A new route to polyselenoether macrocycles. Catalytic macrocyclization of 3,3-dimethylselenatane by $[Re_2(CO)_9]$

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3,3-Dimethylselenatane, $\overline{\mathrm{SeCH_2CMe_2C}}\mathrm{H_2}$, DMSe is cyclooligomerized catalytically at 115 °C in the presence of $[\mathrm{Re_2(CO)_9}(\overline{\mathrm{SeCH_2CMe_2C}}\mathrm{H_2})]$ to yield three new polyselenoether macrocycles 3,3,7,7-tetramethyl-1,5-diselenacyclooctane, 3,3,7,7,11,11-hexamethyl-1,5,9-triselenacyclododecane, 3,3,7,7,11,11,15,15-octamethyl-1,5,9,13-tetraselenacyclohexadecane and polymer of DMSe; all three macrocycles are characterized crystallographically; in all cases the *gem*-dimethyl groups are directed toward the exterior of the rings; interestingly, some methylene groups are directed to the interior.

In recent studies we have shown that $[\mathrm{Re_2(CO)_9(NCMe)}]$ and other third-row transition-metal carbonyl complexes can serve as effective catalysts for the ring-opening cyclooligomerization of thietanes to polythioether macrocycles.[1] Polythioether macrocycles have attracted attention for their ability to serve as ligands for transition metals.[2] Polyselenoether macrocycles have an equally good potential to serve as ligands,[3] but the number of known polyselenoether macrocycles is very small.[4]

We have now found that $[\mathrm{Re_2(CO)_9}(\overline{\mathrm{SeCH_2CMe_2C}}\mathrm{H_2})]$ **1** serves as a catalyst for the ring-opening macrocyclization of 3,3-dimethylselenatane, $\overline{\mathrm{SeCH_2CMe_2C}}\mathrm{H_2}$, DMSe, to yield three new polyselenoether macrocycles.† 15.0 mg of **1** was dissolved in 0.750 g of DMSe[5] and the solution was heated to 115 °C for 8 h.‡ This yielded a residue of 340 mg after removal of the unreacted DMSe. The products were separated by TLC to yield 4.3 mg of 3,3,7,7-tetramethyl-1,5-diselenacyclooctane **2**, 104.1 mg of 3,3,7,7,11,11-hexamethyl-1,5,9-triselenacyclododecane **3** and 12.0 mg of 3,3,7,7,11,11,15,15-octamethyl-1,5,9,13-tetraselenacyclohexadecane **4**. The remainder is believed to be polymer of DMSe. For **3** this is equivalent to 12.0 turnovers or 1.5 turnovers h^{-1}.

All three macrocycles were characterized crystallographically, and structural diagrams of each are shown in Figs. 1–3, respectively.§ In all three structures the *gem*-dimethyl groups are directed toward the exterior of the ring. In the solid state **2** and **4** both contain a crystallographically imposed centre of

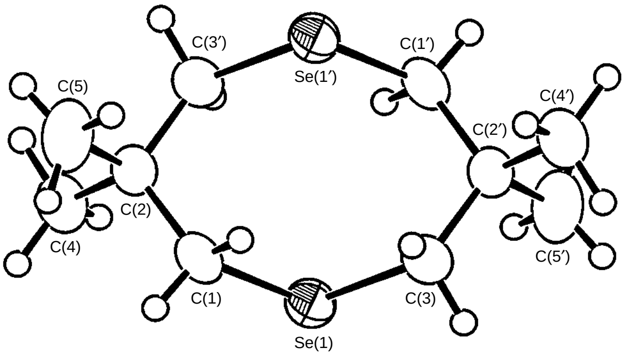


Fig. 1 An ORTEP diagram of 3,3,7,7-tetraamethyl-1,5-diselenacyclooctane **2**. Selected interatomic distances (Å): Se(1)–C(1) 1.961(8), Se(1)–C(3) 1.974(8), C(1)–C(2) 1.52(1), C(2)–C(3′) 1.52(1).

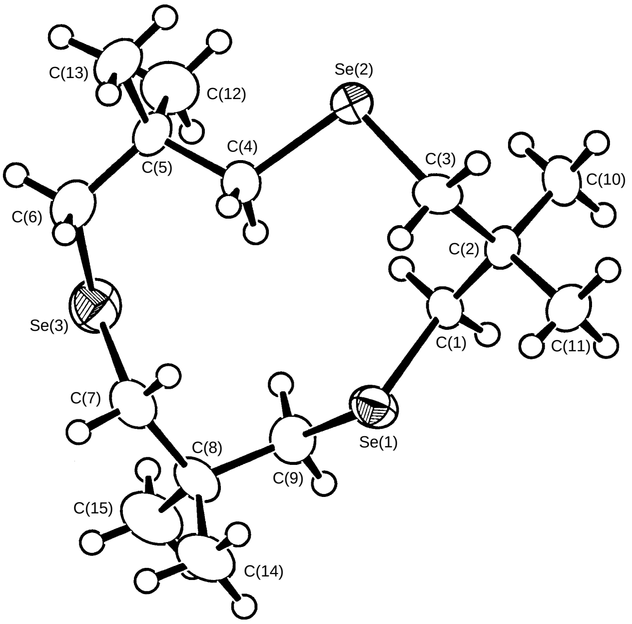


Fig. 2 An ORTEP diagram of 3,3,7,7,11,11-hexamethyl-1,5,9-triselenacyclododecane **3**. Selected interatomic distances (Å): Se (1)–C(1) 1.965(8), Se(1)–C(9) 1.953(9), Se(2)–C(3) 1.952(9), Se(2)–C(4) 1.957(9), Se(3)–C(6) 1.97(1), Se(3)–C(7) 1.97(1).

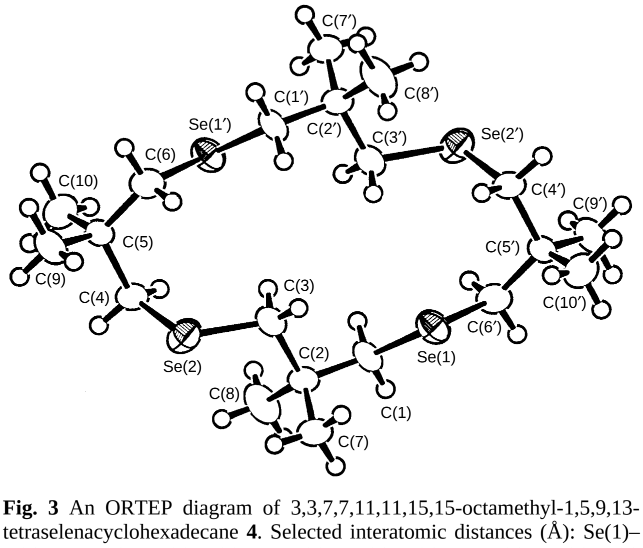
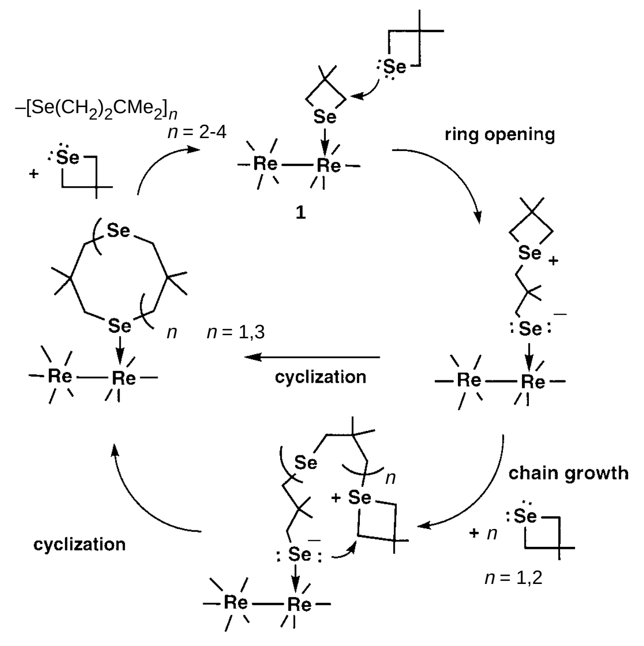


Fig. 3 An ORTEP diagram of 3,3,7,7,11,11,15,15-octamethyl-1,5,9,13-tetraselenacyclohexadecane **4**. Selected interatomic distances (Å): Se(1)–C(1) 1.961(9), Se(1)–C(6) 1.967(9), Se(2)–C(3) 1.961(9), Se(2)–C(4) 1.956(9), C(1)–C(2) 1.54(1), C(2)–C(3) 1.57(1), C(4)–C(5) 1.55(1), C(5)–C(6) 1.51(1).



Scheme 1

symmetry. All Se–C distances are similar, Se(1)–C(1) 1.961(8) and Se(1)–C(3) 1.974(8) Å for **2**; Se(1)–C(1) 1.965(8), Se(1)–C(9) 1.953(9), Se(2)–C(3) 1.952(9), Se(2)–C(4) 1.957(9), Se(3)–C(6) 1.97(1) and Se(3)–C(7) 1.97(1) Å for **3**; and Se(1)–C(1) 1.961(9), Se(1)–C(6) 1.967(9), Se(2)–C(3) 1.961(9) and Se(2)–C(4) 1.956(9) Å for **4** and all are similar to those found in the unsubstituted selenoether macrocycles: [12]aneS_4, [18]aneSe_6, [16]aneSe_4, [24]aneSe_6 and [14]aneSe_4.[4c] It has been suggested that *gem*-dimethyl groups on the ring of polythioether macrocycles will force the sulfur atoms to turn toward the interior of the ring and enhance their ligand properties.[6] This is only partially supported by the results for the selenium compounds described here. Although conformations of **3** and **4** differ from those of their unsubstituted sulfur and selenium homologues 1,5,9-trithiacyclododecane¶ and 1,5,9,13-tetraselenacyclohexadecane,[4c] the selenium atoms are not directed inward. In fact, it is methylene groups, C(4) on **3** and C(3) on **4**, that are most dramatically turned toward the interior of the macrocycles.

In the absence of **1**, no significant amounts of the macrocycles or polymer are formed from DMSe under these conditions. We feel that the mechanism involves a series of ring opening additions of DMSe to the DMSe ligand in a $Re_2(CO)_9$ complex followed by a recyclization, similar to that established for the macrocyclizations of thietane[1c] and 3-methylthietane,[1f] see Scheme 1. To date, our studies have been limited to DMSe due to the lower stability of the less substituted selenatanes. Efforts to prepare metal complexes of these new macrocycles are now in progress.

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Footnotes

† $[Re_2(CO)_9(\overline{SeCH_2CMe_2CH_2})]$ **1** was obtained in 88% yield from the reaction of $[Re_2(CO)_9(NCMe)]$ with 3,3-dimethylselenatane in hexane at reflux for 2 h.

Analytical data: **1**, ^1H NMR ($CDCl_3$): δ 3.58 (d, 2 H, J_{HH} 9.4 Hz), 3.20 (d, 2 H, J_{HH} 9.7 Hz), 1.41 (s, 3 H), 1.22 (s, 3 H). IR ν(CO)/cm^{-1} (hexane): 2102.2w, 2040.5m, 2016.0w, 1995.0s, 1988.5s, 1976.8m, 1967.1m, 1954.4w, 1933.5m. Anal. Found (Calc.): C 21.99 (21.74), H 1.31 (1.30)%.

‡ **2**, ^1H NMR ($CDCl_3$), δ 2.90 (s, 8 H), 0.97 (s, 12 H); ^{13}C NMR, δ 44.46 (2 C), 37.72 (1 C), 28.64 (2 C); ^{77}Se NMR ($CDCl_3$), δ 56.05; MS (^{80}Se), *m/z* 300 [$\mathbf{2}^+$], 230 ($\mathbf{2}^+ - C_5H_{10}$), 69 (C_5H_9).

3, ^1H NMR ($CDCl_3$) δ, 2.81 (s, 12 H), 1.54 (s, 18 H); ^{13}C NMR 37.91 (2 C), 36.09 (1 C), 28.32 (2 C); ^{77}Se NMR, δ 54.46 (s, 3 Se); MS (^{80}Se), *m/z* 450 [$\mathbf{3}^+$], 230 [$\mathbf{3}^+ - SeC_{10}H_{20}$], 150 ($\mathbf{3}^+ - Se_2C_{10}H_{20}$), 69 ($C_5H_9$). Anal. Calc. for **3** ($Se_3C_{15}H_{30}$): C, 40.28; H, 6.76. Found: C, 40.27; H, 6.65%.

4, ^1H NMR ($CDCl_3$), δ 2.75 (s, 16 H), 1.05 (s, 24 H); ^{13}C NMR, δ 39.99 (2 C), 36.43 (1 C), 27.69 (2 C); ^{77}Se NMR, δ 53.90 (s, 4 Se). MS (^{80}Se), *m/z* 600 ($\mathbf{4}^+$) 300 ($\mathbf{4}^+ - Se_2C_{10}H_{20}$), 230 ($\mathbf{4}^+ - Se_2C_{15}H_{30}$), 150 ($\mathbf{4}^+ - Se_3C_{15}H_{30}$), 69 ($C_5H_9$).

§ *Crystal data*: **2**, $C_{10}H_{20}Se_2$, monoclinic, space group $C2/c$, a = 10.534(3), b = 7.602(2), c = 15.612(3) Å, β = 96.88(2)°, U = 1241.1(5) $Å^3$, Z = 4. 873 unique reflections, R = 0.043, R_w = 0.049 for 631 reflections with $I > 3\sigma(I)$. **3**, $C_{15}H_{30}Se_3$, monoclinic, space group $P2_1/a$, a = 11.660(3), b = 10.975(2), c = 14.578(3) Å, β = 98.57(2)°, U = 1860(2) $Å^3$, Z = 4. 2570 unique reflections, R = 0.045, R_w = 0.049 for 1697 reflections with $I > 3\sigma(I)$. **4**, $C_{20}H_{40}Se_4$, triclinic, space group $P\bar{1}$, a = 8.669(1), b = 9.719(2), c = 7.402(1) Å, α = 94.23(2), β = 94.72(1), γ = 79.34(2)°, U = 1860(2) $Å^3$, Z = 1. 1591 unique reflections, R = 0.043, R_w = 0.046 for 1241 reflections with $I > 3\sigma(I)$. For all structures data were collected on a Rigaku AFC6S diffractometer using Mo-Kα radiation. L_p and absorption corrections were applied in all analyses.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/376.

¶ The molecular structure of [12]aneSe_3 has not yet been determined. Most likely it is similar to that of [12]aneS_3.[7] The structures of [16]aneS_4 and [16]aneSe_4 are similar.[4c]

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