Formation and Reactions of Novel Types of Bridging Sulfido Anions, (μ-RE)(μ-S$^-$)[$Fe_2(CO)_6$]$_2$(μ_4-S) (E = S, Se): Synthesis and Structures of Double- and Triple-Butterfly Fe/E Cluster Complexes

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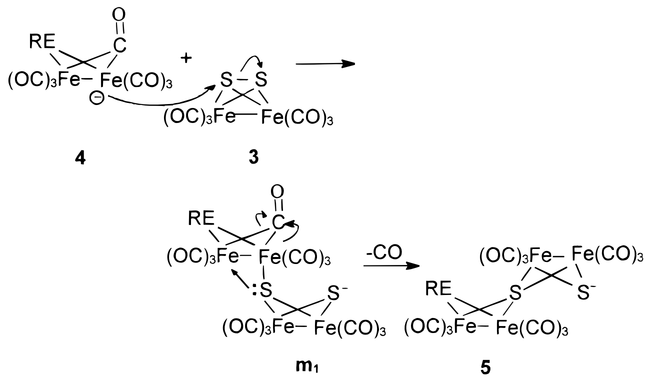
Received June 21, 1999

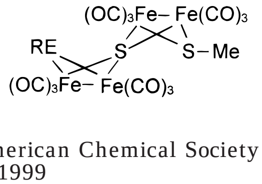
Summary: The [Et_3NH]$^+$ salts of novel anions (μ-RE)(μ-S$^-$)[$Fe_2(CO)_6$]$_2$(μ_4-S) (RE = t-BuS, p-MeC_6H_4Se) have been prepared by reaction of [(μ-RE)(μ-CO)$Fe_2(CO)_6$][Et_3NH] with (μ-S_2)$Fe_2(CO)_6$. While these salts react in situ with MeI to yield the double clusters [(μ-RE)$Fe_2(CO)_6$](μ_4-S)[(μ-MeS)$Fe_2(CO)_6$], their reactions with SO_2Cl_2 in the presence of excess [(μ-RE)(μ-CO)$Fe_2(CO)_6$][Et_3NH] afford the triple clusters [(μ-RE)$Fe_2(CO)_6$]$_2$[(μ_4-S)($Fe_2(CO)_6$)$_2$(μ_4-S)].

Over the past two decades the bridging sulfido anions (μ-S$^-$)$_2$$Fe_2(CO)_6$ (**1**) and (μ-RS)(μ-S$^-$)$Fe_2(CO)_6$ (**2**), derived from reductive cleavage of the S−S bond of the Fe/S complex μ-$S_2Fe_2(CO)_6$ (**3**) by corresponding nucleophiles such as Et_3BHLi,[1] alkyllithium species RLi,[2] and Grignard reagents RMgX,[3] have played an important role in the development of the chemistry of butterfly Fe/S cluster complexes.[4] In view of our current interest in the chemistry of butterfly Fe/E (E = S, Se) cluster complexes based on the complex anions [(μ-RE)(μ-CO)$Fe_2(CO)_6$]$^-$ (**4**, E = S, Se),[5] we have begun an investigation of the reaction of [Et_3NH]$^+$ salts of anions **4** with Fe/S complex **3** to see if the S−S bond of **3** could be cleaved by the nucleophiles of Fe-centered anions **4**. Interestingly, we found that this reaction indeed involves the reductive cleavage of the S−S bond of **3**, which was presumably caused by nucleophilic attack of the negatively charged Fe atom of **4** at the S atom of **3** to give intermediates **m$_1$**; then, **m$_1$** might further lose their μ-CO ligands through coordination of the μ_3-S atom to another Fe atom to give the novel bridging sulfido anions **5**, as shown in Scheme 1.

Scheme 1



Although direct structural studies of anions **5** have not been carried out as yet, their reactions suggest the assigned general structure, since reactions with alkyl halides afford products with bridging mercapto ligands, which were fully characterized. In a typical example, the reaction was performed with MeI as follows. A 100 mL Schlenk flask was charged with 0.504 g (1.0 mmol) of $Fe_3(CO)_{12}$ and 10 mL of THF. To the resulting green solution were added 0.11 mL (1.0 mmol) of *t*-BuSH and 0.14 mL (1.0 mmol) of Et_3N, and the mixture was stirred at 25−30 °C for 0.5 h to give a yellow-brown solution of the [Et_3NH]$^+$ salt of **4** (RE = *t*-BuS). To the yellow-brown solution was added 0.344 g (1.0 mmol) of **3**, and the mixture was stirred at room temperature for 2 h to give a brown-green solution of the [Et_3NH]$^+$ salt of **5** (RE = *t*-BuS). To the brown-green solution was added 0.125 mL (2.0 mmol) of MeI, and then the mixture was stirred for 12 h at room temperature. After removal of the volatiles the residue was subjected to TLC. Elution with petroleum ether gave a major red band, from which 0.668 g of **6** was obtained in 92% yield. Similarly, **7** was obtained in 46% yield, using *p*-MeC_6H_4SeH instead of *t*-BuSH and carrying out the reaction with **3** at −78 to 0 °C.



6 RE=t-BuS
7 RE=*p*-MeC_6H_4Se

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(1) Seyferth, D.; Henderson, R. S.; Song, L.-C. *J. Organomet. Chem.* **1980**, *192*, C1.

(2) Seyferth, D.; Henderson, R. S. *J. Am. Chem. Soc.* **1979**, *101*, 508.

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(4) For example, see: (a) Seyferth, D.; Song, L.-C.; Henderson, R. S. *J. Am. Chem. Soc.* **1981**, *103*, 5130. (b) Seyferth, D.; Henderson, R. S.; Song, L.-C. *Organometallics* **1982**, *1*, 125. (c) Song, L.-C.; Kadiata, M.; Wang, J.-T.; Wang, R.-J.; Wang, H.-G. *J. Organomet. Chem.* **1988**, *340*, 239. (d) Song, L.-C.; Kadiata, M.; Wang, J.-T.; Wang, R.-J.; Wang, H.-G. *J. Organomet. Chem.* **1990**, *391*, 387. (e) Bose, K. S.; Sinn, E.; Averll, B. A. *Organometallics* **1984**, *3*, 1126.

(5) (a) Song, L.-C.; Yan, C.-G.; Hu, Q.-M.; Wang, R.-J.; Mak, T. C. W. *Organometallics* **1995**, *14*, 5513. (b) Song, L.-C.; Yan, C.-G.; Hu, Q.-M.; Wu, B.-M.; Mak, T. C. W. *Organometallics* **1997**, *16*, 632. (c) Song, L.-C.; Yan, C.-G.; Hu, Q.-M.; Wang, R.-J.; Mak, T. C. W.; Huang, X.-Y. *Organometallics* **1996**, *15*, 1535. (d) Song, L.-C.; Lu, G.-L.; Hu, Q.-M.; Qin, X.-D.; Sun, C.-X.; Yang, J.; Sun, J. *J. Organomet. Chem.* **1998**, *571*, 55. (e) Song, L.-C.; Qin, X.-D.; Hu, Q.-M.; Huang, X.-Y. *Organometallics* **1998**, *17*, 5437. (f) Song, L.-C.; Fun, H.-T.; Hu, Q.-M.; Qin, X.-D.; Zhu, W.-F.; Chen, Y.; Sun, J. *Organometallics* **1998**, *17*, 3454.

10.1021/om9904753 CCC: $18.00
Publication on Web 07/24/1999

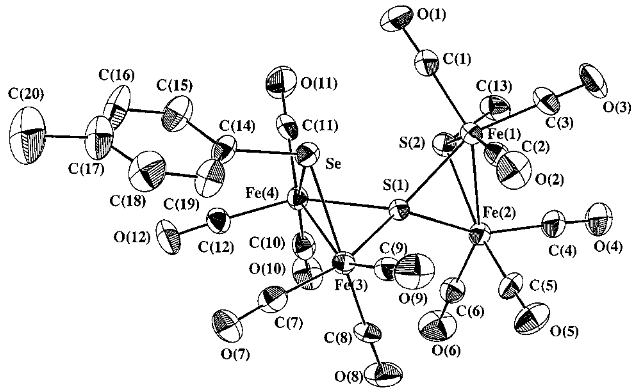


Figure 1. ORTEP drawing of complex **7**. Selected distances (Å) and angles (deg): Fe(1)−Fe(2), 2.515(2); Fe(3)−Fe(4), 2.544(2); S(1)−Fe(1), 2.247(3); S(1)−Fe(3), 2.226(3); Se−Fe(3), 2.391(2); Fe(1)−S(1)−Fe(2), 68.10(8); Fe(3)−S(1)−Fe(4), 69.60(8); S(1)−Fe(1)−Fe(2), 55.92(7); S(1)−Fe(3)−Fe(4), 55.29(7); Fe(3)−Se−Fe(4), 64.19(5).

Products **6** and **7** have been characterized by elemental and spectroscopic analyses;[6] **7** has been characterized as well by X-ray diffraction analysis.[7] Figure 1 represents the molecular structure of **7** with selected bond lengths and angles. As seen in Figure 1, cluster **7** is a chiral molecule, which consists of the two different butterfly-shaped subcluster cores Fe(1)Fe(2)S(1)S(2) and Fe(3)Fe(4)S(1)Se joined to a spiro type of μ_4-S: i.e., the S(1) atom. In addition, it can be seen that the two substituents Me and p-MeC$_6$H$_4$ on the subclusters are attached to S(2) and Se atoms by an equatorial bond and each of the three CO's attached to Fe atom is terminal. Therefore, this structure is consistent with its elemental and spectroscopic data and is similar to other μ_4-S and μ_4-Se double clusters, such as [(μ-MeS)Fe$_2$(CO)$_6$]$_2$(μ_4-S),[8] [(μ-EtS)Fe$_2$(CO)$_6$]$_2$(μ_4-S),[4c] [(μ-EtS)Fe$_2$(CO)$_6$]$_2$(μ_4-Se),[5c] and [(μ-p-MeC$_6$H$_4$Se)Fe$_2$(CO)$_6$]$_2$(μ_4-Se).[9]

Anions **5** have more interesting and useful synthetic applications, as demonstrated by the following preparation of the novel triple butterfly cluster **8**. Addition of 0.172 g (0.50 mmol) of **3** to a brown solution of ca. 1 mmol of the [Et$_3$NH]$^+$ salt of **4** (RE = t-BuS) prepared as described above resulted in formation of a brown-green solution that was stirred at room temperature for 2 h. When this solution was cooled to −78 °C, 0.05 mL (0.5 mmol) of SO$_2$Cl$_2$ was added and the solution turned to red immediately. The mixture was warmed to room temperature and stirred for an additional 2 h. Volatiles were removed in vacuo, and the residue was subjected to TLC. Petroleum ether eluted one major band, from which 0.210 g (38%) of **8** was obtained. Similarly, 23% of **9** was obtained if p-MeC$_6$H$_4$SeH was used instead of t-BuSH.

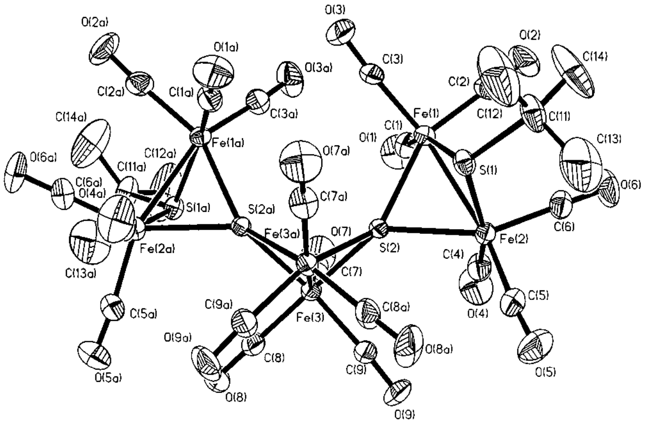
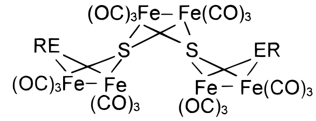


Figure 2. ORTEP drawing of complex **8**. Selected distances (Å) and angles (deg): Fe(1)−Fe(2), 2.504(1); Fe(3)−Fe(3a), 2.563(2); S(2)−Fe(1), 2.277(2); S(2)−Fe(3), 2.253(2); Fe(1)−S(2)−Fe(2), 66.8(1); Fe(3)−S(2)−Fe(3a), 69.3(1); S(2)−Fe(1)−Fe(2), 56.5(1); S(2)−Fe(3)−Fe(3a), 55.4(1).



8 RE=t-BuS
9 RE=p-MeC$_6$H$_4$Se

Products **8** and **9** have been fully characterized by combustion analysis and spectroscopic techniques.[10] To unambiguously confirm their structures, the X-ray diffraction analysis for **8** was undertaken.[11] Figure 2 shows the molecular structure of **8**. As seen in Figure 2, **8** comprises the three butterfly-shaped Fe$_2$S$_2$ subcluster cores Fe(1)Fe(2)S(1)S(2), Fe(3)Fe(3a)S(2)S(2a), and Fe(1a)Fe(2a)S(1a)S(2a). It is unprecedented to have two such μ_4-S (S(2) and S(2a)) atoms. In addition, each Fe atom has three terminal CO ligands, and the two t-Bu groups are bonded to S(1) and S(1a) atoms by an equatorial bond. This molecule is chiral, which has a C_2 axis passing through the two midpoints of Fe(3)−Fe(3a) and S(2)···S(2a). It is noteworthy that the geometric parameters of the middle subcluster core are somewhat different from those of the two identical side subcluster cores. For example, the dihedral angle between Fe(3)−Fe(3a)−S(2) and Fe(3)−Fe(3a)−S(2a) (73.7°) is less than that between Fe(1)−Fe(2)−S(1) and Fe(1)−Fe(2)−S(2) or Fe(1a)−Fe(2a)−S(1a) and Fe(1a)−Fe(2a)−S(2a) (86.1°), and the bond length of Fe(3)−Fe(3a) (2.563(2) Å) is longer than that of Fe(1)−Fe(2) or Fe(1a)-Fe(2a) (2.504(1) Å). However, the basic geometric parameters of this triple-butterfly cluster complex are still comparable with those of double-butterfly clusters.[4c,5c,8,9]

At present, we are not clear concerning the reaction mechanism for production of **8** and **9**. However, on the

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[6] Product **6**: mp 150 °C dec; ^{1}H NMR (CDCl$_3$) δ 1.44 (s, 9H, t-(CH$_3$)$_3$C), 2.14 (s, 3H, CH$_3$) ppm; IR (KBr disk): 2082 (vs), 2052 (vs), 2034 (vs), 1984 (s), 1979 (s), 1972 (s), 1967 (m) cm^{-1}. Anal. Calcd for C$_{17}$H$_{12}$Fe$_4$O$_{12}$S$_3$: C, 28.04; H, 1.65. Found: C, 28.06; H, 1.67. Product **7**: mp 154 °C dec; ^{1}H NMR (CDCl$_3$) δ 2.17 (s, 3H, SCH$_3$), 2.29 (s, 3H, ArCH$_3$), 7.12 (q, AA′BB′, J = 7.5 Hz, 4H, C$_6$H$_4$); ^{77}Se NMR (CDCl$_3$, Me$_2$Se) δ 248.04 ppm; IR (KBr disk) 2082 (m), 2052 (s), 2032 (vs), 1993 (vs), 1970 (s) cm^{-1}. Anal. Calcd for C$_{20}$H$_{10}$Fe$_4$O$_{12}$S$_2$Se: C, 29.68; H, 1.24. Found: C, 29.50; H, 1.66.

[7] X-ray data: red crystals of **7** from CH$_2$Cl$_2$/hexane, triclinic ($P\bar{1}$), a = 8.782(2) Å, b = 9.093(3) Å, c = 19.514(7) Å, α = 86.98(2)°, β = 86.42(2)°, λ = 68.6(2)°, Z = 2, R = 0.058, GOF = 1.60.

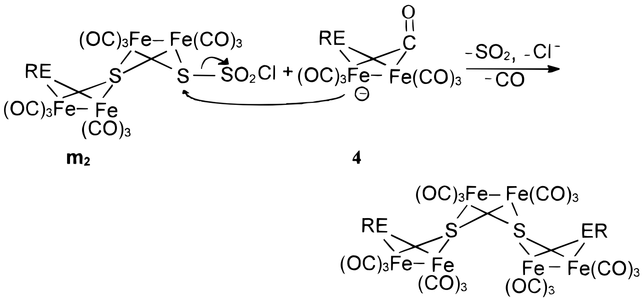
[8] Coleman, J. M.; Wojcicki, A.; Pollick, P. J. Dahl, L. F. *Inorg. Chem.* **1967**, *6*, 1236.

[9] Song, L.-C.; Hu, Q.-M.; Yan, C.-G.; Wang, R.-J.; Mak, T. C. W. *Acta Crystallogr.* **1996**, *C52*, 1357.

[10] Product **8**: mp 180 °C dec; ^{1}H NMR (CDCl$_3$) δ 1.48 (s, 18H, 2(CH$_3$)$_3$C) ppm; IR (KBr disk) 2070 (s), 2041 (vs), 1989 (vs), 1922 (s) cm^{-1}. Anal. Calcd for C$_{26}$H$_{18}$Fe$_6$O$_{18}$S$_4$: C, 28.87; H, 1.68. Found: C, 28.84; H, 1.71. Product **9**: mp 170 °C dec; ^{1}H NMR (CDCl$_3$) δ 2.31 (s, 6H, 2ArCH$_3$), 7.17 (q, AA′BB′, J = 8.3 Hz, 8H, 2C$_6$H$_4$); ^{77}Se NMR (CDCl$_3$, Me$_2$Se) δ 249.78 ppm; IR (KBr disk): 2085 (m), 2069 (s), 2055 (s), 2038 (vs), 2022 (s), 2006 (s), 1992 (vs) cm^{-1}. Anal. Calcd for C$_{32}$H$_{14}$Fe$_6$O$_{18}$S$_2$Se$_2$: C, 30.91; H, 1.14. Found: C, 30.56; H, 1.44.

[11] X-ray data: red crystals of **8** from CH$_2$Cl$_2$/hexane, monoclinic ($C2/c$), a = 27.454(5) Å, b = 9.303(2) Å, c = 20.136(4) Å, β = 128.16(3)°, Z = 4, R = 0.044, S = 0.8.

Scheme 2



8 RE=*t*-BuS
9 RE=*p*-MeC_6H_4Se

basis of the well-known properties of both S-centered monoanions **2** and Fe-centered monoanions **4**[3,5c,d] we might suggest that this type of reaction would involve the intermediates $\mathbf{m_2}$ generated in situ from anions **5** and SO_2Cl_2. These intermediates could further react with an excess amount of **4** via nucleophilic attack of the negatively charged Fe atom of **4** at the bridged S atom attached to the SO_2Cl group, followed by loss of the SO_2Cl group and μ-CO ligand to give **8** and **9** (Scheme 2).

In conclusion, we have prepared a novel type of sulfido anions **5** through new reactions of the Fe/S complex **3** with the $[Et_3NH]^+$ salts of anions **4**. Further study of the chemical reactivities of **5** has led to the synthesis of novel double- and triple-butterfly Fe/E (E = S, Se) clusters **6**–**9** successfully. A detailed mechanism for the novel reaction which affords clusters **8** and **9**, as well as other interesting applications of anions **5** in the synthesis of cluster complexes, particularly the multi-butterfly Fe/E clusters, is under investigation.

Acknowledgment. We are grateful to the National Natural Science Foundation of China, the State Key Laboratory of Elemento-Organic Chemistry, and the Laboratory of Organometallic Chemistry for financial support.

Supporting Information Available: Text giving preparation details and characterization data for complexes **6**–**9** and tables giving data collection and refinement details, atomic coordinates, thermal parameters, and bond lengths and bond angles of the two crystallographically characterized complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

OM9904753