Synthesis of Double and Quadruple Butterfly Fe/S Cluster Complexes via a Novel Type of Reaction of Anions (μ-RS)(μ-S⁻)[Fe₂(CO)₆]₂(μ₄-S) with Succinyl Chloride

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*Summary: The bridging sulfido anions (μ-RS)(μ-S⁻)[Fe₂-(CO)₆]₂(μ₄-S) (**4a**) react with succinyl chloride in THF to give double and quadruple butterfly Fe/S clusters (μ-RS)(μ-RSS)[Fe₂(CO)₆]₂(μ₄-S) (**5a**, R = Et; **6a**, R = t-Bu) and [(μ-RS)Fe₂(CO)₆(μ₄-S)Fe₂(CO)₆]₂(μ-S−S-μ) (**5b**, R = Et; **6b**, R = t-Bu), unexpectedly. Crystal structrues of **6a** and **6b** are described.*

In recent years iron−sulfur cluster complexes have attracted considerable attention because of the novelty and versatility of structures and reactivities of such clusters, as well as their potential applications as models for the active site in non-heme iron proteins such as the ferredoxins.[1] Among the iron−sulfur cluster complexes the single butterfly Fe/S clusters are known to be most studied,[2] then the double[3] and triple[4] butterfly ones, but no quadruple butterfly Fe/S cluster complex has so far appeared in the literature.

We previously reported that the reaction of single butterfly Fe/S cluster anions (μ-RS)(μ-S⁻)Fe₂(CO)₆ (**1**) with organic diacid chlorides ClC(O)ZC(O)Cl (Z = (CH₂)₂, C₆H₄) gave bridged double clusters **2** and Fe₄S₃ double clusters **3**, depending upon the reaction temperature employed[3e] (Scheme 1).

Recently we further reported the preparation of a new type of double butterfly Fe/E cluster anions (μ-RE)(μ-S⁻)[Fe₂(CO)₆]₂(μ₄-S) (**4a**, E = S; **4b**, E = Se),[4b] which have been shown to be very useful as building blocks in the synthesis of novel butterfly, particularly multi-

Scheme 1

Scheme 2
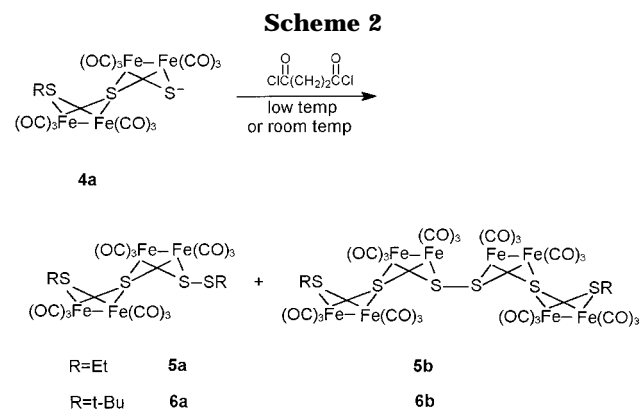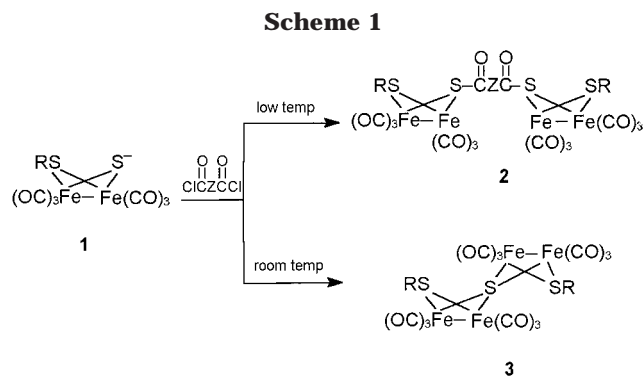
butterfly, Fe/E cluster complexes.[4b] To find out the similarity and differences in chemical behavior between the single and double butterfly anions **1** and **4** and to develop a new synthetic methodology for butterfly Fe/E cluster complexes, we have carried out the reaction of **4a** with succinyl chloride under reaction conditions similar to those in reaction of **1** with organic diacid chlorides as mentioned above.[3e] Interestingly, we found that the reaction of **4a** with succinyl chloride, in contrast to **1**, is independent of the reaction temperature and afforded different types of products from those obtained in reaction of **1**, namely, double and quadruple butterfly clusters (μ-RS)(μ-RSS)[Fe₂(CO)₆]₂(μ₄-S) (**5a**, R = Et; **6a**, R = t-Bu) and [(μ-RS)Fe₂(CO)₆(μ₄-S)Fe₂(CO)₆]₂(μ-S−S-μ) (**5b**, R = Et; **6b**, R = t-Bu) (Scheme 2).

As a typical experiment, the preparation of **5a,b** was performed as follows. A 100 mL Schlenk flask was charged with 0.504 g (1.0 mmol) of Fe₃(CO)₁₂[5] and 10 mL of THF. To the resulting green solution were added 0.08 mL (1.1 mmol) of EtSH and 0.17 mL (1.2 mmol) of

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(1) For reviews, see for example: (a) Adams, R. D.; Tsai, M. *J. Cluster Sci.* **1990**, *1*, 249. (b) Marko′, L.; Marko′-Monostory, B. In *The Organic Chemistry of Iron*; von Gustorf, E. A. K., Grevels, F.-W., Fischer, I., Eds.; Academic Press: New York, 1981; p 283. (c) Ogino, H.; Inomata, S.; Tobita, H. *Chem. Rev.* **1998**, *98*, 2093.
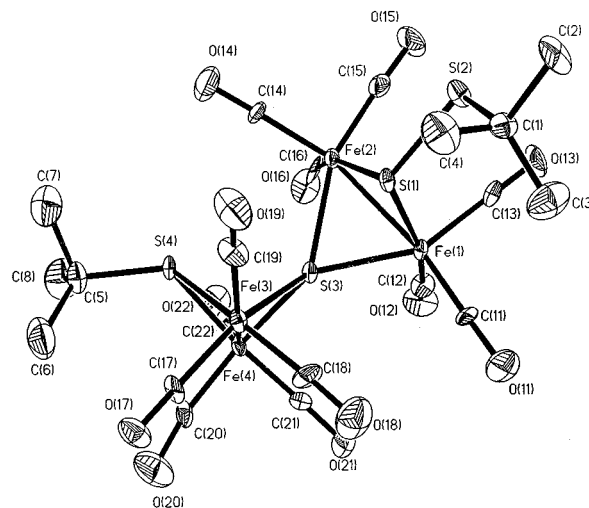(2) For reviews, see for example: (a) Song, L.-C. In *Advances in Organometallic Chemistry*; Huang, Y., Qian, Y., Eds.; Chemical Industry Press: Beijing, 1987; p 181, and references therein. (b) Song, L.-C. *Chem. J. Chin. Univ.* **1996**, *17*, 575, and references therein.
(3) (a) Seyferth, D.; Henderson, R. S.; Song, L.-C. *Organometallics* **1982**, *1*, 125. (b) Bose, K. S.; Sinn, E.; Averill, B. A. *Organometallics* **1984**, *3*, 1126. (c) Seyferth, D.; Kiwan, A. M.; Sinn, E. *J. Organomet. Chem.* **1985**, *281*, 111. (d) Seyferth, D.; Kiwan, A. M. *J. Organomet. Chem.* **1985**, *286*, 219. (e) Song, L.-C.; Kadiata, M.; Wang, J.-T.; Wang, R.-J.; Wang, H.-G. *J. Organomet. Chem.* **1988**, *340*, 239. (f) Song, L.-C.; Kadiata, M.; Hu, Q.-M.; Wang, J.-T. *Acta Chim. Sin. (English ed.)* **1988**, *46*, 203. (g) Song, L.-C.; Kadiata, M.; Wang, J.-T.; Wang, R.-J.; Wang, H.-G. *J. Organomet. Chem.* **1990**, *391*, 387. (h) Song, L.-C.; Yan, C.-G.; Hu, Q.-M.; Wang, R.-J.; Mak, T. C. W.; Huang, X.-Y. *Organometallics* **1996**, *15*, 1535. (i) Song, Z.-X.; Jia, C.-S.; Zhou, Z.-Y.; Zhou, X.-G. *J. Organomet. Chem.* **1999**, *580*, 201.
(4) (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.; Lu, G.-L.; Hu, Q.-M.; Fan, H.-T.; Chen, Y.; Sun, J. *Organometallics* **1999**, *18*, 3258.

Et$_3$N, and the mixture was stirred at room temperature for 0.5 h to give a yellow-brown solution of [Et$_3$NH$^+$]-[(μ-EtS)(μ-CO)Fe$_2$(CO)$_6^-$].[6] To the solution was added 0.400 g (1.16 mmol) of μ-S$_2$Fe$_2$(CO)$_6$,[3a] and the mixture was stirred at room temperature for 2 h to give a brown-green solution of [Et$_3$NH$^+$] salts of (μ-EtS)(μ-S$^-$)[Fe$_2$-(CO)$_6$]$_2$(μ_4-S). The solution was cooled to −78 °C, and 0.055 mL (0.5 mmol) of succinyl chloride was added. After the temperature of the reaction mixture was raised naturally to room temperature by removal of a dry ice bath, the mixture continued to stir at this temperature for 2 h. Solvent was removed under vacuum, and the residue was subjected to TLC. Elution with CH$_2$Cl$_2$/petroleum ether (v/v = 1:20) gave two major bands. From the first orange-red band 0.096 g of **5a** was obtained in 26% yield, whereas from the second red band 0.188 g of **5b** was obtained in 28% yield. Similarly, **6a** and **6b** were obtained in 12% and 37% yields, when using t-BuSH (0.130 mL, 1.1 mmol) instead of EtSH.

Products **5a**,**b** and **6a**,**b** have been characterized by elemental analysis, IR, and ^{1}H NMR spectroscopy,[7] and **6a** and **6b** by X-ray diffraction techniques.[8] Figure 1 and Figure 2 show the molecular structures of **6a** and **6b** with selected bond lengths and angles. As can be seen from Figure 1, **6a** is a chiral molecule, which comprises two butterfly subcluster cores Fe(1)Fe(2)S(1)S(3) and Fe(3)Fe(4)S(3)S(4) joined to a spiran type of μ_4-S, i.e., S(3) atom. In addition, the two substituents t-Bu and t-BuS on the subclusters are bound to S(1) and S(4) atoms by an equatorial type of bond,[9] and each of the three CO's attached to Fe(1), Fe(2), Fe(3), and Fe(4) is terminal. So, this structure is in good agreement with its elemental analysis and spectroscopic data. For example, the IR spectrum of **6a** showed six absorption bands in the range 2082−1970 cm^{-1} characteristic of its terminal carbonyls,[10] and the ^{1}H NMR spectrum

(5) King, R. B. *Orgnometallic Syntheses; Transition-Metal Compounds*; Academic Press: New York, 1965; Vol. 1, p 95.

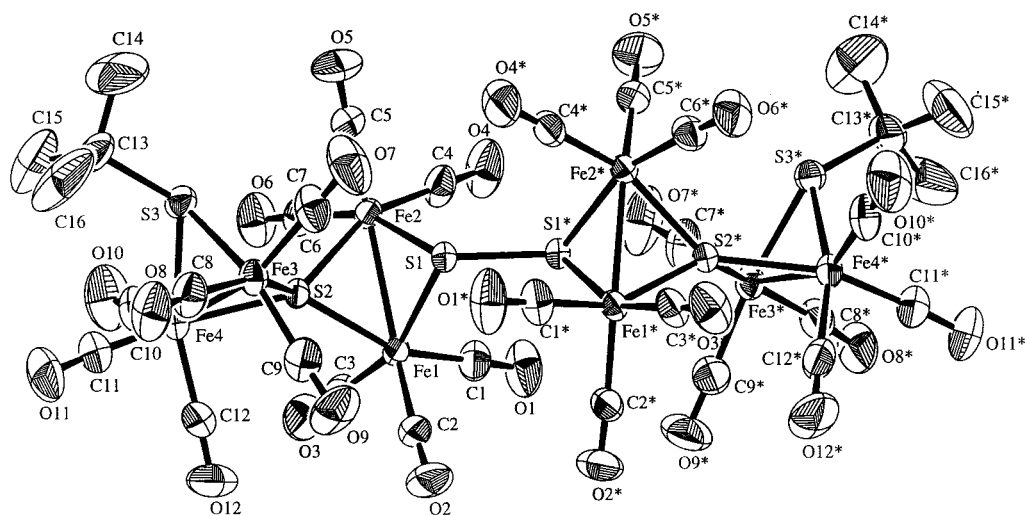(6) Serferth, D.; Womack, G. B.; Dewan, J. C. *Organometallics* **1985**, *4*, 398.

(7) Characterization data for **5a**,**b** and **6a**,**b** are as follows. **5a**: mp 103 °C dec. Anal. Calcd for C$_{16}$H$_{10}$Fe$_4$O$_{12}$S$_4$: C, 25.76; H, 1.34. Found: C, 25.64; H, 1.30. IR (KBr disk): 2085(m), 2057(s), 2034(vs), 2015(s), 1996(s), 1980(vs) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.36 (t, J = 7.1 Hz, 3H, SCH$_2$CH_3), 1.46 (t, J = 7.1 Hz, 3H, S$_2$CH$_2$CH_3), 2.45 (q, J = 7.1 Hz, 2H, SCH_2), 2.95 (q, J = 7.1 Hz, 2H, S$_2$CH_2) ppm. **5b**: mp 162 °C dec. Anal. Calcd for C$_{28}$H$_{10}$Fe$_8$O$_{24}$S$_6$: C, 24.55; H, 0.73. Found: C, 24.97; H, 1.00. IR (KBr disk): 2081(m), 2059(vs), 2037(vs), 1992(s) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.34 (t, J = 6.9 Hz, 6H, 2CH$_3$), 2.43 (q, J = 6.9 Hz, 4H, 2CH$_2$) ppm. **6a**: mp 140 °C dec. Anal. Calcd for C$_{20}$H$_{18}$Fe$_4$O$_{12}$S$_4$: C, 29.95; H, 2.26. Found: C, 29.68; H, 2.27. IR (KBr disk): 2082(m), 2057(s), 2036(vs), 2016(s), 1991(vs), 1970(s) cm^{-1}.^{1}H NMR (CDCl$_3$): δ 1.44 (s, 9H, t-BuS), 1.48 (s, 9H, t-BuS$_2$) ppm. **6b**: mp 174 °C dec. Anal. Calcd for C$_{32}$H$_{18}$Fe$_8$O$_{24}$S$_6$: C, 26.96; H, 1.27. Found: C, 27.39; H, 1.30. IR (KBr disk): 2081(s), 2057(s), 2035(vs), 1987(vs) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.41 (s 18H, 2t-Bu) ppm.

(8) **6a**: Crystal diffraction measurements were made on a CAD-4 diffractometer with Mo Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods: orthorhombic, $P2_12_12_1$ (No. 19), a = 9.022(2) Å, b = 20.309(3) Å, c = 17.112(4) Å, V = 3135(2) Å^3, D_c = 1.699 g cm^{-3}, μ = 2.1228 mm^{-1}, $F(000)$ = 1608, Z = 4, 2951 measured reflections, 2804 independent reflections, R = 0.081, R_w = 0.089. **6b**: Crystal diffraction measurements were made on a Rigaku AFC7R diffractometer with Mo Kα radiation (λ = 0.71069 Å). The structure was solved by direct methods: monoclinic $C2/c$ (No. 15), a = 36.442(5) Å, b = 15.0.692(3) Å, c = 9.171(1) Å, β = 97.66 (1)°, V = 5197(1)Å^3, D_c = 1.822 g cm^{-3}, μ = 2.481 mm^{-1}, $F(000)$ = 2824, Z = 4, 4805 measured reflections, 4567 independent reflections, R = 0.030, R_w = 0.038.

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

(10) Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry;* University Science Books: Mill Valley, CA, 1980; p 81.

Figure 1. ORTEP drawing of complex **6a**. Selected bond lengths (Å) and angles (deg): Fe(1)−Fe(2), 2.527(3); Fe-(3)−Fe(4), 2.545(3); S(1)−Fe(1), 2.242(4); S(3)−Fe(1), 2.253-(3); S(1)−S(2), 2.076(5); Fe(4)−S(4), 2.280(4); Fe(1)−S(1)−S(2), 116.0(2); Fe(1)−S(1)−Fe(2), 68.5(1); Fe(1)−S(3)−Fe(2), 68.0(1); S(1)−Fe(1)−S(3), 75.9(1); S(3)−Fe(3)−S(4), 76.1-(1); Fe(3)−S(4)−Fe(4), 67.8(1).

displayed one singlet at 1.44 ppm for its equatorial t-Bu[11] attached to S(4) and one singlet at 1.48 ppm for the substituent t-BuS attached to S(1), respectively. From Figure 2 it can be seen that **6b** is symmetric with respect to a mirror plane which is through the midpoint of the S1−S1* bond and perpendicular to the S1−S1* bond. In addition, **6b** consists of four butterfly subclusters. The first and second subcluster cores S3Fe3Fe4S2 and S2Fe2Fe1S1 share a spiran S2 atom, whereas the third and fourth subcluster cores S1*Fe1*Fe2*S2* and S2*Fe3*Fe4*S3* are joined to a spiran S2* atom. Figure 2 shows that there is an equatorial type of S1−S1* bond in **6b**, which is necessary to avoid the axial−axial repulsions[3a,9] between the S1* atom and the structural moiety axially attached to the spiran S2 atom, as well as between S1 and that axially attached to the spiran S2* atom. Similar to **6a** the two substituents t-Bu are bonded to the S3 and S3* atoms by an equatorial type of bond, and each of the three CO's attached to each of the iron atoms is terminal. These are consistent with its ^{1}H NMR spectrum showing only one singlet at 1.41 ppm for two identical t-Bu's[11] and its IR spectrum exhibiting four absorption bands in the range 2081−1987 cm^{-1} for all the carbonyls.[10]

As described above, **6a** contains two butterfly Fe$_2$S$_2$ subcluster cores, whereas **6b** contains four. In these subcluster cores, the bond lengths and angles are very similar. Fo example, while the average Fe−Fe bond lengths of **6a** and **6b** are 2.536(3) and 2.517(8) Å, the average Fe−S bond lengths of **6a** and **6b** equal 2.259-(4) and 2.257(1) Å. However, although in **6b** the dihedral angle between the two butterfly wings of each subcluster core is almost the same (95.94° and 95.78°), that in **6a** is quite different (95.7° for subcluster core Fe(1)Fe(2)S-(1)S(3) and 83.6° for Fe(3)Fe(4)S(3)S(4)). It is worth noting that, to our knowledge, **6a** and **6b** are respectively the first double butterfly Fe/S cluster complex

(11) De Beer, J. A.; Haines, R. J. *J. Organomet. Chem.* **1970**, *24*, 755.

Figure 2. ORTEP drawing of complex **6b**. Selected bond lengths (Å) and angles (deg): Fe(1)−Fe(2), 2.5307(7); Fe(3)−Fe(4), 2.5303(8); S(1)−Fe(1), 2.257(1); S(2)−Fe(2), 2.258(1); S(3)−Fe(3), 2.272(1); S(1)−S(1)*, 2.113(2); Fe(1)−S(1)−S(1)*, 106.49(5); Fe(1)−S(2)−Fe(2), 68.48(3); Fe(3)−S(3)−Fe(4), 67.79(4); S(1)−Fe(1)−S(2), 76.01(4); S(2)−Fe(3)−S(3), 75.72(4).

containing a bridging alkylperchalcogenido ligand η^2-RS_2 and the longest multibutterfly Fe/S cluster complex (nonbonded distance C13···C13* = 0.92 nm) prepared and crystallographically characterized so far, although some single, double, and even triple butterfly Fe/E cluster complexes are prepared and crystallographically studied, such as $(\mu\text{-EtS})_2Fe_2(CO)_6$,[12] $[(\mu\text{-MeS})Fe_2(CO)_6]$-$(\mu_4\text{-S})$,[13] $[(\mu\text{-EtS})Fe_2(CO)_6][(\mu\text{-PhS})Fe_2(CO)_6](\mu_4\text{-S})$,[14] $[(\mu\text{-EtS})Fe_2(CO)_6]_2(\mu_4\text{-Se})$,[3h] $[(\mu\text{-}p\text{-MeC}_6H_4Se)Fe_2(CO)_6]_2(\mu_4\text{-Se})$,[15] $[(\mu\text{-PhS})Fe_2(CO)_6][(\mu\text{-S}-\text{S-}\mu)$,[3c] $[(\mu\text{-MeS})Fe_2(CO)_6]_2[\mu\text{-S-}(m\text{-CH}_2C_6H_4CH_2)\text{-S-}\mu]$,[3g] $[(\mu\text{-}t\text{-BuS})Fe_2(CO)_6]_2[\mu_4\text{-}SFe_2(CO)_6\text{-S-}\mu_4]$,[4b] and $[(\mu\text{-}n\text{-BuSe})Fe_2(CO)_6]_2(\mu_4\text{-Se})$.[16]

It should be pointed out that the reaction mechanism is up to now unclear. However, this reaction can be reasonably regarded as including both the hetero-oxidative coupling of **4a** with an excess of $RS^-[Et_3NH^+]$ (formed in the course of preparation of **4a**) and the homo-oxidative coupling of **4a** itself under the action of succinyl chloride (Scheme 3).

It follows that the double butterfly Fe/S cluster anion **4a** is completely different from the single butterfly Fe/S cluster anions **1** in chemical behavior toward both diacid chlorides and SO_2Cl_2. That is, while complexes **1** react with diacid chlorides to give double Fe/S clusters **2** and **3**,[3d,e] reaction of **4a** with succinyl chloride in the presence of mercaptide anions RS^- gives the oxidative coupling type of double and quadruple clusters **5a**,**b** and

Scheme 3
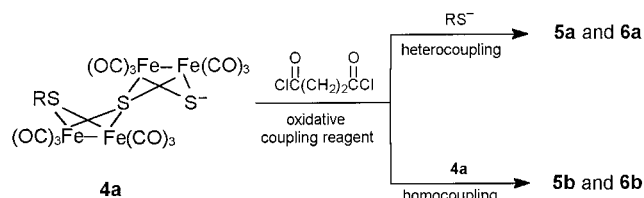
6a,**b**. In addition, while complexes **1** react with SO_2Cl_2 to give the oxidative coupling type of double Fe/S clusters $[(\mu\text{-RS})Fe_2(CO)_6](\mu\text{-S}-\text{S-}\mu)$,[3c,h] reaction of **4a** with SO_2Cl_2 in the presence of excess $[(\mu\text{-RS})(\mu\text{-CO})Fe_2(CO)_6]^-$ anions affords triple butterfly clusters $[(\mu\text{-RS})Fe_2(CO)_6]_2(\mu_4\text{-S})Fe_2(CO)_6(\mu_4\text{-S})]$.[4b]

At present, the mechanisms for the novel reaction that yields double and quadruple clusters **5a**,**b** and **6a**,**b**, as well as other novel reactions of anions **4a** and **4b**, to afford nanometer-scale multibutterfly clusters that may have unique optical and electronic properties are under intensive study.

Supporting Information Available: Details describing synthesis and characterization of complexes **5a**,**b** and **6a**,**b** and details of structural determinations of **6a** and **6b**, including atomic coordinates, equivalent isotropic displacement parameters, bond lengths and angles, and data collection and processing parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

OM9907019

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

(16) Mathur, P.; Trivedi, R.; Satyanarayana, C. V. V. *Organometllics* **1996**, *15*, 1062.