The First Examples of Organometallic Crown Ethers Containing Redox-Active Tetrahedral $Mo_2Fe(\mu_3\text{-}S)$ Cluster Cores via a Novel Self-Assembly Cyclization Reaction

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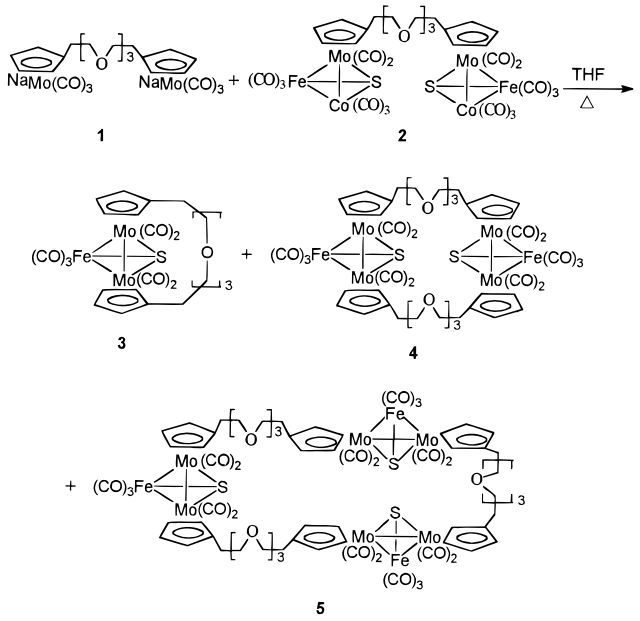
Summary: Three novel organometallic crown ethers with a general formula $[Mo_2Fe(\mu_3\text{-}S)(CO)_7]_n[\eta^5\text{-}C_5H_4CH_2(CH_2OCH_2)_3CH_2C_5H_4\text{-}\eta^5]_n$ (**3**, $n = 1$; **4**, $n = 2$; **5**, $n = 3$) *were synthesized through an unexpected cyclization reaction of* $[\eta^5\text{-}C_5H_4CH_2(CH_2OCH_2)_3CH_2C_5H_4\text{-}\eta^5][(CO)_3MoNa]_2$ (**1**) *with* $[MoCoFe(\mu_3\text{-}S)(CO)_8]_2[\eta^5\text{-}C_5H_4\ CH_2(CH_2OCH_2)_3\text{-}CH_2C_5H_4\text{-}\eta^5]$ (**2**). *The crystal structure of* **3** *and one of the possible pathways for formation of* **3**−**5** *are briefly discussed.*

Since crown ethers were discovered in 1967,[1] a great variety of crown ethers, including those organometallic ones, have been synthesized and widely utilized in numerous fields, such as catalytic organic synthesis, molecular recognition, and chemical sensor technology.[2−7] However, although the first organometallic crown ether $[\eta^5\text{-}C_5H_4OCH_2(CH_2OCH_2)_3CH_2OC_5H_4\text{-}\eta^5]Fe$ appeared in 1986,[8] no organometallic crown ethers that contain metal cluster cores have been reported yet in the literature up to now. Fortunately, we recently found that the polyether chain-bridged dicyclopentadienylbis-(tricarbonylmolybdenumsodium) (**1**),[9] prepared from $Mo(CO)_6$ and $NaC_5H_4CH_2(CH_2OCH_2)_3CH_2C_5H_4Na$[9] in THF at reflux, reacted with the polyether chain-bridged dicyclopentadienyl double cluster $[MoCoFe(\mu_3\text{-}S)(CO)_8]_2\text{-}[\eta^5\text{-}C_5H_4CH_2\ (CH_2OCH_2)_3CH_2C_5H_4\text{-}\eta^5]$ (**2**),[9] through an unexpected self-assembly cyclization reaction, to give three organometallic crown ethers containing a single, double, and triple tetrahedral $[Mo_2Fe(\mu_3\text{-}S)]$ cluster core with a general formula $[Mo_2Fe(\mu_3\text{-}S)(CO)_7]_n[\eta^5\text{-}C_5H_4\text{-}CH_2(CH_2OCH_2)_3CH_2C_5H_4\text{-}\eta^5]_n$ in 53% total yield (**3**, $n = 1$; **4**, $n = 2$; **5**, $n = 3$) (Scheme 1).

Scheme 1



The preparations of **3**−**5** were performed in a Schlenk flask under dry nitrogen. A mixture of $Mo(CO)_6$ (0.264 g, 1.0 mmol), $NaC_5H_4CH_2(CH_2OCH_2)_3CH_2C_5H_4Na$ (0.5 mmol), and THF(10 mL) was refluxed for 20 h. To this reaction mixture was added $[MoCoFe(\mu_3\text{-}S)(CO)_8]_2[\eta^5\text{-}C_5H_4CH_2(CH_2OCH_2)_3CH_2C_5H_4\text{-}\eta^5]$ (**2**, 0.490 g, 0.4 mmol) and THF (30 mL), and the new reaction mixture continued to reflux for 50 h. The solvent was removed in a vacuum to give a residue, which was subjected to TLC separation using 6:5 (v/v) THF/petroleum ether as eluent to give **3** (0.151 g, 25%), **4** (0.106 g, 17%), and **5** (0.068 g, 11%) sequentially.

Cluster crown ethers **3**−**5** have been characterized by elemental analysis, IR, ^1H NMR, and FAB MS spectroscopies,[10] as well as for **3** by X-ray diffraction analysis.[11] For example, in the ^1H NMR spectra of **3**−**5**, while for **3** the α-CH_2 groups and their neighboring β-CH_2 groups show two multiplets respectively in the ranges 2.57−2.84 and 3.47−3.79 ppm, for **4** and **5** the α-CH_2 and β-CH_2 groups display two singlets respectively at ca. 2.64 and ca. 3.60 ppm. The different ^1H NMR behavior of α-CH_2 and β-CH_2 of **3** from that of **4** and **5** might be ascribed to the restricted rotation of the polyether chain in the smaller ring of **3** and the capable free rotation of the polyether chain in the larger rings of **4** and **5**; that is, the restricted rotation in the former

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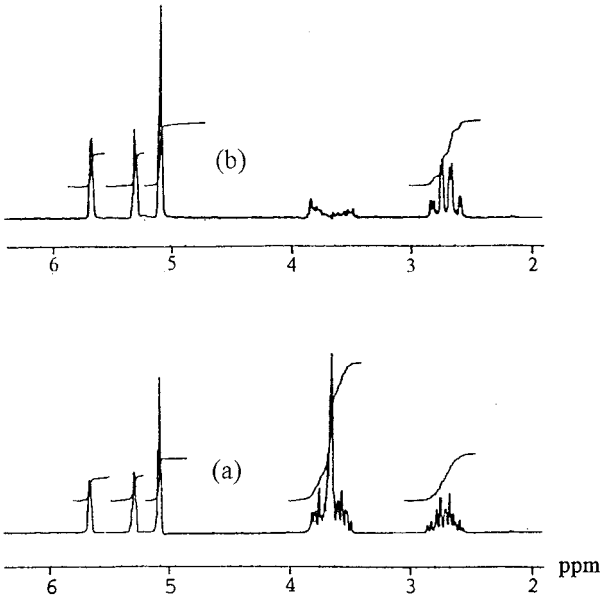

Figure 1. Original ^{1}H NMR (a) and decompling ^{1}H NMR (b) spectra of **3**.

would make the two hydrogen atoms of each α-CH_2 (or β-CH_2) in **3** magnetically unequivalent, showing first a quartet and then a multiplet through coupling between α-CH_2 and β-CH_2, whereas the free rotation in the latter would make the two hydrogen atoms of each α-CH_2 (or β-CH_2) in **4** and **5** become magnetically equivalent to show a singlet. This deduction can be proved by the decoupling ^{1}H NMR spectrum of **3**, in which the complicated multiplet for β-CH_2 in the original spectrum almost disappears and the two very close quartets should be attributed to the very similar two α-CH_2 bonded to the corresponding Cp rings (Figure 1). The FAB MS spectra of **3**−**5** show their molecular ion peaks at M^+, and the ICP analyses of **3**−**5** indicate no Co atom present and a 2:1 stoichiometry of Mo:Fe atoms, which are consistent with the macrocyclic structures shown in Scheme 1.

The X-ray diffraction analysis of **3** showed that there are two crystallographically independent molecules contained in the unit cell with very similar crystallographic data. For simplicity only the ORTEP drawing of one of the two molecules is given in Figure 2. Figure 2 indicates that **3** consists of a distorted tetrahedral $Mo_2Fe(\mu_3\text{-}S)$ cluster core, which carries one ligand, 1,1′-(3, 6, 9-trioxaundecamethylene)dicyclopentadienyl, coordinated to two Mo atoms, two sets of two CO ligands attached to two Mo atoms, and three CO ligands bonded to the Fe atom. This molecule could be viewed as a size-

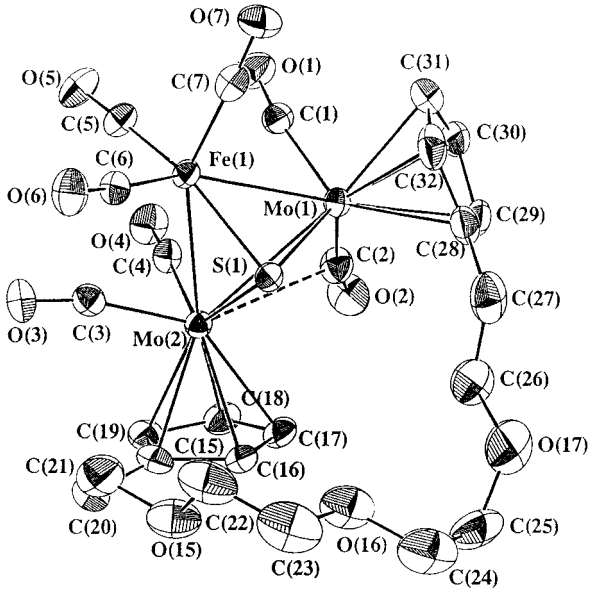

Figure 2. ORTEP drawing of **3** (thermal ellipsoids with 30% probability). Selected bond lengths (Å) and angles (deg.): Mo(1)−Fe(1) 2.796(1), Mo(1)−Mo(2) 3.042(1), Mo(2)−Fe(1) 2.825(1), Fe(1)−S(1) 2.196(2), Mo(1)−S(1) 2.366(2); Fe(1)−Mo(1)−Mo(2) 57.69(3), S(1)−Mo(1)−Fe(1) 49.49(5), Mo(1)−Fe(1)−Mo(2) 65.53(3), Fe(1)−S(1)−Mo(1) 75.50(7).

varied macrocyclic crown ether containing three oxygen atoms and one sulfur atom, depending on which carbon atoms of the two Cp rings C(15)-through-C(19) and C(28)-through-C(32) and which metal atoms of Mo(1), Mo(2), and Fe(1) are involved in counting the ring size.

This molecule is asymmetric, so that the two α-hydrogen atoms attached to C(20) or C(27) and those β-hydrogen atoms attached to C(21) or C(26) are magnetically unequivalent. This is in accordance with the ^{1}H NMR spectrum displayed by α-CH_2 and β-CH_2 groups in **3** described above. In addition, among the seven carbonyls attached to metals, while the three carbonyls attached to Fe(1) and one carbonyl attached to Mo(1), i.e., C(4)O(4), are terminal, the other three carbonyls attached to Mo(1) and Mo(2), i.e., C(1)O(1), C(2)O(2), and C(3)O(3), are semibridging. This is because the asymmetric parameters of C(1)O(1), C(2)O(2), and C(3)O(3) are 0.43, 0.48, and 0.35, which fall within the range of α values for semibridging carbonyls.[12] The existence of both terminal and semibridging CO's confirmed by X-ray diffraction is in good agreement with the fact that the IR spectrum of **3** showed absorption bands ranging from 1840 to 2029 cm^{-1}.

At present, the self-assembly cyclization for the formation of cluster crown ethers **3**−**5** is not completely understood. However, we might suggest a possible pathway (Scheme 2) to account for the reaction, on the

(10) Characterization data for **3**−**5** are as follows. **3**: mp 172 °C dec. Anal. Calcd for $C_{25}H_{24}FeMo_2O_{10}S$: C, 39.29; H, 3.17. Found: C, 39.38; H, 3.11. IR (KBr disk): $\nu_{C\equiv O}$ 2029(vs), 1982(vs), 1952(vs), 1929(vs), 1908(vs), 1895(vs), 1865(vs), 1840(vs) cm^{-1}, ν_{C-O-C} 1108(m) cm^{-1}. ^{1}H NMR(200 MHz, $CDCl_3$): δ 2.57−2.84(m, 4H, $2C_5H_4CH_2$), 3.47−3.79(m, 12H, $6CH_2O$), 5.06(t, 4H, H^2, $H^{2'}$, H^5, $H^{5'}$), 5.28, 5.65(s, s, 4H, H^3, $H^{3'}$, H^4, $H^{4'}$) ppm. MS, *m/z* (^{98}Mo): 768(M^+, 14%). **4**: mp 64−66 °C. Anal. Calcd for $C_{50}H_{48}Fe_2Mo_4O_{20}S_2$: C, 39.29; H, 3.17. Found: C, 39.57; H, 3.09. IR (KBr disk): $\nu_{C\equiv O}$ 2034(vs), 1975(vs), 1886(s), 1830(s) cm^{-1}, ν_{C-O-C} 1102(m) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.65(s, 8H, $4C_5H_4CH_2$), 3.62(s, 24H, $12CH_2O$), 5.19−5.31(m, 16H, $4C_5H_4$) ppm. MS, *m/z* (^{98}Mo): 1536(M^+, 15%). **5**: mp 51−52 °C. Anal. Calcd for $C_{75}H_{72}Fe_3Mo_6O_{30}S_3$: C, 39.29; H, 3.17. Found: C, 39.51; H, 3.19. IR (KBr disk): $\nu_{C\equiv O}$ 2033(vs), 1974(vs), 1886(s), 1830(s) cm^{-1}, ν_{C-O-C} 1109(m) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.63(s, 12H, $6C_5H_4CH_2$), 3.61(s, 36H, $18CH_2O$), 5.15−5.31(m, 24H, $6C_5H_4$) ppm. MS, *m/z* (^{96}Mo): 2292(M^+, 51%).

(11) Crystal data for **3**: M_r 764.25, monoclinic, $P2_1$ (no. 4), a = 11.389(2) Å, b = 17.440(4) Å, c = 14.726(2) Å, β = 109.17(1)°, V = 2762.6(9) Å^3, Z = 4, D_{calc} = 1.837 g cm^{-3}, $F(000)$ = 1520, μ = 15.16 cm^{-1}, Mo Kα radiation (λ = 0.71069 Å), $2\theta_{max}$ = 53.9°, scan mode ω−2θ, no. observations ($I > 3.00\sigma(I)$) 5994, no. variables 747, R = 0.045, R_w = 0.054. The structure was solved by a direct method. The final refinement was accomplished by a full-matrix least-squares method with anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were included but not refined. All calculations were performed on a Micro-Vax II computer using the TEXASAN program system.

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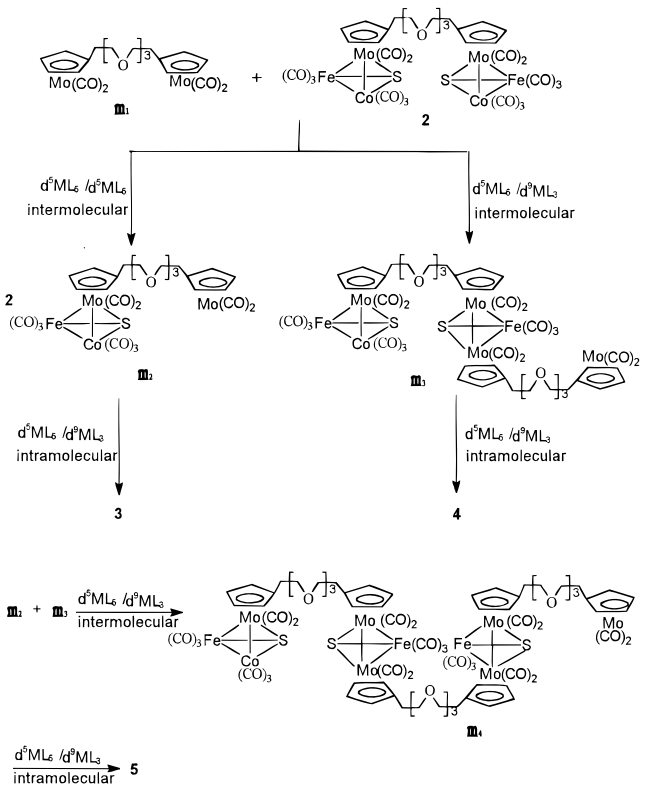
Scheme 2. One of the Possible Pathways for Production of 3−5



basis of the isolobal analogy principle[13] and the known isolobal displacement reaction modes.[14]

First, the bridged bis(molybdenumsodium) salt **1** can be converted into its decarbonylated intermediate $\mathbf{m_1}$. Second, while this intermediate further reacts with double cluster **2** through intermolecular single isolobal d^5ML_5/d^5ML_5 displacement to give two molecules of intermediate $\mathbf{m_2}$, its reaction with **2** via intermolecular single isolobal d^5ML_5/d^9ML_3 displacement gives intermediate $\mathbf{m_3}$. Third, while $\mathbf{m_2}$ undergoes an intramolecular d^5ML_5/d^9ML_3 single isolobal displacement to give single cluster crown ether **3**, the intramolecular single isolobal d^5ML_5/d^9ML_3 displacement affords double cluster crown ether **4**. However, if $\mathbf{m_2}$ reacts with $\mathbf{m_3}$ through intermolecular d^5ML_5/d^9ML_3 single isolobal displacement, then intermediate $\mathbf{m_4}$ will be produced.

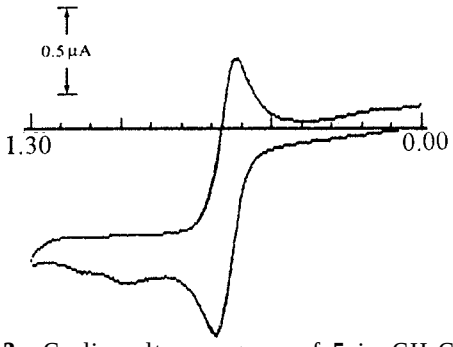


Figure 3. Cyclic voltammogram of **5** in CH_2Cl_2/0.1 M n-Bu_4N PF_6 at 25 °C with a scan rate of 100 mV s^{-1}. Anodic and cathodic peak potentials are given in volts vs the ferrocene/ferrcenium redox couple.

Finally, the intramolecular single isolobal d^5ML_5/d^9ML_3 displacement of $\mathbf{m_4}$ yields triple cluster crown ether **5.**

The cyclic voltammograms of **3**−**5** show a reversible or quasi-reversible one-electron oxidation at anodic peak potentials E_{pa} = +0.693 (**3**), +0.704 (**4**), and +0.694 V (**5**) (for **5** see Figure 3) followed by an irreversible oxidation at more positive potentials, E_{pa} = +1.08 (**3**), +1.05 (**4**), and +0.99 V (**5**) (for **5** see Figure 3). Honrath et al. reported that simple clusters containing tetrahedral cluster cores similar to that of **3**−**5**, namely, clusters with a general formula $CpMFeCo(CO)_8(\mu_3\text{-}E)$ (M = Mo, W; E = S, Se), exhibited one quasi-reversible reduction and one irreversible oxidation.[15] Such differing electrochemical behavior between **3**−**5** and $CpMFeCo(CO)_8(\mu_3\text{-}E)$ could be primarily attributed to the presence of the electron-releasing polyether chain and the absence of more difficultly oxidized Co atoms in **3**−**5.**

Investigations are in hand to examine the scope and limitations for this novel self-assembly cyclization reaction. Redox-switching ability of such cluster crown ethers with respect to alkali metal and transition metal cations is also being studied.

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Supporting Information Available: Details describing synthesis and characterization of complexes **3**−**5** and details of structural determinations of **3**, 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.

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