2612 *Organometallics* **1997,** *16,* 2612−2617

Catalytic Macrocyclization of 3,3-Dimethylthietane by $Re_2(CO)_9(\overline{SCH_2CMe_2C}H_2)$

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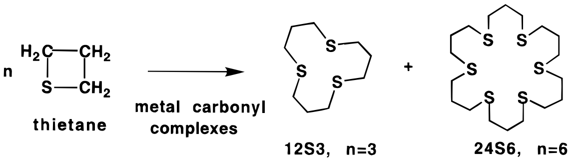
Received February 28, 1997⊗

The reaction of $Re_2(CO)_9(NCMe)$, **1**, with 3,3-dimethylthietane ($\overline{SCH_2CMe_2C}H_2$, 3,3-DMT) yielded the complex $Re_2(CO)_9(\overline{SCH_2CMe_2C}H_2)$, **2**. Compound **2** has been found to react with 3,3-DMT at 100 °C to yield the polythioether macrocycles 3,3,7,7,11,11-hexamethyl-1,5,9-trithiacyclododecane, **3** ($Me_6$12S3), 3,3,7,7,11,11,15,15-octamethyl-1,5,9,13-tetrathiacyclohexadecane, **4** ($Me_8$16S4), and 3,3,7,7,11,11,15,15,19,19-decamethyl-1,5,9,13,17-pentathiacycloeicosane, **5** (Me_{10}20S5), catalytically, but the activity and yields of the macrocycles are low. High molecular weight oligomers of 3,3-DMT are the principal products. A macrocyclization mechanism consisting of a metal-induced ring-opening cyclooligomerization of three, four, and five molecules of 3,3-DMT, respectively, is proposed. The reaction of **3** with $CpMn(CO)_3$ in the presence of UV irradiation yielded the complex $CpMn(CO)_2(\eta^1\text{-}Me_6\text{12S3})$, **6**. The molecular structures of each of the macrocycles **3**, **4**, and **5** and the complexes **2** and **6** were determined by single-crystal X-ray diffraction analyses.

Introduction

We have recently shown that certain third-row transition metal carbonyl complexes are capable of producing macrocyclization of thietanes by ring-opening cyclooligomerization processes.[1] The complexes $Re_3(CO)_{10}(\mu\text{-}\overline{SCH_2CH_2C}H_2)(\mu\text{-}H)_3$,[2] $Re_2(CO)_9(\overline{SCH_2CH_2C}H_2)$,[3] $Os_4(CO)_{11}(\overline{SCH_2CH_2C}H_2)(\mu\text{-}H)_4$,[4] and $W(CO)_5(\overline{SCH_2CH_2C}H_2)$[5] were found to be the most effective catalysts. Macrocycles containing 3−6 equiv of the thietane have been isolated, e.g., eq 1, 12S3 = 1,5,9-trithiacyclododecane and 24S6 = 1,5,9,13,17,21-hexathiacyclotetracosane.



(1)

Polythioether macrocycles have attracted considerable attention for their potential to serve as ligands for transition metals.[6]

We have also observed similar catalytic macrocyclization of 3-methylthietane (3-MT) by 3-MT derivatives of $Re_2(CO)_{10}$ and $W(CO)_6$.[7] We have now investigated the catalytic macrocyclization of 3,3-dimethylthietane ($\overline{SCH_2CMe_2C}H_2$, 3,3-DMT) by the complex $Re_2(CO)_9(\overline{SCH_2CMe_2C}H_2)$, **2**. Three macrocycles 3,3,7,7,11,11-hexamethyl-1,5,9-trithiacyclododecane, **3** ($Me_6$12S3), 3,3,7,7,-11,11,15,15-octamethyl-1,5,9,13-tetrathiacyclohexadecane, **4** ($Me_8$16S4), and 3,3,7,7,11,11,15,15,19,19-decamethyl-1,5,9,13,17-pentathiacycloeicosane, **5** (Me_{10}20S5) have been synthesized and the structures determined crystallographically. These results are reported herein.

Experimental Section

General Data. Reagent grade solvents were stored over 4 Å molecular sieves. All reactions were performed under a nitrogen atmosphere. Infrared spectra were recorded on a Nicolet 5DXB FTIR spectrophotometer. $Re_2(CO)_9(NCMe)$,[8] **1**, and 3,3-dimethylthietane[9] were prepared according to the published procedures. Product separations were performed by thin layer chromatography (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 was performed by Oneida Research Services, Whitesboro, NY.

Preparation of $Re_2(CO)_9(\overline{SCH_2CMe_2C}H_2)$, 2. A 45.0 mg amount of **1** (0.062 mmol) was dissolved in 15 mL of hexane in a 25 mL three-neck round-bottomed flask equipped with a stir bar, reflux condenser, and nitrogen inlet. A 22 μL amount of 3,3-DMT (0.308 mmol) was added, and the resulting solution was heated to reflux with stirring for 2 h. The volatiles were removed *in vacuo*, and the product was isolated by TLC using a hexane/methylene chloride (3/1) solvent mixture to yield 40.8 mg (83%) of $Re_2(CO)_9(\overline{SCH_2CMe_2C}H_2)$, **2**. Spectral data for **2**: IR ν_{CO} (cm^{-1}, hexane): 2103 (w), 2042 (m), 2016 (w), 1996 (vs),

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⊗ Abstract published in *Advance ACS Abstracts*, May 15, 1997.

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1990 (vs), 1977 (w), 1969(m), 1956 (w), 1933 (m). ^{1}H NMR (*δ*, CDCl$_3$): 3.43 (s, 4H), 1.36 (s, 6H). MS *m*/*z* for Re^{187} = 728 − *x*(28), *x* = 1, 3, 6−8; parent ion − X(CO), *x* = 1, 3, 6−8.

Catalytic Macrocyclization of 3,3-DMT by 2. Synthesis of $SCH_2CMe_2(SCH_2CMe_2CH_2)_2CH_2$, 3, $SCH_2CMe_2(SCH_2CMe_2CH_2)_3CH_2$, 4, and $SCH_2CMe_2(SCH_2CMe_2CH_2)_4CH_2$, 5. All of the catalytic reactions were performed under nitrogen by the following procedure. A preweighed amount of crystalline catalyst was placed in a 25 mL three-neck round-bottomed flask equipped with a stir bar, reflux condenser, and nitrogen inlet. Then 2 mL of freshly distilled 3,3-DMT (28.0 mmol) was added, and the solution was stirred and heated to 100 °C by means of an oil bath. A typical reaction and work-up are as follows: 2.0 mL of 3,3-dimethylthietane (28.0 mmol) and 16.0 mg of **2** (0.022 mmol) were heated to 100 °C for 72 h. After the mixture was cooled, the excess 3,3-DMT was removed *in vacuo*. The resulting residue was dissolved in methylene chloride and filtered. After removal of the solvent, the residue weighed 197 mg, 181 mg of organic residue after correcting for the weight of the catalyst. ^{1}H and ^{13}C NMR spectra of this residue indicated that it consisted primarily of high molecular weight oligomers (76%), as well as three other products which were subsequently identified as Me$_6$12S3, **3** (10%), Me$_8$16S4, **4** (3%), and Me$_{10}$20S5, **5** (3%). The residue was filtered through a 6 in. silica gel column with a hexane/methylene chloride (3/1) solvent mixture to remove the high molecular weight oligomers. The macrocycles were then separated by TLC using a hexane/methylene chloride (3/1) solvent mixture to yield 16.0 mg of **3**, 3.0 mg of **4**, and 4.0 mg of **5**. For **3**, this is equivalent to 2.4 turnovers or 0.033 turnovers/h. Repeated attempts to separate the higher macrocycles by chromatography did not yield sufficient amounts of these compounds for complete characterization. Spectral data for **3:** ^{1}H NMR (*δ*, CDCl$_3$) 2.68 (s, 12H), 0.99 (s, 18H). ^{13}C NMR (*δ*, CDCl$_3$): 44.07 (6C), 36.67 (3C), 27.21 (6C). Spectral data for **4**: ^{1}H NMR (*δ*, CDCl$_3$) 2.65 (s, 16H), 1.02 (s, 24H). ^{13}C NMR (*δ*, CDCl$_3$): 45.79 (8C), 36.72 (4C), 27.05 (8C). Spectral data for **5**: ^{1}H NMR (*δ*, CDCl$_3$) 2.62 (s, 20H), 1.01 (s, 30H). ^{13}C NMR (*δ*, CDCl$_3$): 46.06 (6C), 36.95 (3C), 26.81 (6C). Spectral data for polymers: ^{1}H NMR (*δ*, CDCl$_3$) 2.56 (s, 2H), 1.00 (s, 3H). The mass spectra for **3**, **4**, and **5** show the parent ions at 306, 408, and 510 *m*/*e*, respectively, as well as additional ions with weights of 204, 134, and 102 m^+/e corresponding to $(SC_5H_{10})_2^+$, $(SSC_5H_{10})^+$, and 3,3-dimethylthietane. GC/MS of the residues showed evidence for larger macrocycles, but these could not be isolated.

Control Experiments. (a) In a control experiment, 2.0 mL of 3,3-DMT was heated to 100 °C for 72 h in the absence of solvent or any added metal complexes. After the solution was cooled, the unreacted 3,3-DMT was removed *in vacuo*. The contents of the flask were removed by washing with methylene chloride. After removal of the methylene chloride from the collected washings, the total weight of the residue was 4.0 mg. A ^{1}H NMR spectrum of this residue showed that it consisted principally of grease, trace amounts (<25% of the total) of polymer, and **3**.

(b) In a control experiment, 2.0 mL of 3,3-dimethylthietane (28.0 mmol) and 14.4 mg of Re$_2$(CO)$_{10}$ (0.022 mmol) in a 25 mL round-bottomed flask were heated to 100 °C for 72 h. After the mixture was cooled, the excess 3,3-DMT was removed *in vacuo*. The resulting residue was dissolved in methylene chloride and filtered. After removal of the methylene chloride solvent, the residue weighed 21.5 mg. An IR spectrum of a portion of the residue in the CO region showed only the absorptions of Re$_2$(CO)$_{10}$. The organic residue was determined to be 7.1 mg, after correcting for the weight of Re$_2$(CO)$_{10}$. An analysis of this residue by ^{1}H NMR spectroscopy showed that it consisted of polymer (28%, 2.0 mg) and **3** (8%, 0.6 mg). The remainder was unidentified compounds.

Preparation of CpMn(CO)$_2$(η^1-Me$_6$12S3), 6. A 23.4 mg amount of CpMn(CO)$_3$ (0.115 mmol) was dissolved in 20 mL of hexane in a 50 mL three-neck round-bottomed flask equipped with a stir bar, a nitrogen inlet, and an outlet. A 35.5 mg amount of Me$_6$12S3 (0.115 mmol) was added, and the solution was then irradiated for 30 min by using a 360 W high-pressure Hg lamp in the presence of a slow purge of nitrogen through the solution. The volatiles were then removed *in vacuo*, and the residue was dissolved in methylene chloride and filtered through a 6 in. silica gel column. The golden yellow product was separated by TLC using a hexane/methylene chloride (3/1) solvent mixture to yield 12.7 mg (24%) of **6** and 6.0 mg of unknown compound. Spectral and analytical data for **6**: IR ν_{CO} (cm^{-1}, hexane): 1944 (vs), 1938 (s), 1880 (vs), 1875 (s). ^{1}H NMR (*δ*, CDCl$_3$): 4.45 (s, 5H), 2.76 (s, 4H), 2.63 (s, 4H), 2.57 (s, 4H), 1.09 (s, 12H), 0.95 (s, 6H). Anal. Calcd for C$_{22}$H$_{35}$O$_2$S$_3$Mn: C, 54.75; H, 7.31. Found C, 54.79; H, 7.02.

Crystallographic Analysis. Colorless crystals of **2** and **3** suitable for diffraction analysis were grown by slow evaporation of solvent from a solution in hexane at 25 °C. Colorless crystals of **4** and **5** suitable for diffraction analysis were grown by slow evaporation of solvent from a solution in hexane at 0 °C. Golden yellow crystals of **6** suitable for X-ray diffraction analysis were grown from solution in a 1/1 methylene chloride/hexane solvent mixture by slow evaporation of solvent at 25 °C under a nitrogen atmosphere. All crystals used for the diffraction measurements were mounted in thin-walled glass capillaries. Diffraction measurements 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. 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.[10a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[10b] 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 $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02\ I_{net})^2]^{1/2}/Lp$.

Compounds **2** and **3** crystallized in the monoclinic crystal system. The space group $P2_1/n$ was established for both from the patterns of systematic absences observed during the collection of intensity data. Compounds **4**, **5**, and **6** crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement for all three of these structures. 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. The positions of the hydrogen atoms on the DMT ligand in **2** 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. The positions of all of the hydrogen atoms on the macrocycles **3**−**5** and the ligands in **6** were located and refined.

Results

The reaction of **1** with 3,3-DMT has yielded the compound Re$_2$(CO)$_9$($SCH_2CMe_2CH_2$), **2**, in 83% yield. Compound **2** appears to be fully analogous to the

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[10] (a) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1975; Vol. IV, Table 2.2B, pp 99−101. (b) *Ibid*.; Table 2.3.1, pp 149−150.

Table 1. Crystallographic Data for Compounds 2−6

	2	3	4	5	6
empirical formula	$Re_2SO_9C_{14}H_{10}$	$S_3C_{15}H_{30}$	$S_4C_{20}H_{40}$	$S_5C_{25}H_{50}$	$MnS_3O_2C_{22}H_{35}$
fw	726.70	306.41	408.78	510.97	482.64
cryst syst	monoclinic	monoclinic	triclinic	triclinic	triclinic
lattice params					
a (Å)	9.361(2)	11.506(3)	9.334(1)	14.810(5)	10.203(4)
b (Å)	11.978(3)	10.859(3)	10.456(2)	11.067(3)	19.204(6)
c (Å)	17.688(5)	14.224(3)	6.269(1)	10.405(2)	6.619(7)
α (deg)	90.0	90.0	104.78(1)	85.77(2)	96.35(6)
β (deg)	99.10(2)	97.21(2)	96.18(2)	109.02(2)	98.01(6)
γ (deg)	90.0	90.0	83.02(1)	111.15(2)	100.10(3)
V (Å^3)	1957.9(8)	1763.0(8)	586.0(2)	1502.0(9)	1252(1)
space group	$P2_1/n$, No. 14	$P2_1/n$, No. 14	$P\bar{1}$, No. 2	$P\bar{1}$, No. 2	$P\bar{1}$, No. 2
Z	4	4	1	2	2
ρ_{calcd} (g/cm^3)	2.47	1.20	1.16	1.13	1.28
μ(Mo Kα) (cm^{-1})	126.7	4.08	4.07	4.0	7.9
temp (°C)	23	20	20		
$2\theta_{max}$ (deg)	43.0	46.0	45.0	43.0	42.0
no. of obs reflns used ($I > 3\sigma(I)$)	1951	1951	1184	2359	1922
no. of variables	235	284	190	471	253
residuals:[a] R, R_w	0.030; 0.036	0.040; 0.044	0.029; 0.029	0.045; 0.052	0.044; 0.041
goodness of fit, GOF[a]	1.72	2.70	1.71	2.32	2.92
max shift/err on final cycle	0.01	0.01	0.01	0.02	0.00
largest residual peak (e$^-$/Å^3	0.69	0.30	0.16	0.25	0.34
abs corr	DIFABS	none	none	DIFABS	DIFABS

[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 $= [\sum_{hkl}(w(|F_o| - |F_c|))^2/(n_{data} - n_{vari})]^{1/2}$.

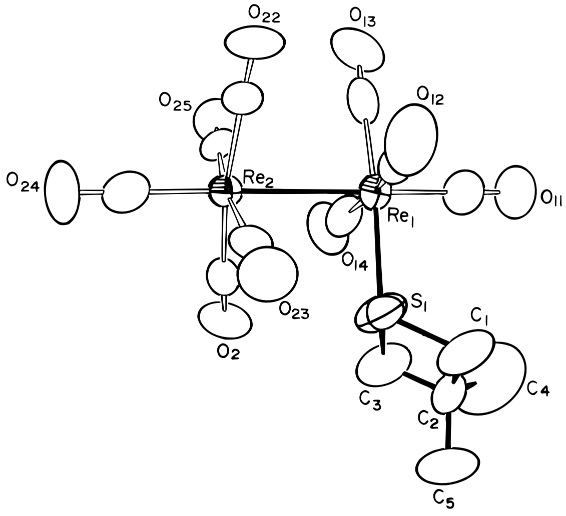

Figure 1. ORTEP diagram of Re$_2$(CO)$_9$(SCH$_2$CMe$_2$CH$_2$), **2**, showing 50% probability thermal ellipsoids. Selected bond distances (Å) and angles (deg) are as follows: Re(1)−Re(2) = 3.042(1), Re(1)−S(1) = 2.485(4), S(1)−C(1) = 1.82(2), S(1)−C(3) = 1.81(2); C(1)−S(1)−C(3) = 73.9(8).

unsubstituted thietane complexes Re$_2$(CO)$_9$(SCH$_2$CH$_2$CH$_2$)[3] and Re$_2$(CO)$_9$(SCH$_2$C(H)MeCH$_2$)[7] that we have prepared previously. This compound was obtained previously in small amounts when solutions of the disubstituted derivative, Re$_2$(CO)$_8$(SCH$_2$CMe$_2$CH$_2$)$_2$, were irradiated.[11] Compound **2** was characterized crystallographically, and an ORTEP diagram of its molecular structure is shown in Figure 1. The molecule is structurally similar to three polythioether macrocycle complexes, Re$_2$(CO)$_9$(12S3), **7**,[3] Re$_2$(CO)$_9$(*c*,*t*,*t*-Me$_3$12S3),[7] **8**, and Re$_2$(CO)$_9$(*c*,*c*,*c*-Me$_3$12S3),[7] **9**, that we have recently reported. In all four of these compounds, the equatorially positioned ligands on the two metal atoms are arranged in a staggered rotational conformation similar to that found in Re$_2$(CO)$_{10}$.[12] The thioether ligand is coordinated to one of the rhenium atoms in an equatorial site. The Re−Re distance in **2** (3.0422(8) Å) is similar to that found in **7** (3.0554(8) Å), **8** (3.069(2), 3.077(1) Å, and **9** (3.0598(6) Å). The Re−S distance in **2** (2.485(4) Å) is also similar to those in **7**, **8**, and **9** (2.498(3), 2.506(3) and 2.510(3) Å, and 2.518(2) Å, respectively). The DMT ring appears to be planar within experimental error. This contrasts with other structural studies of thietane ligands where a slight puckering has been observed.[13] However, examination of the thermal ellipsoids of the methylene carbon atoms of the DMT ligand in **2** reveals significant elongations which are directed perpendicular to the plane of the ring. This leads us to suspect the presence of a small disorder of these atoms that could be a result of a slight puckering of the ring that cannot be resolved by this data.

Compound **2** was found to be capable of producing macrocycles from 3,3-DMT catalytically, but the activity was low. In a typical reaction, 2.0 mL of 3,3-DMT and 16.0 mg of **2** were heated to 100 °C for 72 h in the absence of solvent. The complex appeared to dissolve completely in the 3,3-DMT. After the mixture was cooled, the excess 3,3-DMT was removed *in vacuo* and the resulting residue was dissolved in methylene chloride and filtered. After removal of the solvent, the residue was weighed and analyzed by a combination of ^{1}H and ^{13}C NMR spectra. The residue (181 mg) consisted principally of high molecular weight polymer and **3**, but it also contained small amounts of the larger macrocycles **4** and **5**. The relative amounts by weight of compounds **3** (10%), **4** (3%), and **5** (3%) plus a value for the mass of the combined weight of the remaining

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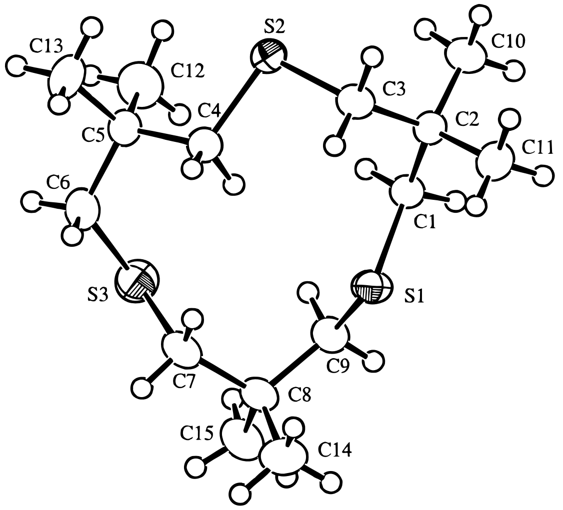


Figure 2. ORTEP diagram of 3,3,7,7,11,11-hexamethyl-1,5,9-trithiaacyclododecane, **3**, showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) are as follows: S(1)−C(1) = 1.827(3), S(1)−C(9) = 1.823(3), S(2)−C(3) = 1.818(3), S(2)−C(4) = 1.822(3), S(3)−C(6) = 1.818(4), (3)−C(7) = 1.826(4), all C−C distances are in the range 1.527(4)−1.544(5).

higher molecular weight oligomers (76%) was determined by integration of the appropriate resonances in the ^{13}C NMR spectrum of the mixture. Separation of the mixture of **3**, **4**, and **5** can be achieved with difficulty by TLC on silica gel using a hexane/methylene chloride (3/1) solvent mixture.

As a control, a sample of the 3,3-DMT was treated identically to those in the catalytic runs in the absence of catalyst. Very small amounts (<1 mg) of 3,3-DMT oligomers which did contain trace amounts of **3** were produced, but the amounts were far less than those obtained in the presence of the catalysts, see Experimental Section. To test for the importance of an accessible coordination site in the catalyst, we also examined $Re_2(CO)_{10}$ for its ability to produce macrocyclization of 3,3-DMT. As in the case of thietane by itself,[3] only very small amounts of macrocycles were found.

Compounds **3** and **5** are new. Compound **4** was obtained previously by the reaction of 2,2-dimethylpropane-1,3-dithiolate with 1,3-dibromo-2,2-dimethylpropane.[14] As a part of this study, all three macrocycles were characterized by single-crystal X-ray diffraction analyses. An ORTEP diagram of the molecular structure of **3** is shown in Figure 2. None of the S−C or C−C bond distances are unusual. The conformation of the 12-membered ring of **3** is quite different from that of its unsubstituted parent, 1,5,9-trithiacyclododecane, **10** (12S3)[15] and 3,7,11-trimethyl-1,5,9-trithiacyclododecane, **11** ($Me_3$12S3),[7] both of which exhibit square-like shapes with four atoms per edge and one of the sulfur atoms in a corner site. In **3**, one edge C(2)−C(8) is five atoms in length, one edge C(2)−S(2) is three atoms in length, and the other two are four atoms in length. The tendency of the *gem*-dimethyl groups to be directed toward the exterior of the ring is clearly one factor that influences the change in conformation of the ring. It has been proposed that an important consequence of this *gem*-dimethyl effect is that the sulfur atoms will be turned inward.[16] This is not confirmed by the observed structure of **3**. In fact, it is the methylene groups that seem to be turned most strongly toward the interior of the ring, e.g., C(4). The ^{1}H and ^{13}C NMR spectra of **3** show only two and three resonances, respectively: ^{1}H NMR δ 2.68 (s, 12H), 0.99 (s, 18H) and ^{13}C NMR δ 44.07 (6C), 36.67 (3C), 27.21 (6C), indicating that the ring is not rigid in solution and that all of the methyl groups and all of the methylene groups are averaged by the dynamical motion.

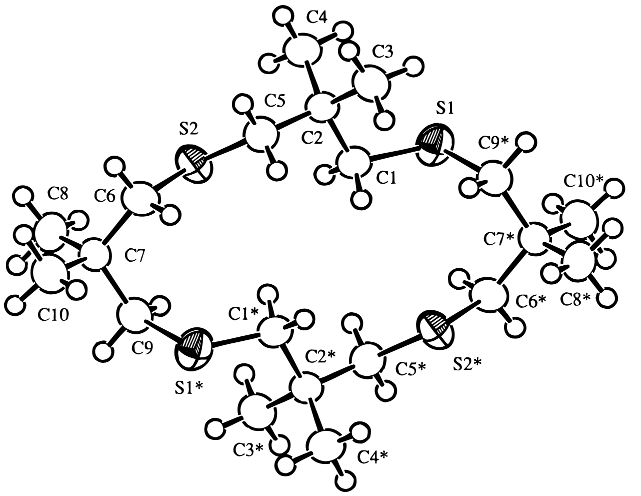
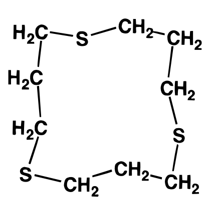


Figure 3. ORTEP diagram of 3,3,7,7,11,11,15,15-octamethyl-1,5,9,13-tetraselenacyclohexadecane, **4**, showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) are as follows; S(1)−C(1) = 1.817(3), S(1)−C(9*) = 1.825(3), S(2)−C(5) = 1.816(3), S(2)−C(6) = 1.819(3), C(1)−C(2) = 1.536(4), C(2)−C(5) = 1.533(4), C(6)−C(7) = 1.529(4), C(7)−C(9) = 1.537(3).



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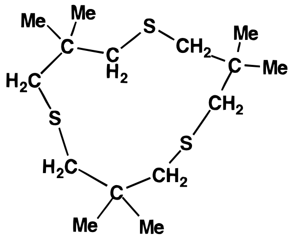

3

An ORTEP diagram of the molecular structure of **4** is shown in Figure 3. Like **3**, the conformation of the 16-membered ring of **4** is quite different from that of its unsubstituted parent, 1,5,9,13-tetrathiacyclohexadecane, **12** (16S4).[17] Compound **12** exhibits a rectangular-like geometry with two chains of four atoms on opposite sides of the molecule and two chains of six

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[14] (a) Yoshida, T.; Adachi, T.; Ueda, T.; Watanabe, M.; Kaminaka, M.; Higuchi, T. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1171. (b) Yoshida, T.; Adachi, T.; Matsumura, K.; Kawazu, K.; Baba, K. *Chem. Lett.* **1991**, 1067. (c) Yoshida, T.; Adachi, T.; Ueda, T.; Akao, H., Tanaka, T.; Goto, F. *Inorg. Chem. Acta* **1995**, *231*, 95.

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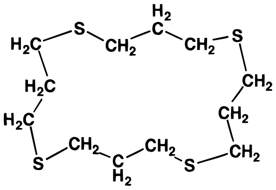
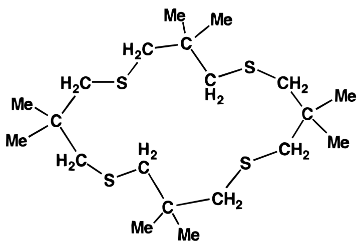
[17] Blake, A. J.; Gould, R. O.; Halcrow, M. A.; Schröder, M. A. *Acta Crystallogr.* **1993**, *B49*, 773.



12



4

atoms in length on the other two sides. Two of the corners of the rectangle are occupied by sulfur atoms. In the solid state, compound **4** contains a crystallographically imposed center of symmetry. As in **3**, the *gem*-dimethyl groups in **4** are clearly directed toward the exterior. The sulfur atoms are not directed toward the exterior of the ring as strongly as in **12**, and again it is a methylene group, e.g., C(1), that is most strongly directed toward the interior of the ring. Nevertheless, **4** has been shown to be capable of serving effectively as a tetradentate ligand with transition metal groupings in the interior of the ring.[14] Certainly, there will be an energy cost for rearranging to a conformation in which the sulfur atoms are directed inward, but this is apparently more than compensated for by the formation of four M−S bonds.

An ORTEP diagram of the molecular structure of **5** is shown in Figure 4. This macrocycle contains 20 atoms with five sulfur atoms regularly spaced through it. As can be seen, the molecule contains no symmetry in the solid state. One sulfur atom S(2) is directed toward the interior of the ring while two, S(3) and S(4), are clearly directed outward. There is no uniform pattern to the orientations of the *gem*-dimethyl groups. The methyl groups on C(14) are directed outward, but one of the methyl groups on C(11) is actually directed inward. The ring is not two-dimensional, as found in **3** and **4**, but is folded and has developed some three-dimensional character, although this is not readily seen in the figure. There are no unusual S−C or C−C bond distances in **4** or **5**.

An ORTEP diagram of the molecular structure of **6** is shown in Figure 5. Compound **6** is a complex between **3** and the 16-electron grouping $CpMn(CO)_2$. The conformation of the Me_612S3 ligand is not significantly different from that of the free molecule. It is coordinated to the manganese through only one of the three sulfur atoms, S(2). The Mn−S bond length, Mn−S(2) = 2.293(2) Å, is slightly longer than found in the bis($CpMn(CO)_2$) thietane complex, $[CpMn(CO)_2]_2(\mu\text{-}SCH_2CH_2CH_2)$, Mn−S = 2.257(1) Å.[18] This may be a result of the substantial steric crowding between *gem*-dimethyl groups of the macrocycle and the ligands on the manganese atom. Indeed, to date, this is the only metal containing grouping that we have been able to attach to **3** to form an isolable complex.

Discussion

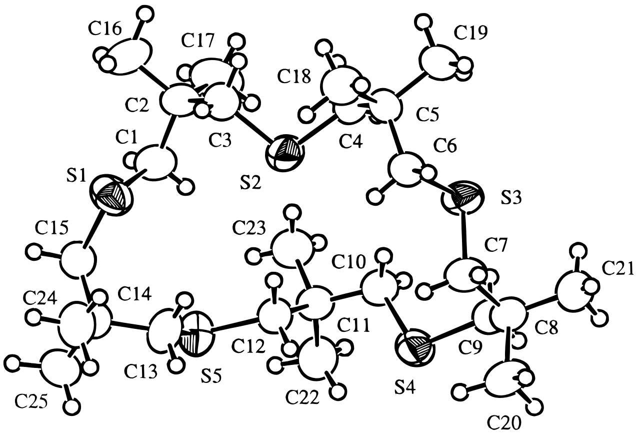


Figure 4. ORTEP diagram of 3,3,7,7,11,11,15,15,19,19-decamethyl-1,5,9,13,17-pentathiaacycloeicosane, **5**, showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) are as follows: S(1)−C(1) = 1.805(6), S(1)−C(15) = 1.824(5), S(2)−C(3) = 1.799(6), S(2)−C(4) = 1.804(6), S(3)−C(6) = 1.821(5), S(3)−C(7) = 1.799(5), S(4)−C(9) = 1.801(5), S(4)−C(10) = 1.804(6), S(5)−C(12) = 1.815(5), S(5)−C(13) = 1.821(6), all C−C distances are in the range 1.519(6)−1.548(8).

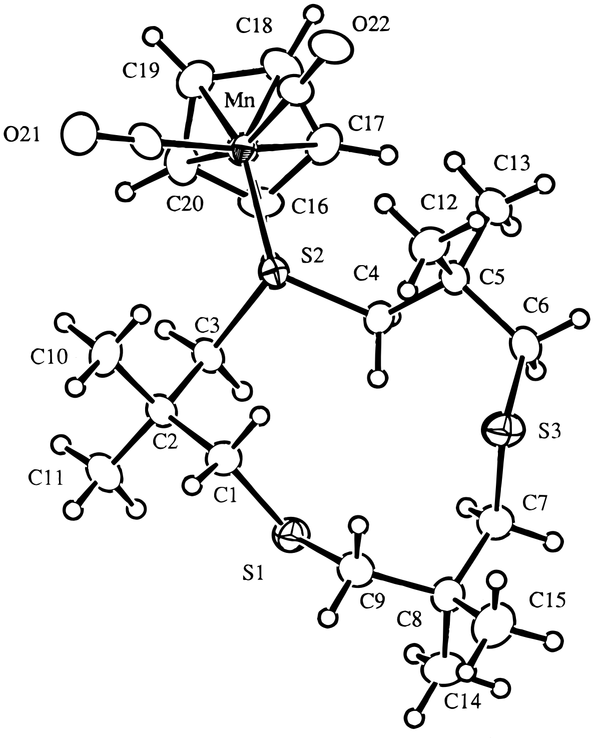


Figure 5. ORTEP diagram of $CpMn(CO)_2(\eta^1\text{-}Me_612S3)$, **6**, showing 40% probablility thermal ellipsoids. Selected interatomic distances (Å) are as follows: Mn−S(2) = 2.293(2), S(1)−C(1) = 1.818(7), S(1)−C(9) = 1.810(7), S(2)−C(3) = 1.831(6), S(2)−C(4) = 1.829(6), S(3)−C(6) = 1.809(7), S(3)−C(7) = 1.823(7), all C−C distances in the macrocycle are in the range 1.520(8)−1.557(8).

In previous studies, we showed that thietane and 3-methylthietane can be readily cyclooligomerized by $Re_2(CO)_9$ complexes of these ligands. In this work, we have described the macrocyclization of 3,3-DMT by the complex **2**. Three macrocycles **3**, **4**, and **5** were obtained. Unfortunately, the catalytic activity is low compared to the reactions of thietane and 3-methylthietane and the bulk of the products are high molecular weight oligomers of 3,3-DMT. For comparison, Table 2 lists the turnover frequencies of the catalytic activity of the three thietane complexes $Re_2(CO)_9$(thietane), $Re_2(CO)_9$(3-MT), and **2** for the formation of the corresponding 12-membered macrocycles.

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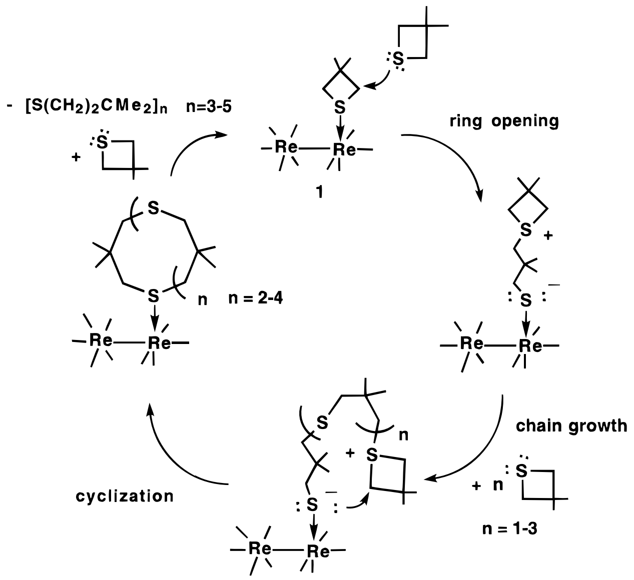
Table 2. Comparison of Catalytic Activity of $Re_2(CO)_9$(thietane) Complexes

catalyst	product	temp (°C)	TOF[a]
$Re_2(CO)_9$(thietane)	12S3	94	6.1
$Re_2(CO)_9$(3-MT)	Me312S3	107	2.0
$Re_2(CO)_9$(3,3-DMT)	Me612S3	100	0.03

[a] TOF = turnover frequency = moles of product/mole of catalyst·h.

Scheme 1



We believe that the mechanism of formation of the macrocycles is the same for all three reactions and is initiated by a ring-opening nucleophilic addition of a free molecule to the thietane to one of the sulfur-bound methylene groups of the thietane ligand, see Scheme 1. This is followed by a series of chain growth ring-opening additions that culminates with a cyclization that leads to formation of a macrocycle. It is notable that $Re_2(CO)_{10}$ is not a good catalyst. We believe this indicates that the 3,3-DMT molecule must be coordinated to the $Re_2(CO)_9$ fragment to be activated. The cycle is completed through regeneration of **2** by a displacement of the macrocycle from the complex by another equivalent of thietane. Rings of any size could be formed by this mechanism simply by extending the growth step.

Two features are now apparent from this series of studies. As the number of substitutents at the 3-position of the thietane increases, the formation of macrocycles is progressively decreased. This is manifested in two ways: (1) the reactivity is clearly lower. The total amount of products that are formed is lower than that of the less substituted thietanes. It appears that the relative rate of ring opening is slower. This can be attributed to steric inhibition caused by the increase in the number of substituents. (2) The quantity of macrocycles decreases relative the quantity of polymer. This may also be a steric effect; namely, the ring closure step that completes the formation of the macrocycle is also inhibited by the increase in the number of substituents at the 3-position. Perhaps as a consequence of this, we observe for the first time significant quantities of the the 16-membered and 20-membered ring macrocycles relative to the 12-membered ring, although the quantites of the larger rings are still too low to consider this synthesis as a procedure for generating synthetically useful amounts of the compounds.

Acknowledgment. These studies were supported by the Division of Chemical Sciences of the Office of Basic Energy Sciences of the U.S. Department of Energy. J.A.Q. wishes to thank the DAAD for a postdoctoral fellowship.

Supporting Information Available: Tables of positional parameters, intramolecular distances, intramolecular angles, and anisotropic thermal parameters for **2**−**6** (28 pages). Ordering information is given on any current masthead page.

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