)Fe$_2$(CO)$_6$] was added 0.16 mL (1.4 mmol) of succinoyl chloride, and the reaction mixture was stirred for 3 h at −78 °C. After the same workup as described above, 0.107 g (9%) of (μ-EtS)$_2$Fe$_2$(CO)$_6$[21] and 0.197 g (18%) of **8a** were obtained.

Compound 8b. The same SO$_2$Cl$_2$ procedure as that of **8a** was followed, but with use of [Et$_3$NH][(μ-n-PrS)(μ-Se)Fe$_2$(CO)$_6$] instead of [Et$_3$NH][(μ-EtS)(μ-Se)Fe$_2$(CO)$_6$]. A 0.072 g amount (6%) of (μ-n-PrS)$_2$Fe$_2$(CO)$_6$[21] and 0.530 g (45%) of [(μ-n-PrS)Fe$_2$(CO)$_6$]$_2$(μ_4-Se) (**8b**) as a dark red solid were obtained. **8b**: mp 103−104 °C. Anal. Calcd for C$_{18}$H$_{14}$Fe$_4$O$_{12}$S$_2$Se: C, 27.41; H, 1.79. Found: C, 27.39; H, 1.28. IR (KBr, disk): $\nu_{C\equiv O}$ 2081.6 (m), 2057.0 (s), 2032.4 (vs), 1991.4 (s), 1975.0 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.08 (t, J = 7.2 Hz, 6H, 2CH$_3$), 1.40−2.04 (m, 4H, 2CH$_2$), 2.48 (t, J = 7.2 Hz, 4H, 2CH$_2$) ppm. MS (EI, ^{80}Se), m/z (relative intensity): 706 (M$^+$ − 3CO, 1.1), 678 (M$^+$ − 4CO, 5.3), 622 (M$^+$ − 6CO, 0.9), 594 (M$^+$ − 7CO, 2.2), 566 (M$^+$ − 8CO, 1.7), 538 (M$^+$ − 9CO, 3.8), 510 (M$^+$ − 10CO, 1.9), 411 (Fe$_4$SeS$_2$Pr$^+$, 3.1), 368 (Fe$_4$SeS$_2^+$, 35.0), 267 (Fe$_2$SeSPr$^+$, 1.0), 224 (Fe$_2$SeS$^+$, 5.0), 192 (Fe$_2$Se$^+$, 2.2), 187 (Fe$_2$SPr$^+$, 2.2), 144 (Fe$_2$S$^+$ 7.2), 56 (Fe$^+$, 16.0), 43 (Pr$^+$, 22).

Compound 8c. The same SO$_2$Cl$_2$ procedure as that of **8a** was followed, but with use of [Et$_3$NH][(μ-t-BuS)(μ-Se)Fe$_2$(CO)$_6$] instead of [Et$_3$NH][(μ-EtS)(μ-Se)Fe$_2$(CO)$_6$]. A 0.094 g amount (7%) of (μ-t-BuS)$_2$Fe$_2$(CO)6,[21] 0.078 g (5%) of (μ-t-BuS)$_2$Fe$_3$(CO)$_9$,[21] and 0.268 g (22%) of [(μ-t-BuS)Fe$_2$(CO)$_6$]$_2$(μ_4-Se) (**8c**) as a dark red solid were obtained. **8c**: mp 116−117 °C. Anal. Calcd for C$_{20}$H$_{18}$Fe$_4$O$_{12}$S$_2$Se: C, 29.41; H, 2.22. Found: C, 29.53; H, 2.17. IR (KBr, disk): $\nu_{C\equiv O}$ 2081.6 (m), 2051.4 (s), 2032.4 (vs) 1991.4 (s), 1972.2 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.46 [s, 18H, 2C(CH$_3$)$_3$] ppm. MS (EI, ^{80}Se), m/z (relative intensity): 762 (M$^+$ − 2CO, 0.7), 678 (M$^+$ − 5CO, 1.7), 650 (M$^+$ − 6CO, 0.9), 622 (M$^+$ − 7CO, 4.0), 594 (M$^+$ − 8CO, 4.5), 566 (M$^+$ − 9CO, 13.4), 538 (M$^+$ − 10CO, 0.7), 510 (M$^+$ − 11CO, 9.1), 482 (M$^+$ − 12CO, 1.0), 425 (Fe$_4$SeS$_2$Bu$^+$, 4.3), 368 (Fe$_4$SeS$_2^+$, 68.8), 281 (Fe$_2$SeSBu$^+$, 2.2), 201 (Fe$_2$SBu$^+$, 3.6), 192 (Fe$_2$Se$^+$, 1.9), 144 (Fe$_2$S$^+$, 11.9), 57 (Bu$^+$, 100), 56 (Fe$^+$, 12.0).

Preparation of 8c through Reaction with Organic Bis Acid Chlorides. (i) Similarly to the ClC(O)(CH$_2$)$_2$C(O)Cl method for **8a**, the same amount of succinoyl chloride was added to the solution of [Et$_3$NH][(μ-t-BuS)(μ-Se)Fe$_2$(CO)$_6$] and the mixture was stirred for 30 min at −78 °C and for 3 h at room temperature. A 0.088 g amount (6%) of (μ-t-BuS)$_2$Fe$_2$(CO)$_6$[21] and 0.337 g (28%) of **8c** were obtained. When 0.305 g (1.5 mmol) of p-phthaloyl chloride was used, 0.098 g (7%) of (μ-t-BuS)$_2$Fe$_2$(CO)$_6$[21] and 0.282 g (23%) of **8c** were obtained. When 0.305 g (1.5 mmol) of p-phthaloyl chloride was used, 0.098 g (7%) of (μ-t-BuS)$_2$Fe$_2$(CO)$_6$[21] and 0.282 g (23%) of **8c** were obtained.

(ii) to the solution of [Et$_3$NH][(μ-t-BuS)(μ-Se)Fe$_2$(CO)$_6$] was added the same amount of succinoyl chloride, and the mixture

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(32) Schermer, E. D.; Baddley, W. H. *J. Organomet. Chem.* **1971**, *30*, 67.

was stirred for 3 h at −78 °C. A 0.268 g amount (20%) of (μ-*t*-BuS)$_2$Fe$_2$(CO)$_6$[21] and 0.105 g (9%) of **8c** were obtained.

Compound 8d. The same SO$_2$Cl$_2$ procedure as that of **8a** was followed, but with use of [Et$_3$NH][(μ-PhS)(μ-Se)Fe$_2$(CO)$_6$] instead of [Et$_3$NH][(μ-EtS)(μ-Se)Fe$_2$(CO)$_6$]. A 0.578 g amount (38%) of (μ-PhS)$_2$Fe$_2$(CO)$_6$[33] and 0.230 g (18%) of [(μ-PhS)Fe$_2$(CO)$_6$]$_2$(μ_4-Se) (**8d**) as a dark red solid were obtained. **8d**: mp 146 °C dec. Anal. Calcd for C$_{24}$H$_{10}$Fe$_4$O$_{12}$S$_2$Se: C, 33.64; H, 1.18. Found: C, 33.69; H, 1.30. IR (KBr, disk): $\nu_{C\equiv O}$ 2081.6 (m), 2057.0 (s), 2032.4 (vs), 1991.4 (s), 1975.0 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.32 (s, 10H, 2C$_6$H$_5$) ppm. MS (EI, ^{80}Se), *m/z* (relative intensity): 802 (M$^+$ − 2CO, 0.9), 746 (M$^+$ − 4CO, 1.3), 718 (M$^+$ − 5CO, 0.7), 690 (M$^+$ − 6CO, 1.4), 662 (M$^+$ − 7CO, 2.1), 634 (M$^+$ − 8CO, 1.5), 606 (M$^+$ − 9CO, 10.3), 578 (M$^+$ − 10CO, 2.5), 550 (M$^+$ − 11CO, 3.3), 522 (M$^+$ − 12CO, 11.4), 445 (Fe$_4$SeS$_2$Ph$^+$, 0.8), 368 (Fe$_4$SeS$_2$$^+$, 100), 301 (Fe$_2$SeSPh$^+$, 6.0), 224 (Fe$_2SeS^+$, 11.2), 221 (Fe$_2SPh^+$, 14.5), 192 (Fe$_2Se^+$, 3.0), 144 (Fe$_2S^+$, 11.6), 77 (Ph$^+$, 20.7), 56 (Fe$^+$, 28.2).

Compound 8e. The same SO$_2$Cl$_2$ procedure as that of **8a** was followed, but with use of [Et$_3$NH][(μ-PhSe)(μ-Se)Fe$_2$(CO)$_6$] instead of [Et$_3$NH][(μ-EtS)(μ-Se)Fe$_2$(CO)$_6$]. A 0.427 g amount (24%) of (μ-PhSe)$_2$Fe$_2$(CO)$_6$[32] and 0.165 g (12%) of [(μ-PhSe)Fe$_2$(CO)$_6$]$_2$(μ_4-Se) (**8e**) as a dark red solid were obtained. **8e**: mp 164 °C dec. Anal. Calcd for C$_{24}$H$_{10}$Fe$_4$O$_{12}$Se$_3$: C, 30.32; H, 1.06. Found: C, 30.33; H, 0.97. IR (KBr, disk): $\nu_{C\equiv O}$ 2081.6 (m), 2057.0 (s), 2032.4 (vs), 1991.4 (s), 1975.0 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.34 (s, 10H, 2C$_6$H$_5$) ppm. MS (EI, ^{80}Se), *m/z* (relative intensity): 702 (M$^+$ − 9CO, 1.7), 618 (M$^+$ − 12CO, 3.0), 464 (Fe$_4$Se$_3$$^+$, 8.3), 461 (Fe$_4Se_2Ph^+$, 100), 272 (Fe$_2Se_2$$^+$, 25.4), 269 (Fe$_2$SePh$^+$, 15.5), 192 (Fe$_2Se^+$, 14.5), 77 (Ph$^+$, 28.7), 56 (Fe$^+$, 51.9).

Preparation of 8e through Reaction with Succinoyl Chloride. To the solution of [Et$_3$NH][(μ-PhSe)(μ-Se)Fe$_2$(CO)$_6$] was added 0.16 mL (1.4 mmol) of succinoyl chloride, and the reaction mixture was stirred for 3 h at −78 °C. A 0.486 g amount (29%) of (μ-PhSe)$_2$Fe$_2$(CO)$_6$[32] and 0.092 g (7%) of **8e** were obtained.

Compound 8f. The same SO$_2$Cl$_2$ procedure as that of **8a** was followed, but with [Et$_3$NH][(μ-*p*-MeC$_6$H$_4$Se)(μ-Se)Fe$_2$(CO)$_6$] instead of [Et$_3$NH][(μ-EtS)(μ-Se)Fe$_2$(CO)$_6$]. A 0.536 g amount (29%) of (μ-*p*-MeC$_6$H$_4$Se)$_2$Fe$_2$(CO)$_6$[6] and 0.195 g (13%) of [(μ-*p*-MeC$_6$H$_4$Se)Fe$_2$(CO)$_6$]$_2$(μ_4-Se) (**8f**) as a dark red solid were obtained. **8f**: mp 163 °C dec. Anal. Calcd for C$_{26}$H$_{14}$Fe$_4$O$_{12}$Se$_3$: C, 31.91; H, 1.44. Found: C, 32.15; H, 1.19. IR (KBr, disk): $\nu_{C\equiv O}$ 2081.6 (m), 2051.6 (s), 2032.4 (vs), 1991.4 (vs) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 2.34 (s, 6H, 2CH$_3$), 7.10, 7.19, 7.34, 7.44 (s, s, s, s, 8H, 2C$_6$H$_4$) ppm. MS (EI, ^{80}Se), *m/z* (relative intensity): 646 (M$^+$ − 12CO, 0.5), 464 (Fe$_4$Se$_3$$^+$, 1.2), 461 (Fe$_4Se_2Ph^+$, 15.1), 272 (Fe$_2Se_2$$^+$, 1.3), 192 (Fe$_2Se^+$, 1.0), 91 (MeC$_6H_4$$^+$, 42.7), 56 (Fe$^+$, 5.2).

Preparation of 9c,d and 10a,b by Reaction of 4 (E = S) with *p*-MeC$_6$H$_4$SO$_2$Cl. To the solution of [Et$_3$NH][(μ-EtS)(μ-S)Fe$_2$(CO)$_6$] prepared above was added 1.144 g (6.0 mmol) of toluene-4-sulfonyl chloride, and the stirring was continued for 0.5 h at −78 °C and for 2 h at room temperature. TLC showed three main products. Solvent was removed under vacuum to leave a red oily residue, which was purified by column chromatography and TLC with petroleum ether and 1:1 (v/v) CH$_2$Cl$_2$/petroleum ether as eluant. The first red band gave 0.075 g (6%) of (μ-EtS)$_2$Fe$_2$(CO)$_6$.[21] The second red band gave 0.241 g (23%) of [(μ-EtS)Fe$_2$(CO)$_6$]$_2$(μ_4-S)[3] (**9c**). The third red band gave 0.408 g (26%) of (μ-EtS)(μ-*p*-MeC$_6$H$_4$SO$_2$S)Fe$_2$(CO)$_6$ (**10a**) as a slightly air-sensitive red solid. **10a**: mp 94 °C dec. Anal. Calcd for C$_{15}$H$_{12}$Fe$_2$O$_8$S$_3$: C, 34.11; H, 2.29. Found: C, 33.79; H, 2.14. IR (KBr, disk): $\nu_{C\equiv O}$ 2081.6 (s), 2040.6 (vs), 2007.8 (s), 1991.4 (vs) cm^{-1}; $\nu_{S=O}$ 1138.3 (m), 1064.4 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.02, 1.44 (t, t, *J* = 7.2 Hz, 3H, CH$_3$), 2.32−2.68 (m, 5H, CH$_2$, *p*-CH$_3$), 7.16−7.96 (m, 4H, C$_6$H$_4$) ppm. MS (EI), *m/z* (relative intensity): 528 (M$^+$, 0.3), 472 (M$^+$ − 2CO, 6.9), 444 (M$^+$ − 3CO, 5.7), 416 (M$^+$ − 4CO, 2.6), 388 (M$^+$ − 5CO, 7.7), 360 (M$^+$ − 6CO, 21.8), 176 (Fe$_2$S$_2$$^+$, 46.8), 155 (MeC$_6H_4SO_2$$^+$, 6.7), 61 (EtS$^+$, 5.4), 56 (Fe$^+$, 8.6).

Compounds 9d and 10b. The same procedure as that for preparation of **9c** and **10a** was followed, but [Et$_3$NH][(μ-*t*-BuS)(μ-S)Fe$_2$(CO)$_6$] was used instead of [Et$_3$NH][(μ-EtS)(μ-S)Fe$_2$(CO)$_6$]. The first red band gave 0.154 g (11%) of (μ-*t*-BuS)$_2$Fe$_2$(CO)$_6$.[21] The second red band gave 0.043 (4%) of [(μ-*t*-BuS)Fe$_2$(CO)$_6$]$_2$(μ_4-S)[21] (**9d**). The third red band gave 0.596 g (36%) of (μ-*t*-BuS)(μ-*p*-MeC$_6$H$_4$SO$_2$S)Fe$_2$(CO)$_6$ (**10b**) as a slightly air-sensitive red solid. **10b**: mp 100−102 °C. Anal. Calcd for C$_{17}$H$_{16}$Fe$_2$O$_8$S$_3$: C, 36.71; H, 2.70. Found: C, 36.96; H, 2.73. IR (KBr, disk): $\nu_{C\equiv O}$ 2081.6 (s), 2040.8 (vs), 1999.6 (vs) cm^{-1}; $\nu_{S=O}$ 1171.1 (m), 1089.1 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.60, 1.72 [s, s, 9H, C(CH$_3$)$_3$], 2.37 (s, 3H, *p*-CH$_3$), 7.15, 7.24, 7.39, 7.48 (s, s, s, s, 4H, C$_6$H$_4$) ppm. MS (EI), *m/z* (relative intensity): 496 (M$^+$ − CO − S, 0.2), 492 (M$^+$ − SO$_2$, 0.3), 233 (Fe$_2$S$_2$Bu$^+$, 3.7), 176 (Fe$_2$S$_2$$^+$, 4.6), 91 (C$_6H_4CH_3$$^+$, 0.8), 57 (Bu$^+$, 76.1), 56 (Fe$^+$, 31.9).

However, when the reaction of [Et$_3$NH][(μ-*t*-BuS)(μ-S)Fe$_2$(CO)$_6$] with *p*-MeC$_6$H$_4$SO$_2$Cl was run at room temperature for 2 h, 0.058 g (4%) of (μ-*t*-BuS)$_2$Fe$_2$(CO)$_6$,[21] 0.710 g (66%) of **9d**,[21] and 0.182 g (11%) of **10b** were obtained.

Preparation of 8a−c,e,f and 11a−e by Reaction of 6 with *p*-MeC$_6$H$_4$SO$_2$Cl. To the solution of [Et$_3$NH][(μ-EtS)(μ-Se)Fe$_2$(CO)$_6$] prepared above was added 1.144 g (6.0 mmol) of toluene-4-sulfonyl chloride, and the stirring was continued for 0.5 h at −78 °C and for 2 h at room temperature. After the same workup as that for the preparation of **9c**,**d** and **10a**,**b**, the first red band gave 0.130 g (11%) of (μ-EtS)$_2$Fe$_2$(CO)$_6$[21] and the second red band gave 0.045 g (4%) of [(μ-EtS)Fe$_2$(CO)$_6$]$_2$(μ_4-Se) (**8a**). The third red band gave 0.931 g (54%) of (μ-EtS)(μ-*p*-MeC$_6$H$_4$SO$_2$)Fe$_2$(CO)$_6$ (**11a**) as a red solid. **11a**: mp 103−104 °C. Anal. Calcd for C$_{15}$H$_{12}$Fe$_2$O$_8$S$_2$: C, 36.32; H, 2.43. Found: C, 36.05; H, 2.39. IR (KBr, disk): $\nu_{C\equiv O}$ 2081.6 (s), 2048.8 (vs), 2016.0 (vs), 1966.8 (vs) cm^{-1}; $\nu_{S=O}$ 1179.3 (s), 1089.1 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.62 (t, *J* = 7.2 Hz, 3H, CH$_3$), 2.24−2.76 (m, 5H, CH$_2$, *p*-CH$_3$), 7.12−7.64 (m, 4H, C$_6$H$_4$) ppm. MS (EI), *m/z* (relative intensity): 300 (M$^+$ − 6CO − C$_2$H$_4$, 0.1), 144 (Fe$_2$S$^+$, 3.0), 91 (MeC$_6$H$_4$$^+$, 11.6), 56 (Fe$^+$, 10.7).

Compounds 8b and 11b. The same procedure as that for **8a** and **11a** was followed, but with use of [Et$_3$NH][(μ-*n*-PrS)(μ-Se)Fe$_2$(CO)$_6$] instead of [Et$_3$NH][(μ-EtS)(μ-Se)Fe$_2$(CO)$_6$]. The first band gave 0.045 g (4%) of (μ-*n*-PrS)$_2$Fe$_2$(CO)$_6$,[21] the second band gave 0.080 g (7%) of [(μ-*n*-PrS)Fe$_2$(CO)$_6$]$_2$(μ_4-Se) (**8b**), and the third band gave 1.011 g (57%) of (μ-*n*-PrS)(μ-*p*-MeC$_6$H$_4$SO$_2$)Fe$_2$(CO)$_6$ (**11b**) as a red solid. **11b**: mp 66−68 °C. Anal. Calcd for C$_{16}$H$_{14}$Fe$_2$O$_8$S$_2$: C, 37.67; H, 2.77. Found: C, 37.56; H, 2.87. IR (KBr, disk): $\nu_{C\equiv O}$ 2081.6 (s), 2048.8 (vs), 1999.6 (vs), 1966.8 (s) cm^{-1}; $\nu_{S=O}$ 1179.3 (s), 1080.9 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.08 (t, *J* = 7.2 Hz, 3H, CH$_3$), 1.68−2.08 (m, 2H, CH$_2$), 2.16−2.76 (m, 5H, SCH$_2$, *p*-CH$_3$), 6.96−7.52 (m, 4H, C$_6$H$_4$) ppm. MS (EI), *m/z* (relative intensity): 481 (M$^+$ − CO, 1.1), 454 (M$^+$ − 2CO, 25.3), 426 (M$^+$ − 3CO, 4.5), 398 (M$^+$ − 4CO, 9.2), 370 (M$^+$ − 5CO, 24.5), 342 (M$^+$ − 6CO, 69.4), 300 (M$^+$ − 6CO − C$_3$H$_6$, 100), 187 (Fe$_2$SPr$^+$, 1.6), 155 (MeC$_6$H$_4$SO$_2$$^+$, 9.7), 144 (Fe$_2S^+$, 57.5), 91 (MeC$_6H_4$$^+$, 44.0), 56 (Fe$^+$, 6.3), 43 (Pr$^+$, 8.7).

Compounds 8c and 11c. The same procedure as that for **8a** and **11a** was followed, but with use of [Et$_3$NH][(μ-*t*-BuS)(μ-Se)Fe$_2$(CO)$_6$] instead of [Et$_3$NH][(μ-EtS)(μ-Se)Fe$_2$(CO)$_6$]. The first red band gave 0.052 g (4%) of (μ-*t*-BuS)$_2$Fe$_2$(CO)$_6$,[21] the second red band gave 0.114 g (9%) of [(μ-*t*-BuS)Fe$_2$(CO)$_6$]$_2$(μ_4-Se) (**8c**), and the third red band gave 1.030 g (57%) of (μ-*t*-BuS)(μ-*p*-MeC$_6$H$_4$SO$_2$)Fe$_2$(CO)$_6$ (**11c**) as a red solid. **11c**: mp 108−110 °C. Anal. Calcd for C$_{17}$H$_{16}$Fe$_2$O$_8$S$_2$: C, 38.96; H, 3.08. Found: C, 38.84; H, 3.04. IR (KBr, disk): $\nu_{C\equiv O}$ 2081.6 (s), 2048.8 (vs), 1999.6 (vs) cm^{-1}; $\nu_{S=O}$ 1154.7 (s), 1089.1 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.58, 1.70 [s, s, 9H, C(CH$_3$)$_3$], 2.36, 2.40 (s, s, 3H, *p*-CH$_3$), 7.08−7.52 (m, 4H, C$_6$H$_4$) ppm. MS (EI), *m/z* (relative intensity): 468 (M$^+$ − 2CO, 1.9), 440 (M$^+$ − 3CO, 0.7), 412 (M$^+$ − 4CO, 0.6), 384 (M − 5CO, 1.6), 356 (M$^+$ −

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[33] Nametkin, N. S.; Tyurin, V. D.; Kukina, M. A. *J. Organomet. Chem.* **1978**, *149*, 355.

Table 4. Crystal Data Collection and Refinement of Compounds 8a and 11a

	8a	**11a**
mol formula	$C_{16}H_{10}Fe_4O_{12}S_2Se$	$C_{15}H_{12}Fe_2O_8S_2$
mol wt	760.72	496.07
cryst syst	orthorhombic	monoclinic
space group	$P2_12_12_1$ (No. 19)	$P2_1/a$ (No. 14)
a/Å	12.103(2)	16.027(4)
b/Å	12.884(3)	7.345(2)
c/Å	17.083(3)	16.665(3)
β/deg	90.00	90.33(2)
V/Å^3	2663.9(9)	1961.6(7)
Z	4	4
density (calcd)/g cm^{-3}	1.90	1.68
F(000)	1488	1000
μ(Mo Kα)/cm^{-1}	37.1	17.2
diffractometer	Siemens P4/PC	Enraf-Nonius CAD4
temp/°C	21 ± 1	23 ± 1
radiation	graphite-monochromatized Mo Kα, $\lambda = 0.710\ 73$ Å	
scan type	ω scan	$\omega/2\theta$ scan
$2\theta_{max}$/deg	46	50
no. of observns, n	1395 ($|F_o| \geq 4\sigma(|F_o|$)	2721 ($|F_o| \geq 3\sigma(|F_o|)$)
no. of variables, p	317	244
$R_F = \sum||F_o| - |F_c||/\sum|F_o|$	0.052	0.048
$R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$	0.048	0.059
$S = [\sum w(|F_o| - |F_c|)^2/(n - p)]^{1/2}$	1.16	1.55
largest Δ/σ in final cycle	0.28	0.02
largest peak in final diff map/e Å^{-3}	1.18	0.54

6CO, 7.6), 300 (M$^+$ − 6CO − C_4H_8, 2.0), 299 ($Fe_2SSO_2C_6H_4$-Me$^+$, 13.6), 267 ($Fe_2SO_2C_6H_4Me^+$, 0.8), 201 (Fe_2SBu^+, 0.5), 144 (Fe_2S^+, 28.5), 91 ($MeC_6H_4^+$, 27.4), 57 (Bu$^+$, 100), 56 (Fe$^+$, 13.8).

Another Route for Preparation of 11c. To the solution of [Et$_3$NH][(μ-t-BuS)(μ-CO)Fe$_2$(CO)$_6$] at 0 °C was added 1.144 g (6.0 mmol) of toluene-4-sulfonyl chloride, and the mixture was stirred for 0.5 h at 0 °C and for 2 h at room temperature. Solvent was removed under vacuum to leave a red solid, which was purified by column chromatography with petroleum ether and 1:1 CH_2Cl_2/petroleum ether as eluant. The first band gave 0.132 g (10%) of (μ-t-BuS)$_2$Fe$_2$(CO)$_6$,[21] and the second band gave 0.433 g (42%) of (μ-t-BuS)(μ-p-MeC$_6$H$_4$SO$_2$)Fe$_2$(CO)$_6$ (**11c**).

Compounds 8e and 11d. The same procedure as that for **8a** and **11a** was followed, but with use of [Et$_3$NH][(μ-PhSe)(μ-Se)Fe$_2$(CO)$_6$] instead of [Et$_3$NH][(μ-EtS)(μ-Se)Fe$_2$(CO)$_6$]. The first band gave 0.567 g (32%) of (μ-PhSe)$_2$Fe$_2$(CO)$_6$,[32] the second band gave 0.046 g (3%) of [(μ-PhSe)Fe$_2$(CO)$_6$]$_2$(μ_4-Se) (**8e**), and the third band gave 0.345 g (17%) of (μ-PhSe)(μ-p-MeC$_6$H$_4$SO$_2$)Fe$_2$(CO)$_6$ (**11d**) as a red solid. **11d**: mp 103−104 °C. Anal. Calcd for $C_{19}H_{12}Fe_2O_8SSe$: C, 38.61; H, 2.05. Found: C, 38.59; H, 1.85. IR (KBr, disk): $\nu_{C\equiv O}$ 2089.8 (vs), 2057.0 (vs), 1991.4 (vs) cm^{-1}; $\nu_{S=O}$ 1171.1 (s), 1089.1 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 2.38, 2.50 (s, s, 3H, CH$_3$), 7.06−7.74 (m, 9H, C$_6$H$_5$, C$_6$H$_4$) ppm. MS (EI, ^{80}Se), m/z (relative intensity): 536 (M$^+$ − 2CO, 8.3), 508 (M$^+$ − 3CO, 4.8), 480 (M$^+$ − 4CO, 3.7), 452 (M$^+$ − 5CO, 6.6), 424 (M$^+$ − 6CO, 42.4), 269 ($Fe_2SeC_6H_5^+$, 24.7), 267 ($Fe_2SO_2C_6H_4Me^+$, 18.2), 192 (Fe_2Se^+, 36.3), 157 ($C_6H_5Se^+$, 52.4), 155 ($MeC_6H_4SO_2^+$, 27.2), 91 ($MeC_6H_4^+$, 88.7), 56 (Fe$^+$, 59.7).

Another Route for Preparation of 11d. A 100 mL three-necked flask equipped with a magnetic stirbar, a rubber septum, and a nitrogen inlet tube was charged with 0.437 g (1.0 mmol) of (μ-Se)$_2$Fe$_2$(CO)$_6$ and 30 mL of THF. To this solution was added a given amount of PhMgBr in diethyl ether at −78 °C until the solution turned deep green. Then, 0.573 g (3.0 mmol) of toluene-4-sulfonyl chloride was added and the mixture instantly became red. After it was stirred for 0.5 h at −78 °C, the reaction mixture was warmed to room temperature and stirred for an additional 2 h. Solvent was removed under vacuum to leave a red residue, which was purified by column chromatography. Petroleum ether eluted a small orange-red band, which was not collected. Further elution with 1:1 (v/v) CH_2Cl_2/petroleum ether yielded a red band, which gave 0.495 g (47%) of (μ-PhSe)(μ-p-MeC$_6$H$_4$SO$_2$)Fe$_2$(CO)$_6$ (**11d**).

Compounds 8f and 11e. The same procedure as that for **8a** and **11a** was followed, but with use of [Et$_3$NH][(μ-p-MeC$_6$H$_4$Se)(μ-Se)Fe$_2$(CO)$_6$] instead of [Et$_3$NH][(μ-EtS)(μ-Se)Fe$_2$(CO)$_6$]. The first band gave 0.686 g (37%) of (μ-p-MeC$_6$H$_4$Se)$_2$Fe$_2$(CO)$_6$,[6] the second band gave 0.022 g (2%) of [(μ-p-MeC$_6$H$_4$Se)Fe$_2$(CO)$_6$]$_2$(μ_4-Se) (**8e**), and the third band gave 0.077 g (4%) of (μ-p-MeC$_6$H$_4$Se)(μ-p-MeC$_6$H$_4$SO$_2$)Fe$_2$(CO)$_6$ (**11e**) as a red solid. **11e**: mp 105 °C dec. Anal. Calcd for $C_{20}H_{14}Fe_2O_8SSe$: C, 39.70; H, 2.33. Found: C, 39.80; H, 2.29. IR (KBr, disk): $\nu_{C\equiv O}$ 2081.6 (s), 2048.8 (vs), 2007.8 (vs), 1975.0 (s) cm^{-1}; $\nu_{S=O}$ 1171.1 (s), 1089.1 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 2.20 (s, 3H, CH_3C$_6$H$_4$Se), 2.28 (s, 3H, CH_3C$_6$H$_4$SO$_2$), 6.72−7.52 (m, 8H, 2C$_6$H$_4$) ppm. MS (EI, ^{80}Se), m/z (relative intensity): 550 (M$^+$ − 2CO, 3.0), 522 (M$^+$ − 3CO, 1.3), 466 (M$^+$ − 5CO, 1.4), 438 (M$^+$ − 6CO, 10.0), 283 ($Fe_2SeC_6H_4Me^+$, 2.1), 267 ($Fe_2SO_2C_6H_4Me^+$, 5.2), 192 (Fe_2Se^+, 12.2), 144 (Fe_2S^+, 2.9), 91 ($MeC_6H_4^+$, 100), 56 (Fe$^+$, 12.2).

Crystal Structure Determination of 8a. Details of crystal parameters, data collection, and structure refinement are given in Table 4. Raw intensities collected on a Siemens P4/PC four-circle diffractometer at room temperature (21 ± 1 °C) were corrected for absorption using ψ-scan data. Patterson superposition yielded the positions of all non-hydrogen atoms, which were subjected to anisotropic refinement. All hydrogen atoms were generated geometrically (C−H bonds fixed at 0.96 Å) and allowed to ride on their respective parent C atoms; they were assigned appropriate isotropic temperature factors and included in the structure-factor calculations. Computations were performed using the SHELXTL PC program package on a PC 486 computer. Analytic expressions of atomic scattering factors were employed, and anomalous dispersion corrections were incorporated.

Crystal Structure Determination of 11a. Details of crystal parameters, data collection, and structure refinement are given in Table 4. Raw intensities were collected on a Enraf-Nonius CAD4 four-circle diffractometer at room temperature (21 ± 1 °C). The structure was solved by a direct method (MITHRIL). The final refinement was carried out by a full-matrix least-squares method with anisotropic temperature factors for non-hydrogen atoms. Computations were performed using the TEXSAN program package on a MICROVAX 3100 computer. Analytic expressions of atomic scattering factors were employed, and anomalous dispersion corrections were incorporated.

Conclusions

In this paper we have demonstrated some interesting similarities and striking differences between two kinds of novel anions, the sulfur-centered anion (μ-RE)(μ-S$^-$)-Fe$_2$(CO)$_6$ (**4**) and selenium-centered anion (μ-RE)(μ-Se$^-$)-Fe$_2$(CO)$_6$ (**6**) (E = S, Se) in reactions with various acid chlorides.

1. Reaction of **4** with SO_2Cl_2 gives the oxidative-coupling products [(μ-RE)Fe$_2$(CO)$_6$]$_2$(μ-S−S) (**5**; E = S, Se), while **6** reacts with SO_2Cl_2 to give the μ_4-Se clusters [(μ-RE)Fe$_2$(CO)$_6$]$_2$(μ_4-Se) (**8**; E = S, Se). For the former reaction, extrusion of SO_2 from the intermediate [(μ-RE)Fe$_2$(CO)$_6$]$_2$(μ-SSO$_2$S-μ) (**M**) has been suggested, while for the latter nuclephilic substitution at the iron atom of the intermediate (μ-RE)(μ-ClSO$_2$Se)Fe$_2$(CO)$_6$ (**M1**) is proposed.

2. With organic bis acid chlorides, such as succinoyl and phthaloyl chlorides, **4** and **6** both afford the μ_4-E (E = S, Se) type of clusters [(μ-RE)Fe$_2$(CO)$_6$]$_2$(μ_4-E).

3. Although the reaction of **4** (E = S) with *p*-MeC$_6$H$_4$-SO$_2$Cl yields the expected Fe$_2$S$_2$ butterfly clusters (μ-RS)(μ-*p*-MeC$_6$H$_4$SO$_2$S)Fe$_2$(CO)$_6$ (**10**), the reaction of **6** produces the unexpected S═O-bridged clusters (μ-RE)-(μ-*p*-MeC$_6$H$_4$SO$_2$)Fe$_2$(CO)$_6$ (**11**). For the formation of **11** the extrusion of an Se atom from the intermediate (μ-RE)(μ-*p*-MeC$_6$H$_4$SO$_2$Se)Fe$_2$(CO)$_6$ (**M2**) has been proposed.

4. [(μ-RE)Fe$_2$(CO)$_6$]$_2$(μ_4-Se) (**8**), (μ-RS)(μ-*p*-MeC$_6$H$_4$-SO$_2$S)Fe$_2$(CO)$_6$ (**10**), and (μ-RE)(μ-*p*-MeC$_6$H$_4$SO$_2$)Fe$_2$-(CO)$_6$ (**11**; E = S, Se), prepared by the reactions mentioned above, are three new types of Fe/S cluster complexes, which have been characterized by spectroscopic methods, while the structures of clusters **8a** (R = Et, E = S) and **11a** (R = Et, E = S) have been confirmed by X-ray crystallography.

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Supporting Information Available: Tables of positional and thermal parameters and bond lengths and angles for **8a** and **11a** (6 pages). Ordering information is given on any current masthead page.

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