Formation and Reactions of Novel Types of Bridging Sulfido Anions, $(\mu$ -RE) $(\mu$ -S⁻)[Fe₂(CO)₆]₂ $(\mu_4$ -S) (E = S, Se): Synthesis and Structures of Double- and Triple-Butterfly Fe/E Cluster Complexes

Li-Cheng Song, *,[†] Guo-Liang Lu,[†] Qing-Mei Hu,[†] Hong-Tao Fan,[†] Yu Chen,[†] and Jie Sun[‡]

Department of Chemistry, Nankai University, Tianjin 300071, China, and Laboratory of Organometallic Chemistry, Shanghai 200032, China

Received June 21, 1999

Summary: The $[Et_3NH]^+$ salts of novel anions $(\mu -RE)$ - $(\mu -S^-)[Fe_2(CO)_6]_2(\mu_4 -S)$ (RE = t-BuS, p-MeC₆H₄Se) have been prepared by reaction of $[(\mu -RE)(\mu -CO)Fe_2(CO)_6][Et_3-NH]$ with $(\mu -S_2)Fe_2(CO)_6$. While these salts react in situ with MeI to yield the double clusters $[(\mu -RE)Fe_2(CO)_6]-(\mu_4 -S)[(\mu -MeS)Fe_2(CO)_6]$, their reactions with SO_2CI_2 in the presence of excess $[(\mu -RE)(\mu -CO)Fe_2(CO)_6][Et_3NH]$ afford the triple clusters $[(\mu -RE)Fe_2(CO)_6]_2[(\mu_4 -S)(Fe_2-(CO)_6)_2](\mu_4 -S)]$.

Over the past two decades the bridging sulfido anions $(\mu - S^{-})_{2}Fe_{2}(\hat{CO})_{6}$ (1) and $(\mu - RS)(\mu - S^{-})Fe_{2}(\hat{CO})_{6}$ (2), derived from reductive cleavage of the S-S bond of the Fe/S complex μ -S₂Fe₂(CO)₆ (**3**) by corresponding nucleophiles such as Et₃BHLi,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 $[(\mu-RE)(\mu-CO) Fe_2(CO)_6]^-$ (4, E = S, Se),⁵ we have begun an investigation of the reaction of [Et₃NH]⁺ 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 \mathbf{m}_1 ; then, \mathbf{m}_1 might further lose

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. 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.



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.

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 Fe₃(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 Et₃N, 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 yellowbrown 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-MeC₆H₄SeH instead of *t*-BuSH and carrying out the reaction with $\mathbf{3}$ at -78 to 0 °C.



6 RE=t-BuS 7 RE=*p*-MeC₆H₄Se



[†] Nankai University.

[‡] Laboratory of Organometallic Chemistry.

⁽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.
(3) Seyferth, D.; Henderson, R. S.; Song, L.-C.; Womack, G. B. J. Organomet. Chem. 1985, 292, 9.

⁽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.



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*-MeC₆H₄ 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)Fe₂- $(CO)_{6}_{2}(\mu_{4}-S),^{8}$ [(μ -EtS)Fe₂(CO)₆]₂($\mu_{4}-S$),^{4c} [(μ -EtS)Fe₂- $(CO)_{6}_{2}(\mu_{4}-Se)^{5c}$ and $[(\mu-p-MeC_{6}H_{4}Se)Fe_{2}(CO)_{6}]_{2}(\mu_{4}-Se)^{.9}$

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 $[Et_3NH]^+$ 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 SO₂Cl₂ 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%



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).

of **9** was obtained if p-MeC₆H₄SeH was used instead of *t*-BuSH.



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_2S_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

⁽⁶⁾ Product **6**: mp 150 °C dec; ¹H NMR (CDCl₃) δ 1.44 (s, 9H, t-(CH₃)₃C), 2.14 (s, 3H, CH₃) ppm; IR (KBr disk): 2082 (vs), 2052 (vs), 2034 (vs), 1984 (s), 1979 (s), 1972 (s), 1967 (m) cm⁻¹. Anal. Calcd for C₁₇H₁₂Fe₄O₁₂S₃: C, 28.04; H, 1.65. Found: C, 28.06; H, 1.67. Product **7**: mp 154 °C dec; ¹H NMR (CDCl₃) δ 2.17 (s, 3H, SCH₃), 2.29 (s, 3H, ArCH₃), 7.12 (q, AA'BB', J = 7.5 Hz, 4H, C₆H₄); ⁷⁷Se NMR (CDCl₃, Me₂Se) δ 248.04 ppm; IR (KBr disk) 2082 (m), 2052 (s), 2032 (vs), 1993 (vs), 1970 (s) cm⁻¹. Anal. Calcd for C₂₀H₁₀Fe₄O₁₂S₂Se: C, 29.68; H, 1.24. Found: C, 29.50; H, 1.66.

⁽⁷⁾ X-ray data: red crystals of **7** from CH₂Cl₂/hexane, triclinic ($P\overline{I}$), 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; ¹H NMR (CDCl₃) δ 1.48 (s, 18H, 2(CH₃)₃C) ppm; IR (KBr disk) 2070 (s), 2041 (vs), 1989 (vs), 1922 (s) cm⁻¹. Anal. Calcd for C₂₆H₁₈Fe₆O₁₈S₄: C, 28.87; H, 1.68. Found: C, 28.84; H, 1.71. Product **9**: mp 170 °C dec; ¹H NMR (CDCl₃) δ 2.31 (s, 6H, 2ArCH₃), 7.17 (q, AA'BB', J = 8.3 Hz, 8H, 2C₆H₄); ⁷⁷Se NMR (CDCl₃, Me₂Se) 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 C₃₂H₁₄-Fe₆O₁₈S₂Se₂: C, 30.91; H, 1.14. Found: C, 30.56; H, 1.44.

⁽¹⁾ X-ray data: red crystals of **8** from CH₂Cl₂/hexane, monoclinic (C2/c), a = 27.454(5) Å, b = 9.303(2) Å, c = 20.136(4) Å, $\beta = 128.16-(3)^\circ$, Z = 4, R = 0.044, S = 0.8.



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 m_2 generated in situ from anions **5** and SO₂Cl₂. 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 SO₂Cl group, followed by loss of the SO₂Cl 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 multibutterfly 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