Positively Charged Crown Thioether Complexes *trans*-[$Mo(CO)_2$(*syn*-Me_9[16]aneS_4)][OSO_2CF_3] and *trans*-[Mo(CO)(OSO_2CF_3)(*syn*-Me_8H[16]aneS_4)]; Difference in π-Acceptor Ability between Tertiary and Secondary Sulfonium Ions

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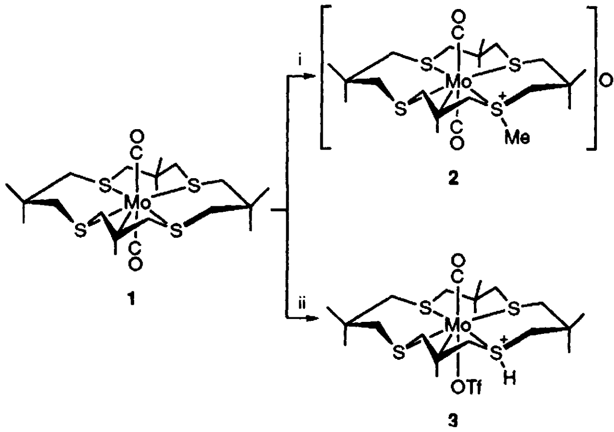
S-Methylation of *trans*-[$Mo(CO)_2$(*syn*-Me_8[16]aneS_4)] (Me_8[16]aneS_4 = 3,3,7,7,11,11,15,15-octamethyl-1,5,9,13-tetrathiacyclohexadecane) with MeOTf (OTf = trifluoromethylsulfonate) gives *trans*-[$Mo(CO)_2$(*syn*-Me_9[16]aneS_4)]OTf, while S-protonation with HOTf proceeds with evolution of CO to afford *trans*-[Mo(CO)(OTf)(*syn*-Me_8H[16]aneS_4)]; the structure of the crown thioether complex containing a tertiary sulfonium ion is elucidated by a single crystal X-ray diffraction study.

Sulfonium ions (R_3S^+) show a marked contrast in their π-acceptor ability[1] from most sulfur ligands such as sulfides and thiolates which behave as a p_π-donor. Despite the unique electronic property, their transition metal complexes are still extremely rare. To the best of our knowledge, the examples so far reported are limited to those of tertiary sulfonium ions $[Ru(SMe_3)(NH_3)_5]^{3+}$,[2] $[M(CO)_4\{Ph_2P(CH_2)_2SMe_2\}]^+$ (M = Mo, W),[1a] and $[(\eta^5\text{-}C_5H_5)Mn(CO)_2(SMe_3)]^+$,[1b] and the complexes of secondary sulfonium ions (R_2SH^+) are virtually unknown. Previously we have shown that Me_8[16]aneS_4 serves as a potential ligand to stabilize zero-valent molybdenum complexes,[3,4] which may be ascribed to the π-acceptor property of polythiamacrocycles.[5,6] Therefore, the crown thioether containing a tertiary or secondary sulfonium ion, Me_8R[16]ane$S_4{}^+$ (R = Me, H) is expected to exhibit more enhanced π-acceptor ability. We report here the preparation



Scheme 1 *Reagents and conditions*: i; 2 MeOTf in toluene, room temp.; ii; HOTf in toluene, room temp. (Tf = SO_2CF_3)

of the first example of the secondary sulfonium ion complex *trans*-[Mo(CO)(OTf)(*syn*-Me_8H[16]aneS_4)] (**3**) together with the tertiary one *trans*-[$Mo(CO)_2$(*syn*-Me_9[16]aneS_4)]OTf (**2**) through S-protonation and -methylation of *trans*-=[$Mo(CO)_2$(*syn*-Me_8[16]aneS_4)] (**1**) with ROTf (R = H, Me), respectively (Scheme 1). In sharp contrast to the methylation where the two CO ligands in **1** remained intact, the extremely facile dissociation of one of the CO ligands observed upon the protonation presents unprecedented chemical evidence for the strong π-acceptor ability of the secondary sulfonium ion compared to the tertiary one.

Treatment of **1** with 2 equiv. of MeOTf in toluene at room temp. and recrystallization of the precipitate from CH_2Cl_2–toluene gave **2** as diamagnetic yellow crystals (73%).† An attempt to alkylate with MeI or Me_3SiBr under N_2 atmosphere failed, **1** was recovered unchanged. The ^1H NMR spectrum shows a Me singlet due to the tertiary sulfonium ion together with four Me singlets and eight CH_2 doublets of the macrocycle. Thus, **2** possess C_s symmetry. This is confirmed by the crystal structure of the BPh_4 salt of **2** (Fig. 1).‡ The Mo atom assumes an essentially octahedral geometry with three thioethers and a tertiary sulfonium ion of *syn*-Me_9[16]aneS_4^+ in the equatorial plane and with two carbonyls at the axial sites. Thus, **2** represents the first example of transition metal complexes possessing both thioether and sulfonium ion in the same molecule, which provides an opportunity to compare directly the electronic features of these two sulfur ligands. The Mo–S distances range from the short Mo–S(1) length [2.310(4) Å] of the sulfonium ion to the long Mo–S(9) [2.489(4) Å] of the thioether *trans* to the S(1) atom, through to those of the remaining thioethers mutually *trans* [Mo–S(5) 2.463(3) and Mo–S(13) 2.461(4) Å]. These Mo–S(thioether) lengths are significantly longer than those (average 2.436(2) Å] found for the parent complex **1**.[3] The extremely short Mo–S(1) separation suggests an extensive π-back donation from the Mo^0 to the sulfonium ion, which in turn reduces the electron density on the Mo atom and weakens the Mo–S(thioether) π-interactions not only in *trans* but also in *cis* positions. The extensive π-donation from the Mo^0 atom to the sulfonium ion is also expected to reduce $d_\pi(Mo) \rightarrow p_\pi^*(CO)$ interactions. Indeed, the ν(CO) bands (1940s and 1820vs cm^{-1}) are higher in frequency than those (1907 and 1767 cm^{-1}) found for the starting crown thioether complex **1**. Consistently, the Mo–C(30) length [2.081(12) Å] of the CO ligand located at the uncongested axial site is significantly longer than the corresponding distance [2.002(8) Å] of **1**. By contrast, the Mo–C(20) separation [1.942(15) Å] of the CO ligand at the congested axial site is comparable with that [1.979(8) Å] of the parent compound.

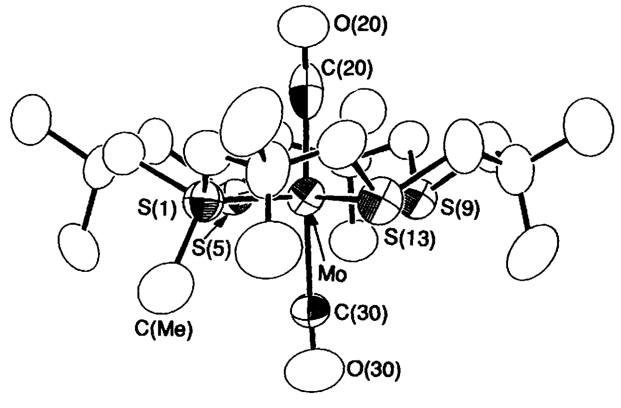


Fig. 1 Molecular structure of the cation of **2**. Selected bond distances (Å) and angles (°): Mo–S(1) 2.310(4), Mo–S(5) 2.463(3), Mo–S(9) 2.489(4), Mo–S(13) 2.461(4), Mo–C(20) 1.942(15), Mo–C(30) 2.081(12), S(1)–C(Me) 1.801(15), C(20)–O(20) 1.20(2), C(30)–O(30) 1.11(2); S(1)–Mo–S(5) 90.5(1), S(1)–M–S(9) 177.0(1), S(1)–Mo–S(13) 90.7(1), S(5)–Mo–S(9) 89.2(1), S(5)–Mo–S(13) 177.5(1), S(9)–Mo–S(13) 89.5(1), C(20)–Mo–S(1) 92.6(4), C(20)–Mo–S(5) 89.2(4), C(20)–Mo–S(9) 90.3(4), C(20)–Mo–S(13) 92.5(4), C(30)–Mo–S(1) 90.5(4), C(30)–Mo–S(5) 90.1(4), C(30)–Mo–S(9) 86.5(4), C(30)–Mo–S(13) 87.7(4), C(20)–Mo–C(30) 176.8(6), Mo–C(20)–O(20) 174(1), Mo–C(30)–O(30) 178(1)

The weakening of one of the axial Mo–CO bonds induced by the introduction of a positive charge into the crown thioether was verified by the facile evolution of one of CO ligands from **1** when it is protonated. Thus, a reaction of **1** with an equimolar amount of HOTf in toluene at ambient conditions gave **3** as pale-yellow crystals (78.5%).† Complex **3** is extremely sensitive towards air and readily soluble in aromatic hydrocarbons. The presence of the secondary sulfonium proton was confirmed by the IR and ^1H NMR spectra, which exhibit a ν(S–H) band at 1895w cm^{-1} and a sharp singlet at δ 11.98. Consistent with the single CO ligand, one ν(CO) band was observed at 1795vs cm^{-1} which is significantly lower in frequency than those of **2**. In sharp contrast to C_s symmetry of the tertiary sulfonium ion complex, the sulfonium proton in the *syn*-Me_8H[16]aneS_4^+ complexes delocalizes over the four S atoms at room temp. in benzene solution. Thus, the ^1H NMR spectrum show only two Me singlets and two CH_2 doublets each assignable to the axial and equatorial ones. Based on the X-ray structure of **2**, it is reasonable to assume that the CO ligand in **3** locates at the congested axial site (Scheme 1). However, the exact determination of the relative positions of the CO and OTf^- ligands at stereochemically different axial sites awaits an X-ray structural study. Finally it is worth noting that the protonation of **1**

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† Satisfactory elemental analyses were obtained for all new compounds. Selected spectral data. For **2**: FAB MS (*m*/*z*) 557 ($[M]^+$), 549 ($[M - CO]^+$), 534 ($[M - CO - Me]^+$); ^1H NMR (δ, $CDCl_3$) 1.08 (s, 6 H, MeC), 1.11 (s, 6 H, MeC), 1.12 (s, 6 H, MeC), 1.32 (s, 6 H, MeC), 2.32 (d, *J* 11.3 Hz, 2 H, CH_2), 2.43 (d, *J* 11.3 Hz, 2 H, CH_2), 2.44 (d, *J* 11.6 Hz, 2H, CH_2), 2.63 (d, *J* 13.1 Hz, 2 H, CH_2), 2.77 (d, *J* 11.6 Hz, 2 H, CH_2), 2.84 (d, *J* 11.3 Hz, 2 H, CH_2), 2.86 (d, *J* 11.3, 2 H, CH_2), 3.74 (s, 3 H, MeS^+) and 4.28 (d, *J* 13.1 Hz, 2 H, CH_2). For **3**: FAB MS (*m*/*z*) 684 ($[M]^+$), 655 ($[M - CO - H]^+$); ^1H NMR (δ, C_6D_6) 0.75 (s, 12 H, Me), 1.11 (s, 12 H, Me), 2.10 (d, *J* 11.3 Hz, 8 H, CH_2), 2.91 (d, *J* 11.3 Hz, 8 H, CH_2) and 11.98 (s, 1 H, HS^+).

‡ *Crystal data* for the BPh_4 salt of **2**, *trans*-{$M(CO)_2$(*syn*-Me_9[16]aneS_4)}$BPh_4 \cdot MeOCH_2CH_2OMe$: $C_{51}H_{73}O_4S_4BMo$, M = 985.13, monoclinic, $P2_1/n$, $a = 14.095(14)$, $b = 10.287(12)$, $c = 36.605(9)$ Å, $\beta = 99.28(4)°$, $U = 5238(9)$ Å^3, $Z = 4$, $D_c = 1.249$ g cm^{-3}, Rigaku AFC-5R diffractometer, λ(Mo-Kα) = 0.71069 Å, $\mu = 4.36$ cm^{-1}, $F(000) = 2088$, specimen 0.5 × 0.3 × 0.1 mm, $R = 0.062$ and $R_w = 0.049$ for 3002 unique reflections [$I > 3\sigma(I)$] and 382 variables. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

accompanying CO dissociation is reversible and the treatment of **3** with 1,8-diazabicyclo[5.4.0]undec-7-ene under CO atmosphere regenerates the parent dicarbonyl compounds.

In conclusion, the preparative study of **2** and **3** as well as the X-ray structure of the latter suggest that the secondary sulfonium ion is probably the strongest π-acid among a wide variety of sulfur ligands and π-acceptor ability of the sulfur ligands in $Me_8R[16]aneS_4^+$ (R = Me, H) increases in the order, secondary sulfonium ion > tertiary sulfonium ion > thioether. The novel electronic feature of the crown thioether containing a sulfonium ion, particularly that of secondary one, may open a new area for the coordination chemistry of macrocyclic sulfur ligands.[7]

This work was partially supported by a Grant-in-Aid for Scientific Research (No. 05804033) from the Ministry of Education, Science, and Culture, Japan.

Received, 27th May 1993; Com. 3/03043A

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