Catalytic Ring Opening of β-Propiothiolactones by Dirhenium and Dimanganese Carbonyl Complexes

Richard D. Adams,* Mingsheng Huang, and Wen Huang

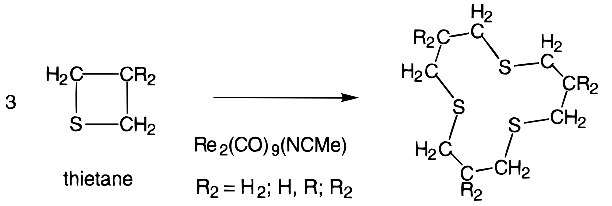
Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208

Received June 23, 1997[⊗]

The catalytic ring opening of β-propiothiolactone, **1**, and 3,3-dimethyl-β-propiothiolactone, **2**, by $Re_2(CO)_9(NCMe)$, $Mn_2(CO)_9(NCMe)$, and $Mn_2(CO)_{10}$ has been investigated. Compound **1** was transformed into polymer $(SCH_2CH_2C{=}O)_n$ (55% yield) and a mixture of new macrocycles $(\overline{SCH_2CH_2C}{=}O)_n$. The major macrocyclic product 1,5,9,13-tetrathiacyclohexadecane-2,6,10,14-tetrone (**3**, $(\overline{SCH_2CH_2C}{=}O)_4$) was isolated in 22% yield. A second macrocycle identified as 1,5,9,13,17,21-hexathiacyclotetracosane-2,6,10,14,18,22-hexone (**4**, $(\overline{SCH_2CH_2C}{=}O)_6$) was isolated in only 2% yield. Compound **2** was converted into polymer $(SCH_2CMe_2C{=}O)_n$ only; however, when applied to silica gel TLC plates, small quantities of macrocycles 3,3,7,711,11,15,15-octamethyl-1,5,9,13-tetrathiacyclohexadecane-2,6,10,14-tetrone, **5**, and 3,3,7,711,11,15,15,19,19,23,23-dodecamethyl-1,5,9,13,17,21-hexathiacyclotetracosane-2,6,10,14,18,22-hexone, **6**, were eluted. Macrocycles **3**−**6** have been characterized crystallographically. The structure of **3** is unusual for a sulfur macrocycle because the sulfur atoms are turned toward the inside of the ring to form a tetrahedral cavity. Compound **4** forms a large 6-sided 24-membered ring and crystallizes from CH_2Cl_2 as an inclusion compound containing 1 equiv of CH_2Cl_2 in the center of the ring. Compounds **5** and **6** are similar to **3** and **4**, but both have lower symmetry due to transannular elongation. The catalytic reactions are promoted by light and inhibited by the radical scavenger TEMPO. It is concluded that these reactions involve radical intermediates formed by photolytic cleavage of the metal−metal bond of the dinuclear catalyst precursors.

Introduction

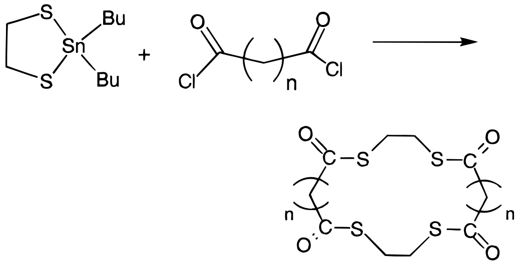
In recent studies we have shown that $Re_2(CO)_9(NCMe)$ can serve as a catalyst for the macrocyclization of the strained ring heterocycles thietanes[1] and selenatanes,[2] e.g., eq 1.[2] Trithia and triselena macrocycles are



(1)

the principal macrocyclic products. These macrocycles have been shown to be effective polydentate ligands for certain transition metals.[3,4]

Polythiolactone macrocycles are a much less studied family of compounds. A number of such macrocycles have been prepared recently by reactions of tin thiolates with acyclic diacyl halides. These compounds are distinguished by the head-to-head and tail-to-tail orientations of the thiolactone groupings (e.g. **A**, eq 2).[5]



(2)

A

We have found that the strained thiolactones β-propiothiolactone, $(\overline{SCH_2CH_2C}{=}O$; **1**) and its 3,3-dimethyl derivative (**2**) can be opened catalytically by certain

---

[⊗] Abstract published in *Advance ACS Abstracts,* September 15, 1997.

(1) (a) Adams, R. D.; Falloon, S. B. *Chem. Rev.* **1995**, *95*, 2587. (b) Adams, R. D.; Falloon, S. B. *J. Am. Chem. Soc.* **1994**, *116*, 10540. (c) Adams, R. D.; Cortopassi, J. E.; Falloon, S. B. *Organometallics* **1995**, *14*, 1748. (d) Adams, R. D.; Falloon, S. B. *Organometallics* **1995**, *14*, 4594. (e) Adams, R. D.; Falloon, S. B.; Perrin, J.; Queisser, J. A.; Yamamoto, J. H. *Chem. Ber.* **1996**, *126*, 313. (f) Adams, R. D.; Queisser, J. A.; Yamamoto, J. H. *Organometallics* **1996**, *15*, 2489. (g) Adams, R. D.; Falloon, S. B.; Perrin, J.; Queisser, J. A.; Wolfe, J. B. *Organometallics* **1997**, *16*, 2612.

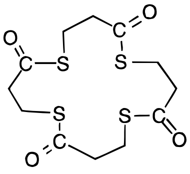
(2) Adams, R. D.; McBride, K. T. *Chem. Commun.* **1997**, 525.

(3) (a) Cooper, S. R. In *Crown Compounds: Toward Future Applications*; Cooper, S. R., Ed.; VCH Publishers: 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.

(4) (a) Batchelor, R. J.; Einstein, F. W. B.; Gay, I. D.; Gu, J.-H.; Pinto, B. M.; Zhou, X.-M. *J. Am. Chem. Soc.* **1990**, *112*, 3706. (b) Batchelor, R. J.; Einstein, F. W. B.; Gay, I. D.; Gu, J.-H.; Pinto, B. M. *J. Organomet. Chem.* **1991**, *411*, 147. (c) Levason, W.; Quirk, J. J.; Reid, G. *J. Chem. Soc., Dalton Trans.* **1996**, 3713. (d) Levason, W.; Quirk, J. J.; Reid, G. *Inorg. Chem.* **1994**, *33*, 6120. (e) Kelly, P. F.; Levason, W.; Reid, G.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1991**, 1716. (f) Adams, R. D.; McBride, K. T.; Rogers, R. D. *Organometallics* **1997**, *16*, 3895.

S0276-7333(97)00524-4 CCC: $14.00

dirhenium and dimanganese carbonyl complexes under mild conditions in the presence of light. Polymers are the principal products. However, macrocycles having head-to-tail orientations of the thiolactone groups (e.g., **B**) are obtained from the reaction solutions. Two macrocycles, a tetramer and a hexamer, formed from **1** and two from **2** have been isolated and structurally characterized. A preliminary report on this work has been published.[6]



B

Experimental Section

General Data. Unless specified otherwise, all reactions were carried out under an atmosphere of nitrogen. All solvents were appropriately dried prior to use. Infrared spectra were recorded on a Nicolet 5DXB FTIR spectrophotometer. $Re_2(CO)_9(NCMe)$,[7] $Mn_2(CO)_9(NCMe)$,[7] β-propiothiolactone[8] ($SCH_2CH_2C{=}O$, **1**), and α,α-dimethyl-β-propiothiolactone[9] ($SCH_2CMe_2C{=}O$, **2**) were prepared according to published procedures. TEMPO (2,2,6,6-tetramethylpiperdinyloxy radical) was purchased from Aldrich and used as received. Lighting was provided from the two fluorescent lamps in the hood lighting system. Reactions were performed in the dark by wrapping the entire reaction vessel with aluminum foil and introducing the solvents and liquid reagents into the flask by syringe through the foil and a rubber stopper. Reaction vessels were made of Pyrex. Precipitated products were separated by filtration. Soluble products were separated by TLC in air on Analtech 0.25 and 0.50 mm silica gel 60 Å F_{254} plates. Elemental analyses were performed by Oneida Research Services, Whitesboro, NY.

Catalytic Ring Opening of 1 with $Re_2(CO)_9(NCMe)$ and Other Catalysts. A 10 mg amount (0.015 mmol) of $Re_2(CO)_9(NCMe)$ was placed in a 50 mL three-necked round-bottomed flask equipped with a stir bar, reflux condenser, and nitrogen inlet. Next, 0.64 mL of freshly distilled **1** (9.45 mmol) and 30 mL of methylene chloride were added. The resulting solution was stirred at 25 °C for 20 h. During this period, a white precipitate, 457 mg, formed and was separated by filtration. The solvent was removed from the filtrate to yield 348/mg of a residue. The major product was identified as 1,5,9,13-tetrathiacyclohexadecane-2,6,10,14-tetrone, **3** (63% of residue by NMR integration). One minor product was identified as 1,5,9,13,17,21-hexathiacyclotetracosane-2,6,10,14,18,22-hexone, **4** (5% of residue). Compounds **3** and **4** were isolated by TLC on silica gel using a hexane/methylene chloride 1/1 solvent mixture to yield 186.3 mg (0.530 mmol) of **3** (22% yield) and 17.4 mg (0.034 mmol) of **4** (2% yield). Spectral data for **3**: ^1H NMR (δ in $CDCl_3$) 3.14 (t, 8H, $^3J_{H-H}$ = 5.8 Hz), 2.87 (t, 8H, $^3J_{H-H}$ = 5.8 Hz); ^{13}C NMR (δ in $CDCl_3$) 198.72 (4C), 42.81 (4C), 25.76 (4C). Anal. Calcd (found): C, 40.89 (38.84); H, 4.57 (4.33). Spectral data for **4**: ^1H NMR (δ in $CDCl_3$) 3.17 (t, 12H, $^3J_{H-H}$ = 6.2 Hz), 2.84 (t, 12H, $^3J_{H-H}$ = 6.2 Hz); ^{13}C NMR (δ in $CDCl_3$) 197.21 (6C), 43.49 (6C), 25.05 (6C). Anal. Calcd (found) for $\mathbf{4}\cdot CH_2Cl_2$: C, 37.18 (37.02); H, 4.27 (3.97). The mass spectra for **3** and **4** show the parent ions at 352 and 528 *m/e*, respectively. Additional ions corresponding to loss of units of the monomer **1** were observed at *m/e* = 440, 352, 264, 176, and 88. The insoluble residue was investigated by solid-state NMR spectroscopy. Data were collected on a Varian Unity Plus console equipped with a 11.2 T Oxford magnet operating at a Larmour frequency of 125.6 MHz for ^{13}C. The spectrum showed three broad peaks at 199, 47, and 25 ppm, respectively, corresponding to the ketonic carbon atom, the sulfur bound methylene group, and the ketone bound methylene group. Anal. Calcd (found) for the insoluble residue: C, 40.89 (40.41); H, 4.57 (4.62); S, 36.36 (36.43). All of these data are consistent with $(SCH_2CH_2C{=}O)_n$.

Table 1. Results of the Catalytic Transformations of Compound 1

catalyst[a]	compound 3 (mg)	polymer (mg)
$Re_2(CO)_9(NCMe)$[b] + light[c]	51	111
$Re_2(CO)_{10}$ + light	0	0
$Mn_2(CO)_9(NCMe)$ + light	35	161
$Mn_2(CO)_{10}$ + light[d]	50	91
$Mn_2(CO)_{10}$ + light + CO	49	90
$Mn_2(CO)_{10}$ no light	0	0
$Mn_2(CO)_{10}$ + light + TEMPO[e]	12	12
$Re_2(CO)_9(NCMe)$ no light	26	61
$Mn_2(CO)_9(NCMe)$ no light	23	114
$Mn_2(CO)_{10}$ + light + TEMPO	12	12
TEMPO[c] + light	0	0
$Re_2(CO)_9(NCMe)$ + light + TEMPO	10	42
$Re_2(CO)_9(NCMe)$ + no light + TEMPO	12	43
$W(CO)_5(NCMe)$ + light	0	0

[a] All reactions were performed at 25 °C using 10 mg of catalyst and 0.20 mL of thiolactone in 15 mL of CH_2Cl_2 solvent for 24 h. [b] An 8.7 mg amount of $Re_2(CO)_9(NCMe)$ and 0.7 mg of $Re_2(CO)_{10}$ were recovered after the reaction. [c] Light = ordinary fluorescent light from the hood system. [d] A 5.3 mg amount of $Mn_2(CO)_{10}$ and 0.5 mg of $Mn(CO)_5Cl$ were recovered after the reaction. [e] TEMPO = 2,2,6,6-tetramethylpiperdinyloxy radical.

A series of similar experiments was conducted using 0.20 mL of **1** in 15 mL of CH_2Cl_2 solvent with 10 mg of one of the following catalysts: $Re_2(CO)_{10}$, $Mn_2(CO)_9(NCMe)$, $Mn_2(CO)_{10}$, or $W(CO)_5(NCMe)$. Some experiments were done in the presence of room light. Some were done in the absence of room light. The experiments in the absence of room light were performed by wrapping the entire reaction apparatus in aluminum foil and injecting the solvent and thiolactone into the flask through a rubber septum via syringe. Some experiments were performed under a CO atmosphere, others were performed in the presence of the radical scavenger TEMPO. These results are listed in Table 1.

Catalytic Ring Opening of 2 by $Re_2(CO)_9(NCMe)$. A 10 mg amount (0.015 mmol) of $Re_2(CO)_9(NCMe)$ was placed in a 50 mL three-necked round-bottomed flask equipped with a stir bar, reflux condenser, and nitrogen inlet. Next, 0.20 mL of freshly distilled **2** (1.79 mmol) and 30 mL of methylene chloride were added, and the solution was stirred at 25 °C for 20 h. The solvent was removed by vacuum distillation to yield 192 mg of a clear, pale yellow, rubbery residue. The ^{13}C NMR spectrum of this material in $CDCl_3$ showed resonances at δ = 204.0 ($C{=}O$), 50.56 (CH_2), 37.33 (C), and 24.70 (CH_3). This material seems to consist almost exclusively of polymers of $(SCH_2CMe_2C{=}O)_n$, 92% yield. However, when this polymer was applied to TLC plates and eluted using a hexane/methylene chloride 1/1 solvent mixture, two small bands were separated to yield, in order of elution, 5.0 mg (0.0108 mmol)

---

(5) (a) Dalla Cort, A.; Ercolani, G.; Iamiceli, A. L.; Mandolini, L.; Mencarelli, P. *J. Am. Chem. Soc.* **1994**, *116*, 7081. (b) Dalla Cort, A.; Ercolani, G.; Mandolini, L.; Mencarelli, P. *J. Chem. Soc., Chem. Commun.* **1993**, 538. (c) Dalla Cort, A.; Ercolani, G.; Iamiceli, A. L.; Mandolini, L.; Mencarelli, P. *J. Org. Chem.* **1992**, *57*, 766. (d) Tor, Y.; Libman, J.; Frolow, F.; Gottlieb, H. E.; Lazar, R.; Shanzer, A. *J. Org. Chem.* **1985**, *50*, 5476. (e) Shanzer, A.; Libman, J. *Synthesis* **1984**, 140.

(6) Adams, R. D.; Huang, M.; Huang, W.; Queisser, J. A. *J. Am. Chem. Soc.* **1996**, *118*, 9442.

(7) Koelle, U. *J. Organomet. Chem.* **1978**, *155*, 53.

(8) Knunyants, I. L.; Kuleshova, N. D.; Lin'kova, M. G. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1965**, 1081.

(9) Lin'kiova, M. G.; Patrina, N. D.; Knunyants, I. L. *Dokl. Akad. Nauk. SSSR, Ser. Khim.* **1959**, *127*, 564; *Chem. Abstr.* **1961**, *54*, 285.

Table 2. Crystal Data for Compounds 3, 4, 5, and 6

	3	4	5	6
formula	$S_4O_4C_{12}H_{16}$	$S_6O_6C_{18}H_{24}{\cdot}CH_2Cl_2$	$S_4O_4C_{20}H_{32}$	$S_6O_6C_{30}H_{48}$
form wt	352.50	613.68	464.71	665.07
cryst syst	monoclinic	trigonal	triclinic	monoclinic
lattice params				
a (Å)	12.932(3)	12.780(2)	13.836(3)	28.429(5)
b (Å)	8.603(2)	12.780(2)	14.232(3)	6.226(2)
c (Å)	15.075(3)	14.792(2)	6.234(2)	24.105(4)
α (deg)	90.00	90.00	95.29(3)	90.00
β (deg)	99.33(2)	90.00	94.57(2)	120.55(1)
γ (deg)	90.00	120.00	94.67(2)	90.00
V (Å^3)	1654.9(5)	2092.2(5)	1213.6(5)	3674(1)
space group	$P2_1/n$ (no. 14)	$R\bar{3}(h)$ (No. 148)	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)
Z value	4	3	2	4
ρ_{calc} (g/cm^3)	1.42	1.46	1.27	1.20
μ(Mo Kα) (cm^{-1})	5.81	7.13	4.13	4.02
no. of obs ($I > 3\sigma(I)$	1378	591	1529	1467
no. of variables	230	73	253	262
goodness of fit (GOF)^a	1.91	3.21	2.90	2.39
max shift in final cycle	0.02	0.00	0.01	0.05
Residuals:^{a} R; R_w	0.046; 0.040	0.055; 0.061	0.066; 0.064	0.047; 0.045
abs corr	none	Difabs	Difabs	none
transmission coeff, max/min		1.00/0.44	1.00/0.69	
largest pk in final diff map (e$^-$/Å^3)	0.57	0.32	0.70	0.48

^{a} $R = \sum_{hkl}(||F_{obs}| - |F_{calc}||)/\sum_{hkl}|F_{obs}|$; $R_w = [\sum_{hkl}w(|F_{obs}| - |F_{calc}|)^2/\sum_{hkl}wF_{obs}{}^2]^{1/2}$, $w = 1/\sigma^2(F_{obs})$; GOF $= [\sum_{hkl}w(|F_{obs}| - |F_{calc}|)^2]/(n_{data} - n_{var})]^{1/2}$.

of 3,3,7,711,11,15,15-octamethyl-1,5,9,13-tetrathiacyclohexadecane-2,6,10,14-tetrone, **5** (2% yield), and 9.6 mg (0.0138 mmol) of 3,3,7,711,11,15,15,19,19,23,23-dodecamethyl-1,5,9,13,17,21-hexathiacyclotetracosane-2,6,10,14,18,22-hexone, **6** (5% yield). Spectral data for **5**: ^{1}H NMR (δ in CDCl$_3$) 3.10 (s, 8H), 1.29 (s, 24H); ^{13}C NMR (δ in CDCl$_3$) 204.77 (4 C=O), 51.02 (4 C), 37.82 (4 C), 25.37 (8 C). Anal. Calcd (found): C, 51.69 (52.67); H, 6.94 (6.96). Spectral data for **6**: ^{1}H NMR (δ in CDCl$_3$) 3.16 (s, 12H), 1.26 (s, 36H); ^{13}C NMR (δ in CDCl$_3$) 204.00 (6 C=O), 50.67 (6 C), 37.49 (6 C), 24.91 (12 C). Anal. Calcd (found): C, 51.69 (51.78); H, 6.94 (6.97).

Crystallographic Analyses. Colorless crystals of each of the compounds **3**−**6** suitable for diffraction analysis were grown by slow evaporation of the solvent from solutions in hexane/methylene chloride solvent mixtures at 25 °C in the open air. 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 were determined and refined from 15 randomly selected reflections obtained by using the AFC6 automatic search, center, index, and least-squares routines. All intensity data were collected at 20 °C. Crystal data, data collection parameters, and results of the analyses are listed in Table 2. All data processing was performed on a Silicon-Graphics INDIGO^2 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.[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 $\sigma(F_o{}^2) = [\sigma(I_{raw})^2 + (0.02\, I_{net})^2]^{1/2}/Lp$.

Compound **3** crystallized in the monoclinic crystal system in the space group $P2_1/n$. Compound **4** crystallized in the trigonal crystal system. The space group $R\bar{3}$ was assumed and confirmed by the successful solution and refinement of the structure. Both 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 were located and refined in both analyses, in **3** by using fixed isotropic thermal parameters and in **4** by using variable isotropic thermal parameters. In the analysis of **4**, 1 equiv of CH$_2$Cl$_2$ cocrystallized from the crystallization solvent was found in the lattice in the center of the ring of the macrocycle. This CH$_2$Cl$_2$ molecule exhibits a $\bar{3}$ disorder. It was satisfactorily refined with isotropic thermal parameters for each of the non-hydrogen atoms.

Compound **5** crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure. 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 positions of the hydrogen atoms on the macrocycle were calculated by assuming idealized 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.

Compound **6** crystallized in the monoclinic crystal system. The pattern of the systematic absences observed during the collection of intensity data was consistent with either of the space groups $C2/c$ or Cc. The structure was solved by direct methods and successfully refined in the higher symmetry centrosymmetric space group $C2/c$. All non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of the hydrogen atoms on the macrocycle were calculated by assuming idealized 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, and their positional parameters were refined employing fixed isotropic thermal parameters.

Results

Syntheses and Structural Analyses. When a solution of Re$_2$(CO)$_9$(NCMe) and **1** in CH$_2$Cl$_2$ solvent was stirred in the presence of room light for 20 h, compound **1** was transformed into a mixture of the polythioester (SCH$_2$CH$_2$C=O)$_n$ (55% yield) and cyclooligomers of **1**. Two of the cyclooligomers, 1,5,9,13-tetrathiacyclohexadecane-2,6,10,14-tetrone, **3**, $n = 4$

---

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

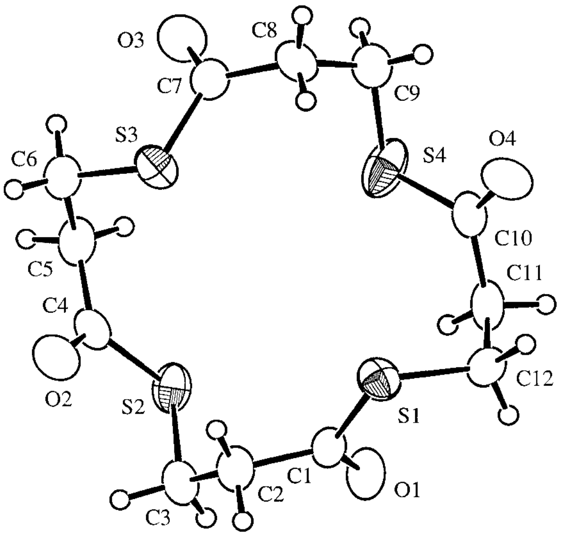


Figure 1. ORTEP diagram of 1,5,9,13-tetrathiacyclohexadecane-2,6,10,14-tetrone, **3**, showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) are S(1)−C(1) = 1.770(6), S(2)−C(4) = 1.761(6), S(3)−C(7) = 1.762(6), S(4)−C(10) = 1.742(6), S(1)···S(2) = 4.457(2), S(1)···S(3) = 4.797(2), S(1)···S(4) = 4.071(3), S(2)···S(3) = 4.293(2), S(2)···S(4) = 4.805(2), S(3)···S(4) = 3.949(2).

(22% isolated yield), and 1,5,9,13,17,21-hexathiacyclotetracosane-2,6,10,14,18,22-hexone, **4**, $n = 6$ (2% isolated yield), were isolated and fully characterized. A ^{13}C NMR spectrum of the reaction mixture indicated the presence of small amounts of a few additional compounds which appear to be higher molecular weight cyclooligomers, which could not be fully characterized. Compounds **3** and **4** were characterized by single-crystal X-ray diffraction analyses. The catalyst was recovered in good yield as a mixture of $Re_2(CO)_9(NCMe)$ and $Re_2(CO)_{10}$. In the absence of CH_2Cl_2 solvent, only polymers are formed in this reaction.

An ORTEP diagram of the molecular structure of **3** is shown in Figure 1. The molecule consists of a 16-membered ring of four ($SCH_2CH_2C{=}O$) repeating units. The conformation differs from saturated polythioether macrocycles[5] in that the sulfur atoms are directed toward the interior of the molecule and form an approximately tetrahedral cavity. The nonbonded S···S distances range from 3.949(2) to 4.805(2) Å, so there are some significant distortions from perfect T_d symmetry. The carbonyl groups are arranged in an alternating up/down pattern such that the molecule exhibits overall an approximate S_4 symmetry.

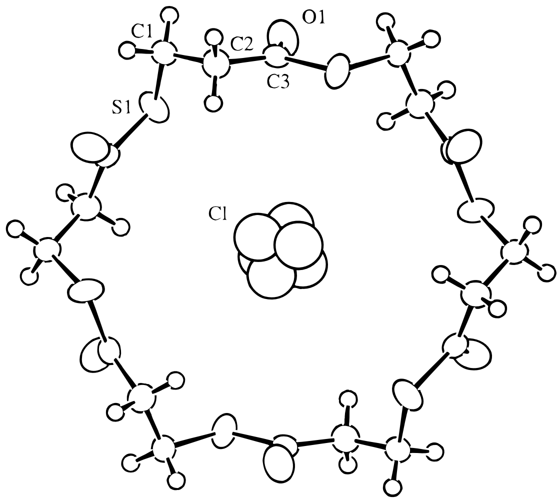


Figure 2. ORTEP diagram of 1,5,9,13,17,21-hexathiacyclotetracosane-2,6,10,14,18,22-hexone, **4**, showing 50% probability thermal ellipsoids. A disordered molecule of CH_2Cl_2 cocrystallized from the crystallization solvent is located in the center of the molecule. Selected interatomic distances (Å) are S(1)−C(3) = 1.764(5), S(1)−C(1) = 1.794(7), S(1)···S(1*) = 9.061(3), S(1)···S(1**) = 7.597(3), S(1)···S(1***) = 4.939(3).

Compound **4** crystallizes from CH_2Cl_2 solvent as a 1:1 CH_2Cl_2 solvate. An ORTEP diagram of the molecular structure of **4** is shown in Figure 2. This molecule consists of a 6-sided 24-membered ring with six ($SCH_2CH_2C{=}O$) units coupled in a head-to-tail fashion. The molecule possesses an exact S_6 symmetry. A crystallographic $\bar{3}$ axis passes through the center of the ring. Three of the carbonyl oxygen atoms lie on one side of the plane of the molecule and the other three lie on the other side. The sulfur atoms are arranged in a similar "crown" fashion. The tendency of **3** and **4** to adopt these novel macrocyclic conformations can be attributed in part to the presence of an *anti* C−S−C(=O)−C torsion angle that is always very close to 180°. The transannular distance S···S is 9.061(3) Å and presents an obvious environment for the formation of inclusion compounds. Indeed, the ability of **4** to form an inclusion compound is demonstrated by the cocrystallization of 1 equiv of CH_2Cl_2 from the crystallization solvent. This is positioned in the center of the molecule and exhibits a $\bar{3}$ disorder. Only the chlorine atoms of the disordered CH_2Cl_2 are seen in the figure.

The ^1H NMR spectra of **3** and **4** each exhibit two resonances as triplets for the inequivalent methylene groups. This indicates that both macrocycles are dynamically active in solution and invert their conformations rapidly on the NMR time scale so that the methylene protons which lie on the exterior of the rings are averaged with those that lie on the interior.

When a solution of $Re_2(CO)_9(NCMe)$ and **2** in methylene chloride was stirred at 25 °C for 20 h, a rubbery residue that seems to be almost exclusively polymers of $(SCH_2CMe_2C{=}O)_n$, yield 92%, was obtained. When this polymer was examined by TLC (hexane/methylene chloride solvent mixture), two small bands identified as 3,3,7,7,11,11,15,15-octamethyl-1,5,9,13-tetrathiacyclohexadecane-2,6,10,14-tetrone, **5** (2% yield), and 3,3,7,7,11,11,15,15,19,19,23,23-dodecamethyl-1,5,9,13,17,21-hexathiacyclotetracosane-2,6,10,14,18,22-hexone, **6** (5% yield), were obtained. The ^1H and ^{13}C NMR spectra for **5** and **6** indicate that they are cyclooligomers of **2**. Both of these compounds were further characterized by single-crystal X-ray diffraction analysis.

An ORTEP diagram of the molecular structure of **5** is shown in Figure 3. This molecule is also a 16-membered macrocycle containing four ($SCH_2CMe_2C{=}O$) repeating units. The conformation of the ring has some similarities to that of **3**, but there are also some significant differences. For example, the sulfur and ketone groups are arranged in an alternating up/down pattern as observed in **3**, but the molecule possesses an elongation along the vector between atoms C(2)−C(8). Accordingly, the nonbonded transannular S···S distances, S(1)···S(3) = 5.053(4) Å and S(2)···S(4) = 5.933(4) Å, are much longer than the adjacent nonbonded

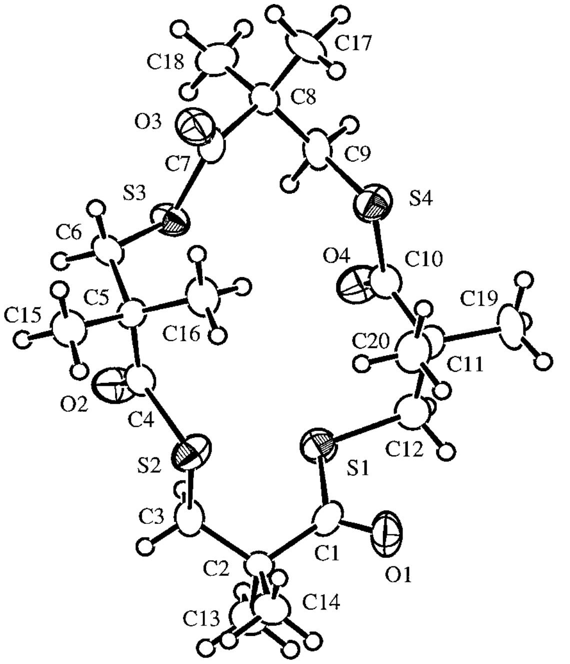


Figure 3. ORTEP diagram of 3,3,7,711,11,15,15-octamethyl-1,5,9,13-tetrathiacyclohexadecane-2,6,10,14-tetrone, **5**, showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) are S(1)−C(1) = 1.75(1), S(1)−C(12) = 1.82(1), S(2)−C(3) = 1.793(9), S(2)−C(4) = 1.80(1), S(3)−C(6) = 1.78(1), S(3)−C(7) = 1.77(1), S(4)−C(9) = 1.79(1), S(4)−C(10) = 1.78(1), S(1)···S(2) = 3.643(4), S(1)···S(3) = 5.053(4), S(1)···S(4) = 4.727(4), S(2)···S(3) = 4.768(4), S(2)···S(4) = 5.933(4), S(3)···S(4) = 3.697(4).

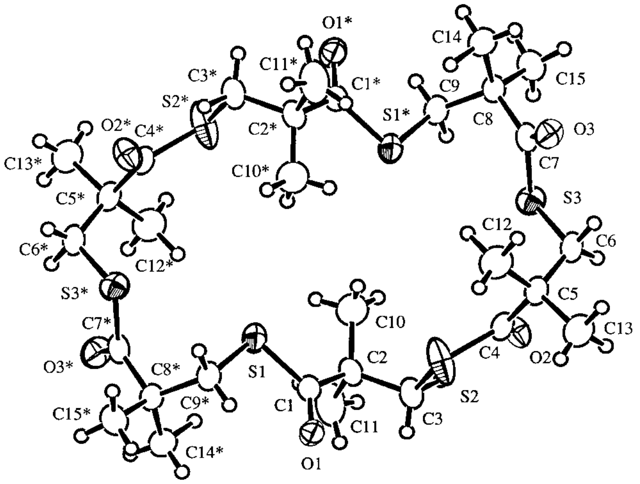


Figure 4. ORTEP diagram of 3,3,7,711,11,15,15,19,19,23,23-dodecamethyl-1,5,9,13,17,21-hexathiacyclotetracosane-2,6,10,14,18,22-hexone, **6**, showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) are S(1)−C(1) = 1.778(5), S(1)−C(9*) = 1.808(6), S(2)−C(3) = 1.796(6), S(2)−C(4) = 1.757(5), S(3)−C(6) = 1.800(6), S(3)−C(7) = 1.775(5), S(1)···S(1*) = 5.490(3), S(1)···S(2) = 5.205(3), S(1)···S(3) = 7.252(2), S(2)···S(2*) = 7.878(4), S(3)···S(3*) = 10.020(2), S(1)···S(3*) = 3.560(2), S(1)···S(2*) = 4.360(2), S(2)···S(3) = 4.578(2), S(2)···S(3*) = 7.764(2).

S···S distances, S(1)···S(2) = 3.643(4) Å and S(3)···S(4) = 3.697(4) Å. Two of the *gem*-dimethyl groups, C(5) and C(11), lie on the same side of the molecule, so that the molecule has an approximate C_2 symmetry.

An ORTEP diagram of the molecular structure of **6** is shown in Figure 4. This molecule consists of a 24-membered ring with six (SCH$_2$CMe$_2$C=O) units coupled in a head-to-tail fashion. The molecule possesses a crystallographically imposed center of symmetry (i.e., the asymmetric crystal unit is occupied by only one-half of the molecule). As in **3**−**5**, there is an alternating up/down pattern of the sulfur atoms and ketone groups, and as with **5**, the structure is elongated along one direction, S(3)···S(3*). Nothing was found in the ring cavity of this compound. The methyl resonances of **5** and **6** are observed as singlets both in the ^{1}H and ^{13}C NMR spectra, indicating that both of these molecules are dynamically active in solution.

Catalysis. The turnover frequency for the catalytic formation of **3** from **1** by Re$_2$(CO)$_9$(NCMe) at 25 °C is 1.76 h^{-1}. The catalytic ring opening of **1** does not occur when Re$_2$(CO)$_{10}$ is substituted for Re$_2$(CO)$_9$(NCMe). This observation would seem to suggest that an accessible coordination site via dissociation of the labile NCMe ligand is a requirement of the catalysis. This led us to investigate the catalytic activity of Mn$_2$(CO)$_9$(NCMe) and Mn$_2$(CO)$_{10}$. Surprisingly, both manganese compounds exhibit considerable activity and both are similar to Re$_2$(CO)$_9$(NCMe), see Table 1, but even more importantly was the observation that Mn$_2$(CO)$_{10}$ was completely inactive as a catalyst in the absence of room light.

The catalysis by Mn$_2$(CO)$_{10}$ and Re$_2$(CO)$_9$(NCMe) was also significantly diminished in the presence of added quantities the radical scavenger TEMPO, 2,2,6,6-tetramethylpiperidinyloxy radical. Small amounts of Mn(CO)$_5$Cl were recovered from the manganese reaction, together with a good return of Mn$_2$(CO)$_{10}$. It is known that the radicals produced by irradiation of Mn$_2$(CO)$_{10}$ in chlorocarbon solvents can abstract chlorine to form Mn(CO)$_5$Cl.[11] Also, it is notable that solutions of the thiolactone and TEMPO in the absence of Mn$_2$(CO)$_{10}$ were completely inactive catalytically, indicating that this oxy radical itself is incapable of activating **1**. These observations suggest that light-generated metal-based radical species may be involved in these reactions.

Re$_2$(CO)$_9$(NCMe) and Mn$_2$(CO)$_9$(NCMe) both showed a low residual but significant activity even in the absence of light. However, when TEMPO was added to a solution of Re$_2$(CO)$_9$(NCMe) in the absence of light, its catalytic activity was decreased even further. It is possible that a second "dark" mechanism may be operating that does not involve radical species or even in the dark there may be catalytically significant quantities of radicals present in the solutions of these two complexes. The inhibition by TEMPO seems to suggest the latter but certainly does not rule out the former.

Finally, the catalytic activity of Mn$_2$(CO)$_{10}$ in light was unaffected when the reaction was performed in the presence of an atomsphere of CO.

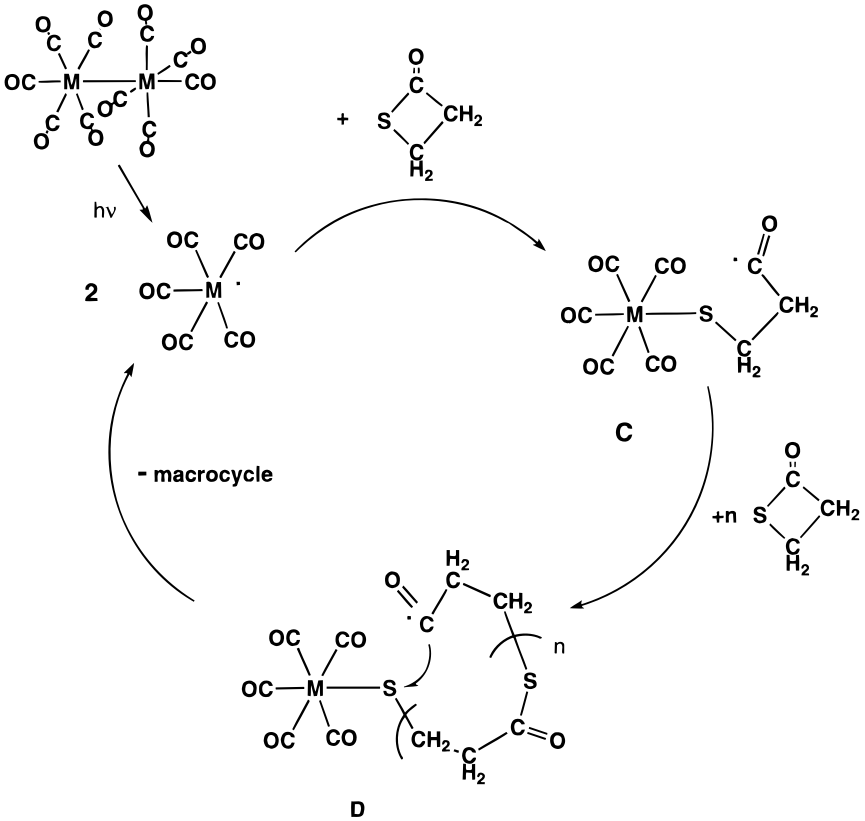
Discussion

The current study was initiated to determine whether or not the rings of β-propiothiolactones can be opened and recyclized by Mn$_2$(CO)$_{10}$, Re$_2$(CO)$_{10}$, or their mono NCMe derivatives. Of these four complexes, only Re$_2$(CO)$_{10}$ is inactive. The transformation of **1** yields two

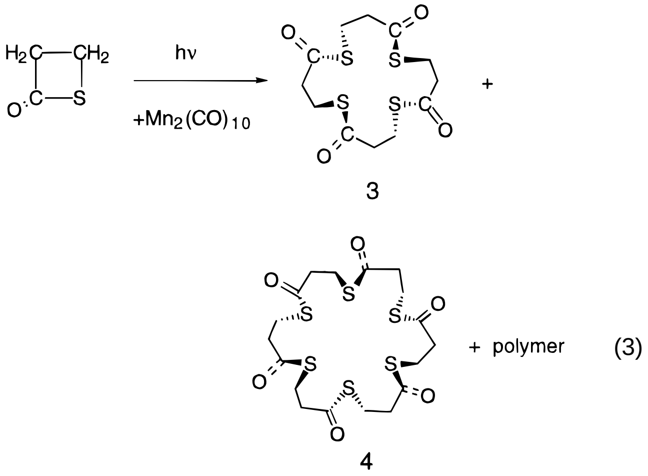
---

[11] (a) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press: New York, 1979; p 136−141. (b) Zhang, H.-T.; Brown, T. L. *J. Am. Chem. Soc.* **1993**, *115*, 107. (c) Kvietok, F. A.; Bursten, B. E. *Organometallics* **1995**, *14*, 2395.

Scheme 1



macrocycles, **3** and **4**, plus polymer as the principal products, eq 3.



(3)

The observation that the catalysis by $Mn_2(CO)_{10}$ is light dependent has two mechanistic implications. It is known that irradiation of the $M_2(CO)_{10}$, M = Mn, Re, compounds leads to (1) decarbonylation that would lead to formation of a "vacant" coordination site and (2) splitting of the metal−metal bond to produce two 17-electron mononuclear radical species.[11] The lack of inhibition of $Mn_2(CO)_{10}$ catalysis in the presence of a CO atmosphere would seem to be contrary to a CO-loss step in the mechanism, while the inhibition of the catalysis by the radical scavenger TEMPO seems to support the importance of radicals in the mechanism. Indeed, it is known that TEMPO will react with $Mn_2(CO)_{10}$ when irradiated to form a stable nonradical complex.[12] The failure of $Re_2(CO)_{10}$ to activate **1** even in the presence of room light can be explained by the higher energy of the absorptions required to split the Re−Re bond in this molecule.

Light-generated $M(CO)_5$ radicals (or $M(CO)_4NCMe$ radicals) could combine with the β-thiolactone (without CO dissociation) by a ring-opening addition of the sulfur atom to the metal atom to generate a metal−thiolate linkage and ketone radical, such as **C**, see Scheme 1. Alternatively, it is possible that the metal atom could add at the ketonic group. However, our efforts to open cyclobutanone with these catalysts have been unsuccessful, thus, we favor the sulfur addition. A series of ring-opening additions of ketone radicals to other molecules of β-thiolactone would lead to growth of the chain. This could lead to polymer or, alternatively, a ketone radical could recombine with the metal-bound sulfur atom at selected chain lengths, **D**, to yield polythiolactone macrocycles and release the metal radical for additional reaction. The absence of catalysis by TEMPO alone suggests that metal-based radical species are required for this new form of catalytic ring opening of thiolactones.

As a further indicator of the importance of the radical character in the reactions, we investigated the potential of $W(CO)_5(NCMe)$ for ring-opening activation of **1**. Such complexes with even numbers of electrons do not exhibit radical character, and as expected, $W(CO)_5(NCMe)$ exhibited no catalytic activity for opening of the ring of **1**.

Nucleophilic ring-opening polymerization of β-thiolactones has been reported previously,[13] but it seems

---

(12) Jaitner, P.; Huber, W.; Huttner, G.; Scheidstager, O. *J. Organomet. Chem.* **1983**, *259*, C1.

unlikely that this mechanism is operative for the light-promoted catalysis produced by these metal carbonyl complexes.

It is curious that $Re_2(CO)_9(NCMe)$ and $Mn_2(CO)_9(NCMe)$ show some residual catalytic activity even in the absence of light. Thus, it is possible that a non-radical mechanism that does not depend on light could also be operative with these compounds. A second mechanism similar to that proposed for the activation of thietanes by these complexes involving displacement of the labile NCMe ligand, coordination of the thiolactone by the sulfur atom, nucleophilic ring opening by free thiolactone, and subsequent cyclization could be envisaged.[1]

The catalytic transformations of **2** by these metal complexes are probably similar to those of **1**. However, the formation of macrocycles is much less effective. It is possible that the small amounts of macrocycles that were obtained from this reaction were derived solely by degradation of the polymer.

By virtue of its large cavity, macrocycle **4** clearly has a potential to form inclusion compounds. Indeed, it has crystallized from the CH_2Cl_2 crystallization solvent with 1 equiv of CH_2Cl_2 in the center of the ring. The tetrahedral cavity formed by the conformation of **3** seems ideally suited for the coordination of a metal atom; however, to date, all of our attempts to introduce a metal into this ring have been unsuccessful. One explanation for this could be related to the presence of the electron-withdrawing ketone group next to each of the sulfur atoms, which should decrease the ability of the sulfur atoms to engage in metal coordination. However, in spite of this, it is still clear that this new family of head-to-tail-oriented polythiolactones does have a potential to exhibit supramolecular properties.[14]

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. We thank Dr. Donald Stec for recording the solid state NMR spectra.

Supporting Information Available: Tables of final atomic positional parameters, intramolecular bond distances and angles, and anisotropic thermal parameters for the structural analyses of **5** and **6** (11 pages). See any current masthead page for ordering information. The corresponding information for the structural analyses of **3** and **4** was deposited previously.[6]

OM970524G

---

(13) (a) Knunyants, I. L.; Linkova, M. G.; Kuleshova, N. D. *Izv. Acad. Nauk SSSR, Ser. Khim.* **1964**, 644. (b) Fles, D.; Tomasic, V.; Samsa, M.; Ahmetovic, D.; Fles, M. *J. Polym. Sci., Polym. Symp.* **1973**, 3221. (c) Fles, D.; Tomasic, V. *J. Polym. Sci.* **1969**, *6*, 809. (d) Jerman, B.; Fles, D. *J. Polym. Sci.* **1976**, *14*, 1117.

(14) (a) Vögtle, F. *Supramolecular Chemistry*; Wiley & Sons: Chichester, U.K., 1991. (b) *Frontiers in Supramolecular Organic and Photochemistry*; Schneider, H.-J., Durr, H., Eds.; VCH: Weinheim, Germany, 1991. (c) *Host Guest Complex Chemistry Macrocycles*; Vögtle, F., Weber, E., Eds.; Springer-Verlag: Berlin, 1985.