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A New Route to Polyselenoether Macrocycles. Catalytic Macrocyclization of 3,3-Dimethylselenetane by $\mathrm{Re_2(CO)_9}\overline{\mathrm{SeCH_2CMe_2C}}\mathrm{H_2}$

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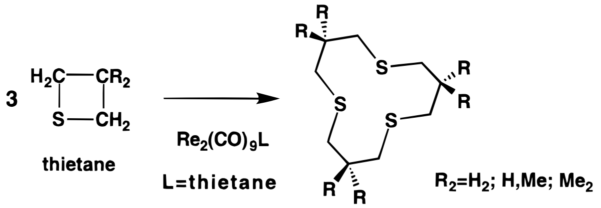
3,3-Dimethylselenetane ($\overline{\mathrm{SeCH_2CMe_2C}}\mathrm{H_2}$, DMSe) was cyclooligomerized catalytically at 115 °C by the complex $\mathrm{Re_2(CO)_9(}\overline{\mathrm{SeCH_2CMe_2C}}\mathrm{H_2)}$ (**1**). Three new polyselenoether macrocycles, 3,3,7,7-tetramethyl-1,5-diselenacyclooctane (**2**; $\mathrm{Me_48Se2}$), 3,3,7,7,11,11-hexamethyl-1,5,9-triselenacyclododecane (**3**; $\mathrm{Me_612Se3}$), and 3,3,7,7,11,11,15,15-octamethyl-1,5,9,13-tetraselenacyclohexadecane (**4**; $\mathrm{Me_816Se4}$), along with a polymer were obtained. Two complexes of **3**, $\mathrm{Re_2(CO)_9(Me_612Se3)}$ (**5**) and $\mathrm{Cu_4I_4(\mu\text{-}Me_612Se3)_2}$ (**6**), were obtained from the reactions with $\mathrm{Re_2(CO)_9(NCMe)}$ and CuI, respectively. All three macrocycles and the complexes **1**, **5**, and **6** were characterized crystallographically. In all cases the *gem*-dimethyl groups of the macrocycles are directed toward the exterior of the rings. Interestingly, some methylene groups are directed toward the interior of the ring. Compound **5** contains an η^1-$\mathrm{Me_612Se3}$ ligand, while compound **6** contains bridging η^2-$\mathrm{Me_612Se3}$ ligands that link $\mathrm{Cu_4I_4}$ clusters into a three-dimensional network in the solid state.

Introduction

Interest in the ligand properties of polythioether macrocycles continues to develop.[1] We have recently developed the first procedures for synthesizing polythioether macrocycles catalytically by ring-opening cyclooligomerization of thietanes (eq 1).[2,3] Third-row



transition-metal carbonyl complexes have proven to be the most effective catalysts for these reactions. Polyselenoether macrocycles also have a good potential to serve as ligands for the transition metals, but the number of known polyselenoether macrocycles is very small[4] and investigations of their ligand properties are even fewer.[5]

We have now prepared the dimethylselenatane complex $\mathrm{Re_2(CO)_9(}\overline{\mathrm{SeCH_2CMe_2C}}\mathrm{H_2)}$ (**1**) and have found that it 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 substituted polyselenoether macrocycles: 3,3,7,7-tetramethyl-1,5-diselenacyclooctane (**2**; $\mathrm{Me_48Se2}$), 3,3,7,7,11,11-hexamethyl-1,5,9-triselenacyclododecane (**3**; $\mathrm{Me_612Se3}$), and 3,3,7,7,11,11,15,15-octamethyl-1,5,9,13-tetraselenacyclohexadecane (**4**; $\mathrm{Me_816Se4}$). Two metal complexes of **3**, $\mathrm{Re_2(CO)_9(Me_612Se3)}$ (**5**) and $\mathrm{Cu_4I_4(Me_612Se3)_2}$ (**6**), were obtained from the reactions of **3** with $\mathrm{Re_2(CO)_9(NCMe)}$ and CuI, respectively. A preliminary report of this work has been published.[6]

Experimental Section

General Data. Reagent grade solvents were stored over 4 Å molecular sieves. All reactions were performed under a

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nitrogen atmosphere unless indicated otherwise. Infrared spectra were recorded on a Nicolet 5DXBO FTIR spectrophotometer. $Re_2(CO)_9(NCMe)$,[7] **1**, and 3,3-dimethylselenatane[8] **(**DMSe**)** were prepared according to the published procedures. CuI was purchased from Strem and was used without further purification. Product separations were performed by TLC in air on Analtech 0.25 and 0.50 mm silica gel 60 Å F_{254} glass plates. Mass spectra were obtained by using electron impact ionization. Elemental analyses were performed by Oneida Research Services, Whitesboro, NY.

Preparation of $Re_2(CO)_9(\overline{SeCH_2CMe_2C}H_2)$ (1). A 40 mg amount of $Re_2(CO)_9NCMe$ was dissolved in 30 mL of hexane in a 50 mL three-neck round-bottom flask equipped with a stirbar, reflux condenser, and nitrogen inlet. A 90 mg amount of 3,3-dimethylselenatane was added and the resulting solution heated to reflux with a slow purge of nitrogen for 2 h. The solution was then cooled and the solvent removed *in vacuo*. The crude residue was then dissolved in a minimal amount of methylene chloride and purified by TLC using hexane as eluant. This yielded 41.2 mg of $Re_2(CO)_9\overline{SeCH_2CMe_2C}H_2$ (**1**; 88%). Analytical and spectral data for **1**: ^1H NMR (δ in $CDCl_3$) 3.58 (d, 2H, $^2J_{H-H} = 9.4$ Hz), 3.20 (d, 2H, $^2J_{H-H} = 9.7$ Hz), 1.41 (s, 3H), 1.22 (s, 3H); IR ν(CO) (cm^{-1} in hexane) 2102 (w), 2040 (m), 2016 (w), 1995 (s), 1988 (s), 1977 (m), 1967 (m), 1954 (w), 1933 (m). Anal. Found (calcd): C, 21.99 (21.74); H, 1.31 (1.30).

Catalytic Macrocyclization of 3,3-Dimethylselenetane by $Re_2(CO)_9$DMSe. A 15 mg amount of **1** was dissolved in 0.75 g of 3,3-dimethylselenatane in a 25 mL round-bottom flask equipped with a stirbar and a reflux condenser. The solution (no solvent was added) was heated to 115 °C in a constant-temperature oil bath and stirred under argon for a period of 8 h. After the mixture was cooled, the unreacted DMSe was removed *in vacuo*. The residue weighed 340 mg. A ^1H NMR spectrum of the residue showed the presence of three compounds: DMSe (unreacted, δ 2.85 (4H) and 1.22 (6H)), 17% by integration; Me_612Se3, 35% by integration; polymer of DMSe (δ 2.65 (4H) and 1.00 (6H)), 36% by integration. The residue was purified by TLC using a hexane/methylene chloride (3/1) solvent mixture as eluant. This yielded, in order of elution, 4.3 mg of $Se_2C_{10}H_{20}$ (**2**, Me_48Se2; 0.6%), 104.1 mg of $Se_3C_{15}H_{30}$ (**3**, Me_612Se3; 14%), and 12 mg of $Se_4C_{20}H_{40}$ (**4**, Me_816Se4; 1.6%). Analytical data for **2**: ^1H NMR (δ in $CDCl_3$) 2.90 (s, 8H), 0.97 (s, 12H); ^{13}C NMR (δ) 44.46 (2C), 37.72 (1C), 28.64 (2C); ^{77}Se NMR (δ in $CDCl_3$) 56.05; MS (*m/e* for ^{80}Se) 300 [Me_48Se2^+], 230 ($Me_48Se2^+ - C_5H_{10}$), 69 [C_5H_9]. Analytical data for **3**: mp 129−131 °C; ^1H NMR (δ in $CDCl_3$) 2.81 (s, 12H), 1.03 (s, 18H); ^{13}C NMR (δ) 37.91 (2C), 36.09 (1C), 28.32 (2C); ^{77}Se NMR (δ) 54.46 (s, 3Se); MS (*m/e* for ^{80}Se) 450 [Me_612Se3^+], 230 [$Me_612Se3^+ - SeC_{10}H_{20}$], 150 [$Me_612Se3^+ - (Se_2C_{10}H_{20})$], 69 [$C_5H_9$]. Anal. Found (calcd) for **3**: C, 40.27 (40.28); H, 6.65 (6.76). Analytical data for **4**: ^1H NMR (δ in $CDCl_3$) 2.75 (s, 16H), 1.05 (s, 24H); ^{13}C NMR (δ) 39.99 (2C), 36.43 (1C), 27.69 (2C); ^{77}Se NMR (δ) 53.90 (s, 4Se); MS (*m/e* for ^{80}Se) 600 [Me_816Se4^+], 300 [$Me_816Se4^+ - Se_2C_{10}H_{20}$], 230 [$Me_816Se4^+ - Se_2C_{15}H_{30}$], 150 [$Me_816Se4^+ - Se_3C_{15}H_{30}$], 69 [$C_5H_9$].

Catalytic Cyclooligomerization of 3,3-Dimethylselenetane by $Re_2(CO)_9NCMe$. Under argon a 10 mg amount of $Re_2(CO)_9NCMe$ was added to a 25 mL round-bottom flask containing a stirbar, reflux condenser, and 500 mg of 3,3-dimethylselenatane. The reaction mixture was heated to 115 °C in an oil bath and was stirred for a period of 17 h. After the mixture was cooled, the unreacted 3,3-dimethylselenatane was removed *in vacuo*. The residue weighed 440 mg. A ^1H NMR spectrum of the residue showed the presence of two major compounds, Me_612Se3 and a polymer of 3,3-dimethylselenatane. Three products were separated from the polymer by TLC: 4 mg of **2** (1%), 92.5 mg of **3** (21%), and 11.5 mg of **4** (3%).

Pyrolysis of DMSe in the Absence of Catalyst. A 500 mg amount of 3,3-dimethylselenatane was added to a 25 mL round-bottom flask equipped with a stirbar and a reflux condenser. The flask was heated to 115 °C in an oil bath with stirring under argon for a period of 17 h. After the mixture was cooled, the unreacted 3,3-dimethylselenatane was removed *in vacuo*. The oily residue weighed 13.2 mg. By ^1H NMR analysis this 13.2 mg was shown to consist of **2**, **3**, **4**, and polymer in the percentages 7/10/3/71.

Preparation of $Re_2(CO)_9(Me_612Se3)$ (5). A 20.0 mg amount of $Re_2(CO)_9(NCMe)$ (0.030 mmol) was dissolved in 20 mL of hexane in a 25 mL three-neck round-bottom flask equipped with a stirbar, a reflux condenser, and a nitrogen inlet. A 20.0 mg amount of Me_612Se3 was added, and the resulting solution was heated to reflux and stirred for 2 h. After the mixture was cooled, the volatiles were removed *in vacuo*, and the product was separated from the unreacted $Re_2(CO)_9(NCMe)$ by TLC using a hexane/methylene chloride (3/1) solvent mixture to yield 18.6 mg of $Re_2(CO)_9(Me_612Se3)$ (**5**; 58% yield). Spectral data for **5**: IR ν_{CO} (cm^{-1} in hexane) 2102 (w), 2038 (m), 2016 (w), 1991 (s), 1976 (m), 1964 (m), 1951 (w), 1930 (m); ^1H NMR (δ in d_8-toluene at 25 °C) 3.42 (d, 2H, $^2J_{H-H} = 12$ Hz), 2.91 (d, 2H, $^2J_{H-H} = 12$ Hz), 2.64 (d, 2H, $^2J_{H-H} = 10.5$ Hz), 2.42 (d, 2H, $^2J_{H-H} = 10.5$ Hz), 2.35 (d, 4H, $^2J_{H-H} = 10.5$ Hz), 1.00 (s, 6H), 0.96 (s, 6H), 0.87 (s, 3H), 0.80 (s, 3H); ^1H NMR (δ in d_8-toluene at 100 °C) 3.24 (s, br, 4H), 2.55 (s, br, 4H), 2.49 (s, 4H), 2.42 (d, 2H, $^2J_{H-H} = 10.5$ Hz), 1.01 (s, 12H), 0.85 (s, 6H). Anal. Found (calcd): C, 26.98 (26.90); H, 2.81 (2.82).

Preparation of $Cu_4I_4(\mu\text{-}\eta^2\text{-}Me_612Se3)_2$ (6). An 18.0-mg amount (0.095 mmol) of CuI and a 20.0-mg amount (0.044 mmol) of Me_612Se3 were stirred at 25 °C in 20 mL of acetonitrile for 30 min. The solvent was then allowed to evaporate under a stream of nitrogen. The crude product was washed with 5 mL of acetonitrile and 5 mL of CH_2Cl_2 to yield 63 mg of **6** (86% yield). ^1H NMR (δ in $NCCD_3$): 2.82 (s, 12H), 1.02 (s, 18H). Anal. Found (calcd) for **6**: C, 22.64 (22.87); H, 3.74 (3.63).

Crystallographic Analysis. Golden yellow crystals of **1** and **5** were grown by slow evaporation of solvent from a solution in benzene at 25 °C. Colorless crystals of **2**, **3**, and **4** suitable for diffraction analysis were grown by slow evaporation of solvent from a solution in hexane at 25 °C. Colorless crystals of **6** were grown by slow evaporation of solvent from a solution in acetonitrile at 25 °C. All crystals used for the diffraction measurements were mounted in thin-walled glass capillaries. Diffraction measurements for compounds **1**−**4** and **6** were made on a Rigaku AFC6S fully automated four-circle diffractometer using graphite-monochromated Mo Kα radiation at 20 °C. The unit cells of the crystals were determined and refined from 15 randomly selected reflections obtained by using the AFC6 automatic search, center, index, and least-squares routines. Diffraction measurements on compound **5** were made on a Siemens CCD area detector-equipped diffractometer with the SMART software (Siemens Corp., Madison, WI). The frame data were integrated using the Siemens SAINT software. A total of 40 845 reflections were collected, of which 7675 were unique. The data were corrected for absorption using George Sheldrick's program SADABS, written explicitly for CCD data. Crystal data, data collection parameters, and results of the analyses are listed in Table 1. All data processing was performed either on a Digital Equipment Corp. VAXstation 3520 computer or a Silicon-Graphics INDIGO^2 workstation by using the TEXSAN structure solving program library obtained from the Molecular Structure Corp., The Woodlands, TX. Neutral atom scattering factors were calculated by the standard procedures.[9a] Anomalous disper-

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Table 1. Crystallographic Data for Compounds 1−6

	1	2	3	4	5	6
formula	$Re_2SeO_9C_{14}H_{10}$	$Se_2C_{10}H_{20}$	$Se_3C_{15}H_{30}$	$Se_4C_{20}H_{40}$	$Re_2Se_3O_9C_{24}H_{30}$	$Cu_4I_4Se_6C_{30}H_{60}\cdot NCCH_3$
fw	773.60	298.19	447.28	596.38	1071.79	1697.42
cryst syst	monoclinic	monoclinic	monoclinic	triclinic	tetragonal	orthorhombic
lattice params						
a (Å)	9.313(3)	10.534(3)	11.660(3)	8.669(1)	11.0155(1)	21.398(4)
b (Å)	11.983(4)	7.602(2)	10.975(2)	9.719(2)	11.0155(1)	21.875(3)
c (Å)	17.898(4)	15.612(3)	14.578(3)	7.402(1)	53.2195(6)	21.175(5)
α (deg)	90.00	90.00	90.00	94.23(2)	90.00	90.00
β (deg)	97.68(2)	96.88(2)	98.57(2)	94.72(1)	90.00	90.00
γ (deg)	90.00	90.00	90.00	79.34(2)	90.00	90.00
V (Å^3)	1979.4(9)	1241.1(5)	1860(2)	609.7(2)	6457.72(7)	9911(3)
space group	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)	$P2_1/a$ (No. 14)	$P\bar{1}$ (No. 2)	$P4_12_12$ (No. 92)	$Pbca$ (No. 61)
Z	4	4	4	1	8	8
ρ_{calc} (g/cm^3)	2.59	1.60	2.58	1.62	2.20	2.28
μ(Mo Kα) (cm^{-1})	141.0	59.1	14.4	60.2	109.2	86.16
temp (°C)	20	20	20	20	25	20
no. of obs rflns ($I > 3\sigma(I)$)	1985	631	1697	1241	3393*	3476
no. of variables	236	95	163	109	339	409
goodness of fit (GOF)[a]	1.86	2.32	2.53	3.86	1.75	2.07
max shift/error on final cycle	0.05	0.00	0.00	0.00	0.00	0.07
residuals: R; R_w[a]	0.036; 0.036	0.043; 0.049	0.045; 0.049	0.043; 0.046	0.054; 0.067	0.048; 0.066
abs cor	DIFABS	empirical	empirical	DIFABS	SADABS	DIFABS
transmissn coeff, max/min	1.00/0.43	1.00/0.42	1.00/0.16	1.00/0.57		1.00/0.42
largest pk in final diff map (e/Å^3)	0.85	0.70	0.52	0.48	1.34	1.17

[a] $R = \sum_{hkl}(||F_o| - |F_c||)/\sum_{hkl}|F_o|$; $R_w = [\sum_{hkl}w(|F_o| - |F_c|)^2/\sum_{hkl}wF_o^2]^{1/2}$, $w = 1/\sigma^2(F_o)$; GOF $= [\sum_{hkl}(w(|F_o| - |F_c|))^2)/(n_{data} - n_{vari})]^{1/2}$.

sion corrections were applied to all non-hydrogen atoms.[9b] Lorentz/polarization (Lp) corrections were applied to the data for each structure. Full-matrix least-squares refinements minimized the function $\sum_{hkl}w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F)$, $\sigma(F) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02I_{net})^2]^{1/2}/Lp$.

Compounds **1**−**3** crystallized in the monoclinic crystal system. For compounds **1** and **3** the space groups $P2_1/c$ and $P2_1/a$, respectively, were established unambiguously from the patterns of systematic absences observed during the collection of the intensity data. The patterns of systematic absences for compound **2** are consistent with either of the space groups Cc and $C2/c$. The centrosymmetric space group $C2/c$ was tested initially and was confirmed by the successful solution and refinement of the structure. Compound **4** crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure. Compound **5** crystallizes in the tetragonal crystal system. The patterns of systematic absences observed in the data are consistent with the space group $P4_12_12$ or its enantiomorph $P4_32_12$. The structure was solved initially in the space group $P4_12_12$. Subsequently, the completed structure was refined in the space group $P4_32_12$ after the structure was inverted. The R factors for the refinement in the space group $P4_32_12$ were significantly higher than those in the space group $P4_12_12$; thus, the latter is deemed to be correct and the results reported here correspond to the refinement in the space group $P4_12_12$. Compound **6** crystallized in the orthorhombic crystal system. The space group $Pbca$ was identified unambiguously on the basis of the patterns of systematic absences observed in the data. In the final stages of analysis a molecule of MeCN from the crystallization solvent was found cocrystallized in the crystal lattice. It was included and satisfactorily refined with isotropic thermal parameters.

All structures were solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. Except for compound **2**, the positions of all hydrogen atoms were calculated by assuming idealized tetrahedral geometries at the carbon atoms with C−H distances of 0.95 Å. The scattering contributions of the hydrogen atoms were included in the structure factor calculations, but their positions were not refined. In the analysis of compound **2**, the hydrogen atoms were located and refined.

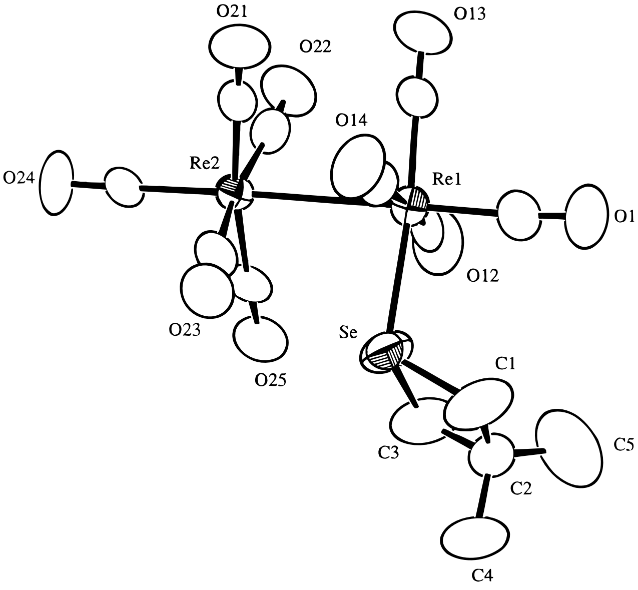

Figure 1. ORTEP diagram of $Re_2(CO)_9(SeCH_2CMe_2CH_2)$ (**1**) showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg): Re(1)−Re(2) = 3.050(1), Re(1)−Se = 2.605(2), Se−C(1) = 1.93(2), Se−C(3) = 1.91(2), C(1)−C(2) = 1.54(3), C(2)−C(3) = 1.51(3); Re(1)−Re(2)−Se = 88.17(5), C(1)−Se−C(3) = 72.2(9).

Results

The compound $Re_2(CO)_9(SeCH_2CMe_2CH_2)$ (**1**) was obtained from the reaction of $Re_2(CO)_9(NCMe)$ with DMSe in 88% yield. Compound **1** was characterized by IR, ^{1}H NMR, and a single-crystal X-ray diffraction analysis. An ORTEP diagram of **1** is shown in Figure 1. The compound is isomorphous and isostructural with its sulfur homologue, $Re_2(CO)_9(SCH_2CMe_2CH_2)$ (**7**).[3c] The DMSe ligand occupies an equatorial coordination site on one of the two rhenium atoms. The *cis*-positioned ligands exhibit a staggered rotational conformation similar to that found in **7** and $Re_2(CO)_{10}$.[10]

The Re−Re distance in **1** is 3.050(1) Å, similar to those found in **7** (3.0422(8) Å) and $Re_2(CO)_{10}$ (3.041(1) Å). The Re−Se distance in **1** is 2.605(2) Å. This compares favorably with the Re−Se distances found in the complexes $ReI(CO)_3(MeSeCH_2CH_2SeMe)$ (2.593(1) and 2.597(1) Å),[11] $Re_2Br_2(CO)_6(\mu\text{-}PhCH_2SeSeCH_2Ph)$ (2.583(3) and 2.599(3) Å),[12] $Re_2Br_2(CO)_6(\mu\text{-}PhSeSePh)$ (2.604(4) Å),[13] and $Re_2Cl_2(CO)_6(\overline{SeCH_2CMe_2CH_2Se})$ (2.601(5) and 2.611(5) Å).[14] There appear to have been no previous crystallographic characterizations of selenatane ligands.

The C−Se−C angle is very acute, 72.2(9)°, but this is only slightly smaller than the C−S−C angle found for the 3,3-dimethylthietane (DMT) ligand in **7**, 73.9(8)°.[9] The ring in **1** is planar. A similar observation was made for the DMT ligand in **7**. This contrasts with other structural studies of thietane ligands where slight puckering of the thietane rings has been observed.[15] The selenium atom has a pyramidal geometry, and the ^1H NMR spectrum of **1** shows two singlets for the methyl resonances (*δ* 1.41 (s, 3H), 1.22 (s, 3H)) and an AB quartet for the methylene groups (3.58 (d, 2H, $^2J_{H-H}$ = 9.4 Hz) and 3.20 (d, 2H, $^2J_{H-H}$ = 9.7 Hz)) at room temperature, as expected. This contrasts with the ^1H NMR spectrum of **7**, which shows singlets for the methyl and methylene resonances and indicates that the pyramidal sulfur atom is rapidly inverting its configuration on the NMR time scale and averaging the inequivalent methyl groups and methylene hydrogen atoms.[16] Clearly, the corresponding process in **1** is not rapid on the NMR time scale.

$Re_2(CO)_9(NCMe)$ and **1** were found to be catalysts for the formation of polyselenoether macrocycles from DMSe when heated in the presence of DMSe and in the absence of solvent to 115 °C. The catalytic activity of **1** is slightly higher than that of $Re_2(CO)_9(NCMe)$. In a typical reaction 15.0 mg of **1** dissolved in 0.75 g of DMSe was heated to 115 °C for 8 h. This yielded a residue of 340 mg of nonvolatile residue after removal of the unreacted DMSe. From this residue 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**) were isolated by TLC separations. The bulk of the products is believed to be a polymer of DMSe. Although the isolated yields are very low for **2** and **4**, for **3** the yield is equivalent to 16.5 turnovers or 2 turnovers/h. This is about 70 times more active than **7** is for the catalytic formation of the sulfur homologue Me_612S3 from DMT.[3c] This could be attributed to the weaker Se−C bonds and higher reactivity of DMSe compared to DMT.

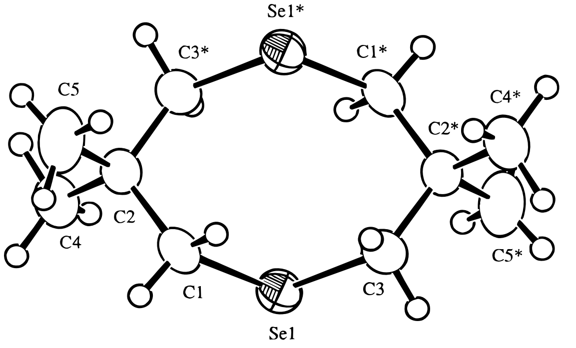

Figure 2. ORTEP diagram of 3,3,7,7-tetramethyl-1,5-diselenacyclooctane (**2**). Selected interatomic distances (Å): Se(1)−C(1) = 1.961(8), Se(1)−C(3) = 1.974(8), C(1)−C(2) = 1.52(1), C(2)−C(3*) = 1.52(1).

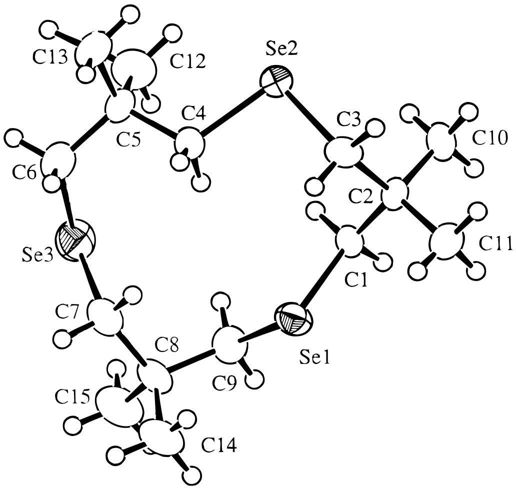

Figure 3. ORTEP diagram of 3,3,7,7,11,11-hexamethyl-1,5,9-triselenacyclododecane (**3**). Selected interatomic distances (Å): Se(1)−C(1) = 1.965(8), Se(1)−C(9) = 1.953(9), Se(2)−C(3) = 1.952(9), Se(2)−C(4) = 1.957(9), Se(3)−C(6) = 1.97(1), Se(3)−C(7) = 1.97(1).

All three of the macrocycles are new, and as a result all were characterized crystallographically. Structural diagrams of each are shown in Figures 2−4, respectively. In all three structures the *gem*-dimethyl groups are directed toward the exterior of the ring. Compounds **2** and **4** both contain a crystallographically imposed center of symmetry in the solid state. All Se−C distances are similar: Se(1)−C(1) = 1.961(8) Å and Se(1)−C(3) = 1.974(8) Å for **2**; Se(1)−C(1) = 1.965(8) Å, Se(1)−C(9) = 1.953(9) Å, Se(2)−C(3) = 1.952(9) Å, Se(2)−C(4) = 1.957(9) Å, Se(3)−C(6) = 1.97(1) Å and Se(3)−C(7) = 1.97(1) Å for **3**; Se(1)−C(1) = 1.961(9) Å, Se(1)−C(6) = 1.967(9) Å, Se(2)−C(3) = 1.961(9) Å, and Se(2)−C(4) = 1.956(9) Å for **4**. These values are similar to those found for related unsubstituted selenoether macrocycles: $C_8H_{16}Se_4$, $C_{12}H_{24}Se_6$, $C_{12}H_{24}Se_4$, $C_{18}H_{36}Se_6$, and $C_{10}H_{20}Se_4$.[4c] For **3** and **4** the conformations of the rings and packing of the molecules in the solid state are completely analogous to those of the sulfur homologues which we have recently reported.[3c]

The reaction of $Re_2(CO)_9(NCMe)$ with **3** yielded the complex $Re_2(CO)_9(Me_612Se3)$ (**5**) in 58% yield. Compound **5** was also characterized crystallographically, and an ORTEP diagram of its molecular structure is shown in Figure 5. Complex **5** is structurally analogous to **1**

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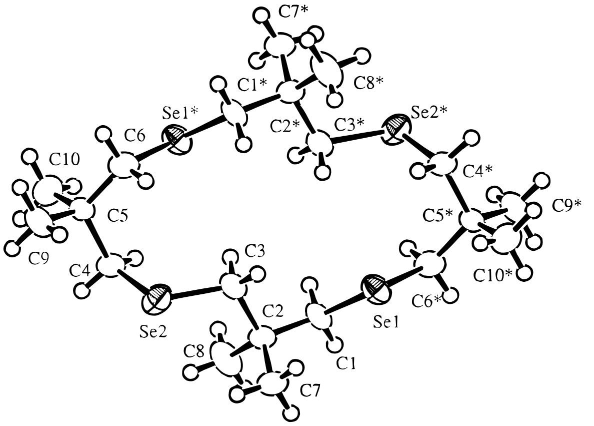


Figure 4. ORTEP diagram of 3,3,7,7,11,11,15,15-octamethyl-1,5,9,13-tetraselenacyclohexadecane (**4**). Selected interatomic distances (Å): Se(1)−C(51) = 1.961(9), Se(1)−C(6) = 1.967(9), Se(2)−C(3) = 1.961(9), Se(2)−C(4) = 1.956(9), C(1)−C(2) = 1.54(1), C(2)−C(3) = 1.57(1), C(4)−C(5) = 1.55(1), C(5)−C(6) = 1.51(1).

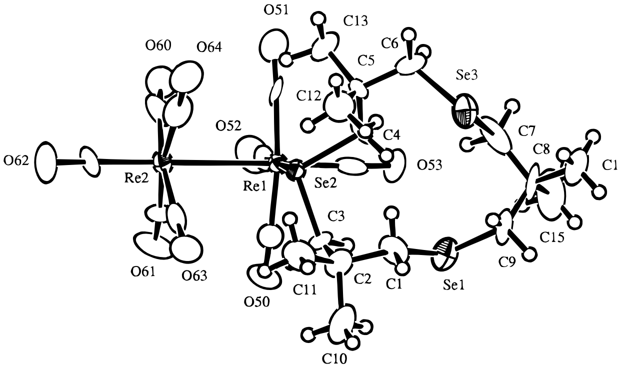


Figure 5. ORTEP diagram of $Re_2(CO)_9(Me_612Se3)$ (**5**) showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg): Re(1)−Re(2) = 3.048(1), Re(1)−Se(2) = 2.657(2), Se(1)−C(1) = 1.93(2), Se(1)−C(9) = 1.97(3), Se(2)−C(3) = 1.98(3), Se(2)−C(4) = 2.02(2), Se(3)−C(6) = 2.20(3), Se(3)−C(7) = 1.92(2); Re(1)−Re(2)−Se(2) = 89.42(5), C(1)−Se(1)−C(9) = 98(1), C(3)−Se(2)−C(4) = 102(1), C(6)−Se(3)−C(7) = 100(2).

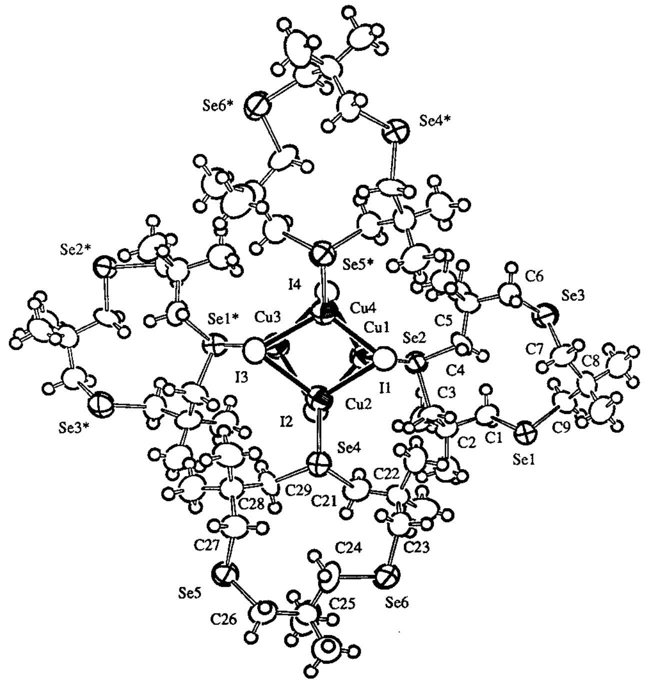


Figure 6. ORTEP diagram of $Cu_4I_4(\mu\text{-}\eta^2\text{-}Me_612Se3)_2$ (**6**) showing the four Me_612Se3 ligands coordinated to the Cu_4I_4 cluster.

and **3** and three trithia crown derivatives of $Re_2(CO)_{10}$ that we have recently reported: $Re_2(CO)_9(12S3)$ (**8**),[3a] $Re_2(CO)_9$(*trans*-Me_312S3) (**9**),[3b] and $Re_2(CO)_9$(*cis*-Me_3-12S3) (**10**).[3b] All of these complexes have η^1 heterocycles in equatorial coordination sites with staggered rotational conformations of the equatorial ligands on the metal atoms. The Re−Re bond distance in **5**, 3.048(1) Å, is similar to that in **1**. The Re−Se distance is slightly, but significantly, longer than that in **1**, 2.657(2) Å. Except for some slight twists (maximum ∼30°), the conformation of the Me_612Se3 ligand in **5** is similar that of the free molecule. Once again, one methylene group C(4) is again directed strongly toward the interior of the ring.

The ^1H NMR spectra of compound **5** are strongly temperature dependent. At 25 °C the spectrum shows four methyl resonances, two of intensity 6 and two of intensity 3, and three sets of AB quartets with *gem* couplings due to the three types of methylene groups. The hydrogen atoms on any one methylene group are inequivalent. This is consistent with the structure as found in the solid state. As the temperature is raised, the methyl resonances of intensity 6 broaden and merge to a sharp singlet at 100 °C. The methyl resonances of intensity 3 undergo a similar broadening and averaging to a sharp singlet at 100 °C. Likewise, the resonances of the methylene groups broaden and average into three singlets at 100 °C. Two of these are still broad at 100 °C. These changes can be explained by intramolecular inversions of configuration at the pyramidally coordinated selenium atom.[16] Note: a dissociation−reassociation mechanism is ruled out, because such a process would lead to an averaging of all of the methyl groups and all of the methylene groups. On the basis of the coalescence temperature of the methylene resonances at 3.42 and 2.91 ppm, ΔG^*_{333} = 15.6(5) kcal/mol.

When **3** was allowed to react with CuI in acetonitrile solvent, the new compound $Cu_4I_4((\mu\text{-}\eta^2\text{-}Me_612Se3)_2$ (**6**) was obtained in 86% yield. Compound **6** was also characterized by a single-crystal X-ray diffraction analysis in the form of a cocrystallized NCMe solvate. An ORTEP drawing of the solid-state structure of **6** is shown in Figure 6. Selected interatomic distances and angles are listed in Tables 2 and 3, respectively. The structure of **6** consists of a three-dimensional network of "cubane-like" Cu_4I_4 clusters linked by four bridging Me_612Se3 ligands. Each copper atom contains one η^1-Me_612Se3 ligand, but only two of these are symmetry-independent. Each Me_612Se3 ligand serves as a bridge to a second Cu_4I_4 cluster. In this way the Me_612Se3 ligands utilize two of the three possible selenium atoms for coordination. The third selenium atom remains uncoordinated. The conformation of the Me_612Se3 ligand is similar to that in **3** and **5**. The ligand has no symmetry of its own, and therefore each selenium atom is inequivalent. For the ligand labeled Se(1), Se(2), Se(3), coordination occurs at the selenium atom Se(1) (to Cu(3) of a neighboring cluster) and Se(2) (to Cu(1)). The latter is analogous to that in **5**. This ligand, as shown in Figure 6, is a mirror image of the one shown in Figure 3. The Me_612Se3 ligand labeled Se(4), Se(5), Se(6) is the exact image of the one shown in Figure 3. For this

Table 2. Selected Intramolecular Distances for 6[a]

I(1)−Cu(1)	2.646(3)	Se(4)−C(21)	2.00(2)
I(1)−Cu(2)	2.686(3)	Se(4)−C(29)	1.97(1)
I(1)−Cu(4)	2.615(3)	Se(5*)−Cu(4)	2.464(3)
I(2)−Cu(1)	2.679(3)	Se(5)−C(26)	1.97(2)
I(2)−Cu(2)	2.728(3)	Se(5)−C(27)	1.97(2)
I(2)−Cu(3)	2.720(3)	Se(6)−C(23)	1.92(2)
I(3)−Cu(2)	2.700(3)	Se(6)−C(24)	1.95(2)
I(3)−Cu(3)	2.704(3)	Cu(1)−Cu(2)	2.780(4)
I(3)−Cu(4)	2.695(3)	C(1)−C(2)	1.57(2)
I(4)−Cu(1)	2.710(3)	C(2)−C(3)	1.59(2)
I(4)−Cu(3)	2.642(2)	C(4)−C(5)	1.53(2)
I(4)−Cu(4)	2.721(3)	C(5)−C(6)	1.52(2)
Se(1)−Cu(3)	2.473(3)	C(7)−C(8)	1.53(2)
Se(1)−C(1)	1.98(2)	C(8)−C(9)	1.57(2)
Se(1)−C(9)	1.97(2)	C(21)−C(22)	1.48(2)
Se(2)−Cu(1)	2.432(3)	C(22)−C(23)	1.53(2)
Se(2)−C(3)	1.97(1)	C(24)−C(25)	1.54(3)
Se(2)−C(4)	1.93(1)	C(25)−C(26)	1.53(2)
Se(3)−C(6)	1.95(2)	C(27)−C(28)	1.56(2)
Se(3)−C(7)	1.97(2)	C(28)−C(29)	1.55(2)
Se(4)−Cu(2)	2.485(3)		

[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

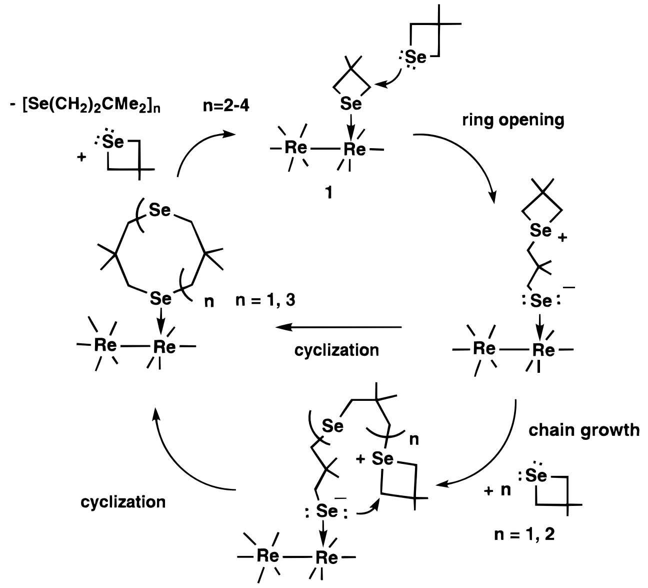
Table 3. Intramolecular Bond Angles for 6[a]

Cu(3)−Se(1)−C(1)	104.2(5)	I(1)−Cu(1)−Se(2)	113.5(1)
Cu(3)−Se(1)−C(9)	97.5(5)	I(2)−Cu(1)−Se(2)	103.0(1)
C(1)−Se(1)−C(9)	96.9(7)	I(4)−Cu(1)−Se(2)	105.3(1)
Cu(1)−Se(2)−C(3)	104.3(5)	Se(2)−Cu(1)−Cu(2)	142.1(1)
Cu(1)−Se(2)−C(4)	109.8(5)	I(1)−Cu(2)−Se(4)	112.4(1)
C(3)−Se(2)−C(4)	96.7(7)	I(2)−Cu(2)−Se(4)	103.1(1)
C(6)−Se(3)−C(7)	98.2(7)	I(3)−Cu(2)−Se(4)	119.2(1)
Cu(2)−Se(4)−C(21)	101.8(5)	Se(4)−Cu(2)−Cu(1)	138.6(1)
Cu(2)−Se(4)−C(29)	100.9(5)	I(2)−Cu(3)−Se(1)	109.2(1)
C(21)−Se(4)−C(29)	97.2(7)	I(3)−Cu(3)−Se(1)	107.4(1)
Cu(4)−Se(5)−C(26)	94.4(5)	I(4)−Cu(3)−Se(1)	120.0(1)
Cu(4)−Se(5)−C(27)	103.3(5)	I(1)−Cu(4)−Se(5)	111.2(1)
C(26)−Se(5)−C(27)	103.6(8)	I(3)−Cu(4)−Se(5)	108.9(1)
C(23)−Se(6)−C(24)	99.6(8)	I(4)−Cu(4)−Se(5)	111.2(1)

[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

ligand Se(4) corresponds to Se(1) in **3**, Se(5) corresponds to Se(3), and Se(6) corresponds to Se(2). The copper atoms are coordinated to Se(4) and Se(5), corresponding to Se(1) and Se(3). Thus, all three types of selenium atoms are engaged in binding to a copper atom at least once. Ligand-supported cubane Cu_4X_4 clusters have been observed for a variety of other ligands.[17,18] In **6** the Cu−Cu distances within a given cluster span a wide range, 2.780(4)−3.201(4) Å, but these are not unusual.

Scheme 1



Likewise, the Cu−I distances are similar to those found previously in a large number of Cu_4I_4 cluster complexes.[17,18] The Cu−Se distances, Cu(1)−Se(2) = 2.432(3) Å, Cu(2)−Se(4) = 2.485(3) Å, Cu(3)−Se(1) = 2.473(3) Å, and Cu(4)−Se(5) = 2.464(3) Å, are also similar to those previously observed for other copper selenoether complexes.[4ab,19] When **6** is dissolved in CD_3CN, only two resonances are observed in the ^1H NMR spectrum at δ 2.82 (s, 12H), 1.02 (s, 18H). This is not consistent with the solid-state structure. These resonances are not significantly different from those of the free molecule **3**; therefore, it is concluded that the Me612Se3 ligands are displaced from the copper atoms when **6** is dissolved.

Discussion

We have prepared the three new polyselenoether macrocycles **2**−**4** by a new procedure, a catalytic ring-opening macrocyclization of DMSe by the complex **1**. In the absence of a catalyst, no significant amounts of the macrocycles or polymer are formed from DMSe under the same conditions. The mechanism is believed to involve a series of ring-opening additions of DMSe to the DMSe ligand in **1**, followed by a recyclization, similar to that established for the macrocyclizations of thietane,[3a] 3-methylthietane,[3b] and 3,3-dimethylthietane (DMT)[3c] (see Scheme 1). The catalytic cycle is completed by substitution of the macrocycle by another DMSe molecule. DMSe is considerably more reactive than DMT, although the yield of **3** is still low and those of **2** and **4** are very low. Note: this is the first time that we have observed the formation of a dimer (**2**) of the substrate in one of these catalytic macrocylization reactions. Unfortunately, the bulk of the DMSe appears to be converted into high-weight polymers. These have not been fully characterized. The catalysis by $Re_2(CO)_9(NCMe)$ is believed to proceed similarly via formation of **1** *in situ* by substitution of the NCMe ligand by DMSe. To date, our studies have been limited to DMSe due to the lower stability of the less substituted selenatanes.

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It has been suggested that the placement of *gem*-dimethyl groups on the rings of polythioether macrocycles will cause the sulfur atoms to turn toward the interior of the ring and enhance their ligand properties.[20] This prediction is only partially supported for the selenium compounds reported here. In fact, it is methylene groups, C(4) on Me_612Se3 and C(3) and C(3*) on Me_816Se4, that are turned most dramatically toward the interior of the ring. Our studies have shown nevertheless that **3** can function as an effective ligand. This was demonstrated by the synthesis of the compounds **5** and **6**. In **5** the Me_612Se3 is monodentate while in **6** it is a bidentate bridging ligand. In both cases, however, the metal atoms are located on the exterior of the ring. The Me_612Se3 ligand is clearly very bulky due to the presence of the *gem*-dimethyl groups, but any steric interactions that are produced upon coordination have not induced any major changes in the conformation of the macrocycle. For **6** the ligand is apparently displaced from the copper atoms upon dissolution in acetonitrile. However, for **5** the ligand remains coordinated in solution and even undergoes rapid inversions of configuration at the coordinated selenium atom without dissociation at 100 °C in toluene solvent.

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Supporting Information Available: Additional material concerning the X-ray crystal structure analyses of the compounds **1**−**6**, including tables of bond lengths and angles and positional and thermal parameters (42 pages). Ordering information is given on any current masthead page.

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