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The First Example of Macrocycles Containing Butterfly Transition Metal Cluster Cores via Novel Tandem Reactions

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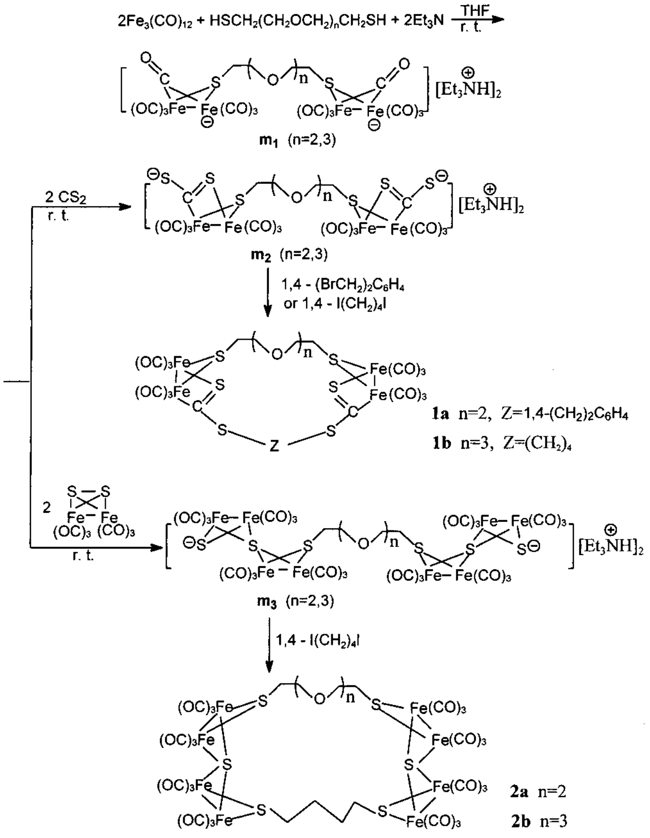
Received January 28, 2002

In a new development in transition metal chemistry, we recently reported a class of macrocycles, which contain tetrahedral Mo_2FeS cluster cores and are formed by a self-assembly cyclization reaction.[1] Macrocycles are of great importance in theory and practical applications.[2,3] Furthermore, the macrocycles containing metal cluster cores along with their synthetic methods are little known up to now.[1,4] So, we are interested in studying the new synthetic methodology by which such macrocycles could be synthesized. Herein we report the synthesis, full characterization, and X-ray structures of the first macrocycles containing butterfly Fe_2S_2C and Fe_2S_2 cluster cores, generated through two novel tandem reactions.

Interestingly, the tandem reactions for production of such macrocycles, for example, **1a**,**b** and **2a**,**b** shown in Scheme 1, involve an intermediate $[Et_3NH]^+$ salt of the ether-chain $CH_2(CH_2OCH_2)_nCH_2$ ($n = 2, 3$)-bridged double μ-CO, double butterfly Fe_2SC dianion $\mathbf{m_1}$**,** formed from the corresponding dithiol, $Fe_3(CO)_{12}$ and Et_3N. More interestingly, the $[Et_3NH]^+$ salt of dianion $\mathbf{m_1}$ reacts in situ with two molecules of CS_2 (via double nucleophilic attack of the two negatively charged Fe atoms in $\mathbf{m_1}$ at the two C atoms in two CS_2 followed by loss of the two μ-CO ligands in $\mathbf{m_1}$) to give another intermediate $[Et_3NH]^+$ salt of double butterfly Fe_2S_2C dianion $\mathbf{m_2}$, which reacts further in situ with 1,4-di(bromomethyl)benzene or 1,4-diiodobutane to afford products **1a**,**b**.[5] Similarly, the $[Et_3NH]^+$ salt of dianion $\mathbf{m_1}$ reacts in situ with two molecules of $(\mu\text{-}S_2)Fe_2(CO)_6$ (via double nucleophilic attack of the two negatively charged Fe atoms in $\mathbf{m_1}$ at one S atom in each $(\mu\text{-}S_2)Fe_2(CO)_6$ followed by loss of the two μ-CO ligands in $\mathbf{m_1}$) to afford an intermediate $[Et_3NH]^+$ salt of the double butterfly Fe_2S_2 anion $\mathbf{m_3}$, which reacts further in situ with 1,4-diiodobutane to yield products **2a**,**b**.[6]

It is worth pointing out that although the single μ-CO, single butterfly monoanion of type $[(\mu\text{-RS})(\mu\text{-CO})Fe_2(CO)_6]^-$ has been known since 1985[7] and is well-studied so far for its chemical reactivities,[8] the novel type of double μ-CO, double butterfly dianion $\mathbf{m_1}$ is now first prepared and investigated. The formation of dianion $\mathbf{m_1}$ can be recognized by the presence of an absorption band characteristic of μ-CO in the IR spectrum of its THF solution. For example, the $[Et_3NH]^+$ salt of dianion $\mathbf{m_1}$ ($Z = CH_2(CH_2OCH_2)_3CH_2$) in THF solution showed an absorption band at 1744 cm^{-1}, which is very close to that displayed by the $[Et_3NH]^+$ salt of monoanion $[(\mu\text{-EtS})(\mu\text{-CO})Fe_2(CO)_6]^-$.[7] Actually, the well-studied chemistry of the single μ-CO cluster monoanion $[(\mu\text{-RS})(\mu\text{-CO})Fe_2(CO)_6]^-$,[7,8] and particularly the fully characterized macrocyclic products **1a**,**b** and **2a**,**b** (vide infra), strongly supports the formation of the intermediate $[Et_3NH]^+$ salt of the double μ-CO, double butterfly dianion $\mathbf{m_1}$. In addition, we have proved that the $[Et_3NH]^+$ salt of dianion $\mathbf{m_1}$ can be formed in quite high yield. This is because we prepared its acyclic derivative $[(\mu\text{-}S{=}C{-}SCH_2Ph)Fe_2(CO)_6]_2[\mu\text{-}SCH_2(CH_2O\ CH_2)_2CH_2S\text{-}\mu]$ through reaction of the corresponding $\mathbf{m_1}$ with CS_2 followed by treatment of the corresponding $\mathbf{m_2}$ with $PhCH_2Br$ in 65% yield. So, in view of the easy availability of dianion $\mathbf{m_1}$ with high yield and because of its high nucleophilic reactivity, it would be potentially very useful in the development of transition metal chemistry.

Scheme 1



The molecular structures of **1a** and **2b** were established by X-ray crystallography.[9] Figure 1 shows that **1a** contains two butterfly subclusters Fe(1)Fe(2)S(2)S(1)C(13) and Fe(3)Fe(4)S(6)S(5)C(22), which are connected by the ether chain and 1,4-di(thiomethyl)benzene group to give a 24-membered macrocycle. The ether chain is bonded to S(2) and S(6) of the subcluster cores by an equatorial type of bond,[10] which is consistent with its ^1H NMR data of the SCH_2 group being greater than 2 ppm.[11] In addition, the 1,4-di(thiomethyl)benzene group is bound to the subclusters through C(13)−S(3) and C(22)−S(4) bonds lying in the planes of Fe(1)Fe(2)S(1)C(13)S(3) and Fe(3)Fe(4)S(5)C(22)S(4), respec-

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10.1021/ja020151x CCC: $22.00

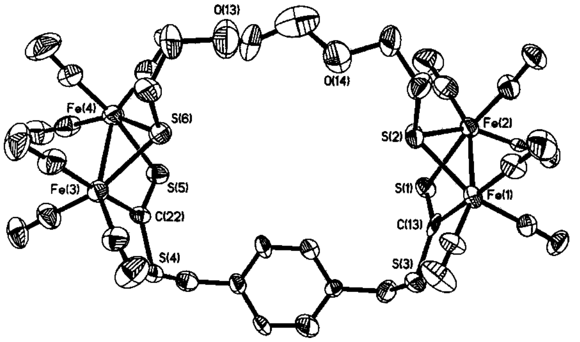

Figure 1. ORTEP diagram of **1a.** Selected bond lengths (Å) and angles (deg): Fe(1)−Fe(2) 2.618(3), Fe(3)−Fe(4) 2.615(3), Fe(2)−S(1) 2.303(3), Fe(1)−S(2) 2.248(4), Fe(1)−C(13) 1.999(13); Fe(1)−S(2)−Fe(2) 71.32(11), Fe(3)−S(6)−Fe(4) 71.13(12), S(1)−Fe(2)−Fe(1) 76.21(11), S(2)−Fe(1)−Fe(2) 54.23 (10).

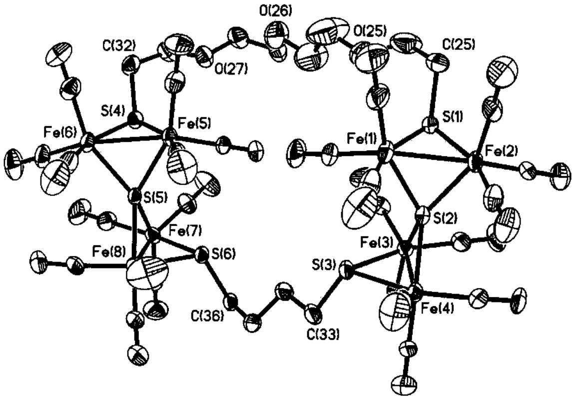

Figure 2. ORTEP diagram of **2b**. Selected bond lengths (Å) and angles (deg): Fe(1)−Fe(2) 2.542(2), Fe(3)−Fe(4) 2.537(2), Fe(1)−S(1) 2.258(4), Fe(1)−S(2) 2.243(3); Fe(1)−S(1)−Fe(2) 68.55(11), Fe(1)−S(2)−Fe(2) 69.27(10), S(1)−Fe(1)−Fe(2) 55.68(9), S(3)−Fe(3)−Fe(4) 55.79(9), S(1)−Fe(1)−S(2) 76.93(11).

tively. The twelve carbonyls bonded to Fe(1), Fe(2), Fe(3), and Fe(4) are terminal, which are in accord with their IR spectra displaying several absorption bands in the range 2074−1981 cm^{-1}.

Figure 2 indicates that **2b** contains four butterfly subcluster cores, in which Fe(1)Fe(2)S(1)S(2) and Fe(3)Fe(4)S(2)S(3) joined to a spiro type of S(2) atom, whereas Fe(5)Fe(6)S(4)S(5) and Fe(7)Fe(8)S(5)S(6) joined to a spiro S(5) atom. In addition, while S(1) and S(4) atoms are bonded to C(25) and C(32) atoms of the ether chain, S(3) and S(6) atoms are bound to C(33) and C(36) atoms of the butylene group to form a 25-membered macrocycle. It should be noted that both the ether chain and the butylene group are attached to the subclusters by an equatorial type of bond,[10] which is necessary to avoid the axial−axial repulsions between the ether chain with the axially bonded subclusters Fe(3)Fe(4)S(2)S(3) and Fe(7)Fe(8)S(5)S(6) or the butylene group with subclusters Fe(1)Fe(2)S(1)S(2) and Fe(5)Fe(6)S(4)S(5).[12] It is also worthy of note that each of the 24 CO's attached to eight Fe atoms from Fe(1) to Fe(8) is terminal, which is in good agreement with its IR spectrum showing several absorption bands in the range 2084−1987 cm^{-1}.

Such macrocycles can be regarded as an unique type of organometallic crown ether and thus they might have some applications in numerous fields, such as catalysis and molecular recognition.[1−3] Studies are underway to apply such tandem reactions for synthesis of other novel macrocyclic and acyclic cluster complexes. New chemical reactivities concerning the double μ-CO, double butterfly dianion $\mathbf{m_1}$ and their applications are also under extensive investigation.

Acknowledgment. We are grateful to the National Natural Science Foundation of China, the State Key Laboratory of Organometallic Chemistry, and the State Key Laboratory of Structural Chemistry for financial support of this work.

Supporting Information Available: An X-ray crystallographic file for **1a** and **2b** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(5) Synthesis of **1a** and **1b** was performed in Schlenk flasks under dry nitrogen. A mixture of $Fe_3(CO)_{12}$ (1.00 g, 2.0 mmol), THF (30 mL), $HSCH_2(CH_2OCH_2)_2CH_2SH$ (0.18 g, 1.0 mmol) or $HSCH_2(CH_2OCH_2)_3CH_2SH$ (0.23 g, 1.0 mmol), and Et_3N (0.28 mL, 2.0 mmol) was stirred at room temperature for ca. 0.5 h to give a brown-red solution containing the $[Et_3NH]^+$ salt of the dianion $[(\mu\text{-CO})Fe_2(CO)_6]_2[(\mu\text{-SCH}_2(CH_2OCH_2)_nCH_2S\text{-}\mu)]$ ($\mathbf{m_1}$, $n = 2$ or 3). To the solution was added CS_2 (0.24 mL, 4.0 mmol) and the mixture was stirred at room temperature for 0.5 h. Then, 1,4-$(BrCH_2)_2C_6H_4$ (0.26 g, 1.0 mmol) for preparation of **1a** or $I(CH_2)_4I$ (0.13 mL, 1.0 mmol) for preparation of **1b** was added and the mixture was stirred at room temperature for 12 h. Solvent was removed under reduced pressure. The residue was subjected to TLC separation using CH_2Cl_2/petroleum ether (v/v = 3:2 or 2:1) as eluent. From the main red band **1a** or **1b** was obtained as a red solid. **1a**: yield 0.144 g (15%); mp 104−106 °C. IR (KBr disk): $\nu_{C\equiv O}$ 2074 (s), 2018 (vs), 1981 (vs); ν_{C-O} 1105 (m); $\nu_{C=S}$ 1014 (m) cm^{-1}. ^1H NMR ($CDCl_3$): 2.81 (br s, 4H, $2SCH_2$), 3.72−3.85 (m, 8H, $4CH_2O$), 4.20−4.45 (m, 4H, $2SCH_2Ar$), 7.15 (s, 4H, C_6H_4) ppm. **1b**: yield 0.110 g (11%); mp 107−108 °C. IR (KBr disk): $\nu_{C\equiv O}$ 2066 (vs), 2024 (vs), 1993 (vs); ν_{C-O} 1107 (m); $\nu_{C=S}$ 1017 (m) cm^{-1}. ^1H NMR ($CDCl_3$): 1.68 (br s, 4H, $SCH_2CH_2CH_2CH_2S$), 2.80 (br s, 8H, $4SCH_2$), 3.65−4.05 (m, 12H, $6CH_2O$) ppm.

(6) Synthesis of **2a** and **2b**: To the solution containing the $[Et_3NH]^+$ salt of dianion $\mathbf{m_1}$ ($n = 2$ or 3) prepared as described above was added $(\mu\text{-S}_2)Fe_2(CO)_6$ (0.688 g, 2.0 mmol) and the mixture was stirred at room temperature for 2 h. To the resulting mixture was added $I(CH_2)_4I$ (0.13 mL, 1.0 mmol) and the reaction mixture was stirred at room temperature for 24 h. Solvent was removed under reduced pressure. The residue was subjected to TLC separation using CH_2Cl_2/petroleum ether (v/v = 2:1) as eluent. From the main red band **2a** or **2b** was obtained as a red solid. **2a**: yield 0.240 g (16%); mp 170 °C dec. IR (KBr disk): $\nu_{C\equiv O}$ 2084 (m), 2057 (s), 2034 (vs), 1989 (vs); ν_{C-O} 1121(m) cm^{-1}. ^1H NMR ($CDCl_3$): 1.84 (br s, 4H, $CH_2CH_2CH_2CH_2$), 2.30−2.85 (m, 8H, $4SCH_2$), 3.55−3.85 (m, 8H, $4CH_2O$) ppm. **2b**: yield 0.270 g (18%); mp 210 °C dec. IR (KBr disk): $\nu_{C\equiv O}$ 2084 (m), 2043 (s), 2033 (vs), 1987 (s); ν_{C-O} 1116 (w) cm^{-1}. ^1H NMR ($CDCl_3$): 1.80−2.00 (m, 4H, $CH_2CH_2CH_2CH_2$), 2.40−2.80 (m, 8H, $4SCH_2$), 3.60−3.83 (m, 12H, $6CH_2O$) ppm.

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(9) X-ray data for **1a**, with **2b** in parentheses, $C_{28}H_{20}Fe_4O_{14}S_6\cdot{}^1/_2CH_3OH$ ($C_{36}H_{24}Fe_8O_{27}S_6\cdot CH_2Cl_2\cdot 1/2H_2O$): triclinic (triclinic), $P1$ ($P1$), $a = 8.198(3)$ (12.643 (4)) Å, $b = 14.912(6)$ (15.601(6)) Å, $c = 19.402(7)$ (16.768(6)) Å, $\alpha = 104.457(8)$ (82.643(6))°, $\beta = 97.953(8)$ (70.777(6))°, $\gamma = 102.998(8)$ (84.743(7))°, $F(000) = 1018$ (1614), $R = 0.0737$ (0.0688), $R_w = 0.1197$ (0.1470), GOF = 0.862 (0.980).

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JA020151X