

SYNTHESIS OF A NEW MACROCYCLE CONTAINING TIN AND SELENIUM, 1,9-DISELENA-5,5,13,13-TETRAMETHYL-5,13-DISTANNACYCLOHEXADECANE, AND RELATED COMPOUNDS

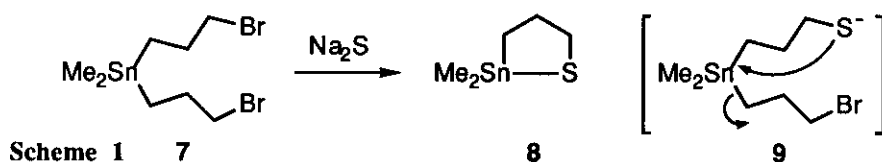
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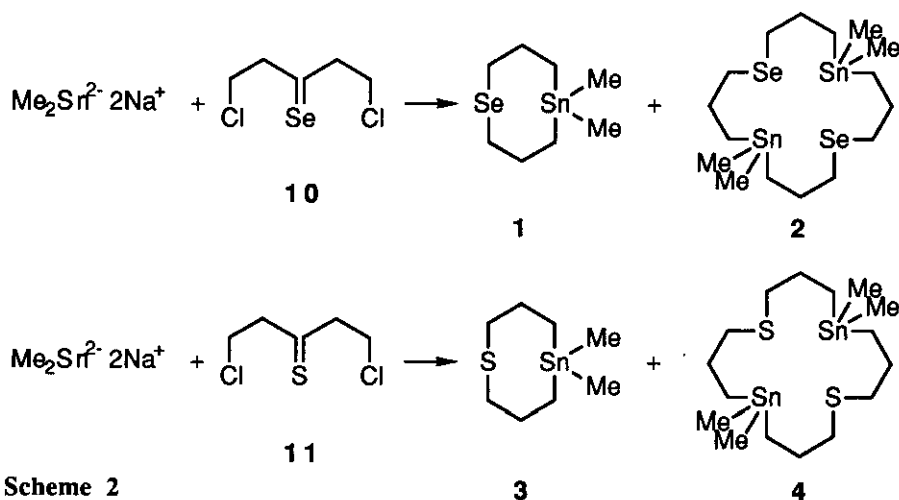
Abstract --- New cyclic compounds containing heavier group 14 and 16 elements, 1-selena- or 1-thia-5,5-dimethyl-5-stannacyclooctane (**1** or **3**) and 1,9-diselena- or 1,9-dithia-5,5,13,13-tetramethyl-5,13-distannacyclohexadecane (**2** or **4**), and its selenonium derivatives have been synthesized.

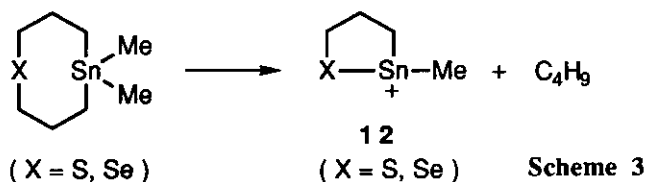
Synthesis and properties of various macrocyclic polyoxaethers (crown ethers) and polythiaethers have been extensively reported.¹ Although the crown ethers coordinate strongly with positively charged species, e.g., alkali or alkaline earth metal cations, the polythiaethers exhibit lower selectivity for those cations. We reported the synthesis of macrocyclic polythiaethers with alkylthio side chains and their sulfoxides which was found to be a good phase-transfer catalyst.² In contrast, the analogous complexation of anions by neutral Lewis acidic macrocycles has received little attention.³ We now report the synthesis of a new type of macrocycle containing two different heavier group 14 and 16 elements, 1,9-diselena-5,5,13,13-tetramethyl-5,13-distannacyclohexadecane (**2**), and its selenonium salts and sulfur derivatives, although only a limited number of macrocyclic stannanes and selenoethers have been reported.^{3,4}

In the beginning, bis(3-bromopropyl)dimethylstannane (**7**) was treated with Na₂S to prepare a new eight-membered ring involving tin and chalcogen, 1-thia-5,5-dimethyl-5-stannacyclooctane (**3**), however the five-membered ring thiastannane, 1-thia-2,2-dimethyl-2-stannacyclopentane (**8**) (26%), was produced instead of **3**.⁵ Probably, the bromide (**7**) reacts with Na₂S to form the thiolate anion (**9**) which subsequently is converted into **8** by an intramolecular nucleophilic displacement of the thiolate ion (Scheme 1).

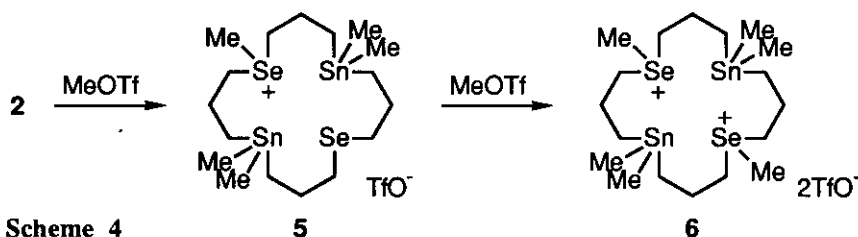


Therefore, a new strategy for the synthesis of cyclic tin-chalcogenide was performed as follows (Scheme 2). To a solution of dichlorodimethylstannane (2.26 g, 10.3 mmol) in anhydrous tetrahydrofuran (THF) (20 ml) and liquid ammonia (50 ml) was added sodium (1.09 g, 47.2 mmol) in small quantities. The mixture was stirred for 4 h at $-60\text{ }^{\circ}\text{C}$. To this solution was added bis(3-chloropropyl)selenide (**10**)⁶ (2.41 g, 10.3 mmol) in anhydrous THF (20 ml) at $-60\text{ }^{\circ}\text{C}$. The mixture was stirred overnight. After evaporation of the solvent, the residue was purified by silicagel column chromatography (eluent, benzene-hexane) to yield the compounds (**1**) (5%) and (**2**) (10%).⁷ Similar reaction of bis(3-chloropropyl)sulfide (**11**) with $\text{Me}_2\text{Sn}\cdot 2\text{Na}$ led to **3** (7%) and **4** (14%).⁸ The eight-membered chalcogena-stannanes (**1**) and (**3**) were highly volatile. The structures of **1-4** were assigned by mass and nmr spectroscopy. The mass spectra on electron impact ionization (70 eV) of cyclic methylstannanes (**1-4**) show the $\text{M}^+ - 15$ peak corresponding to a loss of a methyl group, i.e., no detectable molecular ion under this condition. However, the FAB-mass spectrum of **2** shows a molecular ion, m/z 629 ($\text{M}^+ + 1$), without the observation of the demethylation from the dimethylstannane. Interestingly, the mass spectra (EI) of **1** and **3** exhibit base peaks at m/z 255 for **1** and m/z 209 for **3** when five-membered ring ions (**12**) can be formed by a transannular interaction between tin and selenium or sulfur (Scheme 3).





The synthesis of the selenonium salt of **2** was examined, since little information on the onium salts of macrocyclic polyselenaethers was available. The cyclic selenastannane (**2**) was treated with 1 equiv of methyl triflate, MeOSO₂CF₃ (MeOTf), to give the monoselenonium salt (**5**) in 78% yield (Scheme 4).⁹ The selenonium salt (**5**) was further reacted with 1 equiv of MeOTf to give the bis-selenonium salt (**6**) (67%).¹⁰ The structures of **5** and **6** were characterized by ¹H, ¹³C, ¹⁹F, ⁷⁷Se, and ¹¹⁹Sn nmr spectroscopy and elemental analysis. In particular, the ⁷⁷Se nmr spectrum of **5** in CDCl₃ shows three peaks at δ 162.5, δ 309.9 and δ 310.2; the former one peak is assignable to the selenide, and the latter two peaks are assigned to the selenonium cations. The ⁷⁷Se resonances of selenonium cations for **6** also are two peaks of δ 310.4 and δ 311.0, which may suggest the existence of diastereomers. We are currently exploring the properties of the chalcogena-stannanes and the onium derivatives.



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REFERENCES AND NOTES

1. *Synthesis of Macrocycles*, eds., R. M. Izatt and J. J. Christensen, John Wiley & Sons, New York, 1987.
2. H. Fujihara, K. Imaoka, N. Furukawa and S. Oae, *J. Chem. Soc., Perkin Trans. 1*, 1986, 465.
3. K. Jurkschat, H. G. Kuivila, S. Liu and J. A. Zubieta, *Organometallics*, 1989, **8**, 2755 and references cited therein.
4. *The Chemistry of Organic Selenium and Tellurium Compounds*; Vol. 1 and Vol. 2, eds. S. Patai and Z. Rappoport, Wiley, New York, 1986 and 1988.

5. **8**: ^1H Nmr (CDCl_3) δ 0.54 (s, 6H, CH_3), 1.17 (t, $J = 7$ Hz, 2H, CH_2), 2.04 (q, $J = 7$ Hz, 2H, CH_2), 2.76 (t, $J = 7$ Hz, 2H, CH_2); ^{13}C nmr (CDCl_3) δ -4.56, 14.2, 31.8, 33.3; ms, m/z 224 (M^+), 209 (base peak).
6. Bis(3-chloropropyl)selenide (**10**) was obtained from the reaction of 1-bromo-3-chloropropane with Na_2Se . **10**: bp 135-138 °C (12 mmHg); ^1H nmr (CDCl_3) δ 2.11 (q, $J = 7$ Hz, 4H, CH_2), 2.71 (t, $J = 7$ Hz, 4H, CH_2), 3.65 (t, $J = 7$ Hz, 4H, CH_2); ^{13}C nmr (CDCl_3) δ 20.4, 32.8, 44.2; ms, m/z 234 (M^+).
7. **1**: ^1H Nmr (CDCl_3) δ 0.06 (s, 6H, CH_3), 0.80 (t, $J = 6$ Hz, 4H, CH_2), 1.92 (q, $J = 6$ Hz, 4H, CH_2), 2.60 (t, $J = 6$ Hz, 4H, CH_2); ^{13}C nmr (CDCl_3) δ -6.92, 11.4, 25.1, 28.4; ms, m/z 299 (M^+-15). **2**: ^1H Nmr (CDCl_3) δ -0.04 (s, 12H, CH_3), 0.83 (t, $J = 8$ Hz, 8H, CH_2), 1.76 (q, $J = 8$ Hz, 8H, CH_2), 2.45 (t, $J = 8$ Hz, 8H, CH_2); ^{13}C nmr (CDCl_3) δ -11.2, 11.1, 27.9, 28.6; ^{77}Se nmr (CDCl_3) δ 172.1 (relative to Me_2Se); ^{119}Sn nmr (CDCl_3) δ -2.1 (relative to Me_4Sn); FABms, m/z 629 (M^++1). Anal. Calcd for $\text{C}_{16}\text{H}_{36}\text{Se}_2\text{Sn}_2$: C, 30.81; H, 5.82. Found: C, 31.04; H, 5.84.
8. **3**: ^1H Nmr (CDCl_3) δ 0.04 (s, 6H, CH_3), 0.75-0.80 (m, 4H, CH_2), 1.83-1.92 (m, 4H, CH_2), 2.53-2.57 (m, 4H, CH_2); ^{13}C nmr (CDCl_3) δ -6.93, 10.0, 24.7, 35.4; ms, m/z 251 (M^+-15). Anal. Calcd for $\text{C}_8\text{H}_{18}\text{SSn}$: C, 36.26; H, 6.85. Found: C, 36.01; H, 6.85. **4**: ^1H Nmr (CDCl_3) δ 0.05 (s, 12H, CH_3), 0.92 (t, $J = 8$ Hz, 8H, CH_2), 1.80 (q, $J = 8$ Hz, 8H, CH_2), 2.49 (t, $J = 8$ Hz, 8H, CH_2); ^{13}C nmr (CDCl_3) δ -11.2, 9.94, 27.7, 36.0; ms, m/z 517 (M^+-15). Anal. Calcd for $\text{C}_{16}\text{H}_{36}\text{S}_2\text{Sn}_2$: C, 36.26; H, 6.85. Found: C, 35.99; H, 6.82.
9. **5**: ^1H Nmr (CDCl_3) δ 0.09 (s, 6H, CH_3), 0.10 (s, 6H, CH_3), 0.85-0.98 (m, 8H, CH_2), 1.76-2.10 (m, 8H, CH_2), 2.50-2.55 (m, 4H, CH_2), 2.85 (br s, 3H, CH_3), 3.25-3.43 (m, 4H, CH_2); ^{13}C nmr (CDCl_3) δ -11.1, 9.72, 10.7, 19.4, 23.5, 28.2, 28.3, 43.5; ^{19}F nmr (CDCl_3) δ 83.5 (relative to C_6F_6); ^{77}Se nmr (CDCl_3) δ 162.5, 309.9, 310.2 (relative to Me_2Se); ^{119}Sn nmr (CDCl_3) δ 1.58 (relative to Me_4Sn). Anal. Calcd for $\text{C}_{18}\text{H}_{39}\text{O}_3\text{F}_3\text{SSe}_2\text{Sn}_2$: C, 27.45; H, 4.99. Found: C, 27.21; H, 4.97.
10. **6**: ^1H Nmr (CDCl_3) δ -0.22 (s, 12H, CH_3), 0.43-0.73 (m, 8H, CH_2), 1.50-1.72 (m, 8H, CH_2), 2.31 (br s, 6H, CH_3), 2.78-2.94 (m, 8H, CH_2); ^{13}C nmr (CDCl_3) δ -11.1, 10.1, 10.2, 19.3, 23.7, 23.8, 43.3; ^{19}F nmr (CDCl_3) δ 82.6 (relative to C_6F_6); ^{77}Se nmr (CDCl_3) δ 310.4, 311.0 (relative to Me_2Se); ^{119}Sn nmr (CDCl_3) δ 3.40 (relative to Me_4Sn). Anal. Calcd for $\text{C}_{20}\text{H}_{42}\text{O}_6\text{F}_6\text{S}_2\text{Se}_2\text{Sn}_2$: C, 25.23; H, 4.45. Found: C, 25.22; H, 4.40.