Catalytic Transformations of Thiiranes by (Thiirane)W(CO)$_5$ Complexes

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The thiirane complexes W(CO)$_5$($\overline{\text{SCH}_2\text{CH}_2}$), **1**, W(CO)$_5$(*cis*-$\overline{\text{SCHMeCHMe}}$), **2**, and W(CO)$_5$(*trans*-$\overline{\text{SCHMeCHMe}}$), **3**, have been prepared and characterized. The molecular structure of compound **2** was also determined crystallographically. It was found to contain an S-coordinated *cis*-dimethylthiirane ligand with a pyramidal sulfur atom coordinated to a W(CO)$_5$ group. Compounds **1**−**3** decompose slowly to yield sulfur and the corresponding olefin. Compound **1** and W(CO)$_5$(NCMe) were both found to transform free thiirane into a mixture of cyclic polydisulfides $(SCH_2CH_2S)_n$, **4**−**7**, n = 2, 3, 4, and 5, and ethylene, catalytically. The turnover frequency for the formation of **4** by **1** at 25°C is 6.8 h^{-1}. When the catalytic reaction was performed in the presence of dimethylacetylenedicarboxylate, DMAD, compounds **4** and **5** and the six-membered heterocycle $\overline{\text{SCH}_2\text{CH}_2\text{SC(CO}_2\text{Me)C}}$(CO$_2$Me), **8** were formed, the last by the trapping of a suspected SCH_2CH_2S intermediate. Small amounts of polythioether macrocycles $(CH_2CH_2S)_n$, **12S4**, n = 4, and **15S5**, n = 5, were also formed. (2*R*,3*S*)-dimethylthiirane (*cis*-DMT) and (2*R*,3*R*(2*S*,3*S*))-dimethylthiirane (*trans*-DMT) undergo a combination of isomerization and desulfurization to yield a mixture of *cis*- and *trans*-butene by **2** and **3**, respectively. In the presence of DMAD, the isomerization of the substituted thiiranes is suppressed and small amounts of the cyclic disulfides [$\overline{\text{C(H)CH}_3\text{C(H)CH}_3\text{SS}}$]$_3$, **9**, and [$\overline{\text{C(H)CH}_3\text{C(H)SS}}$]$_2$, **10**, and the cyclic trisulfide (4*S*,5*S*(4*R*,5*R*))-[S$_3$C(H)CH$_3$C(H)CH$_3$], **12**, were formed. The molecular structure of **9** was determined crystallographically and established a pattern of identical *R*,*R*/*S*,*S* stereochemistries at adjacent stereogenic carbon atoms about the ring. A similar stereochemical result was indicated for the stereogenic carbon centers in **12** by preparing the osmium complex Os$_2$(CO)$_6$[μ-(*R*,*R*(*S*,*S*))-SC(H)CH$_3$C(H)CH$_3$S], **13**, from it and determining the configurations at the stereogenic carbon atoms in the SC(H)CH$_3$C(H)CH$_3$S ligand by an X-ray crystallographic analysis. All of the catalytic transformations can be explained by a back-side addition of a sulfur atom from an uncoordinated molecule of thiirane to a carbon atom of a thiirane ligand. This leads to an opening of the thiirane ligand and formation of a zwitterionic thiiranium/thiolato intermediate having the thiolato sulfur atom coordinated to the tungsten atom. Release of the added thiirane from a conformer for the zwitterion would result in isomerization of the thiirane ligand. Alternatively, loss of olefin from the thietanium ion group would yield a (SCH$_2$CH$_2$S)W(CO)$_5$ intermediate that could decompose by loss of SCH$_2$-CH$_2$S groups, which could then combine to form the cyclic disulfides, **4**−**7**. In the presence of DMAD, the SCH_2CH_2S group is trapped to yield **8**. A series of similar ring-opening additions followed by a cyclization could lead to the formation of the polythioether macrocycles **12S4** and **15S5**, but these compounds are minor products even under the best conditions. It was also found that compound **4** has moderate antimicrobial activity toward *Escherichia coli*.

Introduction

Thiiranes exhibit considerable reactivity due in part to their ring strain, which has been estimated to be 19 kcal/mol in the parent molecule.[1] They are readily polymerized when treated with Lewis acids and Lewis bases,[2] and when heated, they are desulfurized to yield elemental sulfur and the corresponding olefin.[2b−d,3] The desulfurization of thiiranes is promoted by complexation to transition metal atoms and adsorption on metal surfaces.[4,5] These reactions can be very fast on a metal surface, even though theoretical studies have shown

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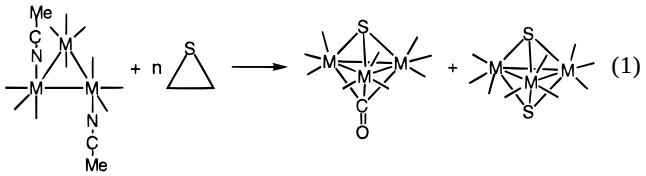
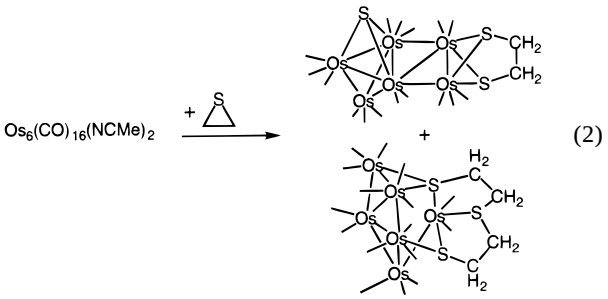
that the concerted elimination of an olefin from a thiirane−metal complex is a forbidden reaction.[6]

Thiirane has been shown to be a good source of monatomic sulfur and has been used for the synthesis of metal cluster complexes.[4a,7] For example, the reaction of thiirane with $M_3(CO)_{10}(NCMe)_2$ (M = Ru, Os) produces mono- and disulfido transition metal cluster complexes (eq 1).[4a]



(1)

It has also been shown that thiirane can react with metal clusters without the complete elimination of the hydrocarbon fragment, as shown by the formation of complexes containing dithiolato ligands from the reactions of thiirane with $Os_6(CO)_{17}(NCMe)$ and $Os_6(CO)_{16}(NCMe)_2$ (eq 2).[8]



(2)

Prior to this work, only two transition metal complexes containing episulfide ligand groupings had been isolated and characterized by a single-crystal X-ray diffraction analysis: $Cr(CO)_4$(*cis*-1,4-cyclohexadiene bis-(episulfide))[9] and $[Cp(PPh_3)_2Ru(\overline{SCH_2CH_2})][OSO_2CF_3]$.[10]

We have now investigated the reactions of thiirane, 2*R*,3*S*-dimethylthiirane (*cis*-DMT), and 2*R*,3*R*(2*S*,3*S*)-dimethylthiirane (*trans*-DMT) with $W(CO)_5(NCMe)$. We have found that these reactions lead to the formation of a new series of thiirane complexes $W(CO)_5(L)$, L = $\overline{SCH_2CH_2}$ (**1**), *cis*-DMT (**2**), and *trans*-DMT (**3**). In the presence of thiirane, compound **1** produces the cyclic disulfides $(SCH_2CH_2S)_2$, **4**, $(SCH_2CH_2S)_3$,[1] **5**, $(SCH_2CH_2S)_4$, **6**, and $(SCH_2CH_2S)_5$, **7**, with a concomitant formation of ethylene, catalytically. The substituted thiiranes are isomerized in the presence of **2** and **3**, and the substituted cyclic disulfides can be obtained in small amounts when $MeO_2CC{\equiv}CCO_2Me$, DMAD, is added to the reaction solutions. In this report, the results of our studies of the synthesis and characterization of these complexes and their reactions with additional quantities of the thiiranes and mixtures of thiiranes with DMAD are presented. A preliminary report of this work has been published.[11]

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. Thiirane and $MeO_2CC{\equiv}CCO_2Me$ (DMAD) were purchased from Aldrich. The DMAD was used without further purification. $W(CO)_6$ was purchased from Strem Chemicals and was used without furthur purification. $W(CO)_5(NCMe)$,[12a] $Cr(CO)_5(NCMe)$,[12a] $Os_3(CO)_{10}(NCMe)_2$,[12b] (2*R*,3*S*)-dimethylthiirane (*cis*-DMT),[12c] and (2*R*,3*R*(2*S*,3*S*))-dimethylthiirane (*trans*-DMT)[12c] were synthesized by known procedures. All thiiranes were vacuum distilled before each use. Thin layer chromatography (TLC) separations were performed in air by using silica gel (60 Å, F_{254}) on plates (Analtech, 0.25 mm). Elemental analyses were performed by Oneida Research Sevices, Whitesboro, NY. Mass spectra were collected using a VG SE-70 in the direct inlet mode using electron impact ionization. Spin simulations were performed using the Acorn NMR, Inc. program "Nuts NMR Data Processing Software" in the iteration mode on an IBM compatible computer.

Synthesis of $W(CO)_5(\overline{SCH_2CH_2})$, 1. $W(CO)_5(NCMe)$ (200.0 mg, 0.570 mmol) was allowed to react with 60 μL of thiirane (1.0 mmol) in 100 mL of hexane solvent for 48 h at 25 °C. The solvent was removed, and the residue was separated on silica gel by column chromatography using a CH_2Cl_2/hexane (1/4) solvent mixture. Three bands were separated in order of elution: 10.3 mg of $W(CO)_6$, 25.3 mg of $W(CO)_5(\overline{SCH_2CH_2})$ (**1**) (12%), and 90.4 mg of unreacted $W(CO)_5(NCMe)$. Spectral data for **1**. IR, ν_{CO} (cm^{-1}, hexane): 2077 (w), 1947 (s), 1936 (m). ^1H NMR (δ, $CDCl_3$): 2.96 (4H, $^3J_{H-H(cis)}$ = 7.75 Hz, $^3J_{H-H(trans)} = -2.72$ Hz, $^2J_{H-H} = 8.23$ Hz), 2.68 (4H, ^3J-$J_{H-H(cis)}$ = 7.75 Hz, $^3_{H-H(trans)} = -2.72$ Hz, $^2J_{H-H} = 8.23$ Hz). ^{13}C NMR (δ, CD_2Cl_2): 198.3 (s, 1C), 197.4 (s, 4C), 31.5 (s, 2C). MS (*m*/*e*): 384, 356, 328, 300, 272, 244, 216 = $M^+ - (xCO + C_2H_4)$, $x = 1-5$.

Synthesis of $W(CO)_5$(cis-DMT), 2. A 100.0 mg amount of $W(CO)_5(NCMe)$ (0.285 mmol) was placed in to a 50 mL round-bottom flask. Dry hexane (10 mL) and 100 μL of *cis*-DMT (1.1 mmol) were added, and the solution was allowed to stir at 25 °C for 19 h. The solvent was removed *in vacuo*, and the residue was separated by column chromatography on silica gel using a 1/4 CH_2Cl_2/hexane solvent mixture. Two yellow bands eluted: $W(CO)_5$(*cis*-DMT), **2** (43.1 mg, 37% yield), and unreacted $W(CO)_5(NCMe)$ (57.3 mg). Spectral data for $W(CO)_5$-((2*R*,3*S*)-dimethylthiirane), **2**. IR, ν_{CO} (cm^{-1}, hexane): 2075 (w), 1940 (vs), 1931 (m). ^1H NMR (δ, $CDCl_3$): major isomer 3.28 (2H, $^3J_{H-H} = 6.09$ Hz, $^4J_{H-H} = -0.26$ Hz, $^5J_{H-H} = 0.05$ Hz, $^2J_{H-H'} = 8.04$ Hz), 1.55 (6H, $^3J_{H-H} = 6.09$ Hz, $^4J_{H-H}$ =

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−0.26 Hz, $^5J_{H-H}$ = 0.05 Hz, $J_{H-H'}$ = 8.04 Hz); minor isomer 3.16 (m, 2H), 1.46 (2H); ratio major isomer/minor isomer = 14/1. ^{13}C NMR (δ, CD_2Cl_2): 198.79 (1CO), 197.59 (4CO), 51.66 (2C), 14.88 (2C). Anal. Calcd (found) for **2**: C, 26.16 (26.04); H, 1.94 (1.88).

Synthesis of W(CO)$_5$(trans-DMT), 3. A 200.0 mg amount of W(CO)$_5$(NCMe) (0.570 mmol) was placed in a 50 mL round-bottom flask. Dry hexane (10 mL) and 100 μL of *trans*-DMT (1.1 mmol) were added, and the solution was allowed to stir at 25 °C for 20 h. The solvent was removed *in vacuo*, and the resulting residue was separated by column chromatography on silica gel with a 1/4 CH_2Cl_2/hexane solvent mixture. Two yellow bands separated: W(CO)$_5$(*trans*-DMT) (70.3 mg, 30%) and unreacted W(CO)$_5$(NCMe) (88.2 mg). Spectral data for **3**. IR, ν_{CO} (cm^{-1}, hexane): 2075 (w), 1945 (vs), 1940 (s), 1931 (m). ^{1}H NMR (δ, $CDCl_3$): 2.81 (1H, dq, $^3J_{H-H}$ = 7.6 Hz, $^3J_{H-H}$ = 5.7 Hz), 2.77 (1H, dq, J_{H-H} = 7.6 Hz, $^3J_{H-H}$ = 5.7 Hz), 1.64 (3H, d, $^3J_{H-H}$ = 5.7 Hz), 1.56 (3H, d, $^3J_{H-H}$ = 5.7 Hz). ^{13}C NMR (δ, CD_2Cl_2, aliphatic region): 52.7 (1C), 46.9 (1C), 20.8 (1C), 19.7 (1C). Anal. Calcd (found) for **3**: C, 26.16 (25.70); H, 1.94 (1.93).

Catalytic Transformations of Thiirane by W(CO)$_5$(NCMe). (a) In a CH_2Cl_2 Solution. A solution consisting of 2.0 mL of thiirane, 1.0 mL of CH_2Cl_2, and 10.0 mg of W(CO)$_5$(NCMe) in a 10 mL round-bottom flask was stirred at 25 °C for 6 h. After removal of the volatile components, the residue was extracted with CH_2Cl_2 to yield a residue (290.1 mg) after removal of the extraction solvent. Separation by TLC on silica gel yielded the following compounds: 190.1 mg (66%) of $(SCH_2CH_2S)_2$,[13a] **4**, 45.3 mg (16%) of $(SCH_2CH_2S)_3$,[13b] **5**, 17.0 mg (6%) of $(SCH_2CH_2S)_4$,[13c] **6**, and 15.2 mg (5%) of $(SCH_2CH_2S)_5$, **7**. Spectral data for **4**. ^{1}H NMR (δ, $CDCl_3$): 3.14 (8H). ^{13}C NMR (δ, $CDCl_3$): 37.8 (s, 4C). MS (*m*/*e*) calcd (found): 183.9509 (183.9507). Spectral data for **5**. ^{1}H NMR (δ, $CDCl_3$): 3.17 (12H). ^{13}C NMR (δ, $CDCl_3$): 39.5 (s, 6C). MS (*m*/*e*) calcd (found): 275.9263 (275.9272). Spectral data for **6**. ^{1}H NMR (δ, $CDCl_3$): 3.07 (16H). ^{13}C NMR (δ, $CDCl_3$): 39.1 (s, 8C). MS (*m*/*e*) calc (found): 367.9018 (367.9018). Spectral data for **7**. ^{1}H NMR (δ, $CDCl_3$): 3.03 (20H). ^{13}C NMR (δ, $CDCl_3$): 38.6 (s, 10C). MS (*m*/*e*) Calcd (found): 459.8772 (459.8768). There were no significant differences in the results when the reaction was performed in complete darkness or in the presence of room light.

(b) In the Absence of Solvent. A 10.0 mg amount of W(CO)$_5$(NCMe) was dissolved in 1.0 mL of pure thiirane in a 50 mL round-bottom flask. The solution was allowed to stir at 25 °C for 6 h. The remaining thiirane was then removed *in vacuo*. From this residue, 358.4 mg of the product mixture was extracted with CH_2Cl_2. A ^{1}H NMR spectrum of this extract showed the following products (% yield based on integration of the appropriate resonances): **4** (64%), **5** (7%), **6** (20%), and **7** (9%).

Reaction of W(CO)$_5$(NCMe) and Thiirane Followed by NMR Spectroscopy. A 10.1 mg amount of W(CO)$_5$(NCMe) was placed in a NMR tube with 500 μL of CD_2Cl_2 and 100 μL of thiirane. The reaction was allowed to stand at 25 °C for 24 h. After this time, a NMR spectrum was recorded and the resulting spectrum showed the resonances of **4**−**7**, plus a prominent singlet at 5.39 ppm (in CD_2Cl_2) which corresponds to the position of free ethylene.

Long-Term Trial of W(CO)$_5$(NCMe). A 10.0 mL amount of thiirane was placed into a 100 mL flask with 20.0 mg (0.057 mmol) of W(CO)$_5$(NCMe). This solution was stirred at 25 °C for 48 h. The solution was then dried *in vacuo*, and 5.01g of a brown residue was isolated. This solid was dissolved with 75 mL of CH_2Cl_2 and filtered. The filtrate was dried *in vacuo*, and a brown solid was isolated (4.38 g). A ^{1}H NMR spectrum of this residue showed the products **4**, **5**, **6**, and **7** were present in the relative amounts of 56%, 27%, 13%, and 4%, respectively. This is equivalent to a total of 233.6 turnovers for **4** and a turnover frequency of 4.8 turnovers/h.

Catalytic Transformations of Thiirane by 1. Thiirane (2.0 mL) and 1 mL of CH_2Cl_2 were placed into a 100 mL flask with 10.0 mg (0.029 mmol) of **1**. This solution was stirred at 25 °C for 6 h. The volatiles were then removed *in vacuo* to leave 334 mg of brown residue. This residue was extracted with 20 mL of CH_2Cl_2 and filtered, and the solvent was removed *in vacuo* to yield 310 mg of brown solid. A ^{1}H NMR spectrum of this solid showed that it consisted of **4**, **5**, **6**, and **7** in the relative amounts of 70%, 13%, 8%, and 9%, respectively. For **4**, this corresponds to a total of 217 mg (41 turnovers) and a turnover frequency of 6.8 h^{-1}.

Transformations of Thiirane by W(CO)$_6$. A 10.0 mg amount of W(CO)$_6$ was placed into a 10 mL round-bottom flask. Thiirane (1.0 mL) and 1 mL of CH_2Cl_2 were added, and the solution was allowed to stir at 25 °C for 6 h. A very small amount of white solid (4.1 mg) remained in the flask after removal of the volatiles. This was shown by a combination of mass spectral and ^{1}H NMR analyses to be a mixture of four known compounds: 1,4,7-trithiacyclononane, **9S3**, 1,4,7,10-tetrathiacyclododecane, **12S4**, 1,4,7,10,13-pentathiacyclopentdecane, **15S5**, and 1,4,7,10,13,16-hexathiacyclooctadecane, **18S6**. None of the compounds **4**−**7** were present.

Catalytic Transformations of Thiirane by Cr(CO)$_5$(NCMe). A 10.0 mg amount of Cr(CO)$_5$(NCMe) and 1.0 mL of pure thiirane were stirred for 6 h at 25 °C. Only 28.1 mg of product was formed. This was shown by ^{1}H NMR analysis to consist of **4** (75%), **5** (8%), **6** (3%), and **7** (13%).

Decomposition of W(CO)$_5$(*cis*-DMT), 2. Compound **2** (20.0 mg, 0.0486 mmol) was placed into a NMR tube with 500 μL of CD_2Cl_2. C_6Me_6 (10.0 mg) was added to serve as a quantitative reference. The solution was maintained at 25 °C for 48 h. At this time, *cis*-2-butene (3.0 mg, 0.0519 mmol) was observed by ^{13}C NMR. There was no evidence for the formation of **3**. The NMR tube was emptied and the volatile components were removed to yield 20.3 mg of residue, which was dissolved in CH_2Cl_2 and separated by TLC with pure hexane as the eluting solvent to yield: S_8 (0.6 mg, 0.002 mmol), W(CO)$_6$ (3.2 mg, 0.0091 mmol), and 5.0 mg of **2**.

Decomposition of W(CO)$_5$(*trans*-DMT), 3. A 20.0 mg amount of **3** (0.0486 mmol) was placed into a NMR tube with 0.50 mL of CD_2Cl_2. C_6Me_6 (10.0 mg) was added to serve as a quantitative reference. The solution was shaken and maintained at 25 °C for 74 h. During this time, the formation of *trans*-2-butene (0.9 mg, 0.017 mmol), but no *cis*-2-butene, was observed by ^{13}C NMR. There was no evidence for the formation of **2**. The NMR tube was emptied and the volatile components were removed to yield 19.1 mg of residue, which was dissolved in CH_2Cl_2 and separated by TLC to yield: S_8 (0.7 mg, 0.003 mmol), W(CO)$_6$ (8.1 mg, 0.0231 mmol), and **3** (4.0 mg, 0.0097 mmol).

Catalytic Transformations of *cis*-DMT by 2. A 20.0 mg amount of **2** was placed in a NMR tube and 500 μL of CD_2Cl_2 and 500 μL of *cis*-DMT were added. C_6Me_6 (10.0 mg) was added to serve as a quantitative reference. The sample was shaken and then placed in a water bath at 25 °C for 48 h. The formation of *cis*- and *trans*-2-butene and *trans*-DMT were measured by ^{13}C NMR spectroscopy by integration of the appropriate resonances: *cis*-2-butene (127 mg, 2.26 mmol) δ = 124.0 (2C), 12.4 (2C), *trans*-2-butene (25 mg, 0.44 mmol) δ = 126.0 (2C), 17.9 (2C), and *cis*-DMT (16 mg, 0.18 mmol) and *trans*-DMT (143 mg, 1.62 mmol) δ = 39.9 (2C), 21.7 (2C). At the end of the period, the NMR tube was emptied and the volatiles were removed. The residue (88.3 mg) was separated by TLC to yield: S_8 (40.3 mg, 0.16 mmol), W(CO)$_6$ (4.1 mg, 0.011 mmol), and **2** (10.1 mg, 0.025 mmol).

Catalytic Transformations of *trans*-DMT by 3. A 20.0 mg of W(CO)$_5$(*trans*-DMT), **3**, was placed in a NMR tube, and 500 μL of CD_2Cl_2 and 500 μL of *trans*-DMT were added. The solution was placed in a water bath at 25 °C for 74 h. After this period, the compounds *cis*-2-butene (134 mg, 2.39 mmol), *trans*-2-butene (95 mg, 170 mmol), *cis*-DMT (1.5 mg, 0.017

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mmol), and *trans*-DMT (468 mg, 5.32 mmol) were observed by ^{13}C NMR spectrocopy. The NMR tube was emptied and the volatile components were removed to yield a residue of 106.1 mg, which was separated by TLC to yield three bands: S_8 (24.3 mg, 0.094 mmol), $W(CO)_6$ (14.1 mg, 0.039 mmol), and the starting complex **3** (4.1 mg, 0.010 mmol).

Catalytic Transformations of Thiirane by $W(CO)_5$(NCMe) in the Presence of $MeO_2CC\equiv CCO_2Me$. A solution of thiirane (1.0 mL), $MeO_2CC\equiv CCO_2Me$ (1.0 mL), and $W(CO)_5$(NCMe) (10.0 mg) was allowed to stir at 25 °C for 6 h in a 10 mL round-bottom flask. The volatiles were removed, and the residue was extracted with CH_2Cl_2 and then separated by TLC on silica gel using hexane solvent to yield **4** (11.3 mg) and **5** (7.1 mg). The base line was removed with acetone and yielded 20.2 mg 1,4,7,10-tetrathiacyclododecane (**12S4**) when it was concentrated. The mother liquor from this crystallization was then separated by TLC using a 1/1 hexane/CH_2Cl_2 solvent mixture to yield, in order of elution an additional 10.1 mg of **12S4**, 8.2 mg of **15S5**, and 58.5 mg of $\overline{SCH_2CH_2SC(CO_2Me)C(CO_2Me)}$, **8**.

Catalytic Transformations of *cis*-DMT by 2 in the Presence of $MeO_2CC\equiv CCO_2Me$. A 10.0 mg amount of **2** was combined with 200 μL of DMAD, 200 μL of CD_2Cl_2, 200 μL of *cis*-DMT, and 10.0 mg of C_6Me_6 (to serve as a quantitative internal reference) in a NMR tube. This solution was shaken by hand and then maintained at 25 °C for 48 h. After this period, a ^{13}C NMR spectrum was recorded and it showed signals representing *cis*-butene (53 mg, 0.95 mmol) and (4*R*,5*R*(4*S*,5*S*))-[$S_3C(H)CH_3C(H)CH_3$], **12** (49 mg, 0.32 mmol). There were no detectable quantities of *trans*-DMT or *trans*-2-butene.

Catalytic Transformations of *cis*-DMT by 2 in the Presence of $MeO_2CC\equiv CCO_2Me$. A 10.0 mg amount of **2** was combined with 1.0 mL of DMAD, 1.0 mL of CH_2Cl_2, and 1.0 mL of *cis*-DMT for 48 h at 25 °C. The volatiles were removed *in vacuo* to yield 310.2 mg of oily residue.

(a) Workup. The residue was then separated by TLC on silica gel by using hexane solvent. Six bands were separated. In order of elution, the first four bands were identified as sulfur (2.1 mg, 0.0082 mmol), $[\overline{C(H)CH_3C(H)CH_3SS}]_3$, **9** (10.3 mg, 0.028 mmol), $[\overline{C(H)CH_3C(H)CH_3SS}]_2$, **10** (9.3 mg, 0.038 mmol), and DMAD (50.3 mg, 0.342 mmol). Bands 5 and 6 were small and were not characterized. The base line of the plate was washed off with acetone. The base line fraction was separated by TLC in a second attempt by using pure CH_2Cl_2 to give **11** (48.2 mg, 0.0803 mmol). Spectral data for **9**. ^1H NMR (δ, $CDCl_3$): 3.60 (bs, 2H), 3.28 (dt, 2H), 3.05 (bs, 2H), 1.36 (d, 6H), 1.29 (d, 6H), 1.20 (d, 6H). ^{13}C NMR (δ, CD_2Cl_2 at 25 °C): 49.7 (4C), 48.6 (2C), 16.0 (4C), 15.9 (2C). MS Calcd (found): 360.0202 (360.0195). Spectral data for **10**. ^1H NMR (δ, $CDCl_3$): 3.28 (dt, 2H), 2.57 (bs, 2H), 1.50 (d, 6H), 1.30 (d, 6H). ^{13}C NMR (δ, CD_2Cl_2 at room temperature): 52.5 (bs, 6C), 20.5 (4C), 15.9 (2C). ^{13}C NMR (δ, CD_2Cl_2, −90 °C): 45.0 (6C), 21.6 (6C). MS Calcd (found): 240.0135 (240.0133). Spectral data for **11**. ^1H NMR (δ, $CDCl_3$): 3.90 (s, 3H), 3.89 (s, 3H), 3.83 (s, 3H), 3.78 (s, 3H), 3.75 (s, 3H), 3.70 (s, 3H), 3.66 (s, 3H), 3.65 (s, 3H) ^{13}C NMR (δ, $CDCl_3$, room temperature): 166.6 (1C), 165.3 (1C), 164.90 (1C), 163.8 (1C), 163.4 (1C), 161.4 (2C), 161.3 (1C), 143.2 (1C), 141.5 (1C), 137.6 (1C), 133.2 (2C), 127.6 (1C), 125.9 (1C), 113.7 (1C) 56.4 (1C), 54.1 (2C), 53.5 (1C), 53.4 (1C), 53.3 (1C), 53.0 (1C), 52.7 (1C). Anal. Calcd (found): C, 48.00 (47.87); H, 4.00 (3.90).

(b) Alternative Workup. The oily residue can alternatively be separated by preparative GC (10 m, 15% SE-30, column temperature of 125 °C) to yield 9.1 mg of (4*S*,5*S*(4*R*,5*R*))-[$S_3C(H)CH_3C(H)CH_3$], **12**, as a yellow liquid. Spectral data for **12**. ^1H NMR (δ, $CDCl_3$): 3.50 (dq, 2H, $^3J_{H-H}$ = 6.80 Hz, $^3J_{H-H}$ = 4.40 Hz, $^4J_{H-H}$ = −0.15 Hz, $^4J_{H-H}$ = 0.05 Hz), 1.46 (dd, 6H, $^3J_{H-H}$ = 6.80 Hz, $^3J_{H-H}$ = 4.40 Hz, $^4J_{H-H}$ = −0.15 Hz, $^4J_{H-H}$ = 0.05 Hz). ^{13}C NMR (δ, CD_2Cl_2): 45.0 (6C), 21.6 (6C). MS Calcd (found): 151.9788 (151.9788).

Table 1. Bioactivity Test Results for 2 and 3

microorganism	**2**, 200 μg/disk zone of inhibition	**3**, 200 μg/disk zone of inhibition
E. Coli	7 mm	3 mm
M. Luteus	2 mm	1 mm
B. Cereus	3 mm	1 mm

Reaction of 12 with $Os_3(CO)_{10}(NCMe)_2$. The sample of **12** obtained in the preceding reaction (9.1 mg, 0.0591 mmol) was allowed to react with 115 mg (0.123 mmol) of $Os_3(CO)_{10}(NCMe)_2$ in 50 mL of CH_2Cl_2 at reflux for 20 h. After this time, the solvent was removed *in vacuo* and the residue was separated by TLC on silica gel using hexane solvent. Six bands were eluted. The principal products were contained in the first band $Os_2(CO)_6$[μ-(*R*,*R*(*S*,*S*))-$SC(H)CH_3C(H)CH_3S$], **13** (14.1 mg, 34%), and the last band was $Os_3(CO)_{10}(\mu$-S),[14] 17.2 mg (30%). Bands 2−5 were obtained in small amounts and could not be fully characterized. Spectral data for **13**. IR, ν_{CO} (cm^{-1}, hexane): 2084 (m), 2053 (vs), 2006 (vs), 1989 (s), 1979 (m). ^1H NMR (δ, $CDCl_3$): 1.97 (m, 2H), 1.37 (m, 6H). Anal. Calcd (found): C, 17.95 (17.82); H, 1.20 (1.15).

Attempted Reaction of Dimethyl Acetylenedicarboxylate with Thiirane in the Absence of Tungsten. DMAD (1.0 mL) and 1.0 mL of thiirane were stirred at 25 °C for 48 h. At the end of this period, the solvent was removed *in vacuo* and a NMR of the residue was taken. The spectrum showed no evidence for the formation of compound **4**.

Attempted Reaction of Dimethyl Acetylenedicarboxylate with 4 in the Presence of $W(CO)_5$(NCMe). A 100 mg amount of **4** was placed into a 50 mL round-bottom flask with 500 μL of DMAD and 10.0 mg of $W(CO)_5$(NCMe), and the mixture was stirred at 25 °C for 24 h. At the end of this period, the solvent was removed *in vacuo* and a NMR of the residue was taken. The spectrum showed no evidence for the formation of compound **8**.

Stability Test of *trans*-DMT in the Absence of Catalyst. A 100 μL amount of (2*R*,3*R*(2*S*,3*S*))-dimethylthiirane was placed into a NMR tube with 500 μL of CD_2Cl_2 and allowed to stir at 25 °C for 48 h. ^1H NMR spectra acquired at the start and finish of the time period were identical.

Stability Test of *cis*-DMT in the Absence of Catalyst. A 100 μL amount of 2*R*,3*S*-dimethylthiirane was placed into a NMR tube with 500 μL of CD_2Cl_2 and allowed to stir at 25 °C for 48 h. ^1H NMR spectra acquired at the start and finish of the time period were identical.

Stability Test of *trans*-DMT in the Presence of $W(CO)_6$. A 10.0 mg amount of $W(CO)_6$ was placed into a NMR tube. (2*R*,3*R*(2*S*,3*S*))-Dimethylthiirane (100 μL) and 500 μL of CD_2Cl_2 were added. The solution was allowed to stir at 25 °C for 48 h. ^1H NMR spectra acquired at the start and finish of the time period were identical.

Stability of 2*R*,3*S*-Dimethylthiirane in the Presence of $W(CO)_6$. A 100 μL amount of $W(CO)_6$ was placed into a NMR tube. *cis*-DMT (100 μL) and 500 mL of CD_2Cl_2 were added. The solution was allowed to stir at 25 °C for 48 h. ^1H NMR spectra acquired at the start and finish of the time period were identical.

Bioactivity Assay. Compounds **4** and **5** were tested for their antimicrobial activity using a standard disk diffusion assay. The compounds were applied to 6 mm cotton disk using CH_2Cl_2 at varying concentrations. The air-dried disks were placed on a lawn of tester microorganisms, which had been prepared by inoculation of a bed of LB (Luria−Bertani) agar. At 200 μg/disk, **4** exhibited moderate activity against *Escherichia coli*, producing a 7 mm zone of inhibition and a weak activity against both *Micrococcus luteus* and *Bacillus cereus* (2 mm zone and 3 mm zone, respectively). Compound **5** showed less activity, displaying 3, 1, and 1 mm zones of inhibition against *E. coli*, *M. luteus*, and *B. cereus*, respectively. Both **4** and **5** were inactive at 100, 50, 20, 2, and 0.5 μg/disk.

(14) Adams, R. D.; Horvath, I. T.; Kim, H. S. *Organometallics* **1989**, *3*, 548.

Table 2. Crystallographic Data for Compounds 2, 9, 11, and 13

	2	9	11	13
formula	$WSC_9O_5H_8$	$S_6C_{12}H_{24}$	$SO_{16}C_{24}H_{24}$	$Os_2S_2O_6C_{10}H_8$
fw	412.07	360.68	600.50	668.69
cryst syst	monoclinic	orthorhombic	monoclinic	monoclinic
lattice params				
a (Å)	5.828(1)	10.142(8)	19.853(4)	9.836(1)
b (Å)	18.204(2)	10.161(5)	17.281(2)	10.152(2)
c (Å)	11.998(2)	18.04(1)	8.148(2)	16.186(2)
β (deg)	91.672(1)	90.00	101.5(3)	98.998(1)
V (Å^3)	1272.4(3)	1860(2)	2739.4(1)	1596.3(4)
space group	$P2_1/n$ (No. 14)	$P2_12_12_1$ (No. 19)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
Z	4	4	4	4
ρ_{calcd} (g/cm^3)	2.15	2.58	1.49	2.78
μ (Mo Kα) (cm^{-1})	92.54	14.42	1.96	161.72
temp (°C)	20	20	20	20
$2\theta_{max}$ (deg)	51	47	45	46
no. of obsd rflns ($I > 3\sigma(I)$)	1720	1814	2242	1721
no. variables	178	163	371	182
goodness of fit	1.39	4.05	2.00	1.67
max shift/error on final cycle	0.12	0.00	0.00	0.00
residuals: R; R_w[a]	0.024; 0.025	0.087; 0.086	0.047; 0.044	0.032; 0.032
abs cor	empirical	DIFABS	empirical	empirical
transmissn coeff, max/min	1.00/0.29	1.00/0.390	1.00/0.93	1.00/0.38
largest pk in final diff (e$^-$/Å^3)	0.5	0.5	0.30	1.2

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

Control disks using solvent only were inactive. All experiments were done in triplicate. Zones of inhibition were measured from the edge of the disk to the edge of the clear zone. The results are presented in Table 1.

Crystallographic Analyses. Yellow crystals of **2** and clear crystals of **11** suitable for X-ray diffraction analysis were grown by slow evaporation of a methylene chloride solution at 25 °C. Clear crystals of **9** suitable for X-ray diffraction analysis were grown by slow evaporation of a 50/50 methylene chloride/ethyl acetate solution at 25 °C. Yellow crystals of **13** suitable for X-ray diffraction analysis were grown by slow evaporation of a 1/1 methylene chloride/hexane solution at 25 °C. The crystals used in the diffraction measurements were mounted inside thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6S automatic diffractometer by using graphite-monochromated Mo Kα radiation. The unit cells were determined 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 on a Silicon Graphics INDIGO2 computer by using the TEXSAN structure solving program library obtained from the Molecular Structure Corp., The Woodlands, TX. Lorentz-polarization (Lp) corrections were applied. Neutral atom scattering factors were calculated by the standard procedures.[15a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[15b] Full-matrix least-squares refinements minimized the function: $\sum_{hkl} w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$ and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02I_{net})^2]^{1/2}/Lp$.

The crystallographic space group $P2_1/n$ was uniquely identified for compounds **2**, **11**, and **13** by the patterns of systematic absences observed during the collection of intensity data. The structures were solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. For compound **2**, all of the hydrogen atoms were located and refined with isotropic thermal parameters. For compounds **11** and **13**, the scattering contributions of the hydrogen atoms were added to the structure factor calculations, but their positions were not refined.

For compound **9**, the crystallographic space group $P2_12_12_1$ was uniquely identified by the patterns 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 scattering contributions of the hydrogen atoms were added to the structure factor calculations, but their positions were not refined.

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

Results

From the reactions of thiirane, (2*R*,3*S*)-dimethylthiirane (*cis*-DMT), and (2*R*,3*R*(2*S*,3*S*))-dimethylthiirane (*trans*-DMT) with $W(CO)_5$(NCMe), we have isolated the series of new complexes, $W(CO)_5(L)$, L = $\overline{SCH_2CH_2}$ (**1**), *cis*-DMT (**2**), and *trans*-DMT (**3**) in the yields 12%, 37%, and 30%, respectively. Compound **1** is the least stable of the three. It has been characterized by IR, ^{1}H NMR, and mass spectrometry. Compounds **2** and **3** were characterized by IR, ^{1}H NMR, and elemental analyses. Compound **2** was also characterized by a single-crystal X-ray diffraction analysis, and an ORTEP diagram of its molecular structure is shown in Figure 1. The *cis*-DMT ligand is coordinated to the tungsten atom through one of the lone pairs of electrons on the sulfur atom. The W−S distance of 2.560(2) Å is similar to the W−S distances found in the related compounds: $W(CO)_5$-($\overline{SCH_2CH_2CH_2}$),[16] 2.540(3) Å; $W(CO)_5$(1,5,9-trithiacyclododecane),[16] 2.564(2) Å; $W(CO)_5[(MeS)_2C{=}PPh_2$-Me],[17] 2.555(2) Å; $W(CO)_5[\overline{SC(H)MeSC(H)MeSC(H)}$-Me],[18] 2.553(6) Å; $W(CO)_5[S(Bu^t)CH_2S(Bu^t)]$,[19] 2.571(5) Å; $W(CO)_5[\overline{SCH_2CH_2NHC{=}OCH_2}]$,[20] 2.551(14) Å. The S−C and C−C distances within the thiirane ligand,

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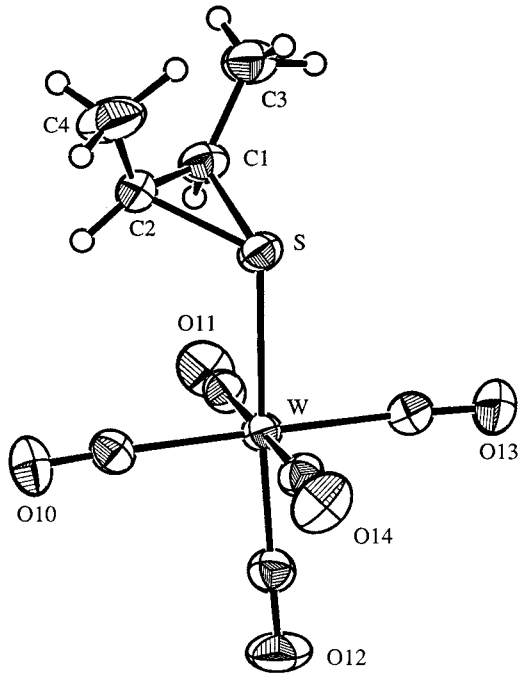
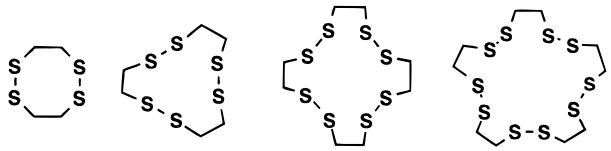


Figure 1. ORTEP diagram of the molecular structure of **2**, showing 40% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg) are as follows: W−S = 2.560(2), S−C(1) = 1.841(7), S−C(2) = 1.835(7), C(1)−C(2) = 1.45(1); W−S−C(1) = 115.1(3), W−S−C(2) = 114.8(3), C(1)−S−C(2) = 46.3(3), S−C(1)−C(2) = 66.6(4), S−C(2)−C(1) = 67.1(4).

S−C(1) = 1.841(7) Å, S−C(2) = 1.835(7) Å, C(1)−C(2) = 1.45(1) Å, are slightly shorter than those found in the *cis*-1,4-cyclohexadiene bis(episulfide) complex: $Cr(CO)_4$-[*cis*-1,4-cyclohexadiene bis(episulfide)], S−C = 1.915(7) and 1.856(7) Å, C(1)−C(2) = 1.513(9) Å.[9] In free thiirane, the S−C and C−C distances are 1.815(3) and 1.484(3) Å, respectively.[21] The sulfur atom has a pyramidal geometry, W−S−C(1) = 115.1(3)° and W−S−C(2) = 114.8(3)°. The methyl groups are directed away *exo* from the tungsten atom in order to minimize the steric interactions with the carbonyl ligands. The presence of a small set of additional resonances observed in the ^1H NMR spectrum indicates that the compound exists in solution as a mixture of two isomers in a 14/1 ratio. The major isomer is presumably the *exo*-isomer, as found in the solid state analysis. The minor isomer presumably has *endo* methyl groups. The H−H coupling constants in the thiirane ligands of all three complexes are similar to those found for the free molecules.[22,23]

Catalytic Transformations of Thiirane. When solutions of **1** or $W(CO)_5$(NCMe) were allowed to stir at 25 °C in the presence of an excess of thiirane, the cyclic disulfides $(SCH_2CH_2S)_2$[13a] (**4**), $(SCH_2CH_2S)_3$[13b] (**5**), $(SCH_2CH_2S)_4$[13c] (**6**), and $(SCH_2CH_2S)_5$ (**7**) were produced catalytically with a concomitant formation of ethylene. From a reaction containing 2.0 mL of thiirane, 1.0 mL of CH_2Cl_2, and 10.0 mg of $W(CO)_5$(NCMe) stirred for 6 h at 25 °C, we were able to isolate 190.1 mg of **4** (66% yield), 45.3 mg of **5** (16% yield), 17.0 mg of **6** (6% yield), and 15.2 mg of **7** (5%). For **4**, this is equivalent to 37.2 catalytic turnovers and a turnover frequency of 6.2 h^{-1}. The turnover frequency for formation of **4** was 6.8 h^{-1} when **1** was used as the catalyst. There was no signifi-

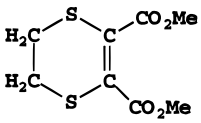


4, 66% **5**, 16% **6**, 6% **7**, 5%

cant difference between the yields when the reactions were performed in room light or in complete darkness. Similar results were obtained when CH_2Cl_2 was omitted; however, in the absence of $W(CO)_5$(NCMe), no cyclic disulfides were formed. Likewise, no cyclic disulfides were formed when the reaction was performed in the presence of $W(CO)_6$. In the complete absence of tungsten, trace amounts of the thioether macrocycles 1,4,7-trithiacyclononane, **9S3**, 1,4,7,10-tetrathiacyclododecane, **12S4**, 1,4,7,10,13-pentathiacyclopentdecane, **15S5**, and 1,4,7,10,13,16-hexathiacyclooctadecane, **18S6**, where formed. These were also formed in trace amounts in the presence of the $W(CO)_6$.

For the sake of comparison, a test of the ability of $Cr(CO)_5$(NCMe) to produce catalytic formation of the cyclic disulfides was performed. Each of the disulfides **4** (75%), **5** (8%), **6** (3%), and **7** (13%) were formed, but the total weight was only 28.1 mg, about $^1/_{10}$ of that obtained when $W(CO)_5$(NCMe) was used.

In an effort to trap possible intermediates, the catalytic reaction was performed in the presence of a large excess of $MeO_2CC{\equiv}CCO_2Me$, DMAD. Under these conditions, compounds **4** and **5** were still obtained, although in much smaller amounts. Curiously, significant amounts of the thioether macrocycles **9S3**, **12S4**, **15S5**, and **18S6** were formed, but most significantly the major product was the known compound $\overline{SCH_2CH_2SC(CO_2Me)C(CO_2Me)}$, **8**.[24] We believe that this is a result



8

of a reaction of DMAD with a SCH_2CH_2S intermediate of some form, since we showed in an independent test that the cyclic disulfide **4** does not react with DMAD to yield **8**, even in the presence of $W(CO)_5$(NCMe). Also, no **8** is formed when thiirane is mixed with DMAD in the absence of $W(CO)_5$(NCMe) or in the presence of $W(CO)_6$ over a period of 24 h at 25 °C.

Catalytic Transformations of *cis*-DMT by 2. A 20.0 mg amount of **2** was dissolved in a solution of 500 μL of CD_2Cl_2 and 500 μL of *cis*-DMT and maintained at 25 °C for 48 h. The reaction was followed by ^{13}C NMR spectroscopy using C_6Me_6 as a quantitative internal reference. During this period, 127 mg (2.26 mmol) of *cis*-2-butene, 25 mg (0.44 mmol) of *trans*-2-butene, and 143 mg (1.62 mmol) of *trans*-DMT were formed. A 40.3 mg (0.16 mmol) amount of elemental sulfur was collected after the removal of the volatiles and separation

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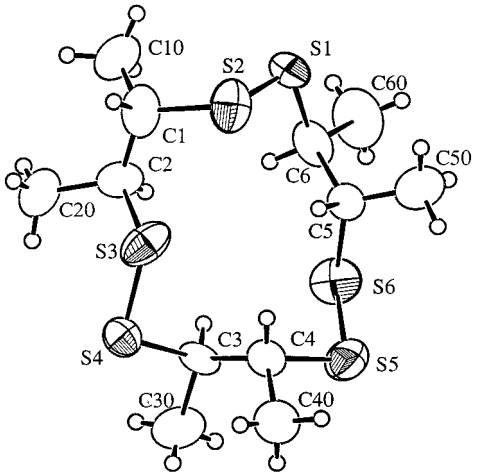


Figure 2. ORTEP diagram of the molecular structure of hexamethyl-1,2,5,6,9,10-hexathiacyclododecane, **9**, showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) as follows: S(1)−S(2) = 2.002(5), S(3)−S(4) = 1.999(5), S(5)−S(6) = 1.994(5), S(1)−C(6) = 1.77(1), S(2)−C(1) = 1.80(1), S(3)−C(2) = 1.94(1), S(4)−C(3) = 1.86(1), S(5)−C(4) = 1.80(1), S(6)−C(5) = 1.87(1), C(1)−C(2) = 1.42(2), C(3)−C(4) = 1.51(1), C(5)−C(6) = 1.50(2).

by TLC. There was no evidence for the formation of any cyclic disulfides under these conditions.

As a control, the decomposition of **2** in the absence of added *cis*-DMT was also determined under similar conditions. In this case, only *cis*-2-butene (45% in situ yield) and elemental sulfur (39% isolated yield) were formed.

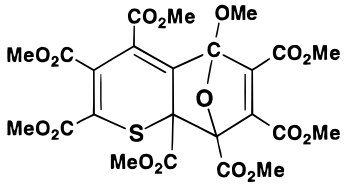
Catalytic Transformations of *trans*-DMT by 3. Similarly, the transformations of *trans*-DMT by **3** were investigated. From a mixture of 20.0 mg of **3** and 500 μL of *trans*-DMT in 500 μL of CD_2Cl_2, *cis*-2-butene (134 mg, 2.39 mmol), *trans*-2-butene (95 mg, 1.70 mmol), and a small amount of *cis*-DMT (1.5 mg, 0.017 mmol) were formed after 74 h at 25 °C, as determined by ^{13}C NMR spectroscopy. After removal of the volatiles, 24.3 mg of elemental sulfur was isolated. There was no evidence for the formation of any cyclic disulfides under these conditions.

The thermal decomposition of 20.0 mg of **3** in the absence of *trans*-DMT was also studied. After 74 h at 25 °C, *trans*-2-butene (33% yield) had formed, but no *cis*-2-butene was observed by ^{13}C NMR spectroscopy. Elemental sulfur was isolated in 45% yield.

Catalytic Transformations of *cis*-DMT by 2 in the Presence of DMAD. When *cis*-DMT and DMAD (1/1 v/v) were treated with **2** for 48 h at 25 °C, three new compounds were isolated by TLC. Two of these were the trimer and dimer of SC(H)MeC(H)MeS, $[\overline{C(H)CH_3C(H)CH_3SS}]_3$, **9**, $[\overline{C(H)CH_3C(H)CH_3SS}]_2$, **10**, and a new heterocycle 2,3,4,5,8,9,10-heptakismethoxycarbonyl-6-methoxy-3,6-oxy-benzothiopyran, **11**, formed by the coupling of four molecules of DMAD with one atom of sulfur. The quantities of these products are not large, so the catalytic activity is not very efficient; however, we feel that the structures and stereochemistries of these products may be mechanistically significant.

Compound **9** was characterized crystallographically, and an ORTEP diagram of its molecular structure is shown in Figure 2. It is indeed the cyclic tris(disulfide), hexamethyl-1,2,5,6,9,10-hexathiacyclododecane. It crystallized in the noncentric space group $P2_12_12_1$ with one formula equivalent in the asymmetric crystal unit. The molecule is chiral, and the crystal is enantiomerically pure. The stereochemistry at the six stereogenic centers has been satisfactorily refined as 3*S*,4*S*,7*R*,8*R*,11*S*,12*S*, but in the absence of a heavy atom, the overall absolute configuration cannot be unambiguously determined, so the alternative configuration 3*R*,4*R*,7*S*,8*S*,11*R*,12*R* is equally possible. One important unambiguous result is that the stereochemistry at neighboring carbon centers is established to be the same, *R*,*R or S*,*S* for all three C_2 pairs. The S−S bond distances, S(1)−S(2) = 2.002(5) Å, S(3)−S(4) = 1.999(5) Å, and S(5)−S(6) = 1.994(5) Å are slightly shorter than those found in the unsubstituted trimer $(SCH_2CH_2S)_3$, **5**, 2.039(1), 2.039(1), and 2.041(1) Å.[25] Conformationally, however, the two rings are different. Although both have *gauche*-torsion angles at each of the S−S bonds, two of the three C−C bonds in **9** have *trans*-torsion angles, while only one of the C−C bonds in **5** has a *trans*-torsion angle. In addition, there are two adjacent bonds C(5)−C(6) and C(5)−S(6) in **9** that have *trans*-torsion angles, while there is no such occurrence in **5**. The ^1H NMR spectrum of **9** at 25 °C shows three doublets of intensity 6H at 1.36, 1.29, and 1.20 ppm and three broad multiplets at 3.60 (2H), 3.28 (2H), and 3.05 (2H) ppm. This can be explained by a dynamical averaging in solution that is rapid on the NMR time scale. Dynamical averaging has been observed for six-membered heterocycles containing disulfide groups.[26] A possible explanation for the low yields of **9** and **10** can be explained by the inherent instability of substituted cyclic disulfides relative to the corresponding polymers.[27]

Compound **11** was also characterized crystallographically, and an ORTEP diagram of its molecular structure is shown in Figure 3. The molecule could be described as a 2,3,4,5,8,9,10-heptamethoxycarbonyl-6-methoxy-3,6-oxa-bicyclo[2.2.1]benzothiopyran formed by the fusion of four molecules of DMAD with one sulfur atom.



11

The mechanism of formation has not been established, but the oxo bridge is clearly derived from the carbonyl oxygen atom of one of the methoxycarbonyl groups. Similar coupling of DMAD with formation of oxo bridges from the carboxylate groups has been observed previously.[28] The C(1)−C(2), C(3)−C(4), and C(6)−C(7) bonds are double bonds with lengths of 1.345(6), 1.330(6), and 1.318(6) Å, respectively. The S−C bonds

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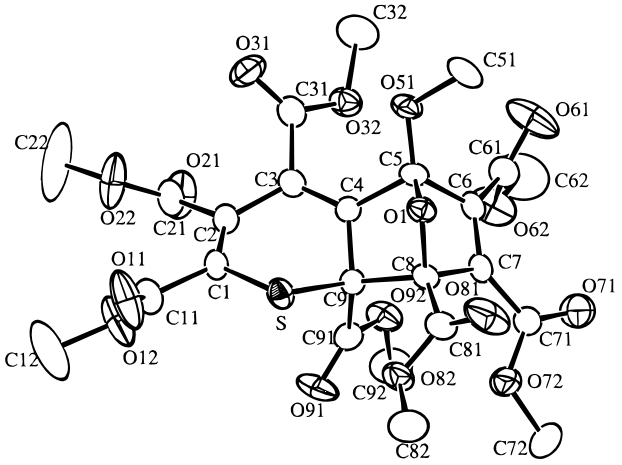


Figure 3. ORTEP diagram of the molecular structure of **11**, showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) as follows: S−C(1) = 1.754(5), S−C(9) = 1.811(5), O(1)−C(5) = 1.455(5), O(1)−C(8) = 1.425(5), C(1)−C(2) = 1.345(6), C(2)−C(3) = 1.473(7), C(3)−C(4) = 1.330(6), C(4)−C(5) = 1.539(7), C(5)−C(6) = 1.533-(6), C(6)−C(7) = 1.318(6), C(7)−C(8) = 1.537(6), C(8)−C(9) = 1.606(6).

S−C(1) = 1.754(5) Å and S−C(9) = 1.811(5) Å are close to single bonds, and the remaining C−C bonds are single bonds, although the C(8)−C(9) bond is unusually long 1.606(6) Å. The bonds to the bridging oxygen atom O(1) are single bonds, O(1)−C(5) = 1.455(5) Å and O(1)−C(8) = 1.425(5) Å.

If the product mixture was separated by preparative gas−liquid chromatography, the new cyclic trisulfide [$S_3C(H)CH_3C(H)CH_3$], **12**, could be isolated as a yellow liquid. Its molecular weight was established by high-resolution mass spectrometry: calcd (found) 151.9788 (151.9788); its ^{1}H NMR and ^{13}C NMR spectra are consistent with this formulation: ^{1}H NMR δ 3.50 (dq, 2H, $^3J_{H-H}$ = 6.80 Hz, $^3J_{H-H}$ = 4.40 Hz, $^4J_{H-H}$ = −0.15 Hz, $^4J_{H-H}$ = 0.05 Hz), 1.46 (dd, 6H, $^3J_{H-H}$ = 6.80 Hz, $^3J_{H-H}$ = 4.40 Hz, $^4J_{H-H}$ = −0.15 Hz, $^4J_{H-H}$ = 0.05 Hz). ^{13}C NMR (δ, CD_2Cl_2): 45.0 (6C), 21.6 (6C). The stereochemistry of the carbon atoms has been assigned as 4*S*,5*S*(4*R*,5*R*) on the basis of a product obtained from it by reaction with $Os_3(CO)_{10}(NCMe)_2$.

The principal products obtained from the reaction of **12** with $Os_3(CO)_{10}(NCMe)_2$ were identified as $Os_2(CO)_6$-[μ-SC(H)CH_3C(H)CH_3S], **13**, (34% yield), and the known compound $Os_3(CO)_{10}(\mu$-S) [13] (30% yield). Compound **13** was characterized crystallographically, and an ORTEP diagram of its molecular structure is shown in Figure 4. The molecule is structurally very similar to that of its unsubstituted parent $Os_2(CO)_6(\mu$-$SCH_2CH_2S)$, **14**, which was recently reported.[29] Compound **13** contains a (1*R*,2*R*)(1*S*,2*S*)-dimethylethanedithiolate ligand bridging a pair of mutually bonded osmium atoms, Os(1)−Os(2) = 2.7164(7) Å. The most important feature of this study is the establishment of the relative stereochemistry at the two methyl-substituted carbon atoms, (1*R*,2*R*), shown in the figure. The compound crystallized in the centric space group $P2_1/n$, so the crystal actually contains a racemic mixture of the (1*R*,2*R*) and (1*S*,2*S*) enantiomers. It is believed that the dimethylethanedithiolate ligand was formed by the loss of one

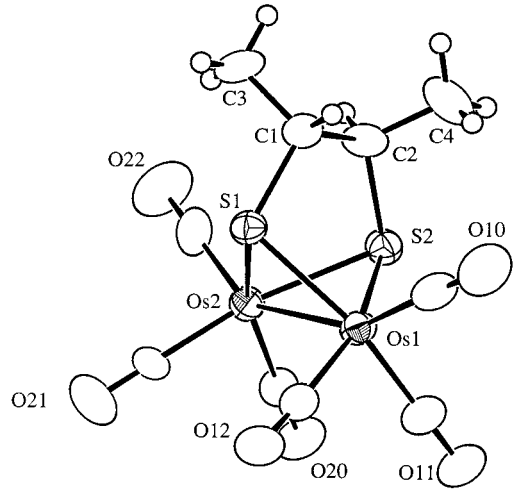
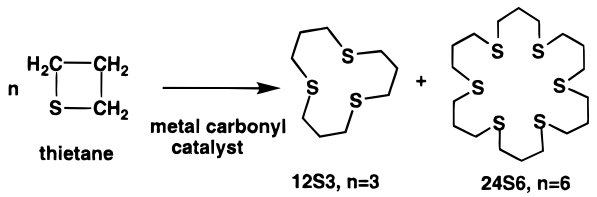


Figure 4. ORTEP diagram of the molecular structure of **13**, showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) as follows: Os(1)−Os(2) = 2.7164-(7), Os(1)−S(1) = 2.407(3), Os(1)−S(2) = 2.402(3), Os(2)−S(1) = 2.410(3), Os(2)−S(2) = 2.391(3), S(1)−C(1) = 1.86(1), S(2)−C(2) = 1.85(1), C(1)−C(2) = 1.50(2).

sulfur atom from **12**. Organic trisulfides are well-known for their ability to release monatomic sulfur,[30] and the formation of approximately 1 equiv of $Os_3(CO)_{10}(\mu$-S) with the formation of **13** is, thus, consistent with previous observations. In most cases, the desulfurization of organic trisulfides proceeds with retention of stereochemistry at the sulfur bound carbon atoms.[30a] Assuming that the loss of sulfur from **12** does not produce any changes in stereochemistry at the carbon atoms, then the configuration at the carbon atoms in **12** and **13** must be the same, (1*R*,2*R*) and (1*S*,2*S*), with overall a racemic mixture of the two enantiomers.

Discussion

In recent studies, we have shown that thietane ligands in certain metal carbonyl complexes,[31] including $W(CO)_5$ complexes,[32] can be transformed catalytically into polythioether macrocycles, eq 3. We have shown



(3)

that the nucleophile-induced opening of thietane rings occurs by back-side addition to the carbon atoms bonded to the sulfur atom.[33] There is evidence that the ring opening of thiiranes by nucleophiles also occurs by back-side addition to one of the carbon atoms.[34]

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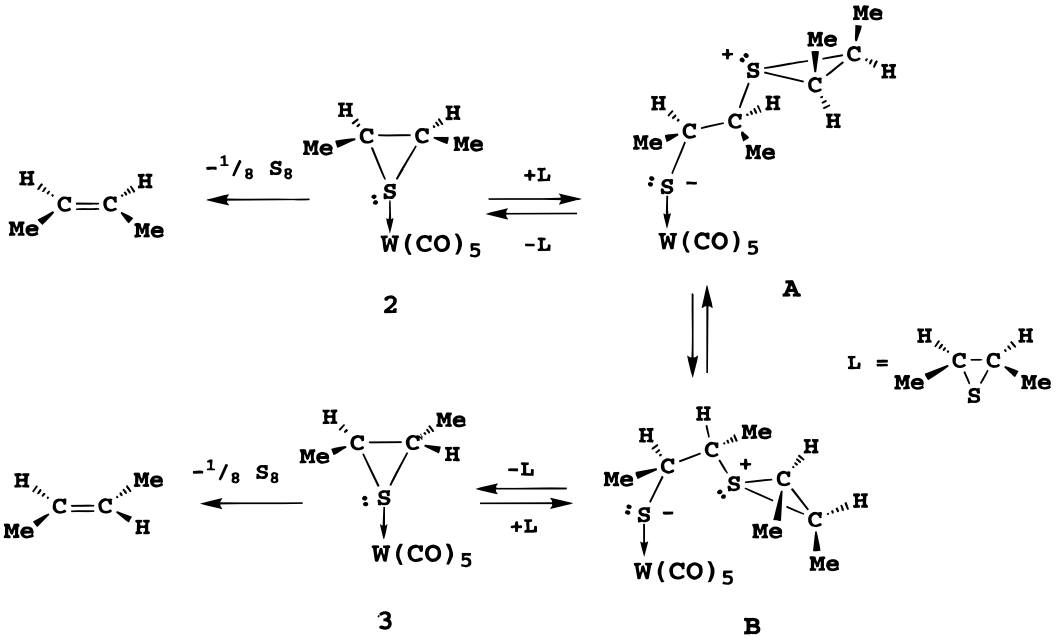
Scheme 1



In this report, we have described the synthesis and characterization of the thiirane complexes **1**−**3** and the observation that **1** produces the transformation of thiirane to cyclic polydisulfides catalytically. Also, *cis*-DMT and *trans*-DMT are catalytically isomerized by **2** and **3**. All observations can be explained by a mechanism which begins with a nucleophilic back-side ring-opening addition of an uncoordinated molecule of thiirane to one of the carbon atoms of a thiirane ligand. This conclusion is based on the changes in the stereochemistry that were observed in the reactions involving DMT.

(1) *cis*-DMT and *trans*-DMT are isomerized in the presence of their tungsten complexes. Back-side addition of the sulfur atom of a free molecule of thiirane to the carbon atom of the thiirane ligand will yield a zwitterionic intermediate, such as **A**, and a change in stereochemistry at the added carbon atom, see Scheme 1. The zwitterion would contain a positively charged dimethylthietanium group and a negatively charged thiolate group. A rotation about the C−C single bond of the zwitterion could lead to a conformer, such as **B**, which would yield the isomeric thiirane complex by release of the added thiirane (i.e., **2** goes to **3** or vice versa).

(2) The matching stereochemistry at adjacent carbon atoms in the cyclic tris(disulfide) **9** and the trisulfide **12** derived from the reaction of *cis*-DMT with **2** in the presence of DMAD is consistent with the inversion of stereochemistry, back-side addition mechanism. The strength of this argument would appear to be mitigated by observation 1; isomerization of the thiirane could have preceded the reactions that led to the formation of **9** and **12**. However, we have observed in an independent test that the isomerization of the substituted thiiranes is completely suppressed when DMAD is present in these catalytic reaction mixtures in the amounts that we studied. Since **9** and **12** are obtained only in the presence of DMAD, it thus seems relatively unlikely that isomerization has compromised the validity of the interpretation of this stereochemical inversion observation.

It is further proposed that the cyclic disulfides **4**−**7**, **9**, and **10** are formed from the same or similar zwitterionic intermediates, **C**, obtained in the isomerization of *cis*- and *trans*-DMT by competing reactions involving the loss of olefin, see Scheme 2. Previous studies have shown that thietanium ions will decompose by loss of olefin.[35] This will lead initially to a zwitterionic $^{+}SCH_2CH_2S^{-}$ group that may rapidly neutralize itself by formation of an S−S bond to yield a cyclic dithietane or perhaps simply transfer one electron from the negatively charged sulfur atom to the positively charged sulfur atom to yield a $^{\bullet}SCH_2CH_2S^{\bullet}$ grouping, which might have a diradical or triplet character while it remains coordinated to a $W(CO)_5$ group. 1,2-Dithietane has not yet been synthesized,[36] although a highly substituted form of it has been.[37] Huttner and co-workers have recently isolated a bis($CpMn(CO)_2$) complex of SCH_2CH_2S and showed that it exhibits a diradical character.[38] The random coupling of SCH_2CH_2S groups from these $W(CO)_5$ intermediates could lead to the formation of the stable cyclic disulfides **4**−**7**, **9**, and **10**. Note that the yields of the rings **4**−**7** decrease as the size of the ring increases. We attribute the lower catalytic activity of $Cr(CO)_5$ to a lower activation of the thiirane in a presumed (thiirane)$Cr(CO)_5$ complex. Less activation would be expected if the Cr−S bond were weaker than the W−S bond.

To try to obtain evidence for the existence of a species containing a SCH_2CH_2S grouping, we performed the reaction that leads to the rings **4**−**7** in the presence of DMAD. Interestingly, we observed the formation of the known compound **8**. We believe that this is a result of a trapping of some transient SCH_2CH_2S species by 1 equiv of DMAD, since we observed that the cyclic disulfides do not react with DMAD to yield **8**, see Scheme 2.

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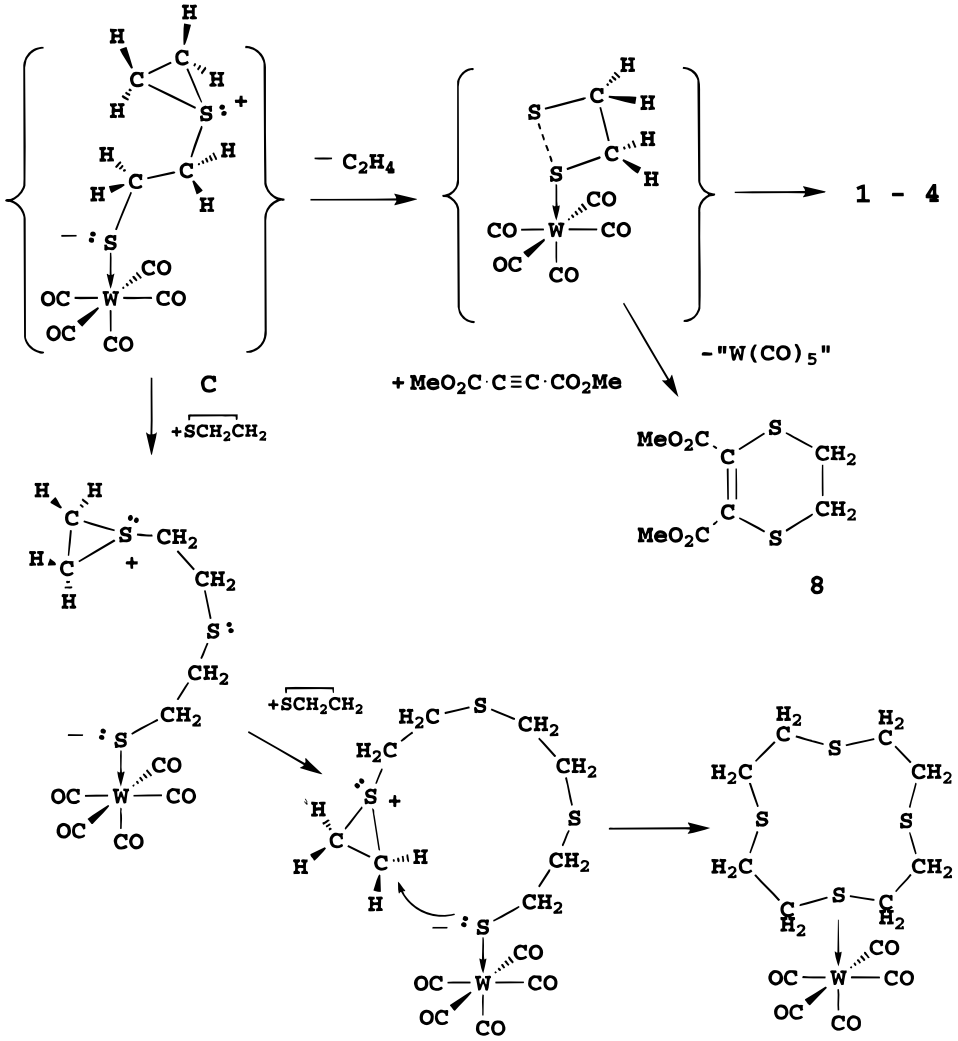
Scheme 2



Another interesting result of the study of the thiirane transformations in the presence of DMAD was the formation of small but significant quantites of the polythioether macrocycles **12S4** and **15S5**. The formation of such products is easily explained by a series of ring-opening additions of thietane to the thietanium grouping in the intermediate **C** that is terminated by an intramolecular ring-opening coupling of the thiolato sulfur atom with a thietanium group to form the macrocycle, see Scheme 2. This would be similar to the mechanisms proposed for the catalytic formation of thioether macrocycles from thietanes by metal carbonyl complexes.[31,32] The reason for the increased formation of thioether macrocycles when DMAD is present in the reaction mixtures has not been established, but perhaps associations between DMAD and the thietanium groupings suppresses the olefin-elimination step that leads to desulfurization and the thioether macrocyclization process thus becomes relatively more important.

Cyclic disulfides have been shown to exhibit a variety of antimicrobial properties.[39] Accordingly, it was decided to test two of the cyclic disulfides, **4** and **5**, for their antimicrobial activity using a standard disk diffusion assay. Each compound was applied to a 6 mm cotton disk using CH_2Cl_2 in five different amounts. The air-dried disks were placed on a lawn of three standard assay microorganisms, *E. coli*, *M. luteus*, and *B. cereus*, which had been prepared by inoculation on a bed of LB agar. At 200 μg/disk, compound **4** exhibited a moderate activity against *E. coli*, producing a 7 mm zone of inhibition, and weak activities against both *M. luteus* (2 mm inhibition zone) and *B. cereus* (3 mm inhibition zone). Compound **5** exhibited less activity, displaying 3, 1, and 1 mm zones of inhibition against *E. coli*, *M. luteus*, and *B. cereus*, respectively. Compounds **4** and **5** were both inactive at the levels 100, 50, 20, 2, and 0.5 μg/disk.

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.

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Supporting Information Available: Tables of final atomic positional parameters, bond distances, bond angles, and anisotropic thermal parameters for the structural analysis of **2**, **9**, **11**, and **13** (24 pages). Ordering information is given on any current masthead page.

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