

Synthesis and structural characterization of chiral thiacycrows: the crystal and molecular structure of (*R,R,R*)-2,6,10-trimethyl-1,5,9-trithiacyclododecane

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Dedicated to Professor F.A. Cotton on the occasion of his 70th birthday.

Abstract

The chiral polythioether macrocycles (*R,R,R*)-2,6,10-trimethyl-1,5,9-trithiacyclododecane [(*R,R,R*)-Me₃12S3] (**8**), and (*R,R,R,R*)-2,6,10,14-tetramethyl-1,5,9,13-tetrathiacyclohexadecane, [(*R,R,R,R*)-Me₄16S4] (**9**), have been synthesized from (*R*)-2-methylthietane (**7**) by using the dirhenium carbonyl catalyst Re₂(CO)₉[(*R*)-2-SC(H)MeCH₂CH₂] (**10**). The catalytic activity is low, 0.21 turnovers per hour, but is significantly above the uncatalyzed level. Compound **8** was characterized by a single-crystal X-ray diffraction analysis that was able to establish the absolute configuration. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Macrocyclization; Rhenium; Thiacycrows; Chiral macrocycle

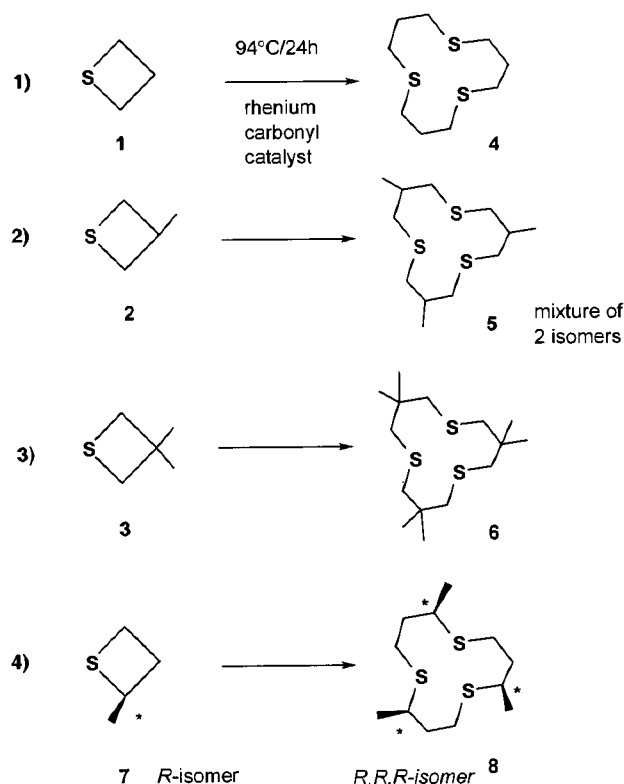
1. Introduction

Recently, we have shown that polythioether macrocycles, or thiacycrows, can be obtained catalytically from the family of strained ring thioethers known as thietanes including: thietane (**1**) [1,2], 3-methylthietane (**2**) [3], and 3,3-dimethylthietane (**3**) [4] by using rhenium and tungsten carbonyl catalysts. The principal products of these reactions are the trithiacyclododecanes: 12S3 (**4**), Me₃12S3 (**5**), and Me₆12S3 (**6**), respectively (Eqs. (1–3)).

Thiacycrows have attracted attention because of their potential to serve as ligands for the transition metals [5]. Metal complexes containing chiral phosphine ligands have been shown to be of great value in producing catalysis with asymmetric induction [6]. Although the number of examples of catalysts derived from metal complexes containing thiacycrown ligands have been very few [7], it can be anticipated that complexes containing chiral thiacycrows would also have the potential to promote enantioselective catalysis similar to that found with other chiral chelating phosphine ligands.

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In the hope of preparing a trithiacyclododecane with three identical stereocenters, we have investigated the macrocyclization of (*R*)-2-methylthietane **7** by dirhenium carbonyl complexes (Eq. (4)). These studies have resulted in the preparation of the (*R,R,R*)-2,6,10-trimethyl-1,5,9-trithiacyclododecane [(*R,R,R*)-Me₃12S3] (**8**) and (*R,R,R,R*)-2,6,10,14-tetramethyl-1,5,9,13-tetrithiacyclohexadecane [(*R,R,R,R*)-Me₄16S4] (**9**).

2. Results

The reaction of Re₂(CO)₉(NCMe) (**11**) with (*R*)-2-MT has yielded the compound Re₂(CO)₉[(*R*)-SC(H)-MeCH₂CH₂] (**10**), in 75% yield. Compound **10** can be anticipated to be structurally analogous to the related thietane complexes Re₂(CO)₉(SCH₂CH₂CH₂) (**12**) [2], Re₂(CO)₉(SCH₂C(H)MeCH₂) (**13**) [3], and Re₂(CO)₉-(SCH₂CMe₂CH₂) (**14**) [4], that we have previously reported. We were unable to obtain a single crystal of compound **10** for an X-ray diffraction analysis. If **10** follows the trend of other rhenium thioether complexes, the molecule should be structurally similar to **14** and the three thiacycrown complexes, Re₂(CO)₉(12S3) (**15**), Re₂(CO)₉(*c,c,t*-Me₃12S3) (**16**), and Re₂(CO)₉(*c,c,c*-Me₃-12S3) (**17**), that we have recently reported [2,3]. In all four of these compounds, the thioether ligand occupies a position *cis* to the Re–Re bond and the equatorially positioned ligands on the two metal atoms are arranged in a staggered rotational conformation similar to that found in Re₂(CO)₁₀.

Compound **10** was found to be capable of producing macrocycles from (*R*)-2-MT catalytically, but the activity was relatively low. In a typical reaction, a 15.0-mg amount of **10** was dissolved in 0.6 ml of (*R*)-2-MT and heated to 100°C for 24 h. The catalyst appeared to dissolve completely. After cooling, the excess (*R*)-2-MT was removed in vacuo and the resulting residue was dissolved in methylene chloride and filtered. After removal of the solvent, the residues were weighed and analyzed by ¹³C-NMR. The residue consisted principally of materials believed to be low-molecular-weight polymers, but it also contained substantial amounts of the macrocycles **8** and **9** and some larger macrocycles that could not be isolated in pure forms. The relative amounts by weight of compounds **8** and **9** were 15 and 5%, respectively as determined by integration of the appropriate resonances in the ¹³C-NMR spectrum of the mixture. Separation of the mixture of **8** and **9** can be achieved by TLC on silica gel using a 3:1 hexane–methylene chloride solvent mixture for elution.

As a control, a sample of the (*R*)-2-MT was treated identically to those in the catalytic runs in the absence of catalyst **10**. Only trace amounts of (*R*)-2-MT oligomers, including some **8**, were produced, but the amounts were much less than those obtained in the

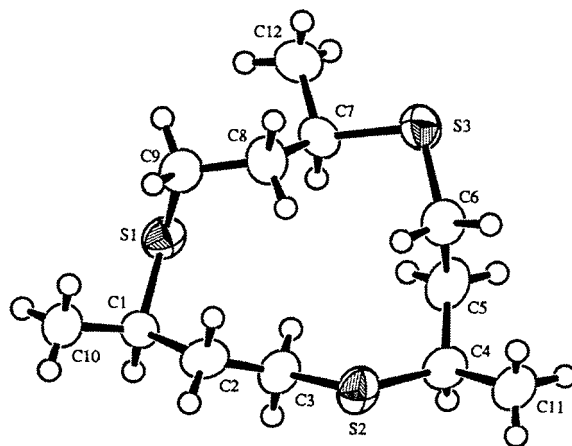


Fig. 1. An ORTEP diagram of **8** showing 40% probability thermal ellipsoids.

presence of the catalysts [4]. To test for the importance of coordination to the catalyst, we also examined Re₂(CO)₁₀ which has no labile ligands or vacant sites for thietane activation. Only very small amounts of macrocycles were obtained.

Compounds **8** and **9** are new. Compound **8** was characterized by single-crystal X-ray diffraction analysis (Table 1). An ORTEP diagram of the molecular structure of **8** is shown in Fig. 1.

Selected interatomic distances and angles are listed in Tables 2 and 3. First of all, it is observed that each of the carbon atoms C(1), C(4) and C(7) have the same

Table 1
Crystallographic data for compound **8**

Formula	S ₃ C ₁₂ H ₂₄
Formula weight	264.50
Crystal system	Orthorhombic
Lattice parameters	
<i>a</i> (Å)	8.9060(2)
<i>b</i> (Å)	31.2668(6)
<i>c</i> (Å)	5.3106(2)
<i>V</i> (Å ³)	1478.7(6)
Space group	<i>P</i> 2 ₁ 2 ₁ 2 (no. 18)
<i>Z</i> value	4
ρ_{calc} (g cm ⁻³)	1.19
μ (Mo–K α) (cm ⁻¹)	4.75
Temperature (°C)	20
No. of observations (<i>I</i> > 3 σ (<i>I</i>))	5322
No. of variables	233
Goodness-of-Fit ^a	1.29
Max. shift/error on final cycle	0.06
Residuals ^a : <i>R</i> ; <i>R</i> _w	0.0395; 0.0457
Abs. corr.	None
Largest peak in final diff. map (e Å ⁻³)	0.62

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

Table 2
Intramolecular bond distances for **8**^a

Atom	Atom	Distance (Å)	Atom	Atom	Distance (Å)
S(1)	C(1)	1.849(3)	C(2)	C(3)	1.533(4)
S(1)	C(9)	1.824(3)	C(4)	C(5)	1.530(4)
S(2)	C(3)	1.803(3)	C(4)	C(11)	1.531(4)
S(2)	C(4)	1.836(3)	C(5)	C(6)	1.523(5)
S(3)	C(6)	1.819(3)	C(7)	C(8)	1.520(4)
S(3)	C(7)	1.842(3)	C(7)	C(12)	1.515(5)
C(1)	C(2)	1.520(4)	C(8)	C(9)	1.537(4)
C(1)	C(10)	1.519(5)			

^a Estimated standard deviations in the least significant figure are given in parentheses.

Table 3
Intramolecular bond angles for **8**^a

Atom	Atom	Atom	Angle (°)	Atom	Atom	Atom	Angle (°)
C(1)	S(1)	C(9)	104.0(2)	S(2)	C(4)	C(11)	106.2(3)
C(3)	S(2)	C(4)	102.6(2)	C(5)	C(4)	C(11)	112.9(3)
C(6)	S(3)	C(7)	103.9(2)	C(4)	C(5)	C(6)	115.8(3)
S(1)	C(1)	C(2)	113.9(2)	S(3)	C(6)	C(5)	114.8(3)
S(1)	C(1)	C(10)	112.4(2)	S(3)	C(7)	C(8)	112.2(2)
C(2)	C(1)	C(10)	112.5(3)	S(3)	C(7)	C(12)	106.4(2)
C(1)	C(2)	C(3)	114.3(3)	C(8)	C(7)	C(12)	114.8(3)
S(2)	C(3)	C(2)	111.2(3)	C(7)	C(8)	C(9)	114.9(3)
S(2)	C(4)	C(5)	113.6(2)	S(1)	C(9)	C(8)	115.2(2)

^a Estimated standard deviations in the least significant figure are given in parentheses.

stereochemical configuration. An analysis of the absolute configuration showed that it was *R*, the same as that of the starting material. None of the S–C or C–C bond distances has abnormal length. The conformation of the 12-membered ring is slightly different from that of its unsubstituted parent **4** (12S3) [8], **5** (Me₃12S3) [3], both of which exhibit square-like shapes with four atoms per edge and one sulfur atom in a corner site (see Fig. 2). In **8**, one edge C(1)–C(4) is five atoms in length, the edge C(1)–C(9) is three atoms in length, and the other two are four atoms in length. This is similar to the structure of **6** (Me₆12S3) [4]. The tendency of the three methyl groups to be directed toward the exterior of the ring is clearly one factor that influences the conformation of the ring. In the case of **6**, the methylene groups seem to be turned strongly toward the interior of the ring as a result outward orientation of the *gem*-dimethyl groups. In the case of **8**, methylene groups also seem to be turned toward the interior of the ring, e.g. C(8), due to the exterior methyl groups, although to a lesser extent. The ¹H- and ¹³C-NMR spectra of **8** show five and four resonances, respectively: ¹H-NMR δ = 2.89 (m, 3H), 2.72 (m, 3H), 2.55 (m, 3H), 1.82 (m, 6H), 1.26 (d, 9H, ³J_{H–H} = 7.0 Hz) and ¹³C-NMR δ = 39.74 (3C), 37.31 (3C), 26.08 (3C), 21.13 (3C). This indicates that the ring is not rigid in solution and that all of the similar groupings are averaged by dynamical intercon-

versions. The ¹³C-NMR spectrum shows that the methyl groups are equivalent as indicated by the structure analysis.

The ¹³C-NMR of compound **9** shows only four resonances, 38.80 (4C), 36.20 (4C), 26.65 (4C), 21.73 (4C). This is consistent with the proposed symmetric structure, 2,6,10,14-tetramethyl-1,5,9,13-tetrathiacyclohexadecane, but since we were unable to obtain crystals of **9** suitable for X-ray diffraction analysis, we were unable to determine its absolute configuration experimentally. The absolute configuration of **9** was therefore assumed by analogy to compound **8**.

3. Discussion

In previous studies, we have observed that thietane, 3-methylthietane and 3,3-dimethylthietane can be cyclotrimerized by their Re₂(CO)₉ complexes [1–4]. In this study, we have shown that **7** can be cyclotrimerized by the dirhenium complex **10** to yield two new thiacycrows, **8** and **9**. The catalytic activity is low and similar to that of the synthesis of **6** from **3**. For comparison, Table 4 lists the turnover frequencies of the catalytic activity of the four thietane complexes **10**, **12**, **13** and **14** for the formation of the corresponding 12-membered ring thiacycrows.

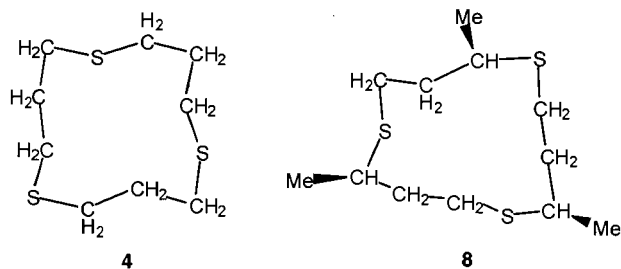
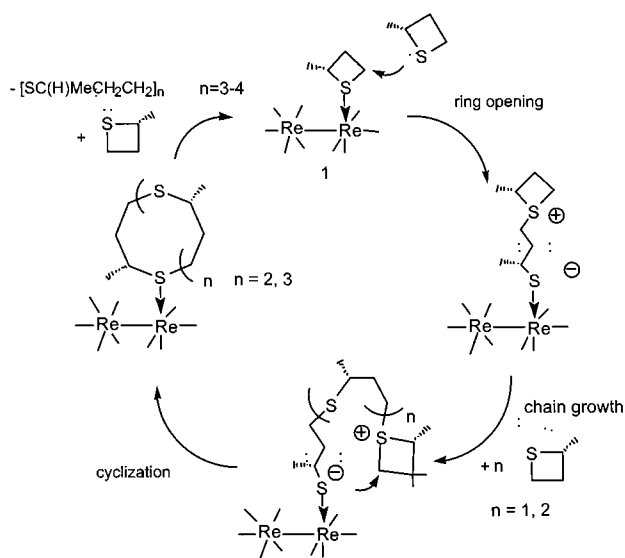


Fig. 2. Structure of **4** and **8** showing square-like shapes with four atoms per edge in **4** and five and three atoms per edge in **8**.

It is proposed that the mechanism of formation for these macrocycles is the same as for the other catalytic reactions. It begins with a ring-opening nucleophilic addition of a free molecule of the thietane to the sulfur-bound methylene group of the thietane ligand (see Scheme 1). This is followed by a series of similar chain growth ring-opening additions that culminate with a cyclization that leads to the formation of a macrocycle. As in the other catalytic ring-opening cyclooligomerization processes of thietanes, it was observed that $\text{Re}_2(\text{CO})_{10}$ is not a good catalyst. This indicates that the (*R*)-2-MT ligand must be coordinated to the $\text{Re}_2(\text{CO})_9$ fragment in the course of the macrocyclization process. The cycle is completed through regeneration of **10** by displacement of the macrocycle from the complex by another equivalent of the thietane. Rings of any size could be formed by this mechanism simply by extending the growth step, and the formation of **9** is believed to occur similarly.

The reactivity of 2-MT is clearly lower than that of 3-MT. As the position of the methyl substituent becomes closer to the sulfur atom, the reactivity de-



Scheme 1.

Table 4

Comparison of catalytic activities of some $\text{Re}_2(\text{CO})_9$ (thietane) complexes

Catalyst	Product	Temperature (°C)	TOF ^a
$\text{Re}_2(\text{CO})_9$ (thietane)	12S3	94	6.1
$\text{Re}_2(\text{CO})_9$ (3-MT)	Me_3 12S3	107	2.0
$\text{Re}_2(\text{CO})_9$ (3,3-DMT)	Me_6 12S3	100	0.03
$\text{Re}_2(\text{CO})_9$ (<i>R</i>)-2-MT)	(<i>R,R,R</i>)- Me_3 12S3	100	0.21

^a TOF, turnover frequency = mol of product/mol of catalyst·h.

creases. This can be attributed to steric effects, namely the methyl group inhibits nucleophilic attack at the substituted carbon atom (see Table 4).

In summary, we have observed for the first time significant quantities of the chiral 12-membered and 16-membered ring thiocrowns. There are still some difficulties in obtaining them enantiomerically pure, in part because it is not now possible to synthesize their precursor 2-methylthietane in an enantiomerically pure form.

4. Experimental

4.1. 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 5DXBO FTIR spectrophotometer. ¹H- and ¹³C-NMR spectra were recorded on a Varian Mercury spectrometer operating at 400 and 125.76 MHz, respectively. $\text{Re}_2(\text{CO})_9(\text{NCMe})$ [**9**] and (*R*)-2-methylthietane [**10**] ($\approx 81\%$ *ee*) were prepared according to the published procedures. The separation of products was performed by TLC in air on Analtech 0.25 and 0.50 mm silica gel 60 Å F₂₅₄ glass plates. Mass spectra were obtained using electron impact ionization. Optical rotations were measured on a Perkin–Elmer polarimeter using a 10 cm cell. Elemental analysis was performed by Oneida Research Services, Whitesboro, NY.

4.2. Preparation of $\text{Re}_2(\text{CO})_9[(R)\text{-}2\text{-SC(H)MeCH}_2\text{CH}_2]$ (**10**)

A 20.0-mg amount of $\text{Re}_2(\text{CO})_9(\text{NCMe})$ (**11**), (0.030 mmol) was dissolved in 15 ml of acetone in a 25 ml 3-neck round-bottomed flask equipped with a stir bar, reflux condenser and a nitrogen inlet. A 10.0 μl amount of (*R*)-2-methylthietane (0.124 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 3:1 hexane–methylene chloride solvent mixture to yield 16.0 mg

(75%) of $\text{Re}_2(\text{CO})_9[(R)\text{-SC(H)MeCH}_2\text{CH}_2]$ (**10**). Spectral data for **10**: IR ν_{CO} (cm^{-1} in hexane): 2103 (w), 2042 (m), 2016 (w), 1993 (vs), 1976 (w), 1968 (m), 1956 (w), 1931 (m). $^1\text{H-NMR}$ (δ in CDCl_3): 4.13 (m, 1H), 3.54 (m, 1H), 3.38 (m, 1H), 2.80 (m, 1H), 2.63 (m, 1H), 1.43 (d, 3H, $^3J_{\text{H-H}} = 6.7$ Hz). MS m/z for $\text{Re}^{187} = 712 - x(28)$, $x = 1-6$; parent ion $-x(\text{CO})$, $x = 1-6$.

4.3. Catalytic macrocyclization of (*R*)-2-methylthietane: synthesis of $\text{SC(H)MeCH}_2(\text{CH}_2\text{SC(H)MeCH}_2)_2\text{CH}_2$ (8**), and $\text{SC(H)MeCH}_2(\text{CH}_2\text{SC(H)MeCH}_2)_3\text{CH}_2$ (**9**)**

All of the catalytic reactions were performed under nitrogen by the following procedure. A pre-weighed amount of crystalline catalyst was placed in a 25 ml greaseless round-bottomed flask equipped with a stir bar, reflux condenser and a nitrogen inlet. Then, 0.6 ml of freshly distilled (*R*)-2-MT (7.5 mmol) was added, the reaction mixture was evacuated and filled with nitrogen twice, and the solution was stirred at 100°C in an oil bath. The results of this reaction are shown below.

A typical reaction and work-up are as follows: 0.6 ml of (*R*)-2-methylthietane (7.5 mmol) and a 15.0-mg amount of **10** (0.021 mmol) were heated to 100°C for 24 h. After cooling, the excess (*R*)-2-MT was removed in vacuo. ^1H - and ^{13}C -NMR spectra of this residue indicated that it consisted primarily of low-molecular-weight oligomers (53%) as well as what appears to be a mixture of sulfur-containing macrocycles, the major components being identified as (*R,R,R*)-2,6,10-trimethyl-1,5,9-trithiacyclododecane [(*R,R,R*)- $\text{Me}_3\text{12S3}$] (**8**) (15%), and (*R,R,R,R*)-2,6,10,14-tetramethyl-1,5,9,13-tetrathiacyclohexadecane [(*R,R,R,R*)- $\text{Me}_4\text{16S4}$] (**9**) (5%). The residue was extracted with hexane to remove the macrocycles. Upon evaporation of the solvent, the hexane-soluble fraction weighed 85 mg. The macrocycles were then separated by TLC using a 2:1 hexane–methylene chloride solvent mixture to yield 28.0 mg of **8** and 9.0 mg of **9**. For **8**, this is equivalent to 5.0 turnovers or 0.21 turnovers h^{-1} . Repeated attempts to separate the higher macrocycles by chromatography did not yield sufficient amounts of these compounds for complete characterization. Spectral data for **8**: $^1\text{H-NMR}$ (δ in CDCl_3): 2.89 (m, 3H), 2.72 (m, 3H), 2.55 (m, 3H), 1.82 (m, 6H), 1.26 (d, 9H, $^3J_{\text{H-H}} = 7.0$ Hz). $^{13}\text{C-NMR}$ (δ in CDCl_3): 39.74 (3C), 37.31 (3C), 26.08 (3C), 21.13 (3C). $[\alpha]_{\text{D}}^{293\text{K}} = -34.4^\circ$ (conc. = 3.1 mg ml^{-1} , CH_2Cl_2). $^1\text{H-NMR}$ (δ in CDCl_3) for **9**: 2.94 (m, 4H), 2.71 (m, 4H), 2.63 (m, 4H), 1.81 (m, 8H), 1.29 (d, 12H, $^3J_{\text{H-H}} = 6.8$ Hz). $^{13}\text{C-NMR}$ (δ in CDCl_3) for **9**: 38.80 (4C), 36.20 (4C), 26.65 (4C), 21.73 (4C). $^{13}\text{C-NMR}$ (δ in CDCl_3) for polymer: 39.14 (1C), 36.85 (1C), 27.72 (1C), 21.62 (1C). The mass spectra for **8** and **9** show the parent ions at 264 and 352 m/e , respectively, as well as additional ions with weights of 209, 120 and 88 m^+/e corresponding to

$[(\text{SC}_4\text{H}_8)_3\text{-C}_4\text{H}_7]^+$, $(\text{SSC}_4\text{H}_8)^+$ and (*R*)-2-methylthietane. GC–MS of the residues indicated the presence of larger macrocycles, such as $\text{Me}_5\text{20S5}$ and $\text{Me}_6\text{24S6}$, as well as some low-molecular-weight polymer, but the macrocycles' small amounts and similar properties prevented their isolation in pure forms.

4.4. Control experiments

(a) In a control experiment, 0.6 ml (*R*)-2-methylthietane (7.5 mmol) was heated to 100°C for 24 h in the absence of solvent or any added metal complexes. After cooling, the unreacted (*R*)-2-MT was removed in vacuo. The resulting residue was dissolved in methylene chloride and filtered. After removal of the methylene chloride from the collected washings, the total weight of the residue was 3.6 mg. A $^1\text{H-NMR}$ spectrum of this residue indicated that it consisted principally of trace amounts of polymer and **8**.

(b) In a control experiment, 0.6 ml of (*R*)-2-methylthietane (7.5 mmol) and 15.0 mg of $\text{Re}_2(\text{CO})_{10}$ (0.023 mmol) in a 25 ml round-bottomed flask were heated to 100°C for 24 h in the absence of solvent. After cooling, the unreacted (*R*)-2-MT was removed in vacuo. The resulting residue was dissolved in methylene chloride and filtered. After removal of the methylene chloride from the collected washings, the total weight of the residue was 20.5 mg. An IR spectrum of a portion of the residue in the CO region showed only the absorptions of $\text{Re}_2(\text{CO})_{10}$. An analysis of the $^1\text{H-NMR}$ spectrum of this residue indicated that it consisted of trace amounts of polymer and **8**.

4.5. Crystallographic analysis

Colorless crystals of **8** suitable for diffraction analysis were grown by slow evaporation of solvent from a solution in hexane at 25°C. The crystal used for the diffraction measurements was mounted in a thin-walled glass capillary. Diffraction measurements on compound **8** were made on a Siemens CCD area detector-equipped diffractometer with the SMART software (Siemens Corp. Madison, WI). The frame data were integrated using the Siemens SAINT software. 9314 reflections were collected of which 5322 data $> 3\sigma(I)$ were obtained. Crystal data, data-collection parameters, and results of the analyses are listed in Table 1. All data processing was performed either on a Silicon-Graphics INDIGO [2] Workstation by using the TEXSAN structure solving program library obtained from the Molecular Structure Corp., The Woodlands, TX. Neutral atom scattering factors were calculated by the standard procedures [11a]. Anomalous dispersion corrections were applied to all non-hydrogen atoms [11b]. Lorentz/polarization (L_p) corrections were applied to the data for each structure. Full-matrix least-squares refinements minimized the function:

$\sum_{hkl} w (|F_{\text{obs.}}| - |F_{\text{calc.}}|)^2$, where $w = 1/\sigma(F)^2$. $\sigma(F) = \sigma(F_{\text{obs.}}^2)/2F_{\text{obs.}}$ and $\sigma(F_{\text{obs.}}^2) = [\sigma(I_{\text{raw}})^2 + (0.02 I_{\text{net}})^2]^{1/2}/L_p$.

Compound **8** crystallized in the orthorhombic crystal system. The space group $P2_12_12$ was established from the pattern of systematic absences observed during the collection of intensity 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 positions of the hydrogen atoms on the $\text{Me}_3\text{I}_2\text{S}_3$ 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. Refinement of the enantiomorph with the (*R,R,R*)-molecule converged with the *R*-factors $R_1 = 0.0395$ and $R_2 = 0.0457$. Refinement of this enantiomer with 2304 selected reflections yielded a Flack parameter of $-0.1(1)$ indicating that this is the correct enantiomorph. Refinement of the enantiomorph containing the (*S,S,S*)-molecule converged with the *R*-factors $R_1 = 0.0401$ and $R_2 = 0.0462$. Refinement of this enantiomer yielded a Flack parameter of $1.1(1)$. The former was thus clearly indicated to be correct and was retained.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 133355. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK [Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk, or www: <http://www.ccdc.cam.ac.uk>].

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