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Synthetic and Structural Investigations on Double- and Single-Butterfly Fe/E (E = S, Se) Cluster Complexes Containing Diselenolate Ligands

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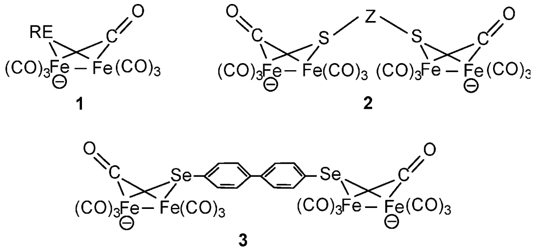
The first examples of diselenolate ligand-containing butterfly Fe/E (E = S, Se) complexes are now reported. When ca. 1 equiv of dilithium reagent 4-$LiC_6H_4C_6H_4Li$-4′ containing *n*-BuBr (prepared from 1 equiv of 4,4′-dibromobiphenyl and *n*-BuLi) was treated with 2 equiv of elemental selenium and $Fe_3(CO)_{12}$ followed by treatment with excess CS_2 and MeI, both double-butterfly complex (4-μ-$SeC_6H_4C_6H_4Se$-μ-4′)[(μ-S=CSMe)$Fe_2(CO)_6$]$_2$ (**4**) and single-butterfly complex (4-*n*-$BuSeC_6H_4C_6H_4Se$-μ-4′)[(μ-S=CSMe)$Fe_2(CO)_6$] (**4***) were produced in 11% and 20% yields, respectively. However, when ca. 1 equiv of dilithium reagent 4-$LiC_6H_4C_6H_4Li$-4′ without *n*-BuBr (*n*-BuBr was removed by evaporation of the initially prepared dilithium reagent containing *n*-BuBr) reacted with 2 equiv of elemental selenium and $Fe_3(CO)_{12}$ followed by treatment with excess CS_2 and MeI, only the double-butterfly complex **4** was obtained in a higher yield (21%) without any single-butterfly complex being isolated. Other double-butterfly complexes, such as (4-μ-$SeC_6H_4C_6H_4Se$-μ-4′)[(μ-S=CSR)$Fe_2(CO)_6$]$_2$ (**5**, R = Et; **6**, $PhCH_2$; **7**, PhC=NPh; **8**, $Cp(CO)_2Fe$), (4-μ-$SeC_6H_4C_6H_4Se$-μ-4′)[(μ-SePh)$Fe_2(CO)_6$]$_2$ (**9**), and (4-μ-$SeC_6H_4C_6H_4Se$-μ-4′)[(μ-CH_2SMe)$Fe_2(CO)_6$]$_2$ (**10**), could be similarly prepared via the latter method by using electrophiles CS_2/EtBr, CS_2/$PhCH_2Br$, CS_2/PhC(Cl)=NPh, CS_2/$Cp(CO)_2FeI$, PhSeBr, and $MeSCH_2Cl$ instead of CS_2/MeI, respectively. A possible pathway for production of the double- and single-butterfly complexes **4**−**10** and **4*** has been proposed, in which the versatile two-μ-CO-containing double-butterfly dianion (4-μ-$SeC_6H_4C_6H_4Se$-μ-4′)[(μ-CO)$Fe_2(CO)_6$]$_2^{2-}$ (**3**) and the one-μ-CO-containing single-butterfly monoanion (4-*n*-$BuSeC_6H_4C_6H_4Se$-μ-4′)[(μ-CO)$Fe_2(CO)_6$]$^-$ (**3***) are involved. All the new complexes were fully characterized by elemental analysis and spectroscopy, as well as by X-ray crystallography for **4*** and **10**.

Introduction

Butterfly Fe/E (E = S, Se) cluster complexes have received ever more attention in recent years, largely because of their novel chemistry[1−3] and the close relevance to Fe-only hydrogenases, a naturally occurring class of enzymes, which mediate the uptake and production of hydrogen in microorganisms.[4−6] Among such complexes the single-butterfly monoanions [(μ-RE)(μ-CO)$Fe_2(CO)_6$]$^-$ (**1**, E = S, Se)[2] and the dithiolato-bridged double-butterfly dianions (μ-SZS-μ)[(μ-CO)$Fe_2(CO)_6$]$_2^{2-}$ (**2**)[7−9] (Scheme 1) are of great interest, since they are easily available and possess high nucleophilicity toward electrophiles. While the one-μ-CO-containing monoanions **1** were first prepared 15 years ago by Seyferth's group,[10,11] we prepared the two-μ-CO-containing dianions **2** just recently.[7,8] Now, these μ-CO-containing butterfly anions have been demonstrated to be very useful reagents for synthesizing a wide variety of Fe/E cluster complexes. To further develop the chemistry of Fe/E cluster complexes, we recently started to investigate if the first Se analogue of dianions **2**, namely, the diselenolato-bridged double-butterfly dianion (4-μ-$SeC_6H_4C_6H_4Se$-μ-4′)[(μ-CO)$Fe_2(CO)_6$]$_2^{2-}$ (**3**) (Scheme 1), could be prepared and how its chemical reactivities are toward electrophiles. Herein we report our results obtained from this study, which include the formation of dianion **3** and its in situ reactions with some electrophiles to give a series of double-

Scheme 1



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(1) Ogino, H.; Inomata, S.; Tobita, H. *Chem. Rev.* **1998**, *98*, 2093.

(2) Song, L.-C. In *Trends in Organometallic Chemistry*; Atwood, J. L., Corriu, R., Cowley, A. H., Lappert, M. F., Nakamura, A., Pereyre, M. Eds.; Research Trends: Trivandrum, India, 1999; Vol. 3, p 1.

(3) Song, L.-C. *Acc. Chem. Res.* **2005**, *38*, 21.

(4) Darensbourg, M. Y.; Lyon E. J.; Smee, J. J. *Coord. Chem. Rev.* **2000**, *206*−*207*, 533.

(5) Rauchfuss, T. B. *Inorg. Chem.* **2004**, *43*, 14.

(6) Liu, X.; Ibrahim, S. K.; Tard, C.; Pickett, C. J. *Coord. Chem. Rev.* **2005**, *249*, 1641.

(7) Song, L.-C.; Fan, H.-T.; Hu, Q.-M. *J. Am. Chem. Soc.* **2002**, *124*, 4566.

(8) Song, L.-C.; Fan, H.-T.; Hu, Q.-M.; Yang, Z.-Y.; Sun, Y.; Gong F.-H. *Chem. Eur. J.* **2003**, *9*, 170.

(9) Song, L.-C.; Gong, F.-H.; Meng T.; Ge, J.-H.; Cui, L.-N.; Hu, Q.-M. *Organometallics* **2004**, *23*, 823.

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

(11) Seyferth, D.; Womack, G. B.; Archer, C. M.; Dewan, J. C. *Organometallics* **1989**, *8*, 430.

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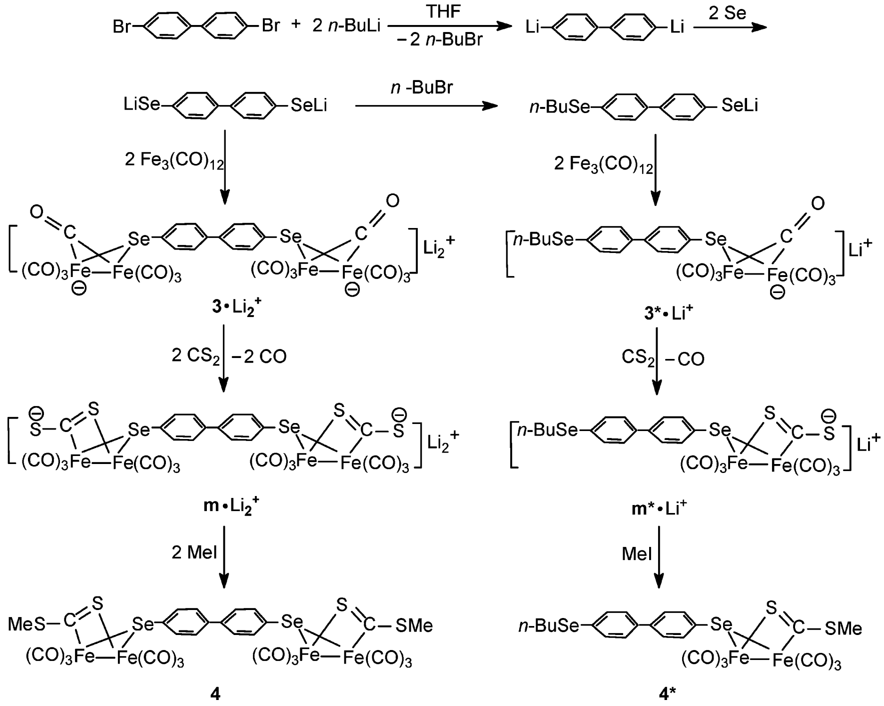
Scheme 2



butterfly Fe/E cluster complexes each containing a diselenolate ligand 4-μ-Se$C_6H_4C_6H_4$Se-μ-4′. In addition, we also report one single-butterfly cluster complex, which contains a *n*-butyl-substituted diselenolate ligand 4-*n*-BuSe$C_6H_4C_6H_4$Se-μ-4′, produced from one of the reactions involved in this study.

Results and Discussion

Rational Synthesis of Double-Butterfly Complexes (4-μ-Se$C_6H_4C_6H_4$Se-μ-4′)[(μ-S=CSR)$Fe_2(CO)_6$]$_2$ (4, R = Me; 5, Et; 6, PhCH_2; 7, PhC=NPh; 8, Cp$(CO)_2$Fe), (4-μ-Se$C_6H_4C_6H_4$Se-μ-4′)[(μ-SePh)$Fe_2(CO)_6$]$_2$ (9), and (4-μ-Se$C_6H_4C_6H_4$Se-μ-4′)[(μ-CH_2SMe)$Fe_2(CO)_6$]$_2$ (10) and Single-Butterfly Complex (4-*n*-BuSe$C_6H_4C_6H_4$Se-μ-4′)[(μ-S=CSMe)$Fe_2(CO)_6$] (4*). We initially found that when 1 equiv of 4,4′-dibromobiphenyl in THF reacted sequentially with 2 equiv of *n*-BuLi, selenium powder, and $Fe_3(CO)_{12}$ followed by treatment with excess CS_2 and MeI, the double-butterfly complex **4** and single-butterfly complex **4*** were produced in 11% and 20% yields, respectively. To account for the formation of complexes **4** and **4***, we have proposed a possible pathway, as shown in Scheme 2. Scheme 2 shows that (i) the metal−halogen exchange between 4,4′-dibromobiphenyl and *n*-butyllithium gives dilithium reagent 4-Li$C_6H_4C_6H_4$Li-4′ and *n*-BuBr; (ii) the insertion reaction of 4-Li$C_6H_4C_6H_4$Li-4′ with elemental selenium produces bis-SeLi species 4-LiSe$C_6H_4C_6H_4$SeLi-4′; (iii) the bis-SeLi species reacts with $Fe_3(CO)_{12}$ to generate a lithium salt of the desired double-butterfly two-μ-CO-containing dianion **3**; (iv) the lithium salt of dianion **3** reacts further with two molecules of CS_2 (presumably via nucleophilic attack of the two negatively charged Fe atoms in **3** at the two molecules of CS_2 followed by loss of the two μ-CO ligands in **3**) to give the lithium salt of an S-centered dianion **m**; and (v) the lithium salt of dianion **m** is alkylated by two molecules of MeI to afford the double-butterfly product **4**. However, in contrast to production of **4**, Scheme 2 also shows that the bis-SeLi species can also react with the in situ formed *n*-BuBr to give the mono-SeLi species *n*-BuSe$C_6H_4C_6H_4$SeLi-4′. This species reacts further with $Fe_3(CO)_{12}$ to produce the lithium salt of the one-μ-CO-containing monoanion **3***. Then the lithium salt of **3*** reacts with CS_2 to give the lithium salt of an S-centered monoanion **m***, and finally the lithium salt of **m*** is alkylated with MeI to give the single-butterfly product **4***. The above suggested pathway for production of **4** and **4*** is mainly speculative, but seems to be reasonable. This is because (i) the above-mentioned metal−halogen exchange to give 4-Li$C_6H_4C_6H_4$Li-4′ and *n*-BuBr was previously reported;[12] (ii) the insertion of elemental E (E = S, Se) into the C−Li bond of the monolithium reagent RLi to give RELi is a well-known process;[13a−c] (iii) the reaction of RSLi with $Fe_3(CO)_{12}$ is one of the known reactions for preparing the one-μ-CO-containing monoanion $[(\mu\text{-RS})(\mu\text{-CO})Fe_2(CO)_6]^-$;[14] and (iv) the above-described reaction modes regarding dianion **3** and monoanion **3*** are well-based on the μ-CO chemistry of the other μ-CO-containing butterfly cluster anions.[2,7−9,15]

On the basis of our initially studied results, we thought that if we had removed *n*-BuBr from the originally prepared solution containing dilithium reagent 4-Li$C_6H_4C_6H_4$Li-4′ and the in situ generated *n*-BuBr, the sequential reaction described above would afford only the double-butterfly complex **4** in a higher yield without any single-butterfly complex **4*** being produced. In fact, this conjecture was proved by our experiments. Thus, treatment of 1 equiv of 4,4′-dibromobiphenyl in THF with 2 eqiuv of *n*-BuLi gave rise to a mixture containing 4-Li$C_6H_4C_6H_4$Li-4′ and *n*-BuBr. Volatiles including *n*-BuBr were removed at reduced pressure to leave an off-white solid 4-Li$C_6H_4C_6H_4$Li-4′. After redissolving it in THF, 2 equiv of elemental selenium and $Fe_3(CO)_{12}$ were added to give a brown-red solution. This solution contains the lithium salt of dianion **3**, which showed a μ-CO medium absorption band at 1742 cm^{-1} in its IR spectrum. This is consistent with the other μ-CO-containing butterfly cluster anions.[8,10,15] Further treatment of this solution with excess

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[12] Baldwin, R. A.; Cheng, M. T. *J. Org. Chem.* **1967**, *32*, 1572.

[13] (a) Haller, W. S.; Irgolic, K. J. *J. Organomet. Chem.* **1972**, *38*, 97. (b) Seebach, D.; Beck, A. K. *Chem. Ber.* **1975**, *108*, 314. (c) Henriksen, L. In *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Ed.; Wiley: New York, 1987; Vol. 2, p 398.

[14] Seyferth, D.; Hoke, J. B.; Dewan, J. C. *Organometallics* **1987**, *6*, 895.

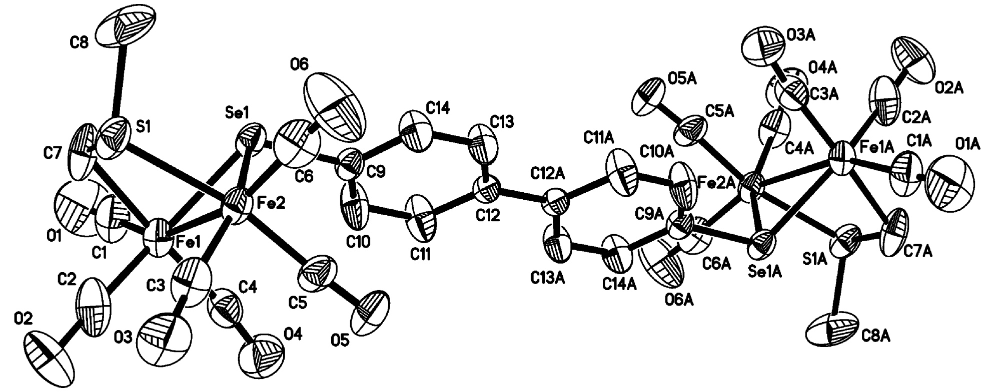
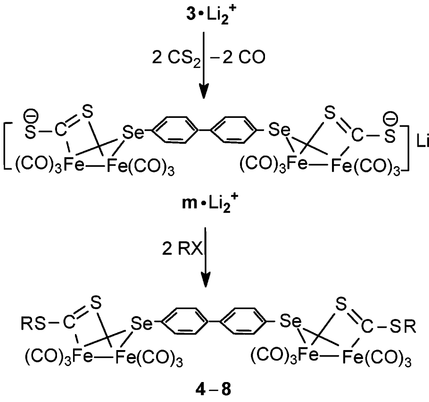


Figure 1. ORTEP view of **10** with 30% probability level ellipsoids.

Scheme 3



	4	5	6	7	8
R	Me	Et	PhCH$_2$	PhC=NPh	Cp(CO)$_2$Fe

CS_2 gave the intermediate **m**·Li_2^+, which reacted with excess MeI to afford the double-butterfly complex **4** in 21% yield, indeed without any single-butterfly complex **4*** being observed (Scheme 3). Since our main purpose is to prepare dianion **3** and to study its new chemistry, we continued carrying out the other reactions of this lithium salt of dianion **3** without *n*-BuBr. As a result, when the electrophiles CS_2/EtBr, CS_2/PhCH$_2$Br, CS_2/PhC(Cl)=NPh, and CS_2/Cp(CO)$_2$FeI reacted (instead of CS_2/MeI) with the brown-red solution containing the lithium salt of dianion **3** in the absence of *n*-BuBr, the corresponding double-butterfly complexes **5**−**8** were similarly produced via the intermediate **m**·Li_2^+ (Scheme 3). In addition, when the electrophile PhSeBr or MeSCH$_2$Cl reacted (instead of the two electrophiles CS_2/MeI) with the lithium salt of dianion **3**, the double-butterfly complexes **9** and **10** were obtained presumably via nucleophilic attack of the two negatively charged iron atoms of **3** at two molecules of PhSeBr or MeSCH$_2$Cl followed by displacement of the two μ-CO ligands in intermediates $\mathbf{m}_1$ and $\mathbf{m}_2$, respectively (Scheme 4).

It should be noted that the isolated yields of products **4**−**10** (21−12%) and **4*** (20%) were calculated on the basis of starting material 4,4′-dibromobiphenyl. Therefore, it is apparent that the multistep (usually 5−6 steps) reactions involved in their synthesis are the main reason for such low yields. In addition, some byproducts (not fully separated and identified due to their very small amounts) were also observed, such as those derived from *n*-C_4H_9SeLi generated by insertion of elemental Se with unreacted *n*-C_4H_9Li.

Spectroscopic Characterization of Double-Butterfly Complexes 4−10 and Single-Butterfly Complex 4*. Crystal Structures of 10 and 4*. Products **4**−**10** and **4*** are air-stable solids, which were characterized by elemental analysis and IR and ^{1}H (^{77}Se) NMR spectroscopy. The IR spectra of **4**−**10** and **4*** showed several strong absorption bands in the range 2067−1967 cm^{-1} for their terminal carbonyls, and those of **4**−**8** and **4*** displayed an additional medium band at around 1000 cm^{-1} for their coordinated C=S double bonds.[16−18] The ^{77}Se NMR spectra of **4**−**10** and **4*** not only indicated the presence of their Se atoms but also provided some information about their conformational isomers in terms of different (axial or equatorial) orientations of the substituents attached to the bridged Se atoms.[19−23] For example, from the ^{77}Se NMR spectra of **4**−**10** and **4***, we can conclude that **9** exists as an isomeric mixture and the others exist as only one conformer. This is because **9** displayed five singlets for its bridged Se atoms, whereas the others each showed only one singlet for their bridged Se atoms. In the five singlets displayed by **9** two singlets at ca. 278 ppm and three singlets around 318 ppm can be assigned respectively to its bridged Se atoms bonded to phenyl and biphenylene groups, whereas the singlets displayed in the range 357−478 ppm by complexes **4**−**8**, **10**, and **4*** should be attributed to the bridged Se atoms attached to their biphenylene groups. Although we cannot further assign their conformers based on only these available ^{77}Se NMR data, the structures of conformers **10** and **4*** have been successfully established by X-ray diffraction techniques.

The ORTEP drawings of **10** and **4*** are shown in Figures 1 and 2, while Tables 1 and 2 present their selected bond lengths and angles, respectively. As can be seen intuitively in Figure 1, complex **10** indeed consists of two identical structural units (μ-CH$_2$SMe)Fe$_2$(CO)$_6$, which are bridged by a diselenolate 4-SeC$_6$H$_4$C$_6$H$_4$Se-4′ ligand to form a double-butterfly Fe/E cluster complex. The X-ray crystallography revealed that the biphenylene group in the diselenolate ligand is attached to the

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(15) Song, L.-C.; Cheng, J.; Gong, F.-H.; Hu, Q.-M.; Yan, J. *Organometallics* **2005**, *24*, 3764.

(16) Seyferth, D.; Womack, G. B.; Archer, C. M.; Fackler, J. P., Jr.; Marler, D. O. *Organometallics* **1989**, *8*, 443.

(17) Patin, H.; Mignani, G.; Mahe, C.; Le Marouille, J.-Y.; Southern, T. G.; Benoit, A.; Grandjean, D. *J. Organomet. Chem*. **1980**, *197*, 315.

(18) Song, L.-C.; Yan, C.-G.; Hu, Q.-M.; Wang, R.-J.; Mak, T. C. W. *Organometallics* **1995**, *14*, 5513.

(19) Buchholz, D.; Huttner, G.; Zsolnai, L.; Imhof, W. *J. Organomet. Chem*. **1989**, *377*, 25.

(20) Song, L.-C.; Yan, C.-G.; Hu, Q.-M.; Sun, J,; Mao, X.-A. *J. Coord. Chem*. **1996**, *39*, 147.

(21) Song, L.-C.; Lu, G.-L.; Hu, Q.-M.; Sun, J.*Organometallics* **1999**, *18*, 2700.

(22) Shaver, A.; Fitzpatrick, P. J.; Steliou, K.; Butler, I. S. *J. Am. Chem. Soc*. **1979**, *101*, 1313.

(23) Seyferth, D.; Henderson, R. S.; Song, L.-C. *Organometallics* **1982**, *1*, 125.

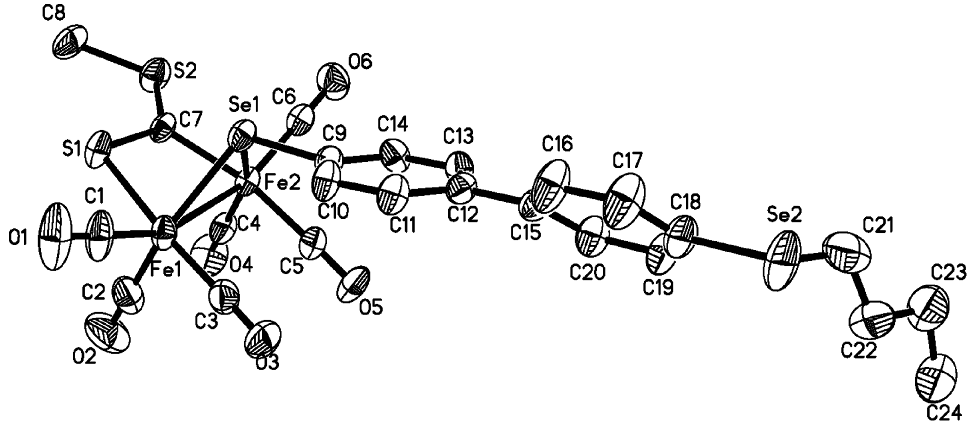

Figure 2. ORTEP view of **4*** with 30% probability level ellipsoids.

Scheme 4

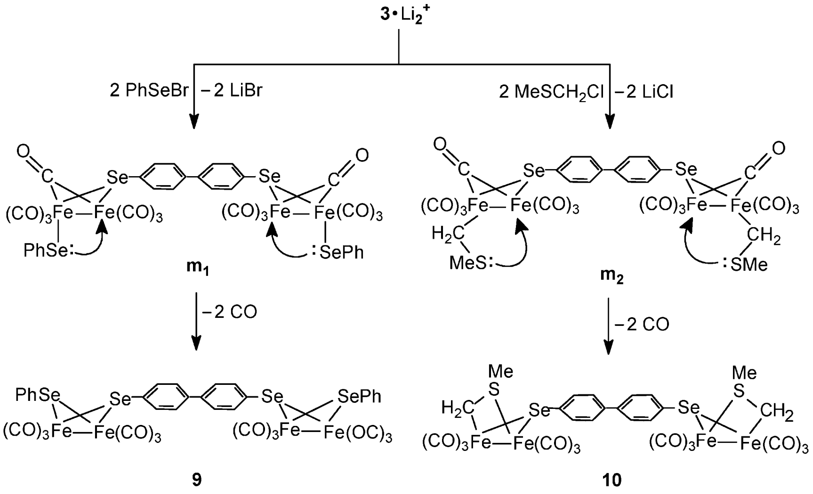

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 10

Fe(1)−C(1)	1.78(2)	Fe(2)−S(1)	2.278(5)
Fe(1)−Se(1)	2.299(3)	S(1)−C(7)	1.78(2)
Fe(1)−Fe(2)	2.628(3)	S(1)−C(8)	1.82(2)
Fe(2)−Se(1)	2.419(2)	Fe(1)−C(7)	2.04(2)
C(7)−Fe(1)−Se(1)	83.2(7)	Se(1)−Fe(2)−Fe(1)	54.01(7)
C(7)−Fe(1)−Fe(2)	81.5(6)	C(7)−S(1)−C(8)	106.4(13)
Se(1)−Fe(1)−Fe(2)	58.35(7)	C(7)−S(1)−Fe(2)	97.9(6)
S(1)−Fe(2)−Se(1)	86.89(15)	S(1)−C(7)−Fe(1)	103.1(11)
S(1)−Fe(2)−Fe(1)	74.82(17)	Fe(1)−Se(1)−Fe(2)	67.64(8)

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 4*

Fe(1)−S(1)	2.304(2)	Se(1)−C(9)	1.946(5)
Fe(1)−Se(1)	2.3796(19)	S(1)−C(7)	1.692(6)
Fe(1)−Fe(2)	2.6572(17)	Se(2)−C(21)	1.755(8)
Fe(2)−Se(1)	2.3900(16)	Se(2)−C(18)	1.921(6)
S(1)−Fe(1)−Se(1)	83.12(6)	S(2)−C(7)−Fe(2)	123.3(3)
S(1)−Fe(1)−Fe(2)	75.82(5)	S(1)−C(7)−Fe(2)	111.8(3)
Se(1)−Fe(1)−Fe(2)	56.33(4)	C(7)−Fe(2)−Fe(1)	77.75(17)
C(21)−Se(2)−C(18)	104.4(4)	Se(1)−Fe(2)−Fe(1)	55.96(5)
S(2)−C(7)−S(1)	124.8(3)	Fe(1)−Se(1)−Fe(2)	67.71(4)

two bridged Se atoms in equatorial orientations (the calculated ∠C(7)···Se(1)−C(9) = 161.0°, ∠S(1)···Se(1)−C(9) = 153.2°). Actually, such a conformer is quite stable since it avoids the strong steric repulsion between the axially bonded biphenylene group and the endo-methyl groups attached to S(1) and S(1A) atoms.[23] In addition, it should be noted that all 12 carbonyls attached to the four Fe atoms are terminal and the whole molecule is centrosymmetric. However, in contrast to **10**, complex **4*** (Figure 2) contains a *n*-butyl-substituted diselenolate 4-*n*-BuSe$C_6H_4C_6H_4$Se-4′ ligand, which is bridged through its Se(1) atom to the two Fe atoms of the (μ-S=CSMe)$Fe_2(CO)_6$ structural unit to consititute a single-butterfly Fe/E cluster complex. Similar to the biphenylene group in **10**, the biphenylene group in **4*** is bound to the bridged Se(1) atom in an equatorial orientation (∠C(7)···Se(1)−C(9) = 159.9°, ∠S(1)···Se(1)−C(9) = 152.3°) to give the most stable conformational isomer, since its methyl group attached to the S(2) atom is an exo-methyl group.[23] In addition, the dihedral angle between two benzene rings of its biphenylene group is 35.2°, which is remarkably different from the corresponding dihedral angle (0°) in **10**. It is worthy of note that the thiocarbonyl C(7)=S(1) in the S(2)−C(7)=S(1) moiety is bridged to Fe(2) through a σ bond (Fe(2)−C(7) = 2.000(5) Å) and to Fe(1) via the donation of an unshared electron pair from S(1) (Fe(1)−S(1) = 2.304(2) Å). Compared to the C=S double bond in free CS_2 (1.554 Å),[24] the bond length of the double bond C(7)=S(1) extends to 1.692(6) Å, but is still shorter than that of the single bond C(8)−S(2) (1.825(6) Å). It follows that the structural feature of **4*** in this respect resembles that of the single-butterfly complex (μ-SePh)(μ-S=$CSCH_2Ph$)$Fe_2(CO)_6$.[18]

In summary, we have synthsized the first diselenolate ligand-containing double- and single-butterfly Fe/E (E = S, Se) cluster complexes **4**−**10** and **4*** by two synthetic methods, which involve using a dilithium reagent 4-Li$C_6H_4C_6H_4$Li-4′ containing the in situ generated *n*-BuBr or without *n*-BuBr. When the dilithium reagent containing *n*-BuBr is used, both the two-μ-CO-containing dianion **3** and the one-μ-CO-containing monoanion **3*** are formed, which react further with electrophiles CS_2/

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(24) Butler, I. S.; Fenster, A. E. *J. Organomet. Chem.* **1974**, *66*, 161.

MeI to produce both the double-butterfly complex **4** and single-butterfly complex **4***. However, when the dilithium reagent without *n*-BuBr is utilized, only the two-μ-CO-containing intermediate dianion **3** is formed, which reacts further with the electrophiles CS_2/MeI, CS_2/EtBr, CS_2/$PhCH_2Br$, CS_2/PhC(Cl)═NPh, CS_2/Cp(CO)$_2$FeI, PhSeBr, and $MeSCH_2Cl$ to produce only the double-butterfly complexes **4**−**10**. It can be expected that dianion **3** and monoanion **3*** will play an important role in development of the chemistry of such butterfly Fe/E cluster complexes, since they all contain the reactive μ-CO functionality.

Experimental Section

General Comments. All reactions were performed using standard Schlenk and vacuum-line techniques under a prepurified N_2 atmosphere. THF was distilled under N_2 from sodium/benzophenone ketyl. *n*-BuLi,[25] $Fe_3(CO)_{12}$,[26] PhSeBr,[27] $MeSCH_2Cl$,[28] and 4,4′-$BrC_6H_4C_6H_4Br$[29] were prepared according to the published methods. Other reactants were purchased from commercial suppliers and used as received. Preparative TLC was carried out on glass plates (26 × 20 × 0.25 cm) coated with silica gel H (10−40 μm). IR spectra were recorded on a Nicolet Magna 560 FTIR or a Bruker Vector 22 infrared spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker AC-P200 NMR spectrometer or a Bruker AC-P 300 NMR spectrometer. ^{77}Se NMR spectra were recorded on a Bruker AV600 NMR spectrometer with Ph_2Se_2 as an external standard, and the chemical shifts were referenced to Me_2Se ($\delta = 0$). Elemental analysis was performed on an Elementar Vario EL analyzer. Melting points were determined on a Yanaco MP-500 apparatus and were uncorrected.

Preparation of Double-Butterfly Complex (4-μ-SeC$_6$H$_4$C$_6$H$_4$Se-μ-4′)[(μ-S═CSMe)Fe$_2$(CO)$_6$]$_2$ (4) along with Single-Butterfly Complex (4-*n*-BuSeC$_6$H$_4$C$_6$H$_4$Se-μ-4′)[(μ-S═CSMe)Fe$_2$(CO)$_6$] (4*). A 100 mL three-necked flask fitted with a magnetic stir-bar, a rubber septum, and a nitrogen inlet tube was charged with 4-$BrC_6H_4C_6H_4Br$-4′ (0.312 g, 1.0 mmol) and THF (20 mL). While stirring, the resulting solution was cooled to −65 °C and then an Et_2O solution of *n*-BuLi (2.0 mmol) was dropwise added. The mixture was stirred for an additional 0.5 h from −65 to 0 °C to give an off-white mixture containing an equimolar amount of 4-$LiC_6H_4C_6H_4Li$-4′ and *n*-BuBr. The mixture was recooled to −15 °C, and then selenium powder (0.158 g, 2.0 mmol) was added. After several minutes the mixture turned orange-red and $Fe_3(CO)_{12}$ (1.00 g, 2.0 mmol) was added to cause vigorous gas evolution. The new mixture was naturally warmed from −15 °C to room temperature and continued stirring for 45 min to give a brown-red solution. To this solution was added CS_2 (0.24 mL, 4.0 mmol), and the mixture was stirred for 1 h. After MeI (0.25 mL, 4.0 mmol) was added, the new mixture was stirred for an additional 12 h. Solvent was removed under vacuum and the residue was subjected to TLC separation using THF/petroleum ether (v/v = 1:20) as eluent. From the first orange-red band, **4*** (0.147 g, 20%) was obtained as a red solid, mp 108−109 °C. Anal. Calcd for $C_{24}H_{20}Fe_2O_6S_2Se_2$: C, 39.02; H, 2.71. Found: C, 38.94; H, 2.85. IR (KBr disk): $\nu_{C\equiv O}$ 2064 (vs), 2026 (vs), 1992 (vs); $\nu_{C=S}$ 1015 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$): 0.90 (t, J = 7.2 Hz, 3H, CH$_2$C*H$_3$*), 1.35−1.52 (m, 2H, C*H$_2$*CH$_3$), 1.63−1.78 (m, 2H, SeCH$_2$C*H$_2$*), 2.60 (s, 3H, SCH$_3$), 2.92 (t, J = 7.2 Hz, 2H, SeCH$_2$), 7.39−7.52 (m, 8H, 2C$_6$H$_4$) ppm. ^{77}Se NMR (CDCl$_3$): 286.9 (s, *n*-BuSe), 477.6 (s, SeFe$_2$) ppm. From the second red band, **4** (0.117 g, 11%) was obtained as a red solid, mp 130 °C (dec). Anal. Calcd for $C_{28}H_{14}Fe_4O_{12}S_4Se_2$: C, 31.94; H, 1.33. Found: C, 31.93; H, 1.28. IR (KBr disk): $\nu_{C\equiv O}$ 2067 (vs), 2027 (vs), 2002 (vs); $\nu_{C=S}$ 1013 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$): 2.60 (s, 6H, 2CH$_3$), 7.37, 7.41, 7.46, 7.50 (q, AA′BB′, 8H, 2C$_6$H$_4$) ppm. ^{77}Se NMR (CDCl$_3$): 476.6 (s) ppm.

Preparation of Double-Butterfly Complex (4-μ-SeC$_6$H$_4$C$_6$H$_4$Se-μ-4′)[(μ-S═CSMe)Fe$_2$(CO)$_6$]$_2$ (4) without Single-Butterfly Complex 4*. In the same equipped flask described above was dissolved 4-$BrC_6H_4C_6H_4Br$-4′ (0.312 g, 1.0 mmol) in THF (20 mL). The resulting solution was cooled to −65 °C, and then a solution of *n*-BuLi (2.0 mmol) in Et_2O was slowly added. The mixture was stirred for an additional 0.5 h from −65 to 0 °C, and then volatiles including the in situ formed *n*-BuBr were removed under vacuum to leave 4-$LiC_6H_4C_6H_4Li$-4′ as an off-white solid. To this solid was added THF (20 mL) cooled to −5 °C to give an off-white suspension. After cooling the suspension to −15 °C, selenium powder (0.158 g, 2.0 mmol) was added. The mixture was stirred for several minutes at this temperature, and then $Fe_3(CO)_{12}$ (1.00 g, 2.0 mmol) was added. The new mixture was naturally warmed from −15 °C to room temperature and continued stirring for 45 min to give a brown-red solution. To this solution was added CS_2 (0.24 mL, 4.0 mmol). After the mixture was stirred for 1 h, MeI (0.25 mL, 4.0 mmol) was added, and the new mixture was stirred for an additional 12 h. Solvent was removed under vacuum, and the residue was subjected to TLC separation using THF/petroleum ether (v/v = 1:20) as eluent. From the main band, **4** (0.221 g, 21%) was obtained as a red solid.

Preparation of (4-μ-SeC$_6$H$_4$C$_6$H$_4$Se-μ-4′)[(μ-S═CSEt)Fe$_2$(CO)$_6$]$_2$ (5). The same procedure was followed as for the preparation of **4** without **4***, except that EtBr (0.436 g, 4.0 mmol) was used instead of MeI and THF/petroleum ether (v/v = 1:25) as eluent. **5** (0.195 g, 18%) was obtained as a red solid, mp 117−118 °C. Anal. Calcd for $C_{30}H_{18}Fe_4O_{12}S_4Se_2$: C, 33.33; H, 1.67. Found: C, 33.50; H, 1.56. IR (KBr disk): $\nu_{C\equiv O}$ 2067 (s), 2028 (vs), 2008 (vs), 1986 (s); $\nu_{C=S}$ 998 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$): 1.28 (t, J = 7.2 Hz, 6H, 2CH$_3$), 3.14 (q, J = 7.2 Hz, 4H, 2CH$_2$), 7.37, 7.41, 7.45, 7.49 (q, AA′BB′, 8H, 2C$_6$H$_4$) ppm. ^{77}Se NMR (CDCl$_3$): 477.1 (s) ppm.

Preparation of (4-μ-SeC$_6$H$_4$C$_6$H$_4$Se-μ-4′)[(μ-S═CSCH$_2$Ph)Fe$_2$(CO)$_6$]$_2$ (6). When $PhCH_2Br$ (0.48 mL, 4.0 mmol) was utilized instead of MeI and THF/petroleum ether (v/v = 1:15) as eluent, **6** (0.227 g, 19%) was obtained as a red solid, mp 122−123 °C. Anal. Calcd for $C_{40}H_{22}Fe_4O_{12}S_4Se_2$: C, 39.87; H, 1.83. Found: C, 39.86; H, 1.92. IR (KBr disk): $\nu_{C\equiv O}$ 2067 (s), 2026 (vs), 2004 (s), 1983 (s); $\nu_{C=S}$ 1011 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$): 4.35 (s, 4H, 2CH$_2$), 7.23−7.45 (m, 18H, 2C$_6$H$_5$, 2C$_6$H$_4$) ppm. ^{77}Se NMR (CDCl$_3$): 478.0 (s) ppm.

Preparation of (4-μ-SeC$_6$H$_4$C$_6$H$_4$Se-μ-4′)[(μ-S═CSC(Ph)═NPh)Fe$_2$(CO)$_6$]$_2$ (7). When PhC(Cl)═NPh (0.862 g, 4.0 mmol) was utilized instead of MeI and THF/petroleum ether (v/v = 1:4) as eluent, **7** (0.212 g, 15%) was obtained as a red solid, mp 142 °C (dec). Anal. Calcd for $C_{52}H_{28}Fe_4N_2O_{12}S_4Se_2$: C, 45.15; H, 2.03, N, 2.03. Found: C, 44.97; H, 2.06; N, 2.29. IR (KBr disk): ν_C≡O 2051 (s), 2009 (vs), 1967(vs); $\nu_{C=N}$ 1592 (w); $\nu_{C=S}$ 1001 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$): 6.95−7.56 (m, 28H, 4C$_6$H$_5$, 2C$_6$H$_4$) ppm. ^{77}Se NMR (CDCl$_3$): 357.4 (s) ppm.

Preparation of (4-μ-SeC$_6$H$_4$C$_6$H$_4$Se-μ-4′)[(μ-S═CSFe(CO)$_2$Cp)Fe$_2$(CO)$_6$]$_2$ (8). When Cp(CO)$_2$FeI (1.22 g, 4.0 mmol) was employed instead of MeI and THF/CH$_2$Cl$_2$/petroleum ether (v/v/v = 1:1:14) as eluent, **8** (0.188 g, 14%) was obtained as a red solid, mp 120 °C (dec). Anal. Calcd for $C_{40}H_{18}Fe_6O_{16}S_4Se_2$: C, 34.88; H, 1.31. Found: C, 34.84; H, 1.37. IR (KBr disk): $\nu_{C\equiv O}$ 2063 (s), 2020 (vs), 1988 (vs); $\nu_{C=S}$ 1000 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$): 4.99 (s, 10H, 2C$_5$H$_5$), 7.38−7.46 (m, 8H, 2C$_6$H$_4$) ppm. ^{77}Se NMR (CDCl$_3$): 462.4 (s) ppm.

Preparation of (4-μ-SeC$_6$H$_4$C$_6$H$_4$Se-μ-4′)[(μ-SePh)Fe$_2$(CO)$_6$]$_2$ (9). The same procedure as for the preparation of **4** without **4***

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[25] Jones, R. G.; Gilman, H. *Organic Reactions*; John Wiley and Sons: New York, 1951; Vol. 6, p 352.

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

[27] Machel, V.; Roger, V. *Bull. Soc. Chim. Fr.* 1970, *27*, 746.

[28] Bordwell, F. G.; Pitt, M. B. *J. Am. Chem. Soc.* **1955**, *77*, 572.

[29] Norman R. *Organic Syntheses*; John Wiley and Sons. Inc.: New York, 1963; Collect. Vol. 4, p 256.

Table 3. Crystal Data and Structural Refinements Details for 10 and 4*

	10	**4***
mol formula	$C_{28}H_{18}Fe_4O_{12}S_2Se_2$ $\cdot 0.5C_4H_8O$	$C_{24}H_{20}Fe_2O_6S_2Se_2$
mol wt	1027.92	738.14
cryst syst	monoclinic	triclinic
space group	$P2(1)/n$	$P\bar{1}$
a/Å	8.609(3)	10.707(7)
b/Å	19.667(6)	11.391(7)
c/Å	13.705(3)	13.432(9)
α/deg	90	96.136(12)
β/deg	90.257(3)	97.556(10)
γ/deg	90	115.678(10)
V/Å^3	2320.4(12)	1438.8(16)
Z	2	2
D_c/g cm^{-3}	1.471	1.704
abs coeff/mm^{-1}	2.931	3.718
cryst size (mm)	0.22 × 0.20 × 0.18	0.25 × 0.20 × 0.20
F(000)	1012	728
$2\theta_{max}$/deg	53.02	52.74
no. of rflns	13 009	8278
no. of indep rflns	4763	5772
index ranges	$-10 \leq h \leq 10$	$-13 \leq h \leq 12$
	$-24 \leq k \leq 23$	$-12 \leq k \leq 14$
	$-17 \leq l \leq 14$	$-13 \leq l \leq 16$
goodness of fit	1.109	1.009
R	0.0620	0.0507
R_w	0.1887	0.1100
largest diff peak and hole (e Å^{-3})	0.880 and −0.372	1.013 and −0.928

was followed, except that PhSeBr (0.472 g, 2.0 mmol) was used instead of both electrophiles CS_2 and MeI. In addition, after addition of PhSeBr the mixture was stirred for 3 h and the eluent for TLC was CH_2Cl_2/petroleum ether (v/v = 1:5). From the major orange-red band, **9** (0.170 g, 14%) was obtained as a red solid, mp 91−93 °C. Anal. Calcd for $C_{36}H_{18}Fe_4O_{12}Se_4$: C, 36.55; H, 1.52. Found: C, 36.57; H, 1.33. IR (KBr disk): $\nu_{C\equiv O}$ 2066 (s), 2027 (vs), 1992 (vs) cm^{-1}. ^{1}H NMR ($CDCl_3$): 7.14−7.40 (m, 18H, $2C_6H_5$, $2C_6H_4$) ppm. ^{77}Se NMR ($CDCl_3$): 277.8, 278.4 (2s, PhSe), 316.5, 316.8, 319.8 (3s, $SeC_6H_4C_6H_4Se$) ppm.

Preparation of (4-μ-SeC$_6$H$_4$C$_6$H$_4$Se-μ-4′)[(μ-CH$_2$SMe)Fe$_2$(CO)$_6$]$_2$ (10). The same procedure was followed as for the preparation of **9**, but $MeSCH_2Cl$ (0.290 g, 3.0 mmol) was employed in place of PhSeBr. From the major red band, **10** (0.115 g, 12%) was obtained as a red solid, mp 95 °C (dec). Anal. Calcd for $C_{28}H_{18}Fe_4O_{12}S_2Se_2$: C, 33.87; H, 1.81. Found: C, 33.99; H, 1.92. IR (KBr disk): $\nu_{C\equiv O}$ 2061 (s), 2019 (vs), 1989 (vs) cm^{-1}. ^{1}H NMR ($CDCl_3$): 1.18, 1.81 (2d, 4H, $2CH_2$), 2.09 (s, 6H, $2CH_3$), 7.46,7.63 (2s, 8H, $2C_6H_4$) ppm. ^{77}Se NMR ($CDCl_3$): 461.7 (s) ppm.

X-ray Structure Determination of 10 and 4*. Single crystals of **10** and **4*** suitable for X-ray diffraction analyses were grown by slow evaporation of the THF/hexane solution of **10** at about −20 °C and the CH_2Cl_2/hexane solution of **4*** at about −4 °C, respectively. A single crystal of **10** or **4*** was mounted on a Bruker SMART 1000 automated diffractometer. Data were collected at room temperature, using a graphite monochromator with Mo Kα radiation (λ = 0.71073 Å) in the $\omega-\phi$ scanning mode. Absorption correction was performed by the SADABS program.[30] The structures were solved by direct methods using the SHELXS-97 program[31] and refined by full-matrix least-squares techniques (SHELXL-97)[32] on F^2. Hydrogen atoms were located by using the geometric method. Details of crystal data, data collections, and structure refinements are summarized in Table 3.

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Supporting Information Available: Full tables of crystal data, atomic coordinates and thermal parameters, and bond lengths and angles for **10** and **4*** in CIF format. This material is available free of charge via the Internet at http://pubs. acs.org.

OM060238H

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(30) Sheldrick, G. M. *SADABS*, A Program for Empirical Absorption Correction of Area Detector Data; University of Göttingen: Germany, 1996.

(31) Sheldrick, G. M. *SHELXS97*, A Program for Crystal Structure Solution; University of Göttingen: Germany, 1997.

(32) Sheldrick, G. M. *SHELXL97*, A Program for Crystal Structure Refinement; University of Göttingen: Germany, 1997.