

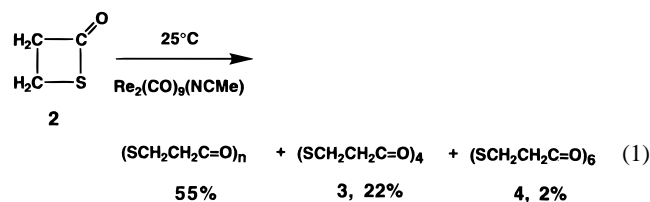
## Catalytic Cyclo-oligomerization of $\beta$ -Propiothiolactone by a Dirhenium Complex. A Convenient Route to New Polythiolactone Macrocycles

Richard D. Adams,\* Mingsheng Huang, Wen Huang, and Joachim A. Queisser

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

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In recent studies, we have shown that  $\text{Re}_2(\text{CO})_9(\text{NCMe})$  (**1**) can serve as a catalyst for the macrocyclization of thietanes.<sup>1</sup> We have now found that **1** also activates  $\beta$ -propiolactone,  $\text{SCH}_2\text{CH}_2\text{C}=\text{O}$  (**2**), toward opening of the heterocyclic ring under mild conditions. The known polymer  $(\text{SCH}_2\text{CH}_2\text{C}=\text{O})_n$ <sup>2</sup> (55% yield) and a mixture of new cyclooligomers  $(\text{SCH}_2\text{CH}_2\text{C}=\text{O})_n$ , two of which, 1,5,9,13-tetrathiacyclohexadecane-2,6,10,14-tetrone (**3**) (22% isolated yield) and 1,5,9,13,17,21-hexathiacyclotetracosane-2,6,10,14,18,22-hexone (**4**),  $n = 6$  (2% isolated yield), have been isolated and characterized crystallographically, eq 1.<sup>3,4</sup>



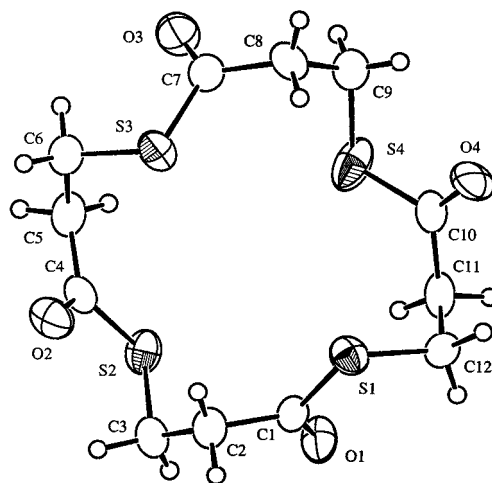
An ORTEP diagram of the molecular structure of **3** is shown in Figure 1. The molecule consists of a 16-membered ring of four  $(\text{SCH}_2\text{CH}_2\text{C}=\text{O})$  repeating units. The conformation differs

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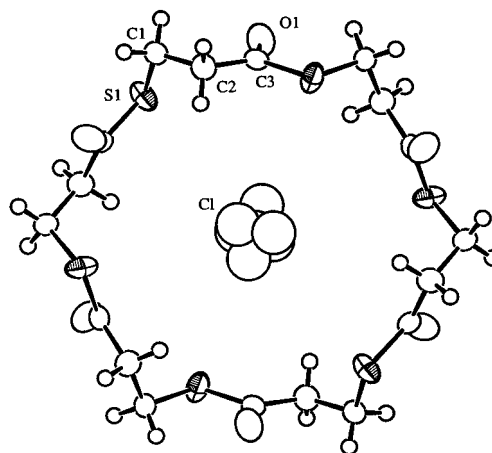
(2) Knunyants, I. L.; Kuleshova, N. D.; Lin'kiova, M. G. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1965**, 1081.

(3) A 10.0 mg amount (0.015 mmol) of  $\text{Re}_2(\text{CO})_9(\text{NCMe})$  (**1**) was placed in a 50 mL three-neck round-bottom flask equipped with a stir bar, reflux condenser, and nitrogen inlet. Then 0.64 mL of freshly distilled thiolactone (9.45 mmol) and 30 mL of methylene chloride were added, and the solution was stirred at a temperature of 25 °C for 20 h. A white precipitate was removed by filtration, 457 mg. This was shown to be the polymer  $(\text{SCH}_2\text{CH}_2\text{C}=\text{O})_n$ , 55% yield.<sup>2</sup> The solvent was removed from the filtrate to yield a residue of 348 mg. 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 has been 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). For **3**: <sup>1</sup>H NMR ( $\delta$  in  $\text{CDCl}_3$ ) 3.14 (t, 8H, <sup>3</sup>J<sub>H-H</sub> = 5.8 Hz), 2.87 (t, 8H, <sup>3</sup>J<sub>H-H</sub> = 5.8 Hz); <sup>13</sup>C NMR ( $\delta$  in  $\text{CDCl}_3$ ) 198.72 (4C), 42.81 (4C), 25.76 (4C). Anal. Calcd: C, 40.89; H, 4.57. Found: C, 38.84; H, 4.33. For **4**: <sup>1</sup>H NMR ( $\delta$  in  $\text{CDCl}_3$ ) 3.17 (t, 12H, <sup>3</sup>J<sub>H-H</sub> = 6.2 Hz), 2.84 (t, 12H, <sup>3</sup>J<sub>H-H</sub> = 6.2 Hz); <sup>13</sup>C NMR ( $\delta$  in  $\text{CDCl}_3$ ) 197.21 (6C), 43.49 (6C), 25.05 (6C). Anal. Calcd for **4**·CH<sub>2</sub>Cl<sub>2</sub>: C, 37.18; H, 4.27. Found: C, 37.02; H, 3.97. The catalysis does not occur when  $\text{Re}_2(\text{CO})_{10}$  is substituted for **1**.

(4) Crystal data for **3**: space group =  $P2_1/n$ ,  $a = 12.932(3)$  Å,  $b = 8.603(2)$  Å,  $c = 15.075(3)$  Å,  $\beta = 99.33(2)^\circ$ ,  $Z = 4$ , 1378 reflections,  $R = 0.046$ . Crystal data for **4**·CH<sub>2</sub>Cl<sub>2</sub>: space group =  $R3$ ,  $a = 12.780(2)$  Å,  $b = 12.780(2)$  Å,  $c = 14.792(2)$  Å,  $Z = 3$ , 591 reflections,  $R = 0.055$ .



**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  $\text{S}(1)-\text{C}(1) = 1.770(6)$ ,  $\text{S}(2)-\text{C}(4) = 1.761(6)$ ,  $\text{S}(3)-\text{C}(7) = 1.762(6)$ ,  $\text{S}(4)-\text{C}(10) = 1.742(6)$ ,  $\text{S}(1)\cdots\text{S}(2) = 4.457(2)$ ,  $\text{S}(1)\cdots\text{S}(3) = 4.797(2)$ ,  $\text{S}(1)\cdots\text{S}(4) = 4.071(3)$ ,  $\text{S}(2)\cdots\text{S}(3) = 4.293(2)$ ,  $\text{S}(2)\cdots\text{S}(4) = 4.805(2)$ , and  $\text{S}(3)\cdots\text{S}(4) = 3.949(2)$ .



**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  $\text{CH}_2\text{Cl}_2$  cocrystallized from the crystallization solvent is located in the center of the molecule. Selected interatomic distances (Å) are  $\text{S}(1)-\text{C}(3) = 1.764(5)$ ,  $\text{S}(1)-\text{C}(1) = 1.794(7)$ ,  $\text{S}(1)\cdots\text{S}(1^*) = 9.061(3)$ ,  $\text{S}(1)\cdots\text{S}(2^*) = 7.597(3)$ , and  $\text{S}(1)\cdots\text{S}(1^*) = 4.939(3)$ .

from saturated polythioether macrocycles<sup>5</sup> in that the sulfur atoms are directed toward the interior of the molecule and form an approximate tetrahedral cavity into which soft Lewis acids, such as transition metals, could be selectively coordinated. The carbonyl groups are arranged in a two up–two down pattern such that the molecule exhibits an overall  $S_4$  symmetry.

Compound **4** crystallizes from  $\text{CH}_2\text{Cl}_2$  solvent as a 1:1  $\text{CH}_2\text{Cl}_2$  solvate. An ORTEP diagram of the molecular structure of **4** is shown in Figure 2. This molecule consists of a six-sided 24-membered ring with six  $(\text{SCH}_2\text{CH}_2\text{C}=\text{O})$  units coupled in a head to tail fashion. The molecule possesses an overall  $S_6$  symmetry which is crystallographically imposed. Three of the carbonyl groups point above the plane of the molecule, and the other three point down. The sulfur atoms are arranged in a similar three up–three down crown fashion. The *trans*-annular distance  $\text{S}\cdots\text{S}$  is 9.061(3) Å and presents an obvious environ-

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ment for the formation of inclusion compounds. The propensity for this is demonstrated by the cocrystallization of 1 equiv of  $\text{CH}_2\text{Cl}_2$  from the crystallization solvent which lies exactly in the center of the molecule. This  $\text{CH}_2\text{Cl}_2$  exhibits a 3-fold rotational disorder, and only the chlorine atoms of the disordered grouping are seen in the figure. The tendency of **3** and **4** to adopt these novel macrocyclic conformations may be attributed in part to the presence of an *anti*-C-S-C(=O)-C torsion angle which is always very close to  $180^\circ$ .<sup>6</sup>

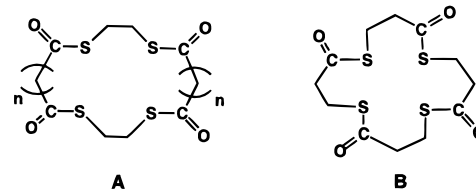
The catalytic ring opening of **2** does not occur when  $\text{Re}_2(\text{CO})_{10}$  is substituted for **1**, which suggests that activation of the  $\beta$ -propiolactone occurs through an interaction with one of the rhenium atoms upon displacement of the NCME ligand, as observed in the reactions of **1** with thietanes.<sup>1c,f</sup> The turnover frequency for the catalytic formation of **3** by **1** at  $25^\circ\text{C}$  is  $1.76\text{ h}^{-1}$ .

Recent studies have provided some of the first examples of polythiolactones from acyclic precursors.<sup>7</sup> These molecules all exhibit head-to-head/tail-to-tail orientations of the thiolactone groupings (**A**). Compounds **3** and **4** are the first members of a

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(7) (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.; Iamiceli, A. L.; Mandolini, L.; Mencarelli, P. *J. Org. Chem. Soc.* **1992**, *57*, 766.

new family of head-to-tail oriented polythiolactones **B** that have a clear and demonstrated potential to exhibit new supramolecular properties.<sup>8</sup>



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**Supporting Information Available:** Details of the reactions and characterization of the products, tables of final atomic positional parameters, intramolecular bond distances and angles, and anisotropic thermal parameters for both of the structural analyses (14 pages). See any current masthead page for ordering and Internet access instructions.

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(8) (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) Vögtle, F., Weber, E., Eds. *Host Guest Complex Chemistry Macrocycles*; Springer-Verlag: Berlin, 1985.