

The Catalytic Ring-Opening Cyclooligomerization (ROC) of Thietane by the Complexes $M(\text{CO})_5\text{L}$ ($M = \text{Cr}$ and W ; $\text{L} = \text{CO}$, Thietane and 1,5,9-Trithiacyclododecane)

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Received November 13, 1995

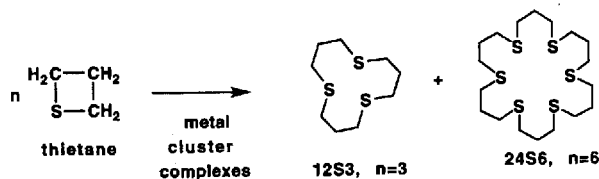
Key Words: Thietane / Catalysis / Tungsten / Macrocyclic

The following four compounds have been synthesized: $M(\text{CO})_5\text{L}$ (**3** and **4**, where $M = \text{Cr}$ and W , and $\text{L} = \text{SCH}_2\text{CH}_2\text{CH}_2$), $\text{W}(\text{CO})_5(12\text{S3})$ (**5**, where $12\text{S3} = 1,5,9\text{-trithia-cyclododecane}$), and $[\text{W}(\text{CO})_5]_2(12\text{S3})$ (**6**). The molecular structures of **4** and **5** were established by single-crystal X-ray diffraction analyses. Both compounds contain a $\text{W}(\text{CO})_5$ group coordinated to one of the sulfur atoms of the heterocycle. The ability of the compounds $M(\text{CO})_6$, **1** and **2** ($M = \text{Cr}$ and W), and **3–5** to catalytically produce ring opening cyclooligomerization (ROC) of thietane into 12S3 and 24S6 ,

($24\text{S6} = 1,5,9,13,17,21\text{-hexathia-cyclotetracosane}$) has been investigated. Compounds **1–3** have relatively low activity. Compounds **4** and **5** have the highest activity and selectivity for 12S3 formation. Crystal Data for **4**: space group = $P2_12_12_1$, $a = 12.906(2) \text{ \AA}$, $b = 13.730(4) \text{ \AA}$, $c = 6.427(1) \text{ \AA}$, $Z = 4$, 1306 reflections, $R = 0.033$; for **5**: space group = $P\bar{1}$, $a = 12.703(1) \text{ \AA}$, $b = 13.510(2) \text{ \AA}$, $c = 5.833(1) \text{ \AA}$, $\alpha = 101.75(1)^\circ$, $\beta = 97.54(1)^\circ$, $\gamma = 101.70(1)^\circ$, $Z = 2$, 2225 reflections, $R = 0.023$.

Polythioether macrocycles have recently attracted considerable interest because of their ability to serve as ligands for the transition metals^[1]. Recently, we have been investigating the ability of polynuclear metal carbonyl complexes to produce ring-opening transformations of thietane ligands^[2–4], and have discovered the first examples of the catalytic formation of the polythioether macrocycles 12S3 (1,5,9-trithiacyclododecane) and 24S6 (1,5,9,13,17,21-hexathia-cyclotetracosane) by ring-opening cyclooligomerization (ROC) of thietane by the following carbonyl cluster complexes: $\text{Re}_3(\text{CO})_{10}[\mu(\text{SCH}_2\text{CH}_2\text{CH}_2)(\mu\text{-H})_3]^{[5]}$, $\text{Re}_2(\text{CO})_9(\text{SCH}_2\text{CH}_2\text{CH}_2)^{[6]}$ and $\text{Os}_4(\text{CO})_{11}(\text{SCH}_2\text{CH}_2\text{CH}_2)(\mu\text{-H})_4^{[7]}$ (see the Equation).

Equation



We have now prepared and investigated the coordination of thietane in the series of complexes $M(\text{CO})_5\text{L}$, **3** and **4** (where $M = \text{Cr}$ and W , and $\text{L} = \text{SCH}_2\text{CH}_2\text{CH}_2$), and $\text{W}(\text{CO})_5(12\text{S3})$, **5**. We have also investigated the ability of these complexes as well as that of the parent carbonyls $M(\text{CO})_6$, **1** and **2** ($M = \text{Cr}$ and W), to produce the thietane ROC catalytically. The results of these studies are reported here.

The thietane-containing complexes $M(\text{CO})_5\text{L}$, **3** and **4**, were obtained by the displacement of NCMe with thietane in the complexes $M(\text{CO})_5(\text{NCMe})$ ($M = \text{Cr}$ and W). The compounds $\text{W}(\text{CO})_5(12\text{S3})$, **5** and $[\text{W}(\text{CO})_5]_2(12\text{S3})$, **6** ($12\text{S3} = 1,5,9\text{-trithia-cyclododecane}$) were obtained in the yields 46% and 8%, respectively from the reaction of $\text{W}(\text{CO})_5(\text{NCMe})$ with 12S3 . Compounds **4** and **5** were characterized by a single-crystal X-ray diffraction analyses, and their molecular structures are shown in Figures 1 and 2, respectively. In both complexes, a $\text{W}(\text{CO})_5$ grouping is coordinated to one sulfur atom in the heterocycle. The tungsten–sulfur distance in **4** [$\text{W–S } 2.540(3) \text{ \AA}$] is slightly shorter than that in **5** [$\text{W–S(1)} 2.564(2) \text{ \AA}$]. In both complexes the W–C bond length for the carbonyl ligand that is trans to the sulfur ligand is significantly shorter than that for the cis ligands, as expected due to the weaker structural trans effect of sulfur compared to CO ; the S–C bond lengths are typical of S–C single bonds (see Figures 1 and 2 for W–C and S–C bond lengths). Naturally, the C–S–C angle in **4** [$77.8(7)^\circ$] is much smaller than those in **5**, which are approximately 100° (see Figure 2). – The thietane ligand in **4** is only slightly puckered; the $\text{C(6)–S–C(8)/C(6)–C(7)–C(8)}$ dihedral angle is 11.2° . This is significantly less than the angle of 28° found for the thietane ligand in $\text{Os}_3(\text{CO})_{11}[\text{SCH}_2\text{CH}_2\text{CH}_2]^{[8]}$. The conformation of the 12S3 ligand is similar to that found in the free molecule and a variety of 12S3 complexes^[6,9,10].

The ^{13}C -NMR spectrum of a ^{13}CO -enriched sample of **4** in the CO region show two resonances at 201.0 (s, 1 CO ,

Figure 1. An ORTEP diagram of $\text{W(CO)}_5(\text{SCH}_2\text{CH}_2\text{CH}_2)$, **4** showing 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles ($^\circ$) are: $\text{W}-\text{S} = 2.540(3)$; $\text{W}-\text{C}(1)_{\text{cis}} = 2.04(1)$; $\text{W}-\text{C}(2)_{\text{cis}} = 2.02(1)$; $\text{W}-\text{C}(3)_{\text{cis}} = 2.05(1)$; $\text{W}-\text{C}(4)_{\text{cis}} = 2.01(1)$; $\text{W}-\text{C}(5)_{\text{trans}} = 1.96(1)$; $\text{S}-\text{C}(6) = 1.80(1)$; $\text{S}-\text{C}(8) = 1.75(1)$; $\text{C}(6)-\text{C}(7) = 1.51(2)$; $\text{C}(7)-\text{C}(8) = 1.50(2)$; $\text{C}(6)-\text{S}-\text{C}(8) = 77.8(7)$

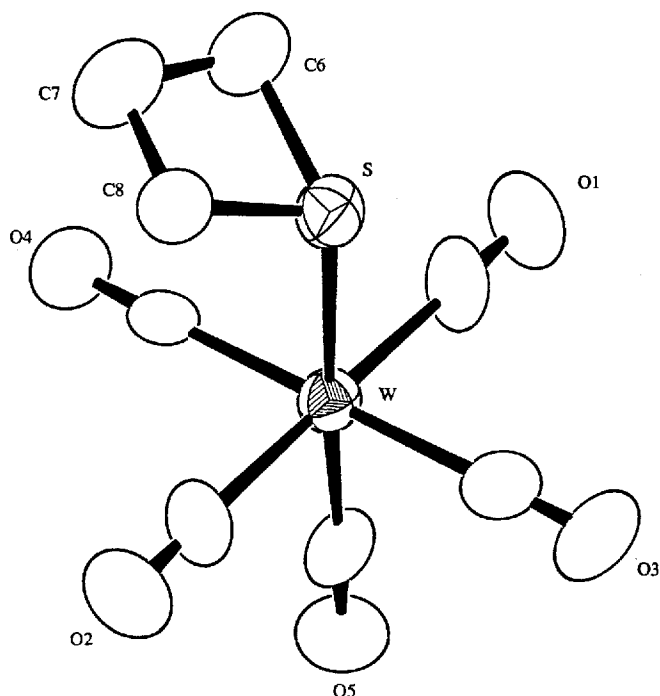
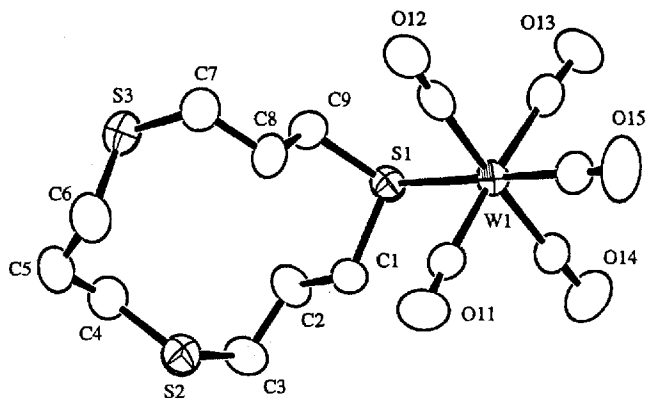


Figure 2. An ORTEP diagram of $\text{W(CO)}_5(12\text{S3})$, **5** showing 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles ($^\circ$) are: $\text{W}-\text{S}(1) = 2.564(2)$; $\text{W}-\text{C}(11)_{\text{cis}} = 2.023(7)$; $\text{W}-\text{C}(12)_{\text{cis}} = 2.036(8)$; $\text{W}-\text{C}(13)_{\text{cis}} = 2.061(8)$; $\text{W}-\text{C}(14)_{\text{cis}} = 2.025(7)$; $\text{W}-\text{C}(15)_{\text{trans}} = 1.972(7)$; $\text{S}(1)-\text{C}(1) = 1.820(6)$; $\text{S}(1)-\text{C}(9) = 1.820(6)$; $\text{S}(2)-\text{C}(3) = 1.808(7)$; $\text{S}(2)-\text{C}(4) = 1.814(7)$; $\text{S}(3)-\text{C}(6) = 1.818(9)$; $\text{S}(3)-\text{C}(7) = 1.815(7)$; $\text{C}(1)-\text{S}(1)-\text{C}(9) = 101.8(3)$; $\text{C}(3)-\text{S}(1)-\text{C}(4) = 100.4(4)$; $\text{C}(1)-\text{S}(1)-\text{C}(9) = 100.1(3)$



$^2J_{\text{W}^{183}\text{W}^{13}\text{C}} = 157.2$ Hz) and 197.5 (s, 4 CO, $^2J_{\text{W}^{183}\text{W}^{13}\text{C}} = 128.7$ Hz) with appropriate couplings to the spin active isotope of tungsten. A similar ^{13}C -NMR spectrum was observed for a ^{13}CO -enriched sample of **5**: 199.9 (s, 1 CO, $^2J_{\text{W}^{183}\text{W}^{13}\text{C}} = 157.6$ Hz), 197.4 (s, 4 CO, $^2J_{\text{W}^{183}\text{W}^{13}\text{C}} = 128.9$ Hz). The ^1H -NMR spectrum of **4** showed only two resonances: 3.80 (t, 4H, $J_{\text{H}-\text{H}} = 7.7$ Hz), 3.03 (q, 2H, $J_{\text{H}-\text{H}} = 7.7$ Hz). This can be explained by the structure observed in the solid state and by assuming rapid inversions of configuration at the

pyramidal sulfur atom. Rapid inversions at pyramidal sulfur in thioether complexes have been observed previously^[11].

Compound **3** is spectroscopically similar to **4** and is thus believed to be structurally similar as well. The structure of compound **6** is believed to contain two W(CO)_5 groups coordinated to neighboring sulfur atoms of the 12S3 ligand, as found in the compound $[\text{Re}_2(\text{CO})_9]_2(12\text{S3})$ ^[6], but this has not been established crystallographically.

Catalytic Cyclooligomerization of Thietane. Compounds **1–5** were tested for their ability to produce ROC of thietane. The results of these tests are given in Table 1. The reactions were performed in thietane in the absence of solvent at the boiling point of thietane, 94°C , and were allowed to run for 24 h. Solvent is not necessary since the compounds dissolve fully in pure thietane. The hexacarbonyl complexes, **1** and **2**, did produce some of the two cyclooligomers 12S3 and 24S6, but the activity is very low compared to **4** and **5** and other known catalysts for this process^[5–7]. Compound **3** produced about twice as much of the products as **1** and **2** did, but again, the activity was still relatively low. Compounds **4** and **5** exhibited significantly higher catalytic activity than **1–3**, and also yielded greater amounts of 12S3 relative to 24S6. The catalytic activity and selectivity for 12S3- and 24S6-formation is virtually the same for **4** and **5**. The average turnover frequency (TOF) for the formation of 12S3 is about 1.1/h over the 24 h reaction period. This is significantly lower than that observed for $\text{Re}_3(\text{CO})_{10}[\mu-\text{SCH}_2\text{CH}_2\text{CH}_2](\mu-\text{H})_3$ ^[5], $\text{Re}_2(\text{CO})_9(\text{SCH}_2\text{CH}_2\text{CH}_2)$ ^[6] and $\text{Os}_4(\text{CO})_{11}(\text{SCH}_2\text{CH}_2\text{CH}_2)(\mu-\text{H})_4$ ^[7]. In one experiment, catalysis was performed using a sample of **4** that had been enriched to 50% with ^{13}CO . The reaction was allowed to run for 5 h. A ^{13}C -NMR spectrum of the entire reaction mixture, taken at the end of this period, showed detectable quantities of only two tungsten carbonyl compounds, **4** and **5**, in a ratio of 4.5/1.

A proposed mechanism for the catalytic cyclotrimerization of thietane by **4** and **5** is shown in the Scheme. The reaction is believed to begin by a ring-opening addition of the sulfur atom, in an uncoordinated molecule of thietane, to one of the methylene groups attached to the sulfur atom of the coordinated thietane ligand in **4**, step A. The activation mechanism probably occurs in the following manner: The tungsten withdraws electron density from the sulfur atom^[6,7], which leads to the formation of a partial positive charge at the sulfur atom and also at the neighboring carbon atoms but to a lesser extent. This is apparently sufficient to allow this nucleophilic addition step to proceed and would yield a zwitterionic intermediate such as **8**. The negatively charged, terminally coordinated thiolate sulfur atom is linked to a positively charged thietanium ring via a trimethylene chain. Similar nucleophilic ring opening reactions have been observed for thietane ligands in bridging coordination modes^[2–4]. The pendant thietanium group should be sufficiently reactive to undergo ring-opening additions with additional uncoordinated thietane molecules spontaneously, step B. The cationic ring-opening polymeri-

Table 1. Results of the catalytic cyclooligomerization of thietane by tungsten carbonyl complexes

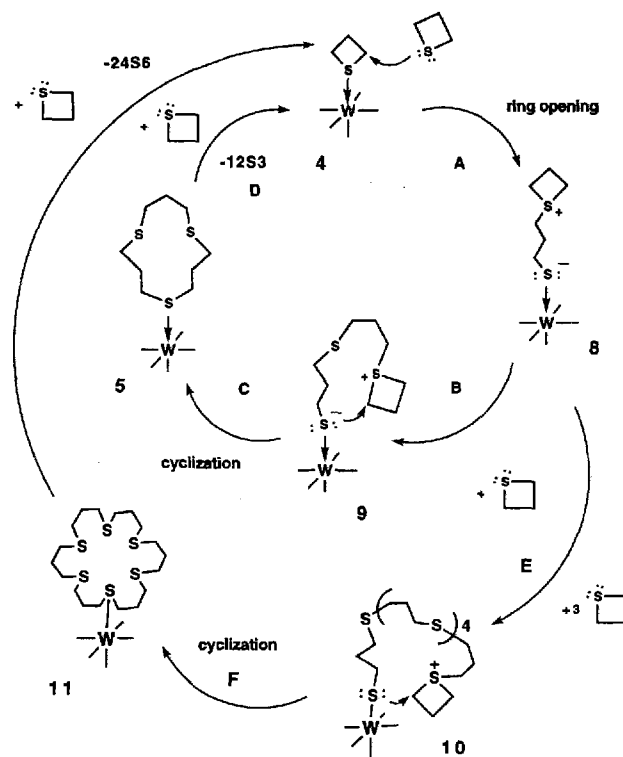
Catalyst ^[a]	Catalyst Amount	Reagent Amount	Products	Ratio ^[b]	Reaction Time	Product Weight ^[c]	TOF for 12S3 ^[d]
1	10.0 mg	6.0 ml	12S3/24S6	0.4/1	24 hr	97 mg	0.07
2	10.0 mg	6.0 ml	12S3/24S6	1.7/1	24 hr	87 mg	0.03
3	10.0 mg	6.0 ml	12S3/24S6	1.2/1	24 hr	199 mg	0.38
4	10.3 mg	6.0 ml	12S3/24S6	2/1	24 hr	312 mg	1.1
4	14.5 mg	6.0 ml	12S3/24S6	2/1	48 hr	628 mg	0.88
5	10.0 mg	6.0 ml	12S3/24S6	2/1	24 hr	211 mg	1.1
None		6.0 ml	12S3/24S6	2/1	24 hr	29 mg ^[e]	-

^[a] Results are the average of two runs. All errors are in the last significant figure. All reactions were performed at the boiling pt. of thietane, 94 °C. — ^[b] These are mol/mol ratios 12S3:24S6 as determined by NMR analysis of the reaction mixtures. — ^[c] These weights are corrected for the effects of weights of noncatalytic decomposition of thietane^[e]. — ^[d] TOF = moles of 12S3/mole of catalyst · hr. — ^[e] A mixture of products containing small amounts of 12S3 and 24S6 in a 2:1 ratio; see ref.^[5].

zation of thietanes by this mechanism is well known^[12]. In principle, polymerization could occur, but instead, after the addition of a second free molecule of thietane, cyclization occurs by addition of the coordinated thiolato sulfur atom to one of the α -carbon atoms in the thietanium ring, step C, and leads to the 12S3 complex 5. The tendency toward cyclization in these complexes is probably enhanced by the zwitterionic nature of the intermediates which should tend to keep the head and tail of the growing chain in proximity to one another. The catalytic cycle is completed by the simple substitution of the 12S3 ligand by thietane, step D. The catalysis observed by 4 is explained by this same catalytic cycle, and, in this regard, it is important to note that the catalytic activity of 5 is not significantly different from that of 4. This mechanism is similar to that proposed for the cyclooligomerization of thietane by $\text{Re}_2(\text{CO})_9(\text{SCH}_2\text{CH}_2\text{CH}_2)^{[6]}$ and $\text{Os}_4(\text{CO})_{11}(\text{SCH}_2\text{CH}_2\text{CH}_2)(\mu\text{-H})_4^{[7]}$, but differs from that of $\text{Re}_3(\text{CO})_{10}[\mu\text{-SCH}_2\text{CH}_2\text{CH}_2](\mu\text{-H})_3^{[5]}$ where the cyclization occurred at a thioether sulfur site, not at the thiolato sulfur atom bonded to the metal atom. The ^{13}C -NMR analysis of the reaction mixture in the CO region indicates the catalytic reactions involving 4 and 5 are clean. There is little decomposition and even after 48 h, the rate of production of 12S3 is only slightly diminished. The formation of 24S6 could be explained by a mechanism similar to that shown for 12S3. The addition of four equivalents of thietane to the intermediate, a combination of steps B and E, prior to the cyclization, step F, would lead to a 24S6 tungsten complex 11 which we have not yet observed (see Scheme 1).

The low catalytic activity exhibited by 1 and 2 can be explained by the unavailability of a coordination site for the activation of the first thietane molecule. Interestingly, the chromium compound 3 has much lower activity than the tungsten compounds. This is consistent with our previous studies which have shown that complexes containing metal atoms from the third transition series are the most effective in producing these ROC catalyses^[5–7]. Currently, we have

Scheme 1



no explanation for the different ratios of 12S3/24S6 formed in the chromium and tungsten catalysis. Furthermore, we have no evidence for the formation of 16S4 (1,5,9,13-tetrathiacyclohexadecane) or 20S5 (1,5,9,13,17-pentathiacyclooctadecane). Similar results were obtained for the catalysis produced by $\text{Re}_2(\text{CO})_9(\text{SCH}_2\text{CH}_2\text{CH}_2)^{[6]}$ and $\text{Os}_4(\text{CO})_{11}(\text{SCH}_2\text{CH}_2\text{CH}_2)(\mu\text{-H})_4^{[7]}$, although small amounts of 16S4 were produced by $\text{Re}_3(\text{CO})_{10}[\mu\text{-SCH}_2\text{CH}_2\text{CH}_2](\mu\text{-H})_3^{[5]}$. Again, we have no explanation for this observation. In the course of these studies we have also labored to prepare and investigate the catalytic activity of the molybdenum mem-

ber of this Group VI series, $\text{Mo}(\text{CO})_5(\overline{\text{SCH}_2\text{CH}_2\text{CH}_2})$. We believe that we were able to prepare it in a fashion analogous to the preparation of **3** and **4**, however, the compound is much less stable than **3** and **4**. Because of this we feel that the results of our investigation of the ROC of thietane by $\text{Mo}(\text{CO})_5(\overline{\text{SCH}_2\text{CH}_2\text{CH}_2})$ are not as reliable as those of **3** and **4** and therefore these studies were not completed.

The results of this study show for the first time that a system of mononuclear metal complexes (**4/5**) is also effective for the ROC of thietane; although in two previous studies of catalysis by metal cluster complexes, it was indicated that the catalysis was performed at the site of a single metal atom^[6,7]. The reason for the higher activity exhibited by the clusters is not yet clear. It could be that the metals used in the cluster studies (rhenium and osmium) are simply more effective than tungsten in the thietane activation step. It will be interesting to see if mononuclear rhenium and osmium complexes are as active as the rhenium and osmium clusters.

These studies were supported by the Division of Chemical Sciences of the Office of Basic Energy Sciences of the U. S. Department of Energy. J. A. Q. thanks the *Deutsche Akademische Austauschdienst* for a research fellowship.

Experimental

General Data. Unless otherwise indicated, all reactions were performed under nitrogen. Reagent grade solvents were stored over 4 Å molecular sieves. $\text{Cr}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ were purchased from Strem Chemicals and were used without further purification. $\text{Cr}(\text{CO})_5(\text{NCMe})$ and $\text{W}(\text{CO})_5(\text{NCMe})$ were prepared according to the published procedures^[13]. Trimethylamine *N*-oxide dihydrate (Aldrich) was dehydrated by using a Dean-Stark apparatus and benzene solvent prior to use. 12S3 was prepared as described in our previous report^[9]. Thietane was purchased from Aldrich and was purified by vacuum distillation before use. All other reagents were purchased from Aldrich and were used as received. Infrared spectra were recorded on a Nicolet 5DXB FTIR spectrophotometer. ¹H-NMR spectra were obtained on Bruker AM-300, WH-400 or AM-500 spectrometers operating at 300 MHz, 400 MHz or 500 MHz, respectively. Mass spectra were run on a VG Model 70SQ mass spectrometer using electron impact ionization. Separations were performed by TLC in air on Analtech 0.25 mm silica gel 60 Å F254 plates. Elemental analyses were performed by Oneida Research Services, Whitesboro, N.Y.

Preparation of $\text{Cr}(\text{CO})_5(\overline{\text{SCH}_2\text{CH}_2\text{CH}_2})$, **3:** A 29.2 mg amount of $\text{Cr}(\text{CO})_5(\text{NCMe})$ (0.12 mmol) was dissolved in 20 ml of methylene chloride in a 25 ml 3-neck round bottom flask equipped with a stir bar, reflux condenser and a nitrogen inlet. 15 µl of thietane (0.20 mmol) was added and the resulting solution was then allowed to stir at 25°C for 1 h. The volatiles were removed in vacuo, and the products were separated by TLC using a hexane/methylene chloride 4/1 solvent mixture, to yield 24.6 mg (77%) of $\text{Cr}(\text{CO})_5(\overline{\text{SCH}_2\text{CH}_2\text{CH}_2})$, **3**, as a yellow oil and 3.0 mg of unreacted $\text{Cr}(\text{CO})_5(\text{NCMe})$. Compound **3** crystallizes from hexane solution at -15°C, but when the solvent is removed and the crystals are dried and warmed to room temperature, they invariably melt. — IR (νCO, cm⁻¹, hexane): $\tilde{\nu}$ = 2069 (w), 1947 (s), 1937 (m). ¹H NMR for **3** (CDCl₃): δ = 3.38 (t, 4H, $J_{\text{H-H}}$ = 7.8 Hz), 2.92 (q, 2H, $J_{\text{H-H}}$ = 7.8 Hz). — C₈H₈CrO₅S (266.19): calcd. C 36.10, H 2.27; found C 35.84, H 2.18.

Preparation of $\text{W}(\text{CO})_5(\overline{\text{SCH}_2\text{CH}_2\text{CH}_2})$, **4:** A 61.0 mg amount of $\text{W}(\text{CO})_5(\text{NCMe})$ (0.17 mmol) was dissolved in 20 ml of methylene chloride in a 25 ml 3-neck round bottom flask equipped with a stir bar, reflux condenser and a nitrogen inlet. 15 µl of thietane (0.20 mmol) was added and this solution was then allowed to stir at reflux for 3 h. The volatiles were removed in vacuo, and the products were separated by TLC using a hexane/methylene chloride 2/1 solvent mixture to yield 25.0 mg (37%) of $\text{W}(\text{CO})_5(\overline{\text{SCH}_2\text{CH}_2\text{CH}_2})$, **4**, and 29 mg of unreacted $\text{W}(\text{CO})_5(\text{NCMe})$. — IR (νCO, cm⁻¹, hexane): $\tilde{\nu}$ = 2075 (m), 1944 (s), 1934 (s). ¹H NMR (CDCl₃): δ = 3.80 (t, 4H, $J_{\text{H-H}}$ = 7.7 Hz), 3.03 (quint, 2H, $J_{\text{H-H}}$ = 7.7 Hz). — C₈H₈O₅SW (398.04): calcd. C 24.14, H 1.52; found C 24.01, H 0.82.

Preparation of $\text{W}(\text{CO})_5(12\text{S3})$, **5:** 100.0 mg of 12S3 (0.45 mmol) was dissolved in 20 ml of methylene chloride and placed in a 50 ml 3-neck round bottom flask equipped with a stir bar, reflux condenser, a nitrogen inlet and a dropping funnel. 40.0 mg of $\text{W}(\text{CO})_5(\text{NCMe})$ (0.11 mmol) was dissolved in 10 ml of methylene chloride and placed in the dropping funnel. The 12S3 solution was brought to reflux and the $\text{W}(\text{CO})_5(\text{NCMe})$ solution was then added to the solution of 12S3 at reflux over a 10 min. period. The reflux of the reaction solution was continued with stirring for 3 h. After cooling, the volatiles were removed in vacuo, and the products were separated by TLC using a hexane/acetone 3/1 solvent mixture to yield 27.8 mg (46%) of $\text{W}(\text{CO})_5(12\text{S3})$, **5**, and 4 mg (8%) of $[\text{W}(\text{CO})_5]_2(12\text{S3})$, **6**, and 3.5 mg of unreacted $\text{W}(\text{CO})_5(\text{NCMe})$. — **5**: IR (νCO, cm⁻¹, hexane): $\tilde{\nu}$ = 2074 (w), 1978 (w), 1941 (s), 1908 (w); ¹H NMR (CDCl₃): δ = 3.00 (t, 4H, $J_{\text{H-H}}$ = 7.0 Hz), 2.73 (t, 4H, $J_{\text{H-H}}$ = 6.3 Hz), 2.63 (t, 4H, $J_{\text{H-H}}$ = 6.0 Hz), 1.98 (q, 4H, $J_{\text{H-H}}$ = 6.6 Hz), 1.82 (q, 2H, $J_{\text{H-H}}$ = 6.3 Hz). — C₁₄H₁₈O₅S₃W (546.32): calcd. C 30.76, H 3.32; found C 30.82, H 3.18. — **6**: IR (νCO, cm⁻¹, hexane): $\tilde{\nu}$ = 2075 (w), 1978 (w), 1943 (s), 1916 (w). — ¹H NMR (CDCl₃): δ = 3.08 (m, 4H), 2.96 (m, 4H), 2.69 (m, 4H), 2.09 (m, 2H), 1.94 (m, 4H). — MS (EI): 870 (M⁺), 546 [M⁺ - W(CO)₅], 546 {M⁺ - [W(CO)₅ + 2 CO]}, 406 {M⁺ - 2[W(CO)₅]}. —

Preparation of ¹³C-Enriched $\text{W}(\text{CO})_6$: 250.0 mg of $\text{W}(\text{CO})_5(\text{NCMe})$ (0.68 mmol) and 7 ml of octane was placed in a 30 ml Parr high-pressure reaction unit. The closed unit was cooled in liquid nitrogen and was evacuated. The CO (99.99% ¹³C) was introduced to the reaction unit at 77 K. The reaction unit was then sealed and placed in an oil bath at 150°C for 24 h. The volatiles were removed in vacuo, and the products were separated by TLC using hexane as the solvent to yield 116 mg of ¹³C-enriched $\text{W}(\text{CO})_6$. A mass spectrum of the product showed that there was an average of three ¹³CO ligands per molecule $\text{W}(\text{CO})_6$ (i.e., 50% enriched with ¹³CO). This was converted to ¹³C-enriched $\text{W}(\text{CO})_5(\text{NCMe})$ by the established procedure^[13].

Preparation of ¹³CO-Enriched **4:** 104.0 mg of ¹³CO-enriched $\text{W}(\text{CO})_5(\text{NCMe})$ (0.28 mmol) was dissolved in 20 ml of methylene chloride in a 25 ml 3-neck round bottom flask equipped with a stir bar, reflux condenser and a nitrogen inlet. 30.0 µl of thietane (0.40 mmol) was added and the resulting solution was then allowed to stir at reflux for 3 h. The volatiles were removed in vacuo, and the products were separated by TLC using a hexane/methylene chloride 2/1 solvent mixture to yield 49.6 mg (44%) of ¹³CO-enriched $\text{W}(\text{CO})_5(\overline{\text{SCH}_2\text{CH}_2\text{CH}_2})$, **4***, and 26.3 mg of unreacted $\text{W}(\text{CO})_5(\text{NCMe})$. — IR (νCO, cm⁻¹, hexane): $\tilde{\nu}$ = 2067 (w), 2059 (br.), 2054 (br.), 2048 (br.), 1973 (m), 1954 (sh, m), 1944 (s), 1917 (s), 1901 (s), 1872 (m). — ¹H NMR (CDCl₃): δ = 3.80 (t, 4H, $J_{\text{H-H}}$ = 7.7 Hz), 3.03 (q, 2H, $J_{\text{H-H}}$ = 7.7 Hz). — ¹³C NMR (CDCl₃): δ = 201.0 (s, 1 CO, ²*J*_{W-¹³C} = 157.2 Hz), 197.5 (s, 4 CO, ²*J*_{W-¹³C} = 128.7 Hz).

Preparation of ^{13}C -enriched $\text{W}(\text{CO})_5(12\text{S}3)$. **5:** 26.5 mg of ^{13}C -enriched $\text{W}(\text{CO})_5(\text{NCMe})$ (0.071 mmol) was dissolved in 20 ml of methylene chloride in a 25 ml 3-neck round bottom flask equipped with a stir bar, reflux condenser and a nitrogen inlet. 16.0 mg of 12S3 (0.072 mmol) was added and the resulting solution was then allowed to stir at reflux for 3 h. The volatiles were removed in vacuo, and the products were separated by TLC using a hexane/methylene chloride 2/1 solvent mixture to yield 6.0 mg (15%) of $\text{W}(\text{CO})_5(12\text{S}3)$, **5***, and 11 mg of unreacted ^{13}C enriched $\text{W}(\text{CO})_5(\text{NCMe})$. — IR ($\nu(\text{CO})$, cm^{-1} , hexane): $\tilde{\nu} = 2066$ (w), 2057 (w), 2047 (w), 1969 (m), 1941 (sh, m), 1917 (s), 1910 (s), 1896 (s), 1865 (m), 1849 (w). — ^1H NMR (CDCl_3): $\delta = 3.80$ (t, 4H, $J_{\text{H-H}} = 7.7$ Hz), 3.03 (q, 2H, $J_{\text{H-H}} = 7.7$ Hz). ^{13}C -NMR (CDCl_3): $\delta = 199.9$ (s, 1 CO, $^{12}\text{J}_{\text{W-}^{13}\text{C}} = 157.6$ Hz), 197.4 (s, 4 CO, $^2\text{J}_{\text{W-}^{13}\text{C}} = 128.9$ Hz).

Catalytic Cyclooligomerizations: All catalytic reactions were performed under nitrogen in 25 ml 3-neck round bottom flasks equipped with a stir bar, reflux condenser, a nitrogen inlet. Pre-weighed amounts of catalyst and thietane were placed in the reaction flask and the flask was briefly evacuated (to remove traces of oxygen), and then filled with nitrogen. The solution was then heated to the reflux temperature of the thietane. Results of these experiments are collected in Table 1. A typical treatment was performed as follows: 6.0 ml of thietane (81 mmol) and 10.3 mg amount of **4** (0.026 mmol) was added to the 25 ml 3-neck round bottom flask. With stirring, the reaction solution was heated to reflux and was maintained at this temperature for 24 h. After cooling, the excess thietane was removed in vacuo. The resulting residue weighed 341 mg. A ^1H -NMR spectrum was taken of a portion of the residue. The spectrum showed only two products. (1) 1,5,9-trithiacyclododecane^[9], 12S3. — ^1H NMR (CDCl_3): $\delta = 2.67$ (t, 12H, $J_{\text{H-H}} = 6.7$ Hz), 1.87 (q, 6H, $J_{\text{H-H}} = 6.7$ Hz). (2) 1,5,9,13,17,21-hexathiacyclotetrasane, 24S6^[10]. — ^1H NMR (CDCl_3): $\delta = 2.60$ (t, 24H, $J_{\text{H-H}} = 7.2$ Hz), 1.84 (q, 12H, $J_{\text{H-H}} = 7.2$ Hz). The relative intensities of the 12S3/24S6 were 1/1 as observed by NMR. This corresponds to a 2/1 12S3/24S6 mol/mol ratio. The products were separated by TLC (on plates of AVICEL F microcrystalline cellulose), using hexane/chloroform/ethyl acetate 2/1/1 solvent mixture as the eluent, to give two bands. The first band contained the pure 12S3^[19] and the second band contained the pure 24S6^[14]. In general, the nonvolatile residues are completely soluble in methylene chloride which indicates the near absence of polymer formation. The results of these tests are listed in Table 1. The product weights in Table 1 are corrected for the weight of compounds produced by the known noncatalytic decomposition of an equivalent amount of thietane over the same period of time^[5].

Catalytic Cyclooligomerization of Thietane by **4, Long-Term Test:** Under nitrogen, 6.0 ml (81.0 mmol) of thietane was added to a 25 ml 3-neck round bottom flask equipped with a stir bar, reflux condenser, a nitrogen inlet containing 12.0 mg of **4** (0.030 mmol). The solution was heated to reflux and was allowed to stir under nitrogen at this temperature for 48 h. After cooling, the unreacted thietane was removed in vacuo. The resulting residue weighed 628 mg. A ^1H -NMR spectrum was taken of a portion of the residue. The spectrum showed the presence of only two products: 12S3 and 24S6 in a 2/1 ratio based on the NMR integration.

Identification of the Complexes After Catalysis Using **4* as the Catalyst:** 6.0 ml of thietane (81.0 mmol) was added to a 25 ml 3-neck round bottom flask equipped with a stir bar, reflux condenser, a nitrogen inlet and 18.0 mg (0.045 mmol) of **4***. The reaction was heated to reflux and was allowed to stir under nitrogen at this temperature for 5 h. After cooling, the excess thietane was removed in

vacuo. A ^{13}C -NMR spectrum was taken of the residue. This showed the presence of only two tungsten carbonyl compounds: **4*** and **5*** in a ratio of 4.5/1.

Crystallographic Analyses: Light yellow crystals of **4** and **5** suitable for X-ray diffraction analysis were grown from solution in a 2/1 CH_2Cl_2 /hexane solvent mixture by slow evaporation of solvent at 25 °C. The crystals used in intensity measurements were mounted in thin-walled glass capillary. Diffraction measurements were made on a Rigaku AFC6S fully automated four-circle diffractometer using graphite-monochromated Mo- K_α radiation. The unit cell was determined and refined from 15 randomly selected reflections obtained by using the AFC6S automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of these analyses are listed in Table 2. All data processing was performed on a Digital Equipment Corp. VAXstation 3520 computer 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^[15a]. Anomalous dispersion corrections were applied to all non-hydrogen atoms^[15b]. Lorentz-polarization (Lp) and absorption corrections (based on three azimuthal psi scans) were applied in each analysis. 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 $\sigma(F_o^2) = [\sigma(I_{\text{raw}})^2 + (0.02 \cdot I_{\text{neq}})^2]^{1/2}/Lp$.

Table 2. Crystallographic data for compounds **4** and **5**

Compound	4	5
Formula	$\text{WSO}_5\text{C}_6\text{H}_6$	$\text{WSO}_5\text{C}_{14}\text{H}_{18}$
Formula weight	398.04	546.32
Crystal system	Orthorhombic	Triclinic
Lattice parameters		
a (Å)	12.906(2)	12.703(1)
b (Å)	13.730(4)	13.510(2)
c (Å)	6.427(1)	5.833(1)
α (°)	90.0	101.75(1)
β (°)	90.0	97.54(1)
γ (°)	90.0	101.70(1)
V (Å ³)	1138.8(3)	944.0(3)
Space group	$P2_12_12_1$ (#19)	$P\bar{1}$ (#2)
Z	4	2
ρ_{calc} (g/cm ³)	2.32	1.92
μ (Mo K α) (cm ⁻¹)	103.4	64.8
Temperature (°C)	20	20
2 θ_{max} (°)	55	45
No. Obs. ($>3\sigma$)	1306	2225
No. Variables	137	209
Goodness of Fit	2.14	1.65
Residuals: R; R_w	0.033; 0.036	0.023; 0.026
Abs. Cor. (3 psi scans)	empirical	empirical
Largest peak in Final	1.93	0.96
Diff. Map (e/Å ³)		

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

Compound **4** crystallized in the orthorhombic crystal system. The space group $P2_12_12_1$ was established uniquely on the basis of 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 nonhydrogen atoms were refined with anisotropic thermal parameters. The positions of the hydrogen atoms on the thietane ligand were calculated by assuming idealized geometries and C–H bond lengths of 0.95 Å. Their contributions were added to the structure factor calculations, but their positions were not refined. At the conclusion of the refinement, a test for the correctness of the crystallographic enantiomorph was made by inverting the coordinates of all

of the atoms and refining again. The residuals after these refinements were significantly larger, indicating the original enantiomorph was correct. The values for the first enantiomorph were retained and are the ones reported here.

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 nonhydrogen atoms were refined with anisotropic thermal parameters. The positions of the hydrogen atoms on the 12S3 ligand were calculated by assuming idealized geometries and C–H bond lengths of 0.95 Å. Their contributions were added to the structure factor calculations, but their positions were not refined. Further details of the crystal structure investigations are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany) on quoting the depository number CSD-59173.

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