# The Catalytic Cyclooligomerization of Thietane by Trirhenium Cluster Complexes. A New Route to Polythiaether Macrocycles

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**Abstract:** The trirhenium complex $Re_3(CO)_{10}[\mu\text{-}SCH_2CH_2CH_2](\mu\text{-}H)_3$ (**1**) reacts with dimethyl sulfide by a ring opening addition to the bridging thietane ligand to yield the zwitterionic complex $Re_3(CO)_{10}[\mu\text{-}SCH_2CH_2CH_2SMe_2](\mu\text{-}H)_3$ (**2**) in 48% yield that contains a sulfonium-substituted thiolate ligand bridging an edge of the cluster. The structure of **2** was established by a single-crystal X-ray diffraction analysis. The reaction of **1** with thietane was found to produce a ring-opening oligomerization of thietane to yield the new complexes $Re_3(CO)_{10}[\mu\text{-}SCH_2CH_2CH_2SCH_2CH_2CH_2SCH_2CH_2CH_2SCH_2CH_2CH_2](\mu\text{-}H)_3$ (**3**), $Re_3(CO)_{10}[\mu\text{-}SCH_2CH_2CH_2SCH_2CH_2CH_2(SCH_2CH_2CH_2)_2SCH_2CH_2CH_2](\mu\text{-}H)_3$ (**4**), and $Re_3(CO)_{10}[\mu\text{-}SCH_2CH_2CH_2SCH_2CH_2CH_2(SCH_2CH_2CH_2)_4SCH_2CH_2CH_2](\mu\text{-}H)_3$ (**5**), depending on how much thietane reagent is used. Compounds **3**, **4**, and **5** were characterized fully as their $PMe_2Ph$ derivatives, **6**, **7**, and **8**. Compound **6** was also characterized by a single crystal X-ray diffraction analysis. Compound **6** contains a bridging thiolato ligand $[\mu\text{-}SCH_2CH_2CH_2SCH_2CH_2CH_2SCH_2CH_2CH_2SCH_2CH_2CH_2]$ that is terminated with the macrocyclic grouping 1,5,9-trithiacyclododecane (12S3), through the formation of a sulfonium center. The macrocycles 12S3, 1,5,9,13-tetrathiacyclohexadecane, (16S4), and 1,5,9,13,17,21-hexathiacyclotetracosane (24S6), were cleaved from the complexes **6**, **7**, and **8**, respectively, by treatment with pyridine. The free macrocycles, 12S3 and 24S6, were obtained catalytically when **1**, **3**, or $Re_3(CO)_{12}(\mu\text{-}H)_3$ was allowed to react with thietane in the absence of solvent at reflux. 3,3,7,7,11,11,15,15,19,19,23,23-Dodecamethyl-1,5,9,13,17,21-hexathiacyclotetracosane ($Me_{12}$-24S6) was obtained catalytically as the only organic product when 3,3-dimethylthietane was allowed to react with $Re_3(CO)_{10}[\mu\text{-}SCH_2CMe_2CH_2](\mu_3\text{-}H)_3$ in the absence of solvent at its refluxing temperature. Crystal data for $2{\cdot}0.5Me_2C{=}O$: space group $P\bar{1}$, $a = 12.295(2)$ Å, $b = 12.341(2)$ Å, $c = 8.568(1)$ Å, $\alpha = 101.76(1)°$, $\beta = 91.37(2)°$, $\gamma = 97.66(2)°$, $Z = 2$, 2344 reflections, $R = 0.040$. Crystal data for **6**: space group $P2_1/n$, $a = 8.637(2)$ Å, $b = 41.80(1)$ Å, $c = 11.418(2)$ Å, $\beta = 111.79(2)°$, $Z = 4$, 2836 reflections, $R = 0.036$.

## Introduction

Polythiaether macrocycles have recently attracted interest for their potential to serve as ligands.[1] To date, virtually all polythiaether macrocycles are prepared via stoichiometric reactions involving thiolate anions[2] or thiolate anion complexes[3] with organic dihalides. Herein, we report a new procedure for the formation of symmetric polythiaether macrocycles that is achieved by the catalytic cyclooligomerization of thietanes in a process that is initiated by the coordination and activation of thietane by trirhenium cluster complexes.

In previous studies we have shown that bridging thietane ligands in metal cluster complexes are activated toward ring-opening addition of nucleophiles.[4,5] We have even found an example of a ring-opening trimerization of 3,3-dimethylthietane by a triosmium cluster complex that was initiated at a bridging thietane ligand and was terminated by an oxidative addition of a C−S bond to the cluster.[6] In recent studies we have found that the bridging thietane ligand in the trirhenium complex $Re_3(CO)_{10}[\mu\text{-}SCH_2CH_2CH_2](\mu\text{-}H)_3$ (**1**) also undergoes ring-opening addition reactions with nucleophiles.[5]

In this report the results of our studies of the reactions of **1** with the thiaethers $Me_2S$ and thietane, itself, are described. It is demonstrated that these thiaethers also produce ring opening of the bridging thietane ligand in **1**, but in the case of thietane a series of ring-opening coupling reactions occurs that is concluded by cyclization processes that yield polythiaether macrocycles. Indeed, the ring-opening cyclization can be performed catalytically under suitable conditions to yield the macrocycles in a free state in substantial amounts. Intermediates that contain the macrocycles linked to the cluster complexes via a $SCH_2CH_2CH_2$ tether have been isolated and characterized. We have also shown that the parent rhenium cluster complex, $Re_3(CO)_{12}(\mu\text{-}H)_3$, may be used as a precursor for this catalysis,

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but the actual catalysis apparently proceeds via the same intermediates that are produced in the reaction of **1** with thietane. A preliminary report of a portion of this work has been published.[7]

## Experimental Section

**General Data.** All reactions were performed under a nitrogen atmosphere. Reagent grade solvents were stored over 4 Å molecular sieves. $Re_3(CO)_{12}(\mu\text{-H})_3$,[8] $Re_3(CO)_{10}[\mu\text{-SCH}_2\text{CH}_2\text{CH}_2](\mu_3\text{-H})_3$,[5] $Re_3(CO)_{10}[\mu\text{-SCH}_2\text{CMe}_2\text{CH}_2](\mu_3\text{-H})_3$,[5] and 3,3-dimethylthietane[9] (3,3-DMT) were prepared by the published procedures. Trimethylamine *N*-oxide dihydrate (Aldrich) was dehydrated by using a Dean-Stark apparatus with benzene as the solvent prior to use. Thietane was purchased from Aldrich and was vacuum distilled before use. Other reagents were purchased from Aldrich and were used as received. Infrared spectra were recorded on a Nicolet 5DXB FTIR spectrophotometer. $^1$H NMR spectra were obtained on a Bruker AM-300 operating at 300 MHz. Separations were performed by TLC in air on Analtech 0.25 mm silica gel 60 Å $F_{254}$ plates. Elemental analyses were performed by Oneida Research Services, Whitesboro, NY.

**Preparation of $Re_3(CO)_{10}[\mu\text{-SCH}_2\text{CH}_2\text{CH}_2\text{SMe}_2](\mu\text{-H})_3$ (2).** A 21.2-mg amount of $Re_3(CO)_{10}[\mu\text{-SCH}_2\text{CH}_2\text{CH}_2](\mu_3\text{-H})_3$ (**1**, 0.023 mmol) was dissolved in 20 mL of methylene chloride in a 25-mL three-neck round-bottom flask equipped with a stir bar, a reflux condenser, and a nitrogen inlet. A 2.0-$\mu$L amount of dimethyl sulfide (0.032 mmol) was added, and the resulting solution was allowed to stir at 25 °C for 18 h. The volatiles were removed *in vacuo*, and the products were separated by TLC using a hexane−acetone 2/1 solvent mixture to yield 10.8 mg of pure $Re_3(CO)_{10}[\mu\text{-SCH}_2\text{CH}_2\text{CH}_2\text{SMe}_2](\mu\text{-H})_3$ (**2**; 48% yield). Compound **2** has poor solubility in most organic solvents, except acetone. IR $\nu$(CO) for **2** ($cm^{-1}$ in acetone): 2097 (w), 2021 (m), 2001 (vs), 1948 (m), 1906 (s). $^1$H NMR spectra for **2** ($\delta$ in acetone-$d_6$): 3.69 (t, 2H, $J_{H-H}$ = 7.4 Hz), 3.22 (s, 6H), 2.53 (t, 2H, $J_{H-H}$ = 7.1 Hz), 2.21 (quintet, 2H, $J_{H-H}$ = 7.4 Hz), −12.48 (s, 1H), −16.54 (s, 2H). Anal. Calcd for **2**·0.5$Me_2C$=O: C, 20.00; H, 1.78. Found: C, 19.19; H, 1.35.

**Reaction of Thietane with 1 in a 3/1 Ratio.** A 28.1-mg amount (0.031 mmol) of **1** was dissolved in 30 mL of methylene chloride in a 50-mL three-neck round-bottom flask equipped with a stir bar, a reflux condenser, and a nitrogen inlet. A 7.0-$\mu$L amount of thietane (0.094 mmol) was added, and the resulting solution was allowed to stir at 25 °C for 36 h. The volatiles were then removed *in vacuo*, and the products were separated by TLC using a hexane−acetone 2/1 solvent mixture to yield 16.5 mg of $Re_3(CO)_{10}[\mu\text{-SCH}_2\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{CH}_2](\mu\text{-H})_3$ (**3**; 47% yield). IR $\nu$(CO) for **3** ($cm^{-1}$ in $CH_2Cl_2$): 2097 (w), 2022 (s), 1996 (vs), 1948 (s), 1906 (s). $^1$H NMR for **3** (500 MHz, $\delta$ in $CD_2Cl_2$): 3.91 (m, 2H), 3.46 (t, 2H, $J_{H-H}$ = 7.4 Hz), 3.36 (m, 2H), 2.91 (q, 2H, $J_{H-H}$ = 5.8 Hz), 2.78 (q, 2H, $J_{H-H}$ = 5.8 Hz), 2.74 (t, 2H, $J_{H-H}$ = 5.1 Hz), 2.59 (t, 4H, $J_{H-H}$ = 7.2 Hz), 2.19 (m, 6H), 1.87 (q, 2H, $J_{H-H}$ = 6.2 Hz), −12.46 (s, 1H), -16.49 (s, 2H). Anal. Calcd for **3**·$Me_2CO$: C, 25.10; H, 2.78. Found: C, 25.66; H, 2.89. Compound **3** has poor solubility in most organic solvents, except acetone.

**Reaction of Thietane with 1 in a 20/1 Ratio.** A 92-mg amount of **1** (0.100 mmol) was dissolved in 25 mL of methylene chloride in a 50-mL three-neck round-bottom flask equipped with a stir bar, a reflux condenser, and a nitrogen inlet. A 150-$\mu$L amount of thietane (2.02 mmol) was added, and the resulting solution was allowed to stir at 25 °C for 18 h. The volatiles were removed *in vacuo*, and the products were separated by TLC using a hexane−acetone 1/1 solvent mixture to yield 59.6 mg of **3** (48% yield) and 30 mg of a mixture of $Re_3(CO)_{10}[\mu\text{-SCH}_2\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{CH}_2(\text{SCH}_2\text{CH}_2\text{CH}_2)_2\text{SCH}_2\text{CH}_2\text{CH}_2](\mu\text{-H})_3$ (**4**) and $Re_3(CO)_{10}[\mu\text{-SCH}_2\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{CH}_2(\text{SCH}_2\text{CH}_2\text{CH}_2)_4\text{SCH}_2\text{CH}_2\text{CH}_2](\mu\text{-H})_3$ (**5**). Compounds **4** and **5** could not be separated in pure form. $^1$H NMR mixture of **4** and **5** ($\delta$ ppm in acetone-$d_6$): 3.80 (m), 2.80 (m), 2.40 (m), 1.88 (m), −12.46 (s), −16.54 (s). The resonance at $\delta$ −16.54 is twice the intensity of the one at $\delta$ −12.46. Treatment of the **4**−**5** mixture with $PMe_2Ph$ yielded two isolable products, **7** and **8**, that were identified as the $PMe_2Ph$ derivatives of **4** and **5**, see below.

**Reaction of 3 with $PMe_2Ph$.** A 41.2-mg amount of **3** (0.033 mmol)-was added to a 50-mL three-neck round-bottom flask equipped with a stir bar, a reflux condenser, a nitrogen inlet, and 40 mL of methylene chloride. A 5.5-$\mu$L amount of dimethylphenylphosphine (0.040 mmol) was added, and the resulting solution was allowed to stir at reflux for 18 h. The volatiles were removed *in vacuo*, and the products were separated by TLC using a hexane−acetone 2/1 solvent mixture to yield 31.2 mg of $Re_3(CO)_9(PMe_2Ph)[\mu\text{-SCH}_2\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{CH}_2](\mu\text{-H})_3$ (**6**; 69% yield). IR $\nu$(CO) for **6** ($cm^{-1}$ in $CH_2Cl_2$): 2032 (s), 1996 (vs), 1926 (m), 1904 (s). $^1$H NMR for **6** ($\delta$ in $CD_2Cl_2$): 7.68 (m, 2H), 7.44 (m, 2H), 7.37 (m, 1H), 3.51 (m, 3H), 3.27 (m, 3H), 3.16 (t, 2H, $J_{H-H}$ = 6.1 Hz), 2.91 (q, 2H, $J_{H-H}$ = 6.5 Hz), 2.78 (q, 3H, $J_{H-H}$ = 5.5 Hz), 2.73 (q, 3H, $J_{H-H}$ = 6.5 Hz), 2.61 (d, 2H, $J_{H-H}$ = 4.1 Hz), 2.47 (d, 2H, $J_{H-H}$ = 6.5 Hz), 2.15 (m, 2H), 1.97 (d, 6H, $J_{P-H}$= 16.5 Hz), 1.87 (t, 2H, $J_{H-H}$ = 6.1 Hz), −12.41 (d, 1H, $J_{P-H}$= 4.2 Hz), −15.40 (d, 2H, $J_{P-H}$ = 16.5 Hz). Anal. Calcd for **6**: C, 27.90; H, 3.04. Found: C, 27.88; H, 2.31.

**Reaction of the Mixture of 4 and 5 with Dimethylphenylphosphine.** A 50-mg amount of the mixture of **4** and **5** was dissolved in 25 mL of acetone in a 50-mL three-neck round-bottom flask equipped with a stir bar, a reflux condenser, and a nitrogen inlet. A 5-$\mu$L amount of dimethylphenylphosphine (0.036 mmol) was added, and the resulting solution was heated to reflux with stirring for 3 h. After the solution was cooled, the volatiles were removed *in vacuo*, and the products were then separated by TLC using a hexane−acetone 1/1 solvent mixture to yield 17.6 mg of $Re_3(CO)_{10}(PMe_2Ph)[\mu\text{-SCH}_2\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{CH}_2(\text{SCH}_2\text{CH}_2\text{CH}_2)_2\text{SCH}_2\text{CH}_2\text{CH}_2](\mu\text{-H})_3$ (**7**) and 18.1 mg of $Re_3(CO)_{10}(PMe_2Ph)[\mu\text{-SCH}_2\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{CH}_2(\text{SCH}_2\text{CH}_2\text{CH}_2)_4\text{SCH}_2\text{CH}_2\text{CH}_2](\mu\text{-H})_3$ (**8**). IR $\nu$(CO) for **7** ($cm^{-1}$ in acetone): 2030 (m), 1999 (vs), 1033 (m), 1905 (s). $^1$H NMR for **7** ($\delta$ in $CD_2Cl_2$): 7.70−7.43 (m, 5H), 3.46−3.18 (m, 6H), 2.78−2.64 (m, 12H), 2.48−2.44 (m, 2H), 2.24−2.16 (m, 4H), 1.97 (d, 6H, $J_{P-H}$ = 8.37 Hz), 1.94−1.87 (m, 6H), −12.48 (d, 1H, $J_{P-H}$ = 4.3 Hz), −15.40 (d, 2H, $J_{P-H}$ = 16.6 Hz). Anal. Calcd for **7**: C, 29.09; H, 3.35. Found: C, 29.30; H, 3.28. IR $\nu$(CO) for **8** ($cm^{-1}$ in acetone): 2029 (s), 1999 (vs), 1995 (vs), 1932 (s), 1903 (vs). $^1$H NMR for **8** ($\delta$ in $CD_2Cl_2$): 7.63−7.38 (m, 5H), 3.68−3.30 (m, 6H), 2.80−2.53 (m, 20H), 2.39 (m, 2H), 2.31−2.24 (m, 6H), 1.99 (d, 6H, $J_{P-H}$ = 8.63 Hz), 1.93−1.79 (m, 8H), −12.57 (s, 1H), −15.43 (d, 2H, $J_{P-H}$ = 16.9 Hz). Hydride resonances in $CDCl_3$ $^1$H NMR for **8** ($\delta$ in $CDCl_3$): −12.72 (s, 1H), −15.41 (d, 2H, $J_{P-H}$ = 17.1 Hz). Anal. Calcd for **8**: C, 31.07; H, 3.84. Found: C, 30.89; H, 3.74.

**Reaction of 6 with Pyridine.** A 31.0-mg amount of **6** (0.025 mmol) was added to a 25-mL three-neck round-bottom flask equipped with a stir bar, a reflux condenser, and a nitrogen inlet. A 5-mL amount of pyridine (63.2 mmol) was added, and the resulting solution was allowed to stir at reflux for 1.5 h. The volatiles were removed *in vacuo*, and the products were separated by TLC using a hexane−acetone 1/1 solvent mixture to yield 1.4 mg of 12S3 (25% yield) and 20.2 mg of $Re_3(CO)_9(\mu\text{-H})_3(PMe_2Ph)[S(CH_2)_3(\text{pyridine})]$ (**9**; 73% yield). IR $\nu$(CO) for **9** ($cm^{-1}$ in acetone): 2030 (s), 1996 (vs), 1933 (s), 1904 (vs). $^1$H NMR for **9** ($\delta$ in acetone-$d_6$): 9.02 (d, 2H, $J_{H-H}$ = 5.4 Hz), 8.75 (t, 1H, $J_{H-H}$ = 7.8 Hz), 8.30 (m, 2H), 7.76 (m, 2H), 7.47 (m, 3H), 4.77 (t, 2H, $J_{H-H}$ = 6.8 Hz), 2.31 (m, 4H), 2.03 (d, 6H, $J_{H-H}$ = 8.6 Hz), −12.45 (d, 1H, $J_{P-H}$ = 4.4 Hz), −15.44 (d, 2H, $J_{P-H}$ = 16.6 Hz). Anal. Calcd for **9**: C, 27.20; H, 2.28. Found: C, 27.72; H, 2.43.

**Reaction of 7 with Pyridine.** A 17.6-mg amount of **7** (0.013 mmol) was added to a 25-mL three-neck round-bottom flask equipped with a stir bar, a reflux condenser, and a nitrogen inlet. A 5-mL amount of pyridine (63.2 mmol) was added, and the resulting solution was allowed to stir at reflux for 1.5 h. The volatiles were removed *in vacuo*, and

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the products were separated by TLC using a hexane−acetone 1/1 solvent mixture to yield 1.2 mg of 1,5,9,13-tetrathiacyclohexadecane[10] (16S4) in 30% yield and 8.5 mg of $Re_3(CO)_9(PMe_2Ph)[\mu\text{-}S(CH_2)_3$-(pyridine)]$(\mu\text{-}H)_3$ (**9**; 57% yield). $^1H$ NMR for **16S4** ($\delta$ in $CDCl_3$): 2.65 (t, 16H, $J_{H-H}$ = 7.1 Hz), 1.89 (quintet, 8H, $J_{H-H}$ = 7.1 Hz).

**Reaction of 8 with Pyridine.** A 20-mg amount of **8** (0.013 mmol) was added to a 25-mL three-neck round-bottom flask equipped with a stir bar, a reflux condenser, and a nitrogen inlet. A 5-mL amount of pyridine (63.2 mmol) was added, and the resulting solution was allowed to stir at reflux for 1.5 h. The volatiles were removed *in vacuo*, and the products were separated by TLC using a hexane−acetone 1/1 solvent mixture to yield 2.1 mg of 24S6 (34% yield) and 8.5 mg of $Re_3(CO)_9(PMe_2Ph)[S(CH_2)_3(pyridine)](\mu\text{-}H)_3$ (**9**; 67% yield).

**Preparation of $Re_3(CO)_{10}[S(CH_2)_3(pyridine)](\mu\text{-}H)_3$.** A 35.1-mg amount of **1** (0.038 mmol) was dissolved in 20 mL of methylene chloride in a 25-mL three-neck round-bottom flask equipped with a stir bar, a reflux condenser, and a nitrogen inlet. A 6.0-$\mu$L amount of pyridine (0.076 mmol) was added, and the resulting solution was allowed to stir at 25 °C for 3 h. The volatiles were removed *in vacuo*, and the products were separated by TLC using a hexane−acetone 1/1 solvent mixture to yield 20.6 mg of $Re_3(CO)_{10}(\mu\text{-}H)_3[\mu\text{-}S(CH_2)_3$-(pyridine)] (**10**, 57% yield). IR $\nu$(CO) for **10** ($cm^{-1}$ in acetone): 2097 (w), 2022 (m), 2001 (vs), 1948 (m), 1905 (s). $^1H$ NMR for **10** ($\delta$ in acetone-$d_6$): 9.24 (d, 2H, $J_{H-H}$ = 5.5 Hz), 8.75 (t, 1H, $J_{H-H}$ = 7.8 Hz), 8.31 (t, 2H, $J_{H-H}$ = 7.0 Hz), 5.01 (t, 2H, $J_{H-H}$ = 6.5 Hz), 2.43 (m, 4H), −12.53 (s, 1H), −16.57 (s, 2H).

**Preparation of $Re_3(CO)_9(\mu\text{-}H)_3(PMe_2Ph)[S(CH_2)_3(pyridine)]$.** A 30-mg amount of **10** (0.032 mmol) was dissolved in 20 mL of acetone in a 25-mL three-neck round-bottom flask equipped with a stir bar, a reflux condenser, and a nitrogen inlet. A 5-$\mu$L amount of $PMe_2Ph$ (0.036 mmol) was added, and the resulting solution was heated to reflux with stirring for 3 h. The volatiles were removed *in vacuo*, and the products were separated by TLC using a hexane−acetone 1/1 solvent mixture to yield 14.3 mg of $Re_3(CO)_9(\mu\text{-}H)_3(PMe_2Ph)[S(CH_2)_3$-(pyridine)] (**9**; 62% yield).

**Reaction of 3 with NaOEt.** NaOEt was prepared by the reaction of a 10-mg amount of sodium (0.43 mmol) with 2 mL of EtOH in a 25-mL three-neck round-bottom flask equipped with a stir bar, a reflux condenser, and a nitrogen inlet. A 20-mg amount of **3** (0.017 mmol) in 5 mL of EtOH was then added, and the resulting solution was allowed to stir at 25 °C for 18 h. The volatiles were removed *in vacuo*, and the products were separated by TLC using a hexane−acetone 2/3 solvent mixture to yield 1.2 mg of 12S3 (32% yield) as a colorless band. The metal-containing product could not be fully characterized, but it appears to be a trirhenium cluster complex with three bridging hydride ligands as indicated by its $^1H$ NMR spectrum, $\delta$ −12.45 (1H) and −16.52 (2H) ppm.

**Catalytic Cyclooligomerization. Reaction of Thietane with 1 in a 5000/1 Ratio.** A 6.0-mL amount of thietane (81 mmol) was added to a 25-mL three-neck round-bottom flask equipped with a stir bar, a reflux condenser, a nitrogen inlet, and 15.2 mg (0.017 mmol) of **1**. The reaction was heated to reflux and was allowed to stir under nitrogen at this temperature for 24 h. After the solution was cooled, the excess thietane was removed *in vacuo*. The resulting residue weighed 632 mg. An NMR spectrum was taken of a portion of the residue and showed the presence of only two compounds, 12S3 and 24S6, in a 1/3.5 ratio based on integration. The macrocycle 12S3 was then isolated by extraction with acetone to yield 172.0 mg (=137 equiv of thietane). This can be obtained as pure crystals by further recrystallization from 1/1 hexane−$CH_2Cl_2$. Extraction of the remaining residue with methylene chloride yielded 392 mg of pure 24S6 (=312 equiv of thietane). 52 mg of insoluble residue remained which is assumed to be a polymer of thietane.

**Identification of the Cluster Species after Catalysis.** A 6.0-mL amount of thietane (81.0 mmol) was added to a 25-mL three-neck round-bottom flask equipped with a stir bar, a reflux condenser, a nitrogen inlet, and 20.8 mg (0.022 mmol) of **1**. The reaction was heated to reflux and was allowed to stir under nitrogen at this temperature for 45 min. The isolation of the metal-containing products is much easier when the reaction is stopped after this shorter reaction period since the yield of macrocycles is much lower, and the excess thietane is easily removed *in vacuo*. An NMR spectrum was taken of the residue taken after removal of the volatiles and only two resonances were observed in the hydride-containing region, −12.46 (s, 1H) and −16.54 (s, 2H) (in acetone-$d_6$), which is characteristic of the mixture of **4** and **5**, see above. However, after treatment of this mixture with dimethylphenylphosphine as described above only the resonances for **8** were observed: $\delta$ (in $CDCl_3$) −12.73 (s, 1H), −15.43 (d, 2H, $^2J_{P-H}$ = 17 Hz).

**Catalytic Cyclooligomerization of Thietane by 3.** Under a nitrogen atmosphere 7.0 mL (94.0 mmol) of thietane was added to a 25-mL three-neck round-bottom flask equipped with a stir bar, a reflux condenser, a nitrogen inlet, and 17.0 mg (0.015 mmol) of **3**. The thietane itself served as the solvent in this reaction. The solution was heated to reflux and was allowed to stir under nitrogen at this temperature for 48 h. After the solution was cooled, the unreacted thietane was removed *in vacuo*. The resulting residue weighed 1.179 g. An NMR spectrum was taken of a portion of the residue. The spectrum showed the two products 1,5,9-trithiacyclododecane [$\overline{SCH_2CH_2CH_2SCH_2CH_2CH_2SCH_2CH_2CH_2}$ (12S3); $^1H$ NMR ($\delta$ in $CDCl_3$) 2.67 (t, 12H, $J_{H-H}$ = 6.7 Hz), 1.87 (q, 6H, $J_{H-H}$ = 6.7 Hz)] and 1,5,9,13,17,21-hexathiacyclotetracosane [24S6;[10] $^1H$ NMR ($\delta$ in $CDCl_3$) 2.60 (t, 24H, $J_{H-H}$ = 7.2 Hz), 1.84 (q, 12H, $J_{H-H}$ = 7.2 Hz)], which were present in a 1/3.5 ratio based on the NMR integration. The products were separated by TLC using a hexane−chloroform−ethyl acetate 2/1/1 solvent mixture as the eluent to give two bands. The first band contained the macrocycle 12S3[10] and the second band contained the macrocycle 24S6.[11]

**Catalytic Cyclooligomerization of Thietane by $Re_3(CO)_{12}(\mu\text{-}H)_3$ (11).** A 7.0-mL amount of thietane (94.0 mmol) was added to a 25-mL three-neck round-bottom flask equipped with a stir bar, a reflux condenser, a nitrogen inlet, and 15.0 mg (0.017 mmol) of **11**. The solution was heated to reflux and allowed to stir under nitrogen at this temperature for 48 h. After the solution was cooled, the excess thietane was removed *in vacuo*. The resulting residue weighed 1.229 g. An NMR spectrum taken of a portion of the residue showed only two products 12S3 and 24S6, which were in a 1/2 ratio based on integration. The products were then separated by TLC using a hexane−chloroform−ethyl acetate 2/1/1 solvent mixture as the eluent to give two bands. The first band contained the 12S3 macrocycle and the second band contained the 24S6 macrocycle. An NMR spectrum was taken of the residue and two hydride resonances were identified. $^1H$ NMR ($\delta$ in acetone-$d_6$) −12.46 (s, 1H), −16.54 (s, 2H), which is characteristic of the mixture of **4** and **5**, see above. However, this treatment of this mixture with dimethylphenylphosphine as described above showed evidence for **8** only by $^1H$ NMR analysis, $\delta$ (in $CDCl_3$) −12.73 (s, 1H), −15.43 (d, 2H, $^2J_{P-H}$ = 17 Hz).

**Catalytic Cyclooligomerization of 3,3-DMT by $Re_3(CO)_{10}[\mu\text{-}\overline{SCH_2CMe_2CH_2}](\mu_3\text{-}H)_3$ (12).** A 7.0-mL amount (68.6 mmol) of 3,3-DMT and 13.2 mg (0.014 mmol) of $Re_3(CO)_{10}[\mu\text{-}\overline{SCH_2CMe_2CH_2}](\mu_3$-$H)_3$ (**12**) were added to a 25-mL three-neck round-bottom flask equipped with a stir bar, a reflux condenser, and a nitrogen inlet. The reaction was brought to reflux and was allowed to stir under nitrogen at this temperature for 24 h. After the solution was cooled, the excess 3,3-dimethylthietane was removed *in vacuo*. The resulting residue weighed 513.1 mg. An NMR spectrum taken of a portion of the residue showed resonances that could be attributed to only one compound that was determined to be 3,3,7,7,11,11,15,15,19,19,23,23-dodecamethyl-1,5,9,13,17,21-hexathiacyclotetracosane, $Me_{12}$-24S6. The product was purified by TLC using a hexane−methylene chloride 4/1 solvent mixture. Only one band of pure $Me_{12}$-24S6 macrocycle was eluted. $^1H$ NMR for $Me_{12}$-24S6 ($\delta$ in $CDCl_3$): 2.93 (s, 36H), 1.01 (s, 24H). The mass spectrum of $Me_{12}$-24S6 showed the parent ion at $m/e$ = 612.

**Crystallographic Analyses.** Yellow crystals of **2** suitable for X-ray diffraction analyses were grown from a solution in acetone by slow evaporation of the solvent at 25 °C. Yellow crystals of **6** suitable for

(10) Rawle, S. C.; Admans, G. A.; Cooper, S. R. *J. Chem. Soc., Dalton Trans.* **1988**, 93.

(11) Ochrymowycz, L. A.; Mak, C.-P.; Michna, J. D. *J. Org. Chem.* **1974**, *14*, 2079.

**Table 1.** Crystallographic Data for Compounds **2** and **6**

| | **2** | **6** |
|---|---|---|
| formula | $Re_3S_2O_{10}C_{15}H_{15}\cdot 0.5(CH_3)_2CO$ | $Re_3PS_4O_9C_{29}H_{38}$ |
| formula wt | 1007.06 | 1248.45 |
| crystal system | triclinic | monoclinic |
| lattice parameters: | | |
| $a$ (Å) | 12.295(2) | 8.637(2) |
| $b$ (Å) | 12.341(2) | 41.80(1) |
| $c$ (Å) | 8.568(1) | 11.418(2) |
| $\alpha$ (deg) | 101.76(1) | |
| $\beta$ (deg) | 91.37(2) | 111.79(2) |
| $\gamma$ (deg) | 97.66(2) | |
| $V$ (Å$^3$) | 1259.7(3) | 3828(2) |
| space group | $P\bar{1}$, No. 2 | $P2_1/n$, No. 14 |
| $Z$ | 2 | 4 |
| $D_{calc}$ (g/cm$^3$) | 2.65 | 2.17 |
| $\mu$(Mo K$\alpha$) (cm$^{-1}$) | 147.8 | 98.9 |
| temp (°C) | 20 | 20 |
| $2\theta_{max}$ (deg) | 43.0 | 41.0 |
| no. of obsd (total unique) | 2891 | 3952 |
| no. of obsd used ($I > 3\sigma(I)$) | 2344 | 2836 |
| no. of variables | 283 | 424 |
| residuals: $R$, $R_w$ | 0.040; 0.043 | 0.036; 0.036 |
| goodness of fit indicator | 2.11 | 1.72 |
| max shift in final cycle | 0.04 | 0.16 |
| largest peak in final diff map (e$^-$/Å$^3$) | 1.45 | 0.78 |
| abs corr | empirical | empirical |

X-ray diffraction were grown from slow diffusion of hexane into a solution of **6** in acetone at 25 °C. All data crystals were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6S fully automated four-circle diffractometer using graphite-monochromated Mo K$\alpha$ radiation. The unit cells were determined and refined from 15 randomly selected reflections obtained by using the AFC6S automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of these analyses are listed in Table 1. All data processing was performed on a Digital Equipment Corp. VAXstation 3520 computer 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.[12a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[12b] Lorentz–polarization (Lp) and absorption corrections were applied in each analysis. Full-matrix least-squares refinements minimized the function: $\sum_{hkl} w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02I_{net})^2]^{1/2}/\text{Lp}$. For each analysis the positions of all hydrogen atoms on the ligands were calculated by assuming idealized geometries. Their contributions were added to the structure factor calculations, but their positions were not refined.

Compound **2** crystallized in the triclinic crystal system. The centrosymmetric space group $P\bar{1}$ was assumed and confirmed by successful solution and refinement of the structure. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All non-hydrogen atoms in the complex were refined with anisotropic thermal parameters. The hydride ligands were located in chemically reasonable positions in a difference Fourier map but could not be adequately refined. In the end they were added to the structure as fixed contributions only. All hydrogen atom positions on the ligand were calculated by assuming idealized geometry and C–H = 0.95 Å. In the final stages of refinement 0.50 equiv of acetone that had cocrystallized from the crystallization solvent was found in the lattice. It exhibited a 2-fold disorder about a crystallographic center of symmetry and was satisfactorily refined using isotropic thermal parameters.

Compound **6** crystallized in the monoclinic crystal system. The space group $P2_1/n$ was established on the basis of the patterns of systematic absences observed during the collection of data. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydride ligands were located and were refined on their position parameters only. All hydrogen atom positions on the ligand were calculated by assuming idealized geometry and C–H = 0.95 Å.

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

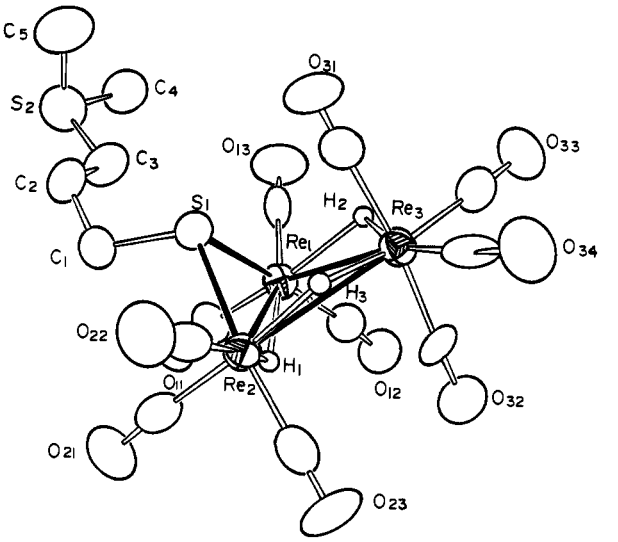



**Figure 1.** An ORTEP diagram of $Re_3(CO)_{10}[\mu\text{-}SCH_2CH_2CH_2SMe_2](\mu\text{-}H)_3$ (**2**) showing 50% probability thermal ellipsoids.

**Table 2.** Intramolecular Distances for **2**[a]

| atom–atom | distance | atom–atom | distance |
|---|---|---|---|
| Re(1)–S(1) | 2.488(5) | S(2)–C(5) | 1.76(2) |
| Re(1)–Re(2) | 3.003(1) | S(2)–C(3) | 1.78(2) |
| Re(1)–Re(3) | 3.243(1) | S(2)–C(4) | 1.81(3) |
| Re(2)–S(1) | 2.482(5) | O–C(av) | 1.15(2) |
| Re(2)–Re(3) | 3.215(1) | C(1)–C(2) | 1.53(3) |
| S(1)–C(1) | 1.85(2) | C(2)–C(3) | 1.50(3) |

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

## Results

Compound **1** has been found to react with dimethyl sulfide by a ring-opening addition to the bridging thietane ligand to yield the zwitterionic complex $Re_3(CO)_{10}[\mu\text{-}SCH_2CH_2CH_2SMe_2](\mu\text{-}H)_3$ (**2**) in 48% yield. Compound **2** was characterized by IR, $^1$H NMR, and single-crystal X-ray diffraction analyses. An ORTEP diagram of the molecular structure of **2** is shown in Figure 1. Selected bond distances and angles are listed in Tables 2 and 3. The molecule contains a triangular trirhenium cluster with one hydride ligand bridging each edge of the cluster. This is typical of the $H_3Re_3$ carbonyl cluster system. On the Re(1)–Re(2) edge of the cluster there is a sulfonium-substituted bridging thiolate group $SCH_2CH_2CH_2SMe_2$. Overall, the molecule is a zwitterion with a formal positive charge located on the sulfur atom S(2). The negative charge is formally located on the sulfur S(1) but is probably delocalized into the $Re_3$ cluster. In solution the molecule has reflection symmetry due to the flexibility of the sulfonium-containing side chain, $\delta$ −12.48 (s, 1H) and −16.54 (s, 2H), for the hydride ligands. This complex has close structural similarities to the zwitterionic complex $Re_3(CO)_{10}[\mu\text{-}SCH_2CH_2CH_2NMe_3](\mu\text{-}H)_3$ and the anionic complex $[Re_3(CO)_{10}[\mu\text{-}SCH_2CH_2CH_2Cl](\mu\text{-}H)_3]^-$ that have been characterized previously.[5]

When **1** was allowed to react with 3 equiv of thietane, $SCH_2CH_2CH_2$, at 25 °C for a period of 18 h, the new complex $Re_3(CO)_{10}[\mu\text{-}SCH_2CH_2CH_2SCH_2CH_2CH_2SCH_2CH_2CH_2SCH_2$-

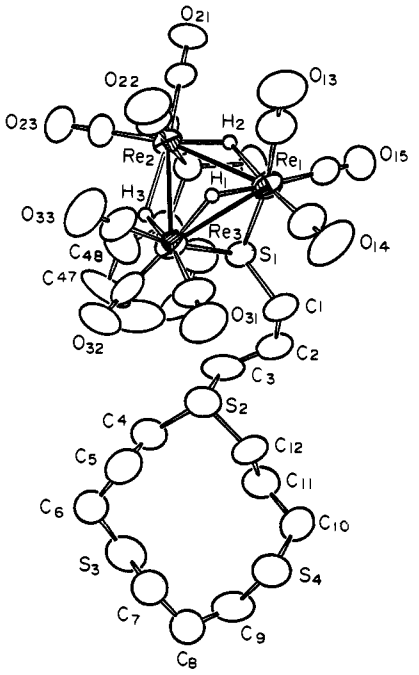



**Figure 2.** An ORTEP diagram of $Re_3(CO)_9(PMe_2Ph)[\mu$-$SCH_2CH_2CH_2$-$SCH_2CH_2CH_2SCH_2CH_2CH_2SCH_2CH_2CH_2](\mu$-$H)_3$ (**6**) showing 50% probability thermal ellipsoids.

**Table 3.** Intramolecular Bond Angles for **2**[a]

| atom−atom−atom | angle | atom−atom−atom | angle |
|---|---|---|---|
| C(11)−Re(1)−S(1) | 93.5(6) | C(23)−Re(2)−Re(3) | 94.4(6) |
| C(11)−Re(1)−Re(2) | 96.6(6) | C(22)−Re(2)−S(1) | 94.5(6) |
| C(11)−Re(1)−Re(3) | 157.8(6) | C(22)−Re(2)−Re(1) | 146.7(6) |
| C(12)−Re(1)−S(1) | 170.9(6) | C(22)−Re(2)−Re(3) | 108.6(6) |
| C(12)−Re(1)−Re(2) | 119.1(7) | S(1)−Re(2)−Re(1) | 52.9(1) |
| C(12)−Re(1)−Re(3) | 95.0(5) | S(1)−Re(2)−Re(3) | 78.3(1) |
| C(13)−Re(1)−S(1) | 96.7(6) | Re(1)−Re(2)−Re(3) | 62.75(3) |
| C(13)−Re(1)−Re(2) | 148.7(5) | C(1)−S(1)−Re(2) | 107.3(7) |
| C(13)−Re(1)−Re(3) | 109.6(5) | C(1)−S(1)−Re(1) | 112.4(6) |
| S(1)−Re(1)−Re(2) | 52.7(1) | Re(2)−S(1)−Re(1) | 74.4(1) |
| S(1)−Re(1)−Re(3) | 77.7(1) | C(5)−S(2)−C(3) | 101(1) |
| Re(2)−Re(1)−Re(3) | 61.83(3) | C(5)−S(2)−C(4) | 99(1) |
| C(21)−Re(2)−S(1) | 96.5(6) | C(3)−S(2)−C(4) | 102(1) |
| C(21)−Re(2)−Re(1) | 99.4(6) | C(2)−C(1)−S(1) | 111(1) |
| C(21)−Re(2)−Re(3) | 161.0(6) | C(3)−C(2)−C(1) | 113(2) |
| C(23)−Re(2)−S(1) | 171.0(6) | C(2)−C(3)−S(2) | 114(1) |
| C(23)−Re(2)−Re(1) | 119.1(6) | O−C(av)−Re | 176(2) |

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

$CH_2CH_2](\mu$-$H)_3$ (**3**) was formed in 47% yield. Compound **3** has been characterized by IR and $^1H$ NMR spectroscopy and by a single-crystal X-ray diffraction analysis of its $PMe_2Ph$ derivative $Re_3(CO)_9(PMe_2Ph)[\mu$-$SCH_2CH_2CH_2SCH_2CH_2CH_2$-$SCH_2CH_2CH_2SCH_2CH_2CH_2](\mu$-$H)_3$ (**6**). The $^1H$ NMR spectrum of **3** contains a complex series of multiplets for the methylene groups [$\delta$ 3.91 (m, 2H), 3.46 (t, 2H, $J_{H-H}$ = 7.4 Hz), 3.36 (m, 2H), 2.91 (q, 2H, $J_{H-H}$ = 5.8 Hz), 2.78 (q, 2H, $J_{H-H}$ = 5.8 Hz), 2.74 (t, 4H, $J_{H-H}$ = 5.1 Hz), 2.59 (t, 2H, $J_{H-H}$ = 7.2 Hz), 2.19 (m, 6H), 1.87 (q, 2H, $J_{H-H}$ = 6.2 Hz)] that integrate to 24 H and are consistent with the presence of 4 equiv of thietane and two hydride resonances [$\delta$ −12.46 (s, 1H), −16.49 (s, 2H)]. Compound **3** was readily converted to its $PMe_2Ph$ derivative in 69% yield by treatment with $PMe_2Ph$ in methylene chloride solvent at reflux for 18 h. An ORTEP diagram of the molecular structure of **6** is shown in Figure 2. Selected bond distances and angles are listed in Table 4 and 5. This zwitterionic complex contains a $Re_3(CO)_9(PMe_2Ph)(\mu$-$H)_3[\mu$-$SCH_2CH_2CH_2]$

**Table 4.** Intramolecular Distances for **6**[a]

| atom−atom | distance | atom−atom | distance |
|---|---|---|---|
| Re(1)−H(1) | 1.8(1) | S(2)−C(12) | 1.82(2) |
| Re(1)−H(2) | 2.0(1) | S(3)−C(6) | 1.78(2) |
| Re(1)−S(1) | 2.466(4) | S(3)−C(7) | 1.80(2) |
| Re(1)−Re(3) | 3.031(1) | S(4)−C(9) | 1.79(2) |
| Re(1)−Re(2) | 3.220(1) | S(4)−C(10) | 1.80(2) |
| Re(2)−H(2) | 1.7(1) | C(1)−C(2) | 1.56(2) |
| Re(2)−H(3) | 2.1(1) | C(2)−C(3) | 1.52(2) |
| Re(2)−P | 2.458(4) | C(4)−C(5) | 1.55(3) |
| Re(2)−Re(3) | 3.211(1) | C(5)−C(6) | 1.51(3) |
| Re(3)−H(3) | 1.6(1) | C(7)−C(8) | 1.53(3) |
| Re(3)−H(1) | 1.9(1) | C(8)−C(9) | 1.50(3) |
| Re(3)−S(1) | 2.461(4) | C(10)−C(11) | 1.53(2) |
| S(1)−C(1) | 1.84(2) | C(11)−C(12) | 1.53(2) |
| S(2)−C(3) | 1.80(2) | C−O(av) | 1.16(2) |
| S(2)−C(4) | 1.80(2) | | |

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

**Table 5.** Intramolecular Bond Angles for **6**[a]

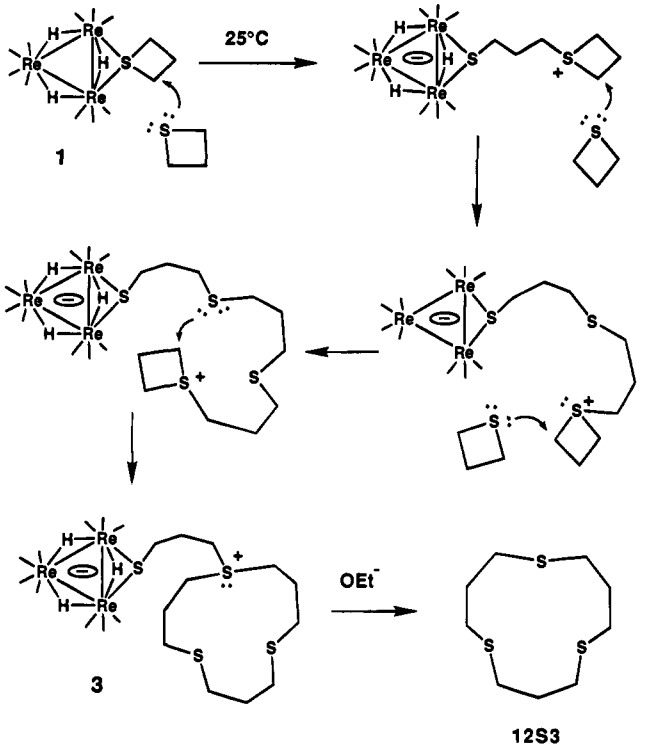
| atom−atom−atom | angle | atom−atom−atom | angle |
|---|---|---|---|
| C(14)−Re(1)−S(1) | 97.8(5) | C(33)−Re(3)−Re(2) | 91.4(5) |
| C(14)−Re(1)−Re(3) | 99.1(6) | Re(1)−Re(3)−Re(2) | 62.03(3) |
| C(14)−Re(1)−Re(2) | 158.4(6) | C(1)−S(1)−Re(3) | 114.1(6) |
| C(13)−Re(1)−S(1) | 169.8(6) | C(1)−S(1)−Re(1) | 109.2(6) |
| C(13)−Re(1)−Re(3) | 121.5(6) | Re(3)−S(1)−Re(1) | 75.9(1) |
| C(13)−Re(1)−Re(2) | 91.3(6) | C(3)−S(2)−C(4) | 102(1) |
| C(15)−Re(1)−S(1) | 94.3(5) | C(3)−S(2)−C(12) | 104.0(9) |
| C(15)−Re(1)−Re(3) | 145.8(5) | C(4)−S(2)−C(12) | 104.1(8) |
| C(15)−Re(1)−Re(2) | 111.5(5) | C(6)−S(3)−C(7) | 100(1) |
| Re(3)−Re(1)−Re(2) | 61.72(3) | C(9)−S(4)−C(10) | 103(1) |
| C(21)−Re(2)−Re(3) | 161.9(5) | C(2)−C(1)−S(1) | 110(1) |
| C(21)−Re(2)−Re(1) | 108.3(5) | C(3)−C(2)−C(1) | 116(1) |
| C(22)−Re(2)−Re(3) | 78.5(5) | C(2)−C(3)−S(2) | 112(1) |
| C(22)−Re(2)−Re(1) | 81.6(5) | C(5)−C(4)−S(2) | 112(2) |
| Re(3)−Re(2)−Re(1) | 56.25(3) | C(6)−C(5)−C(4) | 113(2) |
| C(32)−Re(3)−S(1) | 96.6(5) | C(5)−C(6)−S(3) | 114(1) |
| C(32)−Re(3)−Re(1) | 147.8(5) | C(8)−C(7)−S(3) | 111(2) |
| C(32)−Re(3)−Re(2) | 109.4(5) | C(9)−C(8)−C(7) | 114(2) |
| C(31)−Re(3)−S(1) | 96.9(6) | C(8)−C(9)−S(4) | 113(1) |
| C(31)−Re(3)−Re(1) | 97.6(7) | C(11)−C(10)−S(4) | 114(1) |
| C(31)−Re(3)−Re(2) | 157.2(7) | C(12)−C(11)−C(10) | 110(1) |
| C(33)−Re(3)−S(1) | 169.6(5) | C(11)−C(12)−S(2) | 118(1) |
| C(33)−Re(3)−Re(1) | 119.8(6) | O−C(av)−Re | 176(2) |

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

fragment that is similar to that found in compound **2** with the exception of the $PMe_2Ph$ ligand that occupies an axial coordination site on the metal atom Re(2). The most interesting difference between **2** and **6** is the $SCH_2CH_2CH_2$ chain is terminated with the macrocycle 1,5,9-trithiacyclododecane (12S3) in **6** instead of the $Me_2S$ group as found in **2**. The sulfur atom S(2) is a positively charged sulfonium center. A negative charge is formally located at the thiolate sulfur atom S(1) but is probably also delocalized in the $Re_3$ cluster grouping. The bond distances, angles, and overall conformation of the macrocyclic grouping in **6** are not significantly different from those found in the free molecule, 12S3, or the copper complex, $Cu(12S3)_2Cl_2$.[10] Complex **3** is believed to be structurally similar to that of **6**, having a 12S3 macrocycle tethered to a $Re_3(CO)_{10}(\mu$-$H)_3$ grouping by a $SCH_2CH_2CH_2$ chain.

Complex **3** was apparently formed by a series of three ring-opening additions of thietane to the bridging thietane ligand in **1**, see Scheme 1. The first addition leads to an opening of the ring of the thietane ligand. The added thietane becomes a positively charged thietanium grouping. Because of the strain in the thietanium group it can undergo a ring-opening addition of a second thietane grouping and so on with the third. However, at this stage the thiaether grouping that was formed

**Scheme 1**




in the first addition adds in a ring-opening step to the thietanium ring to produce the 12-membered ring and in the absence of ring strain no further ring-opening additions occur.

When treated with larger amounts of thietane (e.g. 20 equiv), the compounds **4** and **5** that contain thiolate ligands terminated by macrocycles formed by the cyclooligomerization of four and six thietane ligands, respectively, were formed. Compounds **4** and **5** could not be separated and were therefore transformed into their $PMe_2Ph$ derivatives, **7** and **8**, for full and individual characterizations.

When compound **3** was treated with $OEt^-$ at 25 °C for 18 h, the macrocyclic grouping was cleaved from the cluster and the free molecule 12S3 was isolated in 32% yield. The metal-containing product appears to be a trirhenium cluster complex with three bridging hydride ligands, $^1H$ NMR $\delta$ −12.45 (1H) and −16.52 (2H) ppm, but its full characterization has so far eluded us. In a similar fashion when compound **6** was treated with pyridine (py), the 12S3 macrocycle was cleaved from the complex and was isolated in 25% yield. In this case the cluster-containing product was isolated and identified as $Re_3(CO)_9(PMe_2Ph)[\mu\text{-}S(CH_2)_3(py)](\mu\text{-}H)_3$ (**9**). Although it was not characterized crystallographically, this molecule appears to be analogous to **2**, **3**, and **6** with a pyridinium substituent in the place of the $Me_2S$ and 12S3 groupings at the terminus of the $\mu$-$S(CH_2)_3$ chain. Similarly, the macrocycles on compounds **7** and **8** were cleaved from the complexes by treatment with pyridine to yield compound **9**. A summary of these results is given in Scheme 2. Compound **9** was also prepared by a two-step process involving first a ring-opening addition of pyridine to **1** to yield the pyridinium−thiolato complex $Re_3(CO)_{10}(\mu\text{-}H)_3[\mu\text{-}S(CH_2)_3$-(pyridine)] (**10**) in 57% yield and a subsequent treatment of **10** with $PMe_2Ph$ to form **9** in 62% yield.

**Scheme 2**

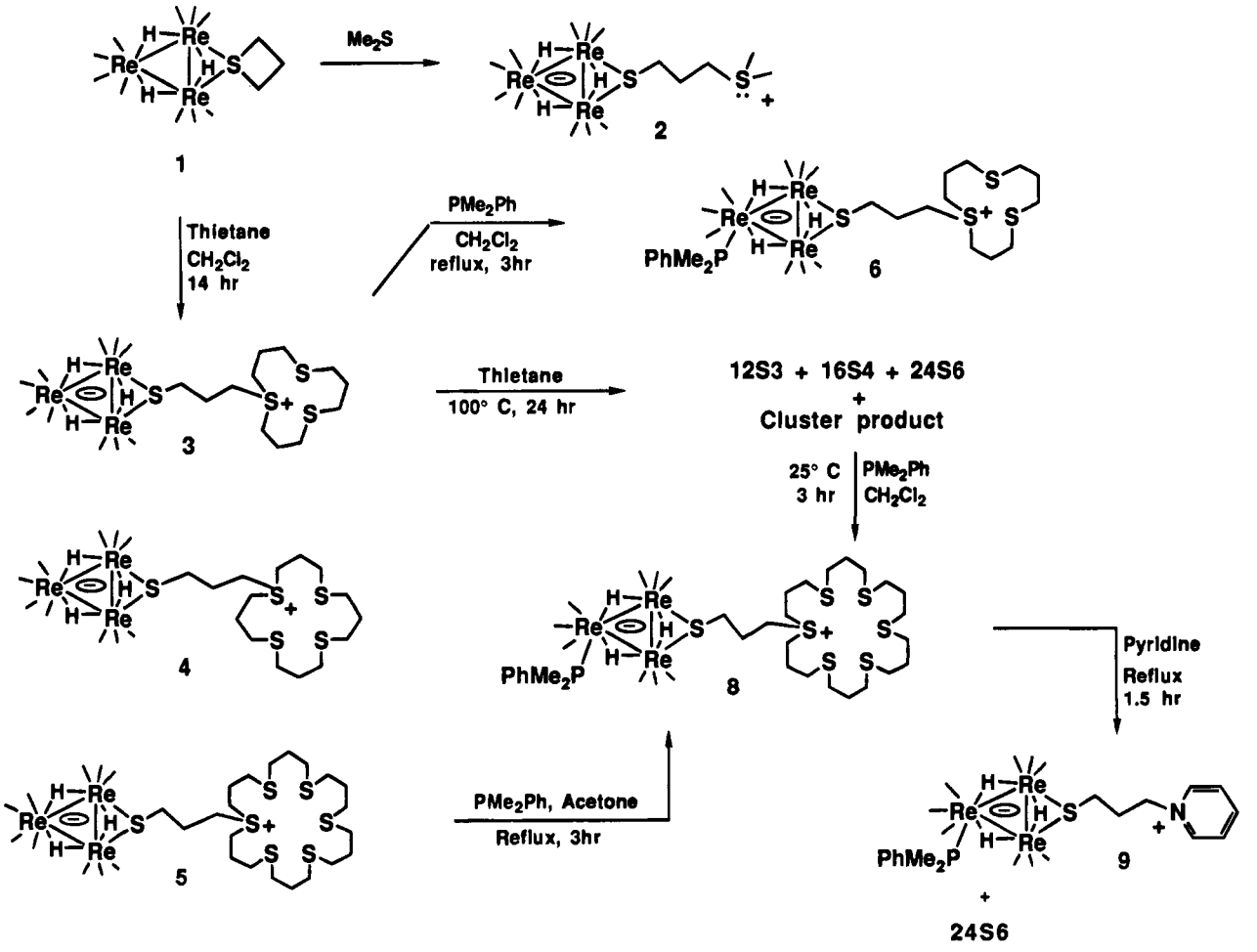
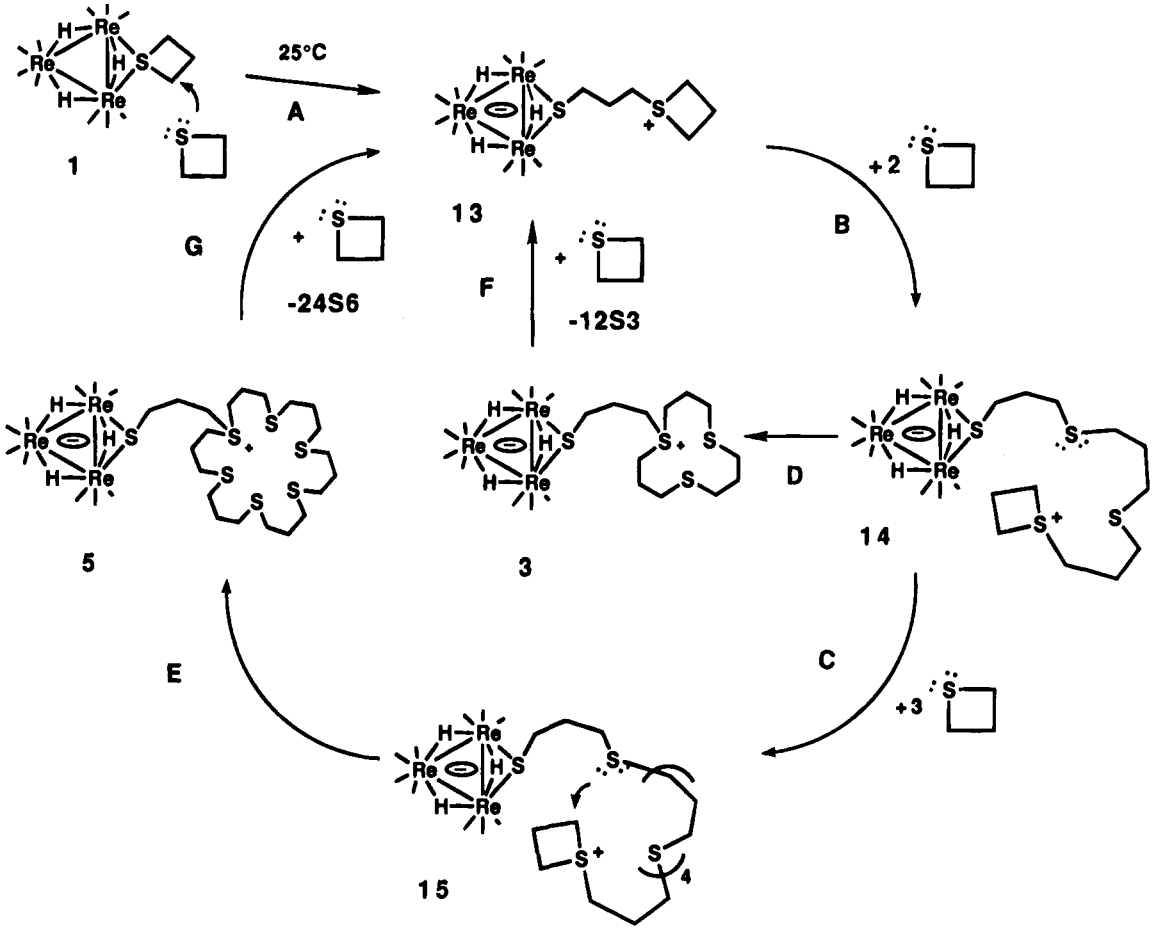


**Table 6.** Summary of the Results of the Catalytic formation of Cyclooligomers by Trirhenium Cluster Complexes

| catalyst[c] | catalyst amount, mg | monomer | monomer amount, mL | products[a] | product radio[b] | reaction time, h | product amount, g |
|---|---|---|---|---|---|---|---|
| **1** | 17.0 | thietane | 6.0 | 24S6/12S3 | 3.5/1 | 24 | 0.632 |
| **3** | 17.0 | thietane | 7.0 | 24S6/12S3 | 3.57/1 | 48 | 1.179 |
| **11** | 15.0 | thietane | 7.0 | 24S6/12S3 | 2/1 | 44 | 1.229 |
| **12** | 13.2 | 3,3-DMT[a] | 7.0 | $Me_{12}$-24S6 | | 24 | 0.513 |

[a] 3,3-DMT = 3,3-dimethylthietane. [b] Determination of the product ratios was performed by $^1$H NMR. [c] **1** = $Re_3(CO)_{10}[\mu\text{-}SCH_2CH_2CH_2](\mu\text{-}H)_3$. **3** = $Re_3(CO)_{10}[\mu\text{-}SCH_2CH_2CH_2SCH_2CH_2CH_2SCH_2CH_2CH_2SCH_2CH_2CH_2](\mu\text{-}H)_3$. **11** = $Re_3(CO)_{12}(\mu\text{-}H)_3$. **12** = $Re_3(CO)_{10}(SCH_2CMe_2CH_2)(\mu\text{-}H)_3$.

**Scheme 3**




It appears that thietane, itself, is also capable of cleaving the macrocycles from the zwitterionic complexes and this has permitted the development of a catalytic procedure for the preparation of the macrocycles. For example, when thietane was allowed to react with **1** at reflux in a 5000/1 ratio in the absence of solvent (ca. 90 °C) for 24 h, the two macrocycles, 12S3 and 24S6, were formed in a 1/3.5 ratio as determined by $^1$H NMR spectroscopy. Ultimately, 172.0 mg (137 equiv of thietane) of pure 12S3, and 392 mg (312 equiv of thietane) of pure 24S6 were isolated. Only 52 mg of insoluble material was formed, which is assumed to be a polymer of thietane. Workup of the mixture by treatment with $PMe_2Ph$ showed significant amounts of the 24S6 macrocycle complex **8**. In a similar fashion, solutions of **3** also produced catalytic cyclooligomerization of thietane in nearly the same amounts. In fact, we found that $Re_3(CO)_{12}(\mu\text{-}H)_3$ (**11**) is an equally effective precursor for the catalytic production of the macrocycles 12S3 and 24S6. Workup of the mixtures obtained from the catalysis produced by **11** has indicated that it was transformed into the macrocycle thiolate complex **5**. A summary of the catalytic studies is given in Table 6.

The catalytic cycles shown in Scheme 3 are proposed to explain the formation of the major macrocyclic products, 12S3 and 24S6, that we have observed. The process is initiated by a ring-opening addition of thietane to the bridging thietane ligand in **1** which leads to the intermediate **13** that contains a thietanium ring. The thietanium ring can react with free thietane in a series of ring-opening additions. These are the propagation steps **B** and **C**. The intermediates **14** and **15** may engage in the chain-terminating steps **D** and **E** to yield the stable compounds **3** and **5**. Finally, there are two regeneration steps **F** and **G** that are probably the slow steps in the cycles. These lead to displacement of the macrocycles and regeneration of the active catalyst **13**.

It would seem that a process such as this should produce substantial amounts of polythietane. Indeed, the cationic polymerization of thietanes via sulfonium intermediates is well-known.[13] We think that the preference for cyclization in these

(13) (a) Goethals, E. J. *Makromol. Chem., Macromol. Symp.* **1991**, *42/43*, 51. (b) Goethals, E. J.; Drijvers, W.; van Ooteghem, D.; Buyle, A. M. *J. Macromol. Sci.—Chem.* **1973**, *A7*, 1375. (c) Goethals, E. J.; Florquin, S. M. *Makromol. Chem.* **1981**, *182*, 3371.

reactions may be controlled by the zwitterionic character of the intermediates that are involved. In particular, in this cluster-promoted oligomerization, the two ends of the growing chain have opposite charges (e.g. intermediates **14** and **15**, Scheme 3). As a result, it is quite likely that the two ends will associate as ion pairs as the chain grows. Since the thiaether group that participates in the cyclization is the one closest to the negatively charged cluster, it will always be proximate to the thietanium ring and thus the tendency for macrocycle formation by reaction of that thiaether link with the thietanium ring will be enhanced. In contrast, in simple cationic polymerization the chain is not connected to the anion and the uncharged terminus of the chain drifts away from the reaction site as the polymer growth occurs. Curiously, the macrocycles that would have been formed by the cyclooligomerization of 4 and 5 equiv of thietane were not produced in significant amounts although the former was observed in the form of the complex **4** when limited amounts of thietane (e.g. 20 equiv) were allowed to react with **1**. The reason for this is not clear at this time.

It is also significant that the thietanium ring does not react with the metal atoms of the cluster as was found in the case of the reaction of thietane with $Os_3(CO)_{10}[\mu\text{-}\overline{SCH_2CMe_2CH_2}]$.[6] In that reaction, the growing chain added to the cluster through a cleavage of one of the metal−metal bonds and cyclization did not occur. In **1**, each of the metal−metal bonds is bridged by a hydride ligand. We think that these bridging hydride ligands protect the cluster from attack by the thietanium rings. It is quite likely that other cluster complexes will also produce catalytic cyclooligomerization of thietanes. A search for other catalysts is in progress.

In previous studies we have made and characterized the related cluster complex, $Re_3(CO)_{10}[\mu\text{-}\overline{SCH_2CMe_2CH_2}](\mu_3\text{-}H)_3$ (**12**).[5] Accordingly, we have tested it for its ability to produce cyclooligomerizations of 3,3-dimethylthietane. Indeed, cyclization proceeds readily at the boiling point of 3,3-dimethylthietane, but only one product, 3,3,7,7,11,11,15,15,19,19,23,23-dodecamethyl-1,5,9,13,17,21-hexathiacyclotetracosane ($Me_{12}$-24S6), was obtained.

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**Supplementary Material Available:** Tables of final atomic positional parameters and anisotropic thermal parameters for the structural analysis (20 pages); listing of structure factor amplitudes (36 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.