Catalytic Macrocyclization of 3-Methylthietane by $Re_2(CO)_9(SCH_2CHMeCH_2)$ and $W(CO)_5(SCH_2CHMeCH_2)$

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The new compounds $Re_2(CO)_9(SCH_2CHMeCH_2)$ (**2**) and $W(CO)_5(SCH_2CHMeCH_2)$, **8**, have been prepared by the reactions of $Re_2(CO)_9(NCMe)$ (**1**) and $W(CO)_5(NCMe)$ (**7**) with 3-methylthietane, ($SCH_2CHMeCH_2$, 3-MT). Compounds **1**, **2**, **7**, and **8** have been found to react with $SCH_2CHMeCH_2$ at reflux to yield substantial amounts of the polythioether macrocycle 3,7,11-trimethyl-1,5,9-trithiacyclododecane ($Me_3$12S3) by a macrocyclization process consisting of a metal-induced ring-opening cyclooligomerization of three molecules of 3-MT. $Me_3$12S3 is formed as two isomers, *cis*,*trans*,*trans*-3,7,11-trimethyl-1,5,9-trithiacyclododecane (*c*,*t*,*t*-$Me_3$12S3, **3**) and *cis*,*cis*,*cis*-3,7,11-trimethyl-1,5,9-trithiacyclododecane (*c*,*c*,*c*-$Me_3$12S3, **4**), due to different orientations of the methyl substituents in the ring. Small amounts of higher macrocycles with the general formula $(SCH_2CHMeCH_2)_n$ ($n > 3$) are also formed, but these could not be isolated in pure forms. A comparison of the two catalysts shows that the rhenium catalyst exhibits a higher activity and higher selectivity for the formation of $Me_3$12S3 than the tungsten complex. The reactions of **1** with **3** and **4** have yielded the new compounds $Re_2(CO)_9(c,t,t\text{-}SCH_2CHMe(CH_2SCH_2CHMe)_2CH_2)$ (**5**) and $Re_2(CO)_9(c,c,cSCH_2CHMe(CH_2SCH_2CHMe)_2CH_2)$ (**6**), respectively. The molecular structures of the free molecule **3** and the complexes **5** and **6** were established by single-crystal X-ray diffraction analyses.

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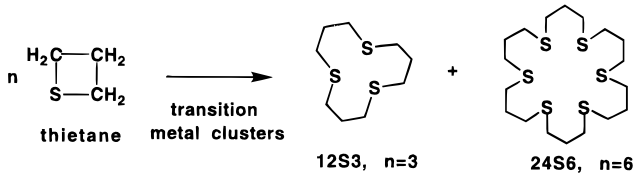
Introduction

In recent studies we have discovered the first examples of the catalytic macrocyclization of thietanes by a ring-opening cyclooligomerization process (ROC) that is promoted by certain metal carbonyl complexes.[1] The polynuclear metal complexes $Re_3(CO)_{10}(\mu\text{-}SCH_2CH_2CH_2)(\mu\text{-}H)_3$,[2] $Re_2(CO)_9(SCH_2CH_2CH_2)$,[3] and $Os_4(CO)_{11}(SCH_2CH_2CH_2)(\mu\text{-}H)_4$[4] were found to be the most effective catalysts, but we have found that the tungsten complex $W(CO)_5(SCH_2CH_2CH_2)$ is also effective.[5] Macrocycles formed by the ROC of three and six thietane molecules are the major products (eq 1; 12S3 = 1,5,9-trithiacyclododecane and 24S6 = 1,5,9,13,17,21-hexathiacyclotetracosane. Polythioether macrocycles have attracted considerable attention in recent years due to their potential to serve as ligands for the transition metals.[6]



(1)

We have now investigated the catalytic macrocyclization of 3-methylthietane (3-MT) by the complexes $Re_2(CO)_9(SCH_2CHMeCH_2)$ and $W(CO)_5(SCH_2CHMeCH_2)$ and have observed the formation of the new macrocycle 3,7,11-trimethyl-1,5,9-trithiacyclododecane, $Me_3$12S3, which is formed as a mixture of two isomers. The results of this study are reported here.

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. ^{1}H NMR spectra were recorded at 400 or 500 MHz. ^{13}C NMR spectra were obtained at 125.76 MHz. $Re_2(CO)_9(NCMe)$[7] (**1**), $W(CO)_5(NCMe)$[8] (**7**), $Mn_2(CO)_9(NCMe)$[9] (**9**), and 3-methylthietane[10] were prepared according to the published procedures. 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

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(1) Adams, R. D.; Falloon, S. B. *Chem. Rev.* **1995**, *95*, 2587.
(2) Adams, R. D.; Falloon, S. B. *J. Am. Chem. Soc.* **1994**, *116*, 10540.
(3) Adams, R. D.; Cortopassi, J. E.; Falloon, S. B. *Organometallics* **1995**, *14*, 1748.
(4) Adams, R. D.; Falloon, S. B. *Organometallics* **1995**, *14*, 4594.
(5) Adams, R. D.; Falloon, S. B.; Perrin, J.; Queisser, J. A.; Yamamoto, J. H. *Chem. Ber.* **1996**, *129*, 313.
(6) (a) Cooper, S. R. In *Crown Compounds: Toward Future Applications*; Cooper, S. R., Ed.; VCH: New York, 1992; Chapter 15. (b) Cooper, S. R.; Rawle, S. C. *Struct. Bonding* **1990**, *72*, 1. (c) Blake, A. J.; Schröder, M. *Adv. Inorg. Chem.* **1990**, *35*, 1. (d) Cooper, S. R. *Acc. Chem. Res.* **1988**, *21*, 141.
(7) Koelle, U. *J. Organomet. Chem* **1978**, *155*, 53.
(8) Ross, B. F.; Grasseli, J. G.; Ritchey, W. M.; Kaesz, H. D. *Inorg. Chem* **1963**, *2*, 1023.
(9) Koelle, U. *J. Organomet. Chem.* **1978**, *155*, 53.
(10) Bordwell, F. G.; Hewett, W. A. *J. Org. Chem.* **1958**, *23*, 636.

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Table 1. Results of the Catalytic Macrocyclizations of 3-Methylthietane

catalyst[a]	catalyst amt (mg)	reagent amt (mL)	wt of products[b] (mg)	mass % of products, 3/4/S_n[c]	reacn time (h)	TOF for Me312S3[d]
1	12.0	4.0	259	60/13/27	24	1.66
2	10.0	4.0	239	60/13/27	24	1.97
2	10.0	4.0	490	27/6/67	48	0.91
5	10.0	4.0	206	60/13/27	24	1.94
7	10.0	4.0	133	26/5/69	24	0.24
8	10.0	4.0	124	26/5/69	24	0.25
9	14.0	2.0	33	33/5/61	24	0.06
$Re_2(CO)_{10}$	11.0	2.0	10	63/13/23	24	0.07
none		4.0	21	55/18/27	24	

[a] All reactions were performed at the boiling point of 3-methylthietane (108−109 °C) in the absence of solvent. [b] The weights are corrected for the weights of catalysts and the anticipated weights of products formed by noncatalyzed transformations of 3-MT. [c] S_n represents the macrocycles with the general formula $(SC_4H_8)_n$ with $n > 3$. [d] TOF = moles for $Me_3$12S3 formation, (**3**+**4**)/(mol of catalyst·h).

using electron impact ionization. Elemental analyses were performed by Oneida Research Services, Whitesboro, NY.

Preparation of $Re_2(CO)_9$(SCH$_2$CHMeCH$_2$) (2). A 20.0-mg amount of **1** (0.030 mmol) was dissolved in 15 mL of acetone in a 25-mL three-neck round-bottom flask equipped with a stirbar, reflux condenser, and nitrogen inlet. A 15-μL amount of 3-MT (0.180 mmol) was added, and the resulting solution was heated to reflux with stirring for 3 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 10.9 mg of $Re_2(CO)_9$(SCH$_2$CHMeCH$_2$) (**2**; 51% yield). Spectral data for **2**: IR ν_{CO} (cm^{-1} in hexane) 2104 (w), 2042 (s), 2016 (w), 1997 (vs), 1990 (vs), 1978 (w), 1969 (m), 1956 (w), 1933 (m); ^{1}H NMR (δ in CD_2Cl_2) 3.57 (m, 2H), 3.48 (m, 3H), 1.24 (d, 3H, $^{32}J_{H-H}$ = 6.3 Hz). The mass spectrum of **2** shows the parent ion at *m/e* 712. Ions at *m/e* 628, 600, 572, and 516 are attributed to the loss of three, four, five, and seven CO ligands from the parent ion.

Catalytic Macrocyclization of 3-MT. Synthesis of (*c,t,t*-SCH$_2$CHMe(CH$_2$SCH$_2$CHMe)$_2$CH$_2$) (3) and (*c,c,c*-SCH$_2$CHMe(CH$_2$SCH$_2$CHMe)$_2$CH$_2$) (4). All 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-bottom flask equipped with a stirbar, reflux condenser, and nitrogen inlet. Then 4 mL of freshly distilled 3-MT (47.5 mmol) was added and the solution was heated to the reflux temperature of 3-MT, 108 °C. The reaction apparatus was wrapped completely in aluminum foil to minimize possible effects of light on the reaction. The results of the experiments are listed in Table 1.

A typical reaction and workup are as follows: 4.0 mL of 3-methylthietane (47.5 mmol) and a 10.0-mg amount of **2** (0.014 mmol) were heated to the reflux temperature of 3-MT for 24 h. After the mixture was cooled, the excess 3-MT was removed in vacuo. The resulting residue was dissolved in methylene chloride and filtered. After removal of the solvent the residue weighed 260 mg. ^{1}H and ^{13}C NMR spectra of this residue indicated that it consisted principally of two products which were subsequently identified as the two configurational isomers of 3,7,11-trimethyl-1,5,9-trithiacyclododecane: *cis*-,*trans*,*trans*-$Me_3$12S3 (**3**) and *cis*,*cis*,*cis*-$Me_3$12S3 (**4**). Spectra for **3:** ^{1}H NMR (δ in $CDCl_3$) 3.10 (dd, 2H, $^2J_{H-H}$ = 12.3 Hz, $^3J_{H-H}$ = 6.2 Hz), 2.76 (dd, 2H, $^2J_{H-H}$ = 13.1 Hz, $^3J_{H-H}$ = 3.1 Hz), 2.71 (dd, 2H, $^2J_{H-H}$ = 14.1 Hz, $^3J_{H-H}$ = 6.6 Hz), 2.43 (dd, 2H, $^2J_{H-H}$ = 13.1 Hz, $^3J_{H-H}$ = 8.0 Hz), 2.15 (dd, 2H, $^2J_{H-H}$ = 14.1 Hz, $^3J_{H-H}$ = 6.9 Hz), 2.06 (dd, 2H, $^2J_{H-H}$ = 12.3 Hz, $^3J_{H-H}$ = 7.5 Hz), 1.99 (m, 2H), 1.96 (m, 1H), 1.08 (d, 3H, $^3J_{H-H}$ = 6.6 Hz), 1.04 (d, 6H, $^3J_{H-H}$ = 6.7 Hz); ^{13}C NMR (δ in $CDCl_3$) 38.26 (2C), 36.36 (2C), 34.40 (2C), 31.69 (2C), 30.01 (1C), 20.04 (2C), 19.62(1C). Spectra for **4**: ^{1}H NMR (δ in $CDCl_3$) 2.65 (dd, 6H, $^2J_{H-H}$ = 13.3 Hz, $^3J_{H-H}$ = 6.7 Hz), 2.54 (dd, 6H, $^2J_{H-H}$ = 13.3 Hz, $^3J_{H-H}$ = 6.1 Hz), 1.97 (m, 3H, $^3J_{H-H}$ = 6.1 Hz, $^3J_{H-H}$ = 6.7 Hz, $^3J_{H-H}$ = 6.8 Hz), 1.06 (d, 9H, $^3J_{H-H}$ = 6.8 Hz); ^{13}C NMR (δ in $CDCl_3$) for **4**: 39.57 (6C), 35.99 (3C), 19.85 (3C). The mass spectra for **3** and **4** show the parent ion at *m/e* 264. Additional ions at *m/e* 209, 120, and 88 are attributed to $M^+ - C_4H_7$, (SSCH$_2$CHMeCH$_2$)$^+$, and (SCH$_2$CHMeCH$_2$)$^+$. GC/mass spectra of the residues indicated the presence of the larger macrocycles $Me_4$16S4, $Me_5$20S5, and $Me_6$24S6 as well as some very high molecular weight compounds containing more than 12 methylthietane units, but their small amounts and similar properties prevented their isolation in pure form. The $Me_3$12S3 isomers were separated from the mixture initially by extraction using hexane solvent. The major isomer **3** can then be obtained pure by crystallization when the hexane solution is cooled to −25 °C. By repeated crystallizations the quantity of **4** in the mother liquor is greatly increased; however, it is very difficult to obtain **4** in pure form. By combinations of column chromatography followed by TLC using a hexane/methylene chloride (3/1) solvent mixture, small amounts of pure **4** can be obtained. The larger macrocycles are almost insoluble in hexane. Repeated attempts to separate the higher macrocycles by chromatography have not yielded pure forms of these compounds.

Preparation of $Re_2(CO)_9$(*c,t,t*-SCH$_2$CHMe(CH$_2$SCH$_2$CHMe)$_2$CH$_2$) (5). A 50.0-mg amount of **1** (0.075 mmol) and 20.0 mg of *c,t,t*-$Me_3$12S3 (**3**; (0.076 mmol) were dissolved in 10 mL of acetone in a 25-mL three-neck round bottom flask equipped with a stirbar, reflux condenser, and nitrogen inlet. The solution was stirred at reflux for 20 h. The volatiles were removed in vacuo, and the product was separated from the starting compounds by TLC using a hexane/methylene chloride (4/1) solvent mixture to yield 12.0 mg of $Re_2(CO)_9$(*c,t,t*-SCH$_2$CHMe(CH$_2$SCH$_2$CHMe)$_2$CH$_2$) (**5**; 18% yield). Light yellow crystals of **5** were obtained out of a hexane solution by slow solvent evaporation at 25 °C. Analytical and spectral data for **5**: IR ν_{CO} (cm^{-1} in hexane) 2103 (w), 2040 (s), 2017 (w), 1991 (vs), 1987 (vs), 1979 (m), 1966 (m), 1952 (w), 1932 (s). ^{1}H NMR (δ in CD_2Cl_2) 3.68 (t, 1H, J_v = 11.9 Hz), 3.28 (dd, 1H, $^2J_{H-H}$ = 13.9 Hz, $^3J_{H-H}$ = 2.0 Hz), 3.05 (dd, 1H, $^2J_{H-H}$ = 13.9 Hz, $^3J_{H-H}$ = 1.7 Hz), 3.01 (dd, 1H, $^2J_{H-H}$ = 13.7 Hz, $^3J_{H-H}$ = 2.6 Hz), 2.90 (dd, 1H, $^2J_{H-H}$ = 11.9 Hz, $^3J_{H-H}$ = 1.9 Hz), 2.74 (dd, 1H, $^2J_{H-H}$ = 10.3 Hz, $^3J_{H-H}$ = 2.6 Hz), 2.60 (m, 3H), 2.32 (m, 1H), 2.15 (dd, 2H, $^2J_{H-H}$ = 14.2 Hz, $^3J_{H-H}$ = 11.2 Hz), 1.82 (m, 1H), 1.74 (m, 2H), 1.17 (d, 3H, $^3J_{H-H}$ = 6.6 Hz), 1.13 (d, 3H, $^3J_{H-H}$ = 6.9 Hz), 1.05 (d, 3H, $^3J_{H-H}$ = 6.5 Hz). The mass spectrum of **5** shows the parent ion at *m/e* 888 with fragment ions corresponding to the loss of the Me12S3 ligand and *x*CO groups from that ion (*x* = 1−5). Anal. Calcd for **5**: C, 28.36; H, 2.70. Found: C, 28.99; H, 2.75.

Preparation of $Re_2(CO)_9$(*c,c,c*-SCH$_2$CHMe(CH$_2$SCH$_2$CHMe)$_2$CH$_2$ (6). A 32.0-mg amount of a mixture of the two $Me_3$12S3 isomers **3** and **4** (0.121 mmol) with a ratio *c,t,t*-Me312S3/*c,c,c*-$Me_3$12S3 of 1/1 (based on ^{1}H NMR integration)

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and 80.0 mg of **1** (0.120 mmol) were dissolved in 10 mL of acetone in a 25-mL three-neck round bottom flask equipped with a stirbar, reflux condenser, and nitrogen inlet. The solution was stirred at reflux for 20 h. The volatiles were removed in vacuo, and the products were separated by TLC using a hexane/methylene chloride (4/1) solvent mixture to yield 9.1 mg of $Re_2(CO)_9$(*c,t,t*-$\overline{SCH_2CHMe(CH_2SCH_2CHMe)_2CH}$) (**5**, 17% yield) and 6.0 mg of $Re_2(CO)_9$(*c,c,c*-$\overline{SCH_2CHMe(CH_2SCH_2CHMe)_2CH_2}$) (**6**; 11% yield). Light yellow crystals of **6** were obtained by crystallization from a solution in hexane by slow evaporation of the solvent at 25 °C. Analytical and spectral data for **6**: IR ν_{CO} (cm^{-1} in hexane) 2103 (w), 2040 (s), 2015 (m), 1993 (vs), 1988 (vs), 1978 (m), 1966 (m), 1953 (w), 1933 (s); ^{1}H NMR (δ in CD_2Cl_2) 3.34 (dd, 2H, J_{H-H}= 13.5 Hz, $^3J_{H-H}$= 4.5 Hz), 2.57 (m, 8H), 2.39 (dd, 2H, $^2J_{H-H}$= 13.5 Hz, $^3J_{H-H}$= 7.0 Hz), 1.96 (m, 2H), 1.78 (m, 1H), 1.12 (d, 6H, $^3J_{H-H}$= 6.6 Hz), 1.02 (d, 3H, $^3J_{H-H}$= 6.7 Hz). The mass spectrum of **6** shows the parent ion at *m/e* 888 with fragment ions corresponding to the loss of the Me12S3 ligand and *x*CO groups from that ion ($x = 1-5$).

Preparation of $W(CO)_5(\overline{SCH_2CHMeCH_2})$ (8). A 40.0-mg amount of $W(CO)_5$(NCMe) (**7**; 0.110 mmol) was dissolved in 20 mL of methylene chloride in a 50-mL three-neck round-bottom flask equipped with a stirbar, reflux condenser, and nitrogen inlet. A 16-μL amount of 3-MT (0.190 mmol) was added, and the resulting solution was stirred at reflux for 2 h. The volatiles were removed in vacuo, and the product was separated by TLC using a hexane/methylene chloride (4/1) solvent mixture to yield 12.0 mg of $W(CO)_5(\overline{SCH_2CHMeCH_2})$ (**8**; 26% yield). Spectral data for **8**: IR ν_{CO} (cm^{-1} in hexane) 2075 (w), 1943 (vs), 1933 (s); ^{1}H NMR (δ in CD_2Cl_2) 3.49 (m, 5H), 1.22 (d, 3H, $^3J_{H-H}$ = 6.0 Hz). The mass spectrum of **8** shows the parent ion at *m/e* 412. The ions at *m/e* 384, 356, 328, 300, and 272 are attributed to the loss of one, two, three, four, and five CO ligands from the parent ion. Additional ions at *m/e* 342, 313, and 286 are attributed to $M^+ - CH_3$ and 2−4CO ligands. The ion at *m/e* 244 is attributed to $M^+ - CH_3$ − 4CO and three CH_2 groups.

Crystallographic Analysis. Colorless crystals of **3** suitable for diffraction analysis were grown by slow evaporation of solvent from a solution in an ethanol/hexane (20/1) solvent mixture at 25 °C. Light yellow crystals of **5** and **6** suitable for diffraction analysis were grown by slow evaporation of solvent from solutions in hexane at 25 °C. 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. 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 2. All data processing was performed either on a Digital Equipment Corp. VAXstation 3520 computer or a Silicon Graphics INDIGO2 workstation by using the TEXSAN motif structure solving program library obtained from the Molecular Structure Corp., The Woodlands, TX. Neutral atom scattering factors were calculated by the standard procedures.[11a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[11b] Lorentz/polarization (Lp) and absorption corrections (empirical based on ψ scans) 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.

Compound **3** crystallized in the monoclinic crystal system.

(11) (a) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1975; Vol. IV, Table 2.2B, pp 99−101. (b) Reference 11a, Table 2.3.1, pp 149−150.

Table 2. Crystallographic Data for Compounds 3, 5, and 6

	3	**5**	**6**
empirical formula	$S_3C_{12}H_{24}$	$Re_2S_3O_9C_{21}H_{24}$	$Re_2S_3O_9C_{21}H_{24}$
fw	264.50	889.01	889.01
cryst syst	monoclinic	triclinic	triclinic
lattice params			
a (Å)	17.310(3)	14.113(5)	11.335(2)
b (Å)	5.352(2)	17.236(5)	12.325(2)
c (Å)	17.394(4)	13.350(7)	11.120(3)
α (deg)	90.0	104.53(3)	99.89(2)
β (deg)	110.97(1)	112.23(3)	99.42(2)
γ (deg)	90.0	76.66(3)	107.64(1)
V (Å^3)	1504.7(6)	2876.3(2)	1419.5(5)
space group	$P2_1/n$, No. 14	$P\bar{1}$, No. 2	$P\bar{1}$, No. 2
Z	4	4	2
ρ_{calc} (g/cm^3)	1.17	2.05	2.08
μ(Mo Kα) (cm^{-1})	4.65	86.74	87.88
temp (°C)	20	20	20
$2\theta_{max}$ (deg)	43.0	40.0	48.0
no. of rflns used ($I > 3\sigma(I)$)	1055	4021	3313
no. of variables	206	631	317
residuals: *R*, R_w[a]	0.045; 0.045	0.028; 0.027	0.033; 0.033
goodness-of-fit indicator	2.32	1.48	1.86
max shift in final cycle	0.00	0.05	0.01
largest peak in final diff map (e/Å^3)	0.50	0.60	1.00
abs cor	DIFAB	empirical	empirical

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

The space group $P2_1/n$ was established from the patterns of systematic absences observed during the collection of intensity data. Compounds **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 of both of the structures. Compound **5** crystallizes with two independent molecules in the asymmetrical unit. All three 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 $Me_3$12S3 ligand 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.

Results

The reactions of **1** and **7** with 3-MT have yielded the compounds $Re_2(CO)_9(\overline{SCH_2CHMeCH_2})$ (**2**) and $W(CO)_5$-$(\overline{SCH_2CHMeCH_2})$ (**8**) in the yields 51% and 26%, respectively. Both compounds appear to be fully analogous to the unsubstituted thietane complexes Re_2-$(CO)_9(\overline{SCH_2CH_2CH_2})$[3] and $W(CO)_5(\overline{SCH_2CH_2CH_2})$[5] that we have prepared previously. The purpose for synthesizing **2** and **8** was to examine their ability to produce catalytic macrocyclization of 3-MT, and indeed this was observed.

In a typical reaction 4.0 mL of 3-MT and a 10.0-mg amount of **2** were heated to the reflux temperature of 3-MT (108 °C) for 24 h. No solvent was added. The

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catalyst appeared to dissolve completely in the 3-MT. After the mixture was cooled, the excess 3-MT was removed in vacuo, and the resulting residue was dissolved completely in methylene chloride and filtered. After removal of the solvent the residues were weighed and analyzed by a combination of ^{1}H and ^{13}C NMR spectra. The residues consisted principally of 3,7,11-trimethyl-1,5,9-trithiacyclododecane ($Me_3$12S3) but also contained some of the larger macrocycles (e.g. $Me_4$16S4). The higher weight products proved to be exceedingly difficult to isolate in their pure forms. The results of our various catalytic tests are given in Table 1. Me_3-12S3 was actually formed as a mixture of two geometrical isomers: *cis*,*trans*,*trans*-$Me_3$12S3 (**3**) and *cis*,*cis*,*cis*-$Me_3$12S3 (**4**), with the former exceeding the latter in a ratio of 60/13 in this particular test (entry 2, Table 1). The relative amounts by weight of compounds **3** and **4** plus a value for the mass of the combined weight of the remaining higher molecular weight macrocycles S_n ($n > 3$) was determined by integration of the appropriate resonances in the ^{13}C NMR spectrum of the mixture. The mixture of **3** and **4** is easily separated from the higher molecular weight products by solvent extraction and filtration using hexane solvent. Much of compound **3** can be separated in a pure form from **4** by crystallization, by cooling concentrated solutions of these extracts. Some additional separation of the remaining mixture of **3** and **4** can be achieved with difficulty by TLC on silica gel using a hexane/methylene chloride (3/1) solvent mixture. 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-MT. As in the case of thietane itself,[3] very little activity was found.

In previous studies we showed that the $W(CO)_5$ fragment also produced the cyclooligomerization of thietane catalytically.[5] Accordingly, we have investigated the tungsten complexes $W(CO)_5$(NCMe) (**7**) and $W(CO)_5(\overline{SCH_2CHMeCH_2})$ (**8**) for their ability to produce methyl-substituted thioether macrocycles from 3-MT. Indeed, **7** and **8** both produce **3** and **4**, but their activity as catalysts is much lower; TOF = 0.24 for **7** versus 1.97 for **2**. The ratio **3**/**4** (26/5) was similar to that produced by **2** (60/13), but the yield of **3** plus **4** relative to the higher weight oligomers (31/69) was much lower than that of **2** (73/27).

To compare with the activity of the rhenium compounds, the manganese compound $Mn_2(CO)_9$(NCMe) (**9**) was prepared and tested with 3-MT. Very little product was formed.

Finally, for completeness a sample of the 3-MT was treated identically with those in the catalytic runs in the absence of catalyst. Indeed, small amounts of 3-MT oligomers containing **3** and **4** in a 55/18 ratio were produced, but the amounts were far less than those obtained in the presence of the catalysts (see Table 1). The results listed in Table 1 were corrected for this noncatalytic "background" oligomerization of 3-MT.

Compound **3** was characterized by a single-crystal X-ray diffraction analysis, and an ORTEP diagram of its molecular structure is shown in Figure 1. The conformation of the 12-membered ring of **3** is virtually identical with that of the unsubstituted molecule 1,5,9-trithiacyclododecane (12S3).[12] The ring has adopted a squarelike shape, in which one of the sulfur atoms S(1) occupies a corner site. The C−S distances in **3** (1.799(6)−1.821(7) Å) are not significantly different from those in 12S3. Unlike 12S3, **3** contains three methyl groups. One is located at the site of the corner carbon C(5), and the other two occupy edge sites of the square on the carbons C(2) and C(8). All three methyl groups are directed to the outside of the ring. If one were to transform the molecule to a planar form that would have the substituents on all of the carbon atoms in an eclipsed arrangement, two of the methyl groups would lie on one side of the ring and one would lie on the other side. For this reason we describe the geometric conformation of the molecule as *cis*,*trans*,*trans*. The ^{1}H NMR spectrum of **3** exhibits two methyl resonances in the form of two doublets at δ 1.08 (3H, $^3J_{H-H}$ = 6.6 Hz) and 1.04 (6H, $^3J_{H-H}$ = 6.7 Hz) ppm at 25 °C. This would be consistent with the structure found in the solid state, provided that the molecule is rapidly averaging its conformations on the NMR time scale. The ^{13}C NMR spectrum for **3** exhibits seven resonances (δ 38.26 (2C), 36.36 (2C), 34.40 (2C), 31.69 (2C), 30.01 (1C), 20.04 (2C, Me), and 19.62 (1C, Me) ppm); which is also consistent with a dynamically rearranging form of the molecule in solution.

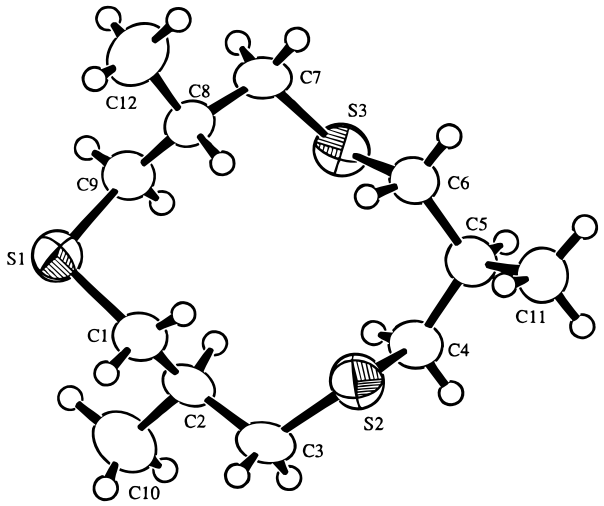

Figure 1. ORTEP diagram of *c*,*t*,*t*-$\overline{SCH_2CHMe(CH_2SCH_2CHMe)_2CH_2}$ (**3**) showing 50% probability thermal ellipsoids. Selected bond distances (Å) and angles (deg) are as follows: S(1)−C(1) = 1.808(7), S(1)−C(9) = 1.818(7), S(2)−C(3) = 1.799(6), S(2)−C(4) = 1.816(6), S(3)−C(6) = 1.821(7), S(3)−C(7) = 1.805(6); C(1)−S(1)−C(9) = 101.1(3), C(3)−S(2)−C(4) = 100.2(3), C(6)−S(3)−C(7) = 100.0(3).

It was not possible to obtain single crystals of **4**, but its ^{1}H NMR spectrum (δ 2.65 (dd, 6H, $^2J_{H-H}$ = 13.3 Hz, $^3J_{H-H}$ = 6.7 Hz), 2.54 (dd, 6H, $^2J_{H-H}$= 13.3 Hz, $^3J_{H-H}$ = 6.1 Hz), 1.97 (m, 3H, $^3J_{H-H}$ = 6.1 Hz, $^3J_{H-H}$ = 6.7 Hz, $^3J_{H-H}$ = 6.8 Hz), 1.06 (9H, $^3J_{H-H}$ = 6.8 Hz) ppm) shows only one methyl resonance, which is consistent with the geometrical form in which all the methyl groups lie on the same side of the ring (i.e. the *cis*,*cis*,*cis* structure). This is further supported by its simple ^{13}C NMR spectrum (δ = 39.57 (6C), 35.99 (3C), 19.85 (3C, Me) ppm), which shows only two ring carbon resonances and

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

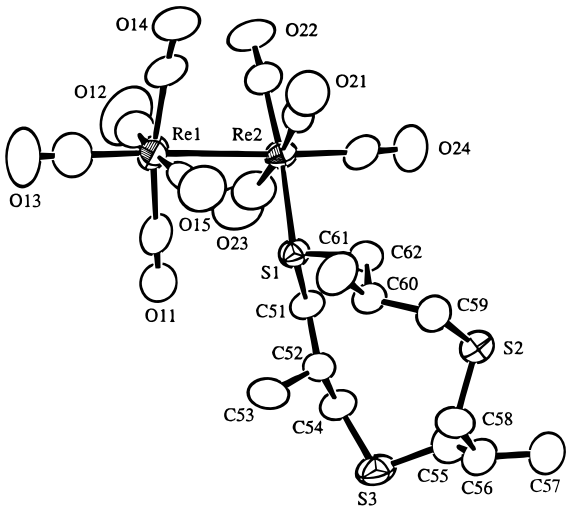

Figure 2. ORTEP diagram of $Re_2(CO)_9$(*c,t,t*-SCH$_2$CHMe-(CH$_2$SCH$_2$CHMe)$_2$CH$_2$) (**5**) showing 50% probability thermal ellipsoids. Selected bond distances (Å) and angles (deg) are as follows: Re(1)−Re(2) = 3.069(2), Re(3)−Re(4) = 3.077(1), Re(2)−S(1) = 2.506(3), Re(4)−S(4) = 2.510(3), S(1)−C(51) = 1.81(1), S(1)−C(62) = 1.83(1), S(2)−C(54) = 1.80(1), S(2)−C(55) = 1.79(1), S(3)−C(58) = 1.81(1), S(3)−C(59) = 1.805(6), S(4)−C(63) = 1.85(1), S(4)−C(74) = 1.83(1), S(5)−C(66) = 1.79(1), S(5)−C(67) = 1.81(1), S(6)−C(70) = 1.81(1), S(6)−C(71) = 1.77(1); C(51)−S(1)−C(62) = 98.7(5), C(54)−S(2)−C(55) = 102.0(5), C(58)−S(3)−C(59) = 100.1(6), C(63)−S(4)−C(74) = 98.6(6), C(66)−S(5)−C(67) = 99.7(7), C(70)−S(6)−C(71) = 101.0(5).

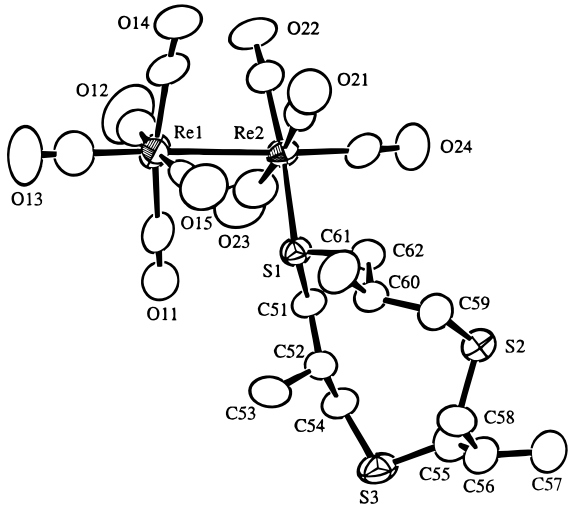

Figure 3. ORTEP diagram of $Re_2(CO)_9$(c,c,c-SCH$_2$CHMe-(CH$_2$SCH$_2$CHMe)$_2$CH$_2$) (**6**) showing 50% probability thermal ellipsoids. Selected bond distances (Å) and angles (deg) are as follows: Re(1)−Re(2) = 3.0598(6), Re(2)−S(1) = 2.518(2), S(1)−C(51) = 1.843(8), S(1)−C(62) = 1.829(9), S(2)−C(58) = 1.81(1), S(2)−C(59) = 1.80(1), S(3)−C(54) = 1.80(1), S(3)−C(55) = 1.81(1); C(51)−S(1)−C(62) = 99.6(4), C(58)−S(2)−C(59) = 103.1(5), C(54)−S(3)−C(55) = 100.6(5).

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one methyl resonance. Compound **4** was further characterized in the form of its mono-$Re_2(CO)_9$ adduct, **6**, which was structurally characterized by a single-crystal X-ray diffraction analysis (see below). The mass spectra of **3** and **4** both show the parent ion and ions corresponding to the elimination of C_4H_8 and complete 3-MT groupings.

Compound **5** is an $Re_2(CO)_9$ adduct of macrocycle **3**. Compound **5** was characterized by a single-crystal X-ray diffraction analysis. The compound crystallizes with two symmetry-independent molecules in the asymmetric crystal unit. Both molecules are structurally similar, and an ORTEP diagram of the molecular structure of one of them is shown in Figure 2. The conformation of the 12-membered ring of the macrocycle is virtually identical with that of the free molecule **3** (see above).[13] The ligand is coordinated to one of the rhenium atoms through one of the two sulfur atoms that lie along the edges of the "square" ring conformation of the ligand: Re(2)−S(1) = 2.506(3) Å [Re(4)−S(4) = 2.510(3) Å]. This is in contrast with that observed for the $Re_2(CO)_9$ adduct of unsubstituted 12S3, $Re_2(CO)_9$-(12S3) (**10**), which we characterized previously.[3] In **10** the rhenium atom was coordinated to the corner sulfur atom (Re−S = 2.498(3) Å). In the bis-$Re_2(CO)_9$ adduct of 12S3, $[Re_2(CO)_9]_2$(12S3) (**11**), one $Re_2(CO)_9$ group is coordinated to the corner sulfur and one is coordinated to one of the edge sulfur atoms of the 12S3 ring.[3] The

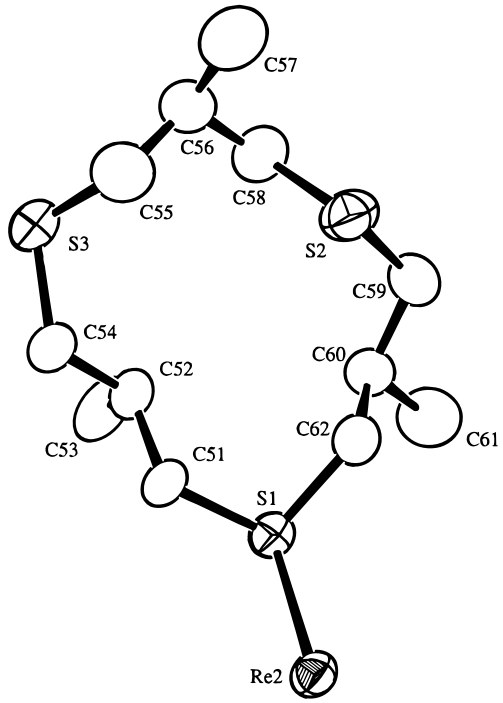


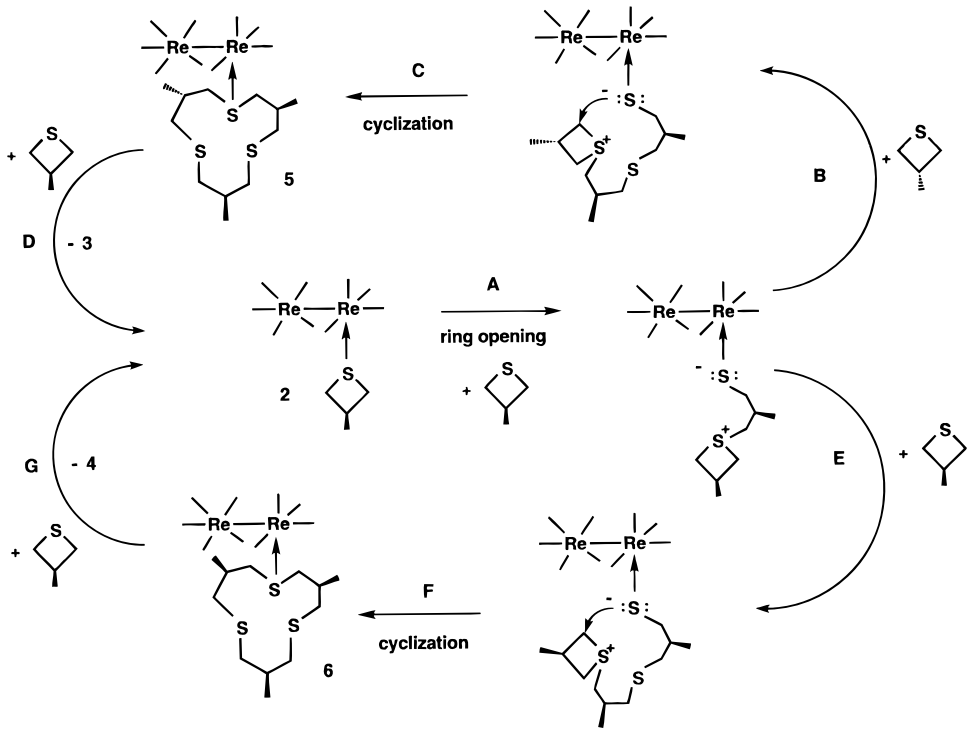
Figure 4. Structural diagram of $Re_2(CO)_9$(c,c,c-SCH$_2$-CHMe(CH$_2$SCH$_2$CHMe)$_2$CH$_2$) (**6**) minus the carbonyl ligands and one of the rhenium atoms.

Re−Re bond distance in **5** (Re(1)−Re(2) = 3.069(2) Å [Re(3)−Re(4) = 3.077(1) Å) is slightly longer than those found in **10** (3.0554(8) Å) and **11** (3.049(1) Å and 3.052(1) Å.

The ^{1}H NMR spectrum of **5** shows three methyl resonances (δ 1.17 (d, 3H, $^3J_{H-H}$ = 6.6 Hz), 1.13 (d, 3H, $^3J_{H-H}$ = 6.9 Hz), 1.05 (d, 3H, $^3J_{H-H}$ = 6.5 Hz)), which is consistent with the solid-state structure. The rhenium atom is coordinated to one of the sulfur atoms lying

(13) (a) Adams, R. D. *J. Cluster Sci.* **1992**, *3*, 263. (b) Adams, R. D.; Pompeo, M. P. *Organometallics* **1992**, *11*, 1460. (c) Adams, R. D.; Belinski, J. A.; Pompeo, M. P. *Organometallics* **1991**, *10*, 2539. (d) Adams, R. D.; Belinski, J. A.; Pompeo, M. P. *Organometallics* **1992**, *11*, 3129. (e) Adams, R. D.; Pompeo, M. P. *J. Am. Chem. Soc.* **1991**, *113*, 1619. (f) Adams, R. D.; Cortopassi, J. E.; Falloon, S. B. *Organometallics* **1992**, *11*, 3794.

Scheme 1



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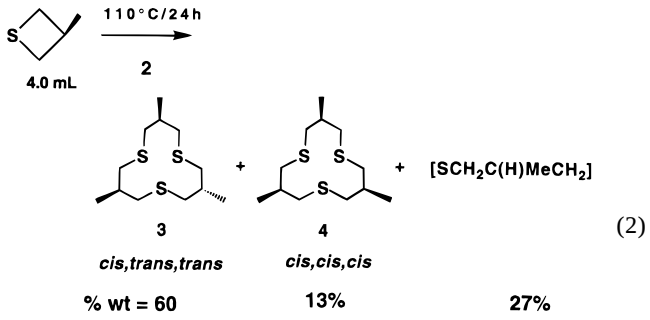
between a *trans* pair of methyl groups, and no matter how dynamic the conformation of the ligand is, the methyl groups cannot be averaged without a cleavage of the Re−S bond.

An ORTEP diagram of the molecular structure of compound **6** is shown in Figure 3. Compound **6** is an $Re_2(CO)_9$ adduct of macrocycle **4**. In this structure we have found for the first time a conformation of the 12-membered ring that does not exhibit the "squared" ring conformation that is found in unsubstituted 12S3[12] and the free molecule **3** described above. The squared ring of 12S3 and **3** is characterized by a *trans* torsion angle at every fourth bond in the ring (the center bond along each edge). All the other bonds possess *gauche* torsion angles. In particular, there is a pair of adjacent C−C bonds, C(51)−C(52) and C(52)−C(54), that both possess *trans* torsion angles (S(1)−C(51)−C(52)−C(54) = 171.7° and S(3)−C(54)−C(52)−C(51) = 160.5°) and the bond S(3)−C(55) has a torsion angle C(54)−S(3)−C(55)−C(56) of 128.5°, which is closer to an "eclipsed" conformation (120°) than a staggered one (60 or 180°); Figure 4 shows a projection of the macrocycle and only the rhenium atom of the $Re_2(CO)_9$ group. One can see that by transforming the ligand to being planar, all of the methyl groups would lie on one side of the ring. Thus, we have defined this ligand as the *cis*,*cis*,*cis* geometric isomer of $Me_3$12S3. The macrocycle is coordinated to the $Re_2(CO)_9$ group through the sulfur atom S(1), (Re(2)−S(1) = 2.518(2) Å). The Re−Re bond distance (Re(1)−Re(2) = 3.0598(6) Å), is similar to those found in **5**, **9**, and **11**. Due to time averaging the ^{1}H NMR spectrum shows only two methyl resonances (δ 1.12 (6H, $^3J_{H-H}$ = 6.6 Hz) and 1.02 (3H, $^3J_{H-H}$ = 6.7 Hz)).

Discussion

The complexes **1** and **2** are both effective catalysts for the macrocyclization of 3-MT to $Me_3$12S3, which is formed as a mixture of the two isomers **3** and **4** (see eq 2).



(2)

It is notable that $Re_2(CO)_{10}$ is not a good catalyst. We believe this indicates that the 3-MT ligand must be coordinated to the $Re_2(CO)_9$ fragment in the course of the macrocyclization process. The mechanism that we propose here is a slight modification of the mechanism that we proposed for the macrocyclization of thietane by $Re_2(CO)_9$ groups[3] and is shown in Scheme 1 for compound **2**. The first step is proposed to be a ring-opening addition of the sulfur atom of an uncoordinated 3-MT molecule to one of the methylene groups of a 3-MT ligand (step **A**). Similar nucleophilic ring-opening reactions have been observed for thietane ligands in bridging coordination modes.[12] The activation mechanism is simply the withdrawal of electron density from the sulfur atom and in turn from the carbon atoms of the 3-MT ligand by the rhenium atom. In Scheme 1 the methyl groups of the two 3-MT molecules are shown oriented in the same direction, but this is not required. This ring-opening addition leads to an intermediate containing a zwitterionic thietanium−thiolato ligand. The uncoordinated four-membered thietanium ring should be sufficiently reactive to add an additional molecule of 3-MT by a similar ring-opening mechanism. The ring-opening polymerization of thietanes via thi-

etanium intermediates is well-known.[14] Two steps are shown, **B** and **E**, which differ only in the orientation of the methyl substituent on the molecule being added (i.e. *anti* for step **B** and *syn* for step **E**). The ligand on the resultant intermediates is a thietanium−thiolate with a thioether link between the two ends. The next step of the reaction is cyclization, which occurs by a ring-opening addition of the thiolato sulfur atom to one of the methylene groups of the thietanium ring (step **C** or step **F**). In the former case the *cis*,*trans*,*trans* macrocycle **3** is formed, while in the latter case the *cis*,*cis*,*cis* isomer **4** is formed. Note that there are other similar routes to the *cis*,*trans*,*trans* isomer **3** which are not shown. On a purely statistical basis the relative ratio **3**/**4** should be 3/1. The results show that this is nearly 5/1 for catalysis by **1**, **2**, **7**, and **8**. This suggests that there may be some long-range steric interactions that lie in favor of the coupling of the thietanes when the methyl groups have *anti* orientations (e.g. steps **B** and **C**). The final step in the catalytic cycle is the simple displacement of the macrocycle by 1 equiv of 3-MT to regenerate **2**.

The results show that the dirhenium catalysts have a much higher preference for formation of the cyclotrimers **3** and **4** than the tungsten catalysts. A similar result was observed for the catalytic macrocyclization of the thietane by these complexes. This would seem to indicate that the cyclization step occurs more readily with rhenium than with tungsten when three thietanes have coupled. We can only speculate about possible reasons for this at this time, but perhaps the presence of the bulky pendant $Re(CO)_5$ grouping in the rhenium case keeps the local concentration of thietane lower in this case, thus leading to a greater chance for cyclization versus continued chain growth.

It was found that the manganese complex **9** is an ineffective catalyst, even though it presumably contained an accessible coordination site in the form of the labile NCMe. In previous studies we have shown that the $Cr(CO)_5$ grouping is a much less effective catalyst than the $W(CO)_5$ grouping and the $H_4Ru_4(CO)_{11}$ grouping is a much less effective catalyst than the $H_4Os_4(CO)_{11}$ grouping for the macrocyclization of thietane. Thus, the present results further indicate that complexes of the third-row transition metals are the most effective catalysts for these reactions. Perhaps, the stronger metal−sulfur bonds involving the third-row metals provide greater activation for the ring-opening step (step **A**).

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 atomic positional parameters, bond distances, bond angles, and anisotropic thermal parameters for all three structural analyses (21 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(14) (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.

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