

Syntheses, Crystal Structures, Spectroscopic Characterization, and Electrochemical Studies of the Ditungsten(III) Complexes $\text{Cl}_3\text{W}(\mu\text{-L})_3\text{WCl}_3$ and $[\text{Cl}_3\text{W}(\mu\text{-L})_2(\mu\text{-Cl})\text{WCl}_3]^-$ ($\text{L} = 1,4\text{-Dithiane}, 1,4\text{-Thioxane}, \text{pms} = \text{Pentamethylene Sulfide}$). C–S Bond Cleavage of the Bridging Thioether(s) in $\text{Cl}_3\text{W}(\mu\text{-L})_3\text{WCl}_3$

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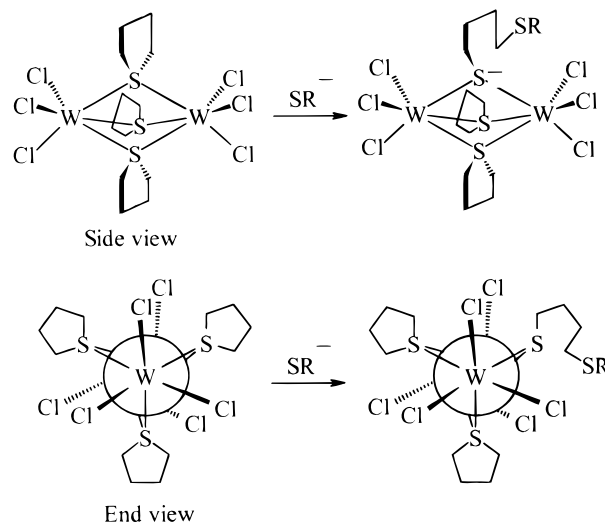
Reduction of WCl_4 with 1 equiv of sodium amalgam, in the presence of either a refluxing toluene or neat solution of the desired thioether, produces a mixture of $\text{Cl}_3\text{W}(\mu\text{-L})_3\text{WCl}_3$ ($\text{L} = 1,4\text{-dithiane}$ (**1**), $1,4\text{-thioxane}$ (**2**), $\text{pms} = \text{pentamethylene sulfide}$ (**3**)) and $[\text{Na}][\text{Cl}_3\text{W}(\mu\text{-L})_2(\mu\text{-Cl})\text{WCl}_3]$ ($\text{L} = 1,4\text{-dithiane}$ (**4**), $1,4\text{-thioxane}$ (**5**), pms (**6**)). **4** and **5** could be converted to **1** and **2**, respectively, in the presence of excess L in refluxing toluene. The structures of **1**, **2**, **3**, **7**, and **8** have been solved. **1**, **2**, and **3** are the first reported crystal structures for ditungsten(III) tris-bridged cyclic thioether complexes. Crystal data are as follows: for an acetone solvate of **1**, monoclinic space group $P2_1/n$ (No. 14), $a = 12.518(3) \text{ \AA}$, $b = 9.475(2) \text{ \AA}$, $c = 27.408(3) \text{ \AA}$, $\beta = 93.34(1)^\circ$, $Z = 4$; for an acetone solvate of **2**, tetragonal space group $P4/ncc$ (No. 130), $a = 25.7603(3) \text{ \AA}$, $b = 25.7603(3) \text{ \AA}$, $c = 18.6771(2) \text{ \AA}$, $Z = 16$; for a hexane solvate of **3**, monoclinic space group $P2_1/n$ (No. 14), $a = 11.874(4) \text{ \AA}$, $b = 21.823(3) \text{ \AA}$, $c = 12.545(3) \text{ \AA}$, $\beta = 100.46(3)^\circ$, $Z = 4$; for an acetonitrile solvate of **7**, monoclinic space group $P2_1/c$ (No. 14), $a = 9.704(5) \text{ \AA}$, $b = 28.241(7) \text{ \AA}$, $c = 15.480(5) \text{ \AA}$, $\beta = 98.55(4)^\circ$, $Z = 4$; for a chloroform solvate of **8**, monoclinic space group $P2_1/a$ (No. 14), $a = 13.531(4) \text{ \AA}$, $b = 25.207(5) \text{ \AA}$, $c = 14.083(3) \text{ \AA}$, $\beta = 115.57(2)^\circ$, $Z = 4$. **1**, **2**, and **3** were all shown to undergo C–S bond cleavage of a bridging thioether by reaction with $[\text{PPh}_4][\text{Sptol}]$ ($\text{ptol} = 4\text{-methyl phenyl}$) to afford the anionic complexes $[\text{PPh}_4][\text{Cl}_3\text{W}(\mu\text{-S}(\text{CH}_2\text{CH}_2)_2\text{E})_2(\mu\text{-SCH}_2\text{-CH}_2\text{ECH}_2\text{CH}_2\text{Sptol})\text{WCl}_3]$ ($\text{E} = \text{S}$ (**9**), O (**10**), CH_2 (**12**)). **1**, **2**, **7**, and **8** undergo reversible one-electron reductions.

Introduction

We reported previously the synthesis and characterization of the ditungsten(III) complex $\text{Cl}_3\text{W}(\text{tht})_3\text{WCl}_3$ ($\text{tht} = \text{tetrahydrothiophene}$ (**12**)).¹ Though the $\text{W}_2\text{S}_3\text{Cl}_6$ core of the molecule was found to be resistant to nucleophilic attack, the complex was significantly modified, via C–S bond cleavage of a bridging thioether, to produce anionic, functionalized thiolate complexes (Scheme 1).²

We are presently involved in developing the chemistry related to thioether ring-opening since the direct syntheses of similar functionalized thiolate species has proved to be difficult. In particular we are interested in whether the anionic functionalized thiolates in ditungsten(III) complexes can be used to bind a secondary metal center. The ultimate goal is to determine their use as metalloligands for neutral or cationic late transition-metal species. One of the main considerations in the evolution of these complexes as metalloligands is the ability to design specific binding sites, that is, modify the functionality of the thiolate. Attempts to achieve this have been made by varying the type of nucleophile used or the nature of the tris-ring thioether bridged precursors. With respect to the latter, this paper reports the preparation and characterization of three new

Scheme 1



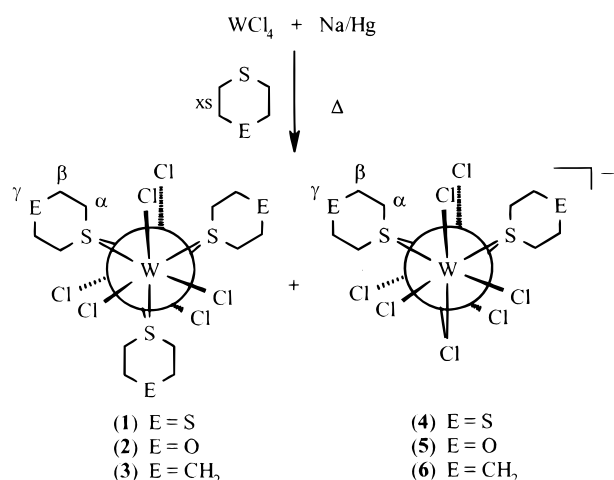
tris-bridged cyclic thioether ditungsten(III) complexes, **1**, **2**, and **3**, followed by investigation into the possibility of nucleophilic attack resulting in their ring-opening.

The successful syntheses of **1–3** were accompanied by the isolation and characterization of the bis-ring thioether bridged ditungsten(III) complexes (**4–6**).

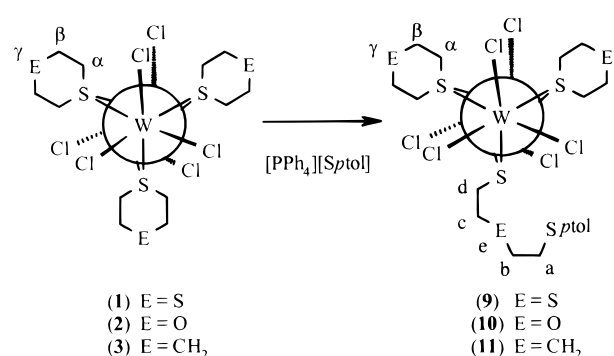
(1) Boorman, P. M.; Gao, X.; Freeman, G. K. W.; Fait, J. F. *J. Chem. Soc., Dalton Trans.* **1991**, 115–120.

(2) Boorman, P. M.; Gao, X.; Fait, J. F.; Parvez, M. *Inorg. Chem.* **1991**, 30, 3886–3893.

Scheme 2



Scheme 3



Experimental Section

General Procedures. All manipulations were carried out using standard glovebox and Schlenk techniques under an atmosphere of dry N₂ or argon. Solvents were dried over the appropriate drying agents, distilled under nitrogen onto molecular sieves, and degassed using argon before use.³ Thietane (trimethylene sulfide), 1,4-thioxane, and pms, as purchased from Aldrich, were dried over molecular sieves and degassed, via freeze-thaw techniques under argon, prior to use. Dithiane, purchased from Aldrich, was purified by sublimation under vacuum onto a coldfinger. WCl₄ was prepared by reduction of WCl₆ with 0.5 mol of W(CO)₆ in refluxing chlorobenzene for 14 h as per literature instructions,⁴ then purified over 24 h by sublimation of volatile impurities at 225 °C in an evacuated and flame-sealed Pyrex tube. Elemental analyses were performed by the University of Calgary, Department of Chemistry, Analytical Services Laboratory. ¹H and ¹³C{¹H} NMR spectra were recorded in CD₃CN or CDCl₃ using a Brüker ACE-200 or ACE-400 NMR spectrometer (designation of the H and C atoms provided in Schemes 2 and 3).

Synthetic Procedures. Cl₃W(μ-L)₃WCl₃ (L = 1,4-dithiane (1), 1,4-thioxane (2) and pms (3)) and [Na][Cl₃W(μ-L)₂(μ-Cl)WCl₃] (L = 1,4-dithiane (4), 1,4-thioxane (5), pms (6)). The previously established synthetic route to preparing tris-thioether bridged ditungsten(III) complexes involves the reduction of WCl₄ using sodium amalgam in the presence of refluxing neat thioether.¹ The same procedure was employed toward the preparation of 1–3 and required a variation in reaction times and the use of toluene as a solvent in the case of the highly volatile solid dithiane. The formation of 1–3 was always accompanied by the formation of the anionic bis-thioether bridged ditungsten(III) complexes, 4–6. The complete preparative procedure for the dithiane complexes is given below as an example.

Cl₃W(μ-1,4-dithiane)₃WCl₃ (1) and [Na][Cl₃W(μ-1,4-dithiane)₂(μ-Cl)WCl₃] (4). Several procedures were attempted. WCl₄ (0.500 g, 1.5 mmol), Na/Hg (2% w/w, 1.76 g; 0.035 g Na), dithiane (0.800 g, 6.7 mmol), and toluene (~5 mL) were placed in a Schlenk tube and refluxed for 45 min, 24 h, and 1 week (the 45 min reaction was locally heated using a heat gun source, the 24 h and 1 week reactions were heated using a heating mantle with Variac). After cooling to room temperature, diethyl ether (50 mL) was added then the supernatant decanted off and the residue was washed with diethyl ether (2 × 100 mL). Extraction using acetone afforded a red solution, the solvent was removed in vacuo, and the red residue washed with diethyl ether (2 × 50 mL). Yields for the respective reaction times were 100, 750, and 400 mg. The ¹H NMR spectra indicated the presence of two species, 1 and 4. It was found that 1 could be isolated by extraction of the red residue using CH₂Cl₂. Purification of 1 and 4 required repeated crystallizations from CH₂Cl₂ and acetone, respectively. Data given below is for the 24 h reaction which gave the best overall yield.

Data for 1: yield, 360 mg (25% of 100% tris). Anal. Calcd for C₁₂H₂₄S₆Cl₆W₂: C, 15.31; H, 2.57. Found: C, 15.34; H, 2.30. ¹H NMR (CD₃CN, ambient, δ): 3.99 (m, 12H, μ-dithiane αH's), 3.55 (m, 12H, μ-dithiane βH's). ¹³C{¹H} NMR (CD₃CN, ambient, δ): 46.96 (s, 6C, μ-dithiane αC's), 29.09 (s, 6C, μ-dithiane βC's).

Data for 4: yield, 360 mg (27% of 100% bis). ¹H NMR (CD₃CN, ambient, δ): δ 4.13 (m, 4H, μ-dithiane αH's), 3.70 (m, 4H, μ-dithiane αH's), 3.68 (m, 4H, μ-dithiane βH's), 3.57 (m, 4H, μ-dithiane βH's). ¹³C{¹H} NMR (CD₃CN, ambient, δ): 47.93 (s, 2C, μ-dithiane αC's), 47.65 (s, 2C, μ-dithiane αC's), 29.34 (s, 2C, μ-dithiane βC's), 29.31 (s, 2C, μ-dithiane βC's). Negative FAB-MS: m/z 857 (Cl₃W(μ-1,4-dithiane)₂(μ-Cl)WCl₃), 617 (Cl₃W(μ-Cl)WCl₃).

Cl₃W(μ-1,4-thioxane)₃WCl₃ (2) and [Na][Cl₃W(μ-1,4-thioxane)₂(μ-Cl)WCl₃] (5). WCl₄ (0.500 g, 1.5 mmol), Na/Hg (2% w/w, 1.76 g; 0.035 g Na), and 1,4-thioxane (3 mL) were reacted together under refluxing conditions. A reaction time of 25 min produced the best overall yield.

Data for 2: yield, 210 mg (15.3% of 100% tris). Anal. Calcd for C₁₂H₂₄S₃O₃Cl₆W₂: C, 16.14; H, 2.71. Found: C, 16.68; H, 2.57. ¹H NMR (CD₃CN, ambient, δ): 4.49 (m, 12H, μ-thioxane βH's), 3.75 (m, 12H, μ-thioxane αH's). ¹³C{¹H} NMR (CD₃CN, ambient, δ): 67.88 (s, 6C, μ-thioxane βC's), 41.87 (s, 6C, μ-thioxane αC's). Negative FAB-MS: m/z 892 (Cl₃W(μ-1,4-thioxane)₃WCl₃).

Data for 5: yield, 1.050 g (81% of 100% bis). Anal. Calcd for C₈H₁₆S₂O₂Cl₇W₂Na: C, 11.34; H, 1.90. Found: C, 11.06; H, 1.97. ¹H NMR (CD₃CN, ambient, δ): 4.61 (m, 4H, μ-thioxane βH's), 4.52 (m, 4H, μ-thioxane βH's), 3.90 (m, 4H, μ-thioxane αH's), 3.45 (m, 4H, μ-thioxane αH's). ¹³C{¹H} NMR (CD₃CN, ambient, δ): 68.38 (s, 2C, μ-thioxane βC's), 68.19 (s, 2C, μ-thioxane βC's), 42.98 (s, 2C, μ-thioxane αC's), 42.78 (s, 2C, μ-thioxane αC's). Negative FAB-MS: m/z 825 (Cl₃W(μ-1,4-thioxane)₂(μ-Cl)WCl₃), 617 (Cl₃W(μ-Cl)WCl₃).

Cl₃W(μ-pms)₃WCl₃ (3) and [Na][Cl₃W(μ-pms)₂(μ-Cl)WCl₃] (6). WCl₄ (0.500 g, 1.5 mmol), Na/Hg (2% w/w, 1.76 g, 0.035 g Na), and pms (5 mL) were reacted together under refluxing conditions. A reaction time of 45 min produced the best overall yield.

Data for 3: yield, 1.00 g (86%). Anal. Calcd for C₁₅H₃₀S₃Cl₆W₂: C, 20.3; H, 3.41. Found: C, 19.6; H, 3.43. ¹H NMR (CD₃CN, ambient, δ): 3.66 (m, 12H, μ-pms αH's), 2.50 (m, 12H, μ-pms βH's), 1.77 (m, 6H, μ-pms γH's).

Data for 6: yield, 110 mg (9.5%). ¹H NMR (CD₃CN, ambient, δ): 3.75 (m, 4H, μ-pms αH's), 3.57 (m, 4H, μ-pms αH's), 2.90 (m, 4H, μ-pms βH's), 2.78 (m, 4H, μ-pms βH's), 2.09 (m, 4H, μ-pms γH's). ¹³C{¹H} NMR (CDCl₃, ambient, δ): 44.89 (m, 2C, μ-pms αC's), 44.78 (m, 2C, μ-pms αC's), 26.26 (m, 4C, μ-pms βC's), 23.48 (m, 2C, μ-pms γC's).

Attempts to Prepare Cl₃W(μ-thietane)₃WCl₃. WCl₄ (0.500 g, 1.5 mmol), Na/Hg (2% w/w, 1.76 g, 0.035 g Na), and thietane (5 mL) were reacted together. Room-temperature reactions of up to 1 month are shown to result in no reaction. Reactions performed at or just below reflux, even for a very short time (10 min), were shown to result in the formation of a brown insoluble polymeric material.

Reaction of [Na][Cl₃W(μ-L)₂(μ-Cl)WCl₃] (L = 1,4-Dithiane (4), 1,4-Thioxane (5)) and Excess L. The general procedure was to reflux

(3) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: Oxford, 1989.

(4) Schaefer King, M. A.; McCarley, R. W. *Inorg. Chem.* **1973**, *12*, 1972.

the desired bis-thioether complex in the presence of excess **L** from 1 to 24 h (in the case of dithiane, included was 10 mL toluene, CH_2Cl_2 , or CH_3CN). The solvent, when necessary, was decanted off, and the residue or slurry was washed with Et_2O (3×20 mL) to remove excess **L** and then extracted first with CH_2Cl_2 to remove the desired tris complex and then with acetone to recover unreacted bis complex.

For reaction of **4** (100 mg, 1.1×10^{-1} mmol) with dithiane (100 mg, 8.3×10^{-1} mmol), the best percent conversion to **1** is 50% after 6 h in refluxing toluene.

For the reaction of **5** (100 mg, 1.2×10^{-1} mmol) with thioxane (3 mL), best percent conversion to **2** is 20% after a 4 h reflux.

[PPh₄][Cl₃W(μ -L)₂(μ -Cl)WCl₃] (L = 1,4-Dithiane (7), 1,4-Thioxane (8)). **4** and **5** were reacted with PPh_4Cl in CH_2Cl_2 (20 mL) at room temperature over a 24 h period. The solvent was then removed in vacuo and the residue washed first with $i\text{PrOH}$ (2×20 mL) to remove unreacted PPh_4Cl and then with Et_2O (3×20 mL) to remove excess $i\text{PrOH}$.

Data for 7: 4 (100 mg 1.1×10^{-1} mmol) was reacted with PPh_4Cl (43 mg, 1.1×10^{-1} mmol). Yield: 100 mg (74%). Anal. Calcd for $\text{C}_{32}\text{H}_{16}\text{S}_4\text{Cl}_7\text{W}_2\text{P}$: C, 32.12; H, 3.03. Found: C, 32.65; H, 2.79. ^1H NMR (CD_3CN , ambient, δ): 4.12 (m, 4H, μ -dithiane $\alpha\text{H}'$'s), 3.54 (m, 4H, μ -dithiane $\alpha\text{H}'$'s), 3.70 (m, 4H, μ -dithiane $\beta\text{H}'$'s), 3.66 (m, 4H, μ -dithiane $\beta\text{H}'$'s). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN , ambient, δ): 47.94 (s, 2C, μ -dithiane $\alpha\text{C}'$'s), 47.88 (s, 2C, μ -dithiane $\alpha\text{C}'$'s), 29.32 (s, 2C, μ -dithiane $\beta\text{C}'$'s), 29.29 (s, 2C, μ -dithiane $\beta\text{C}'$'s).

Data for 8: 5 (100 mg, 1.2×10^{-1} mmol) was reacted with PPh_4Cl (44 mg, 1.2×10^{-1} mmol). Yield: 105 mg (77%). Anal. Calcd for $\text{C}_{32}\text{H}_{16}\text{S}_2\text{O}_2\text{Cl}_7\text{W}_2\text{P}$: C, 33.00; H, 3.12. Found: C, 32.95; H, 3.08. ^1H NMR (CD_3CN , ambient, δ): 3.89 (m, 4H, μ -thioxane $\alpha\text{H}'$'s), 3.44 (m, 4H, μ -thioxane $\alpha\text{H}'$'s), δ 4.59 (m, 4H, μ -thioxane $\beta\text{H}'$'s), 4.50 (m, 4H, μ -thioxane $\beta\text{H}'$'s). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN , ambient, δ): 42.95 (s, 2C, μ -thioxane $\alpha\text{C}'$'s), 42.75 (s, 2C, μ -thioxane $\alpha\text{C}'$'s), 68.32 (s, 2C, μ -thioxane $\beta\text{C}'$'s), 68.14 (s, 2C, μ -thioxane $\beta\text{C}'$'s). Negative FAB-MS: m/z 825 ($\text{Cl}_3\text{W}(\mu$ -1,4-thioxane)₂(μ -Cl)WCl₃), 617 ($\text{Cl}_3\text{W}(\mu$ -Cl)WCl₃).

Reactions with [PPh₄]Sptol. In a typical reaction, 50 mg of the desired complex, **1–8**, and an equimolar amount of $[\text{PPh}_4]\text{Sptol}$ were weighed into a Schlenk tube in a glovebox. The Schlenk tube was evacuated and charged with argon. To this was cannulated over CH_3CN (10–20 mL). Reaction times varied from 12 to 48 h. The solutions containing **1** and **2** were stirred at room temperature and those containing **3–6** while refluxing. After the desired reaction time, the solution was filtered by gravity through a sintered glass frit (size D) and the solvent removed in vacuo. The red residues were washed with diethyl ether (2×10 mL) and dried in vacuo.

[PPh₄][Cl₃W(μ -1,4-dithiane)₂(μ -S(CH₂)₂Sptol)WCl₃] (9). **1** (50 mg, 5.3×10^{-2} mmol) was reacted with $[\text{PPh}_4]\text{Sptol}$ (25 mg, 5.4×10^{-2} mmol). Yield: 60 mg (80%). Anal. Calcd for $\text{C}_{43}\text{H}_{51}\text{S}_7\text{W}_2\text{Cl}_6\text{P}$: C, 36.77; H, 3.66. Found: C, 36.52; H, 3.82. ^1H NMR (CD_3CN , ambient, δ): 8.0–7.7 (m, 20H, PPh_4 aromatic H's), 7.31 (d, 2H, ptol aromatic H's), 7.19 (d, 2H, ptol aromatic H's), 4.00 (m, 2H, μ -dithiane $\alpha\text{H}'$'s), 3.88 (m, 2H, μ -dithiane $\alpha\text{H}'$'s), 3.79 (m, 2H, μ -dithiane $\alpha\text{H}'$'s), 3.71 (m, 2H, μ -dithiane $\alpha\text{H}'$'s), 3.56 (m, 6H, μ -dithiane $\beta\text{H}'$'s), 3.49 (m, 2H, μ -dithiane $\beta\text{H}'$'s), 3.60 (m, 2H, d), 3.16 (m, 2H, a), 2.90 (m, 2H, c), 2.80 (m, 2H, b), 2.32 (s, 3H, ptol methyl H's). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN , ambient, δ): 50.21 (s, 1C, μ -dithiane $\alpha\text{C}'$'s), 48.87 (s, 1C, μ -dithiane $\alpha\text{C}'$'s), 48.81 (s, 1C, μ -dithiane $\alpha\text{C}'$'s), 47.93 (s, 1C, μ -dithiane $\alpha\text{C}'$'s), 41.81 (s, 1C, d), 35.22 (s, 1C, c), 34.32 (s, 1C, b), 32.39 (s, 1C, a), 29.55 (s, 1C, μ -dithiane $\beta\text{C}'$'s), 29.37 (s, 1C, μ -dithiane $\beta\text{C}'$'s), 29.31 (s, 1C, μ -dithiane $\beta\text{C}'$'s), 29.22 (s, 1C, μ -dithiane $\beta\text{C}'$'s), 21.12 (s, 1C, ptol methyl C's).

[PPh₄][Cl₃W(μ -1,4-thioxane)₂(μ -S(CH₂)₂O(CH₂)₂Sptol)WCl₃] (10). **2** (50 mg, 5.6×10^{-2} mmol) was reacted with $[\text{PPh}_4]\text{Sptol}$ (26 mg, 5.6×10^{-2} mmol). Yield quantitative as shown by ^1H NMR of the reaction mixture. Yield: 53 mg (71%). Anal. Calcd for $\text{C}_{43}\text{H}_{51}\text{S}_4\text{O}_3\text{W}_2\text{Cl}_6\text{P}$: C, 38.07; H, 3.79. Found: C, 38.39; H, 3.69. ^1H NMR (CD_3CN , ambient, δ): 8.0–7.6 (m, 20H, PPh_4 aromatic H's), 7.29 (d, 2H, ptol aromatic H's), 7.13 (d, 2H, ptol aromatic H's), 3.43 (m, 2H, μ -thioxane $\alpha\text{H}'$'s), 3.46 (m, 2H, μ -thioxane $\alpha\text{H}'$'s), 3.62 (m, 2H, μ -thioxane $\alpha\text{H}'$'s), 3.75 (m, 2H, μ -thioxane $\alpha\text{H}'$'s), 4.58 (m, 6H, μ -thioxane $\beta\text{H}'$'s), 4.43 (m, 2H, μ -thioxane $\alpha\text{H}'$'s), 3.63 (m, 2H, d) ppm; 3.08 (m, 2H, a) ppm;

3.73 (m, 2H, c) ppm; 3.62 (m, 2H, b), 2.32 (s, 3H, ptol methyl H's). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN , ambient, δ): 45.06 (s, 1C, μ -thioxane $\alpha\text{C}'$'s), 43.80 (s, 1C, μ -thioxane $\alpha\text{C}'$'s), 43.35 (s, 1C, μ -thioxane $\alpha\text{C}'$'s), 43.27 (s, 1C, μ -thioxane $\alpha\text{C}'$'s), 41.00 (s, 1C, d), 72.88 (s, 1C, c), 70.34 (s, 1C, b), 34.51 (s, 1C, a), 21.10 (s, 1C, ptol methyl C's), 68.39 (s, 2C, μ -thioxane $\beta\text{C}'$'s), 68.30 (s, 1C, μ -thioxane $\beta\text{C}'$'s), 68.12 (s, 1C, μ -thioxane $\beta\text{C}'$'s). Negative FAB-MS: m/z 1015 ($\text{Cl}_3\text{W}(\mu$ -1,4-thioxane)₂(μ -S(CH₂)₂O(CH₂)₂Sptol)WCl₃), 807 ($\text{Cl}_3\text{W}(\mu$ -S(CH₂)₂O(CH₂)₂Sptol)WCl₃).

[PPh₄][Cl₃W(μ -pms)₂(μ -S(CH₂)₅Sptol)WCl₃] (11). **3** (50 mg, 5.6×10^{-2} mmol) was reacted with $[\text{PPh}_4]\text{Sptol}$ (26 mg, 5.6×10^{-2} mmol) under refluxing conditions for 48 h. Yield: 67 mg (88%). Anal. Calcd for $\text{C}_{46}\text{H}_{57}\text{S}_4\text{W}_2\text{Cl}_6\text{P}$: C, 40.91; H, 4.25. Found: C, 37.57; H, 4.00. ^1H NMR (CD_3CN , ambient, δ): 8.0–7.7 (m, 20H, PPh_4 aromatic H's), 7.25 (d, 2H, ptol aromatic H's), 7.15 (d, 2H, ptol aromatic H's), 3.74 (m, 2H, μ -pms $\alpha\text{H}'$'s), 3.62 (m, 2H, μ -pms $\alpha\text{H}'$'s), 3.47 (m, 6H, μ -pms α and d H's), 2.91 (t, 2H, a), 2.46 (m, 8H, μ -pms β and d H's), 2.31 (s, 3H, ptol methyl H's), 1.75 (m, 6H, μ -pms γ and c H's), 1.60 (m, 4H, b and e). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN , ambient, δ): 51.93 (s, 1C, μ -pms $\alpha\text{C}'$'s), 50.94 (s, 1C, μ -pms $\alpha\text{C}'$'s), 50.65 (s, 1C, μ -pms $\alpha\text{C}'$'s), 50.25 (s, 1C, μ -pms $\alpha\text{C}'$'s), 44.67 (s, 1C, d), 38.65 (s, 1C, a) 37.13 (s, 1C, c), 34.13 (s, 1C, b), 33.54 (s, 1C, e), 31.75 (s, 1C, μ -pms $\beta\text{C}'$'s), 31.56 (s, 1C, μ -pms $\beta\text{C}'$'s), 31.50 (s, 1C, μ -pms $\beta\text{C}'$'s), 31.42 (s, 1C, μ -pms $\beta\text{C}'$'s), 28.10 (s, 1C, μ -pms $\gamma\text{C}'$'s), 27.94 (s, 1C, μ -pms $\gamma\text{C}'$'s), 21.75 (s, 1C, ptol CH₃).

Crystal Structure Determinations. A red prism of **1** ($0.20 \times 0.20 \times 0.20$ mm) was grown by slow evaporation of an acetone solution. A red prism of **2** ($0.10 \times 0.10 \times 0.10$ mm) was grown by preparing an acetone solution, adding approximately 10% v/v diethyl ether to this solution, and then storing this mixture overnight at -10°C . A red prism of **3** ($0.35 \times 0.18 \times 0.12$ mm) was obtained by slow evaporation of a CH_2Cl_2 solution with approximately 10% v/v hexane added. A red-brown prism of **7** ($0.35 \times 0.30 \times 0.10$ mm) was grown by slow evaporation of an acetonitrile solution. A red prism of **8** ($0.37 \times 0.20 \times 0.15$ mm) was obtained by slow evaporation of a chloroform solution.

1, 3, 7, and 8 were mounted on glass fibers for data collection on the University of Calgary's Rigaku AFC6S diffractometer with graphite-monochromated Mo K α radiation. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections within the range $\sim 18^\circ < 2\theta < \sim 25^\circ$. The data were collected using the ω - 2θ scan techniques to a maximum 2θ value of 50.1° . The diameter of the incident beam collimator was 1.0 mm, the crystal-to-detector distance was 400 mm, and the detector aperture was 9.0×13.0 mm (horizontal $\times$ vertical). Empirical absorption corrections, based on azimuthal scans of several reflections, were applied. All data were corrected for Lorentz and polarization effects. A linear correction factor was also applied to the data to account for fluctuations in the standards over the course of data collection ((**1**) +1.93%, (**3**) -1.68%, (**7**) -6.91%, (**8**) -1.15%). Correction for secondary extinction was applied for structures **1** and **7** (6.96129×10^{-8} and 2.61305×10^{-8} , respectively). The structures were solved by direct methods⁵ and expanded using Fourier techniques.⁶ All non-hydrogen atoms were refined anisotropically except for the C atoms which were refined isotropically. Hydrogen atoms were included but not refined. Neutral atom scattering factors were taken from Cromer and Waber.⁷ Anomalous dispersion effects were included in F_{calc} ,⁸ the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.⁹ The values

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Table 1. Crystallographic Data for $\text{Cl}_3\text{W}(\mu\text{-L})_3\text{WCl}_3$ [$\text{L} = 1,4\text{-Dithiane}$ (**1**), $1,4\text{-Thioxane}$ (**2**), pms (**3**)], $[\text{PPh}_4][\text{Cl}_3\text{W}(\mu\text{-}1,4\text{-dithiane})_2(\mu\text{-Cl})\text{WCl}_3]$ (**7**), and $[\text{PPh}_4][\text{Cl}_3\text{W}(\mu\text{-}1,4\text{-thioxane})_2(\mu\text{-Cl})\text{WCl}_3]$ (**8**)

	(1)	(2)	(3)	(7)	(8)
chemical formula	$\text{C}_{18}\text{H}_{36}\text{O}_2\text{S}_6\text{Cl}_6\text{W}_2$ acetone solvate	$\text{C}_{13.5}\text{H}_{27}\text{O}_{3.5}\text{S}_3\text{Cl}_6\text{W}_2$ acetone solvate	$\text{C}_{16}\text{H}_{33.5}\text{Cl}_6\text{S}_3\text{W}_2$ hexane solvate	$\text{C}_{34}\text{H}_{39}\text{S}_4\text{Cl}_7\text{PW}_2\text{N}$ acetonitrile solvate	$\text{C}_{33}\text{H}_{37}\text{S}_2\text{O}_2\text{Cl}_{10}\text{PW}_2\text{N}$ chloroform solvate
fw (g/mol)	1057.26	921.93	908.54	1236.77	1282.98
space group (no.)	$P2_1/n$ (14)	$P4/ncc$ (130)	$P2_1/n$ (14)	$P2_1/c$ (14)	$P2_1/a$ (14)
a (Å)	12.518(3)	25.7603(3)	11.874(4)	9.704(5)	13.531(4)
b (Å)	9.475(2)	25.7603(3)	21.823(3)	28.241(7)	25.207(5)
c (Å)	27.408(3)	18.6771(2)	12.545(3)	15.480(5)	14.083(3)
β (°)	93.34(1)	90	100.46(3)	98.55(4)	115.57(2)
V (Å ³)	3245.3(9)	12394.0(2)	3196(1)	4195(2)	4333(2)
Z	4	16	4	4	4
ρ_{calc} (g/cm ³)	2.16	1.976	1.888	1.96	1.967
μ (cm ⁻¹)	79.89	81.52	79.00	61.96	60.91
radiation, λ (Å)	Mo K α , 0.710 69	Mo K α , 0.710 73	Mo K α , 0.710 69	Mo K α , 0.710 69	Mo K α , 0.710 69
temp (°C)	-103.0	25(2)	-73.0	-103.0	-103
R, R_w ^a	0.046, 0.048	0.0763, 0.1309	0.051, 0.049	0.065, 0.064	0.0811, 0.0869

^a For structures **1**, **3**, **7**, and **8**, $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = (\sum\omega(|F_o| - |F_c|)^2/\sum\omega F_o^2)^{1/2}$; $\omega = 1/\sigma^2(F_o)$. For structure **2**, $R = \sum(|F_o - F_c|)/\sum(F_o)$; $R_w = \sum[\omega(F_o^2 - F_c^2)^2]$.

for the mass attenuation coefficients are those of Creagh and Hubbell.¹⁰ All calculations were performed using the *teXsan* crystallographic software package.¹¹

Due to the very small size of the crystals obtained for **2**, they were sent to the University of Windsor for structure determination using a CCD diffractometer. A suitable single crystal was selected and mounted with epoxy cement on a glass fiber. Unit-cell parameters were calculated from reflections obtained from 60 data frames collected at different sections of the Ewald sphere. Reflections were collected in the range $1.12 < 2\theta < 21.00^\circ$. The systematic absences in the diffraction data and the determined unit cell parameters were uniquely consistent for the reported space group. A semiempirical absorption correction was applied based on redundant data at varying effective azimuthal angles. A cocrystallized molecule of acetone solvent is located at a 2-fold axis. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were treated as idealized contributions. The structure was solved by direct methods, completed by subsequent Fourier syntheses and refined with full-matrix least-squares methods. All scattering factors and anomalous dispersion coefficients are contained in the SHELXTL 5.03 program library (Sheldrick, G. M. Madison, WI).

The essential data for all crystals are summarized in Table 1.

Results and Discussion

Syntheses. Initially four thioether ring systems were studied: trimethylene sulfide, pms, 1,4-dithiane, and 1,4-thioxane. The former two were an attempt to prepare a precursor, which when ring-opened, created pendant arms of varying lengths. The latter two were attempts to see whether incorporation of a heteroatom into the thioether ring affected ring-opening and consequently if metallo-donor groups could be incorporated via the ring and not necessarily through the nucleophile. The incorporation of a heteroatom was also seen to be a way of decreasing the number of atoms which have no binding ability and which therefore, would be expected to diminish stability as well as potential electronic communication between a host and guest. Placement of a heteroatom in a position para to the sulfur atom was also seen as a way to facilitate the syntheses of metalloligands possessing a crown ether type bracket.

Attempts to prepare the thietane complex, $\text{Cl}_3\text{W}(\mu\text{-S}(\text{CH}_2)_3)_3\text{WCl}_3$ (**13**), were unsuccessful. No reaction was observed at room temperature even after 30 days. When higher temperatures

Table 2. Selected Reactivity Data for Reactions of WCl_4 with Excess Thioether

	1,4-dithiane	1,4-thioxane	pms
overall yield (%)	50	100	85
ratio tris:bis (%)	50:50	20:80	90:10
reaction time	24 h	25 min	45 min

were used, decomposition occurred to yield a brown polymeric material. This result was not surprising as thermal ring-opening and subsequent oligomerization of metal bridging thietanes is known.¹²

Tris-thioether complexes of 1,4-dithiane, 1,4-thioxane, and pms (**1**–**3**), respectively, were all prepared successfully. However, their production was accompanied by that of the anionic bis-thioether bridged complexes (**4**–**6**). Syntheses differ in overall yields, product distribution and reaction time as shown in Table 2. High overall yields and short reaction times reflect the use of liquid thioethers. The reasons for the varying product distribution is unknown.

A crude separation of the tris- and bis-thioether complexes can generally be accomplished by first extracting the tris-complexes from the reaction slurry using CH_2Cl_2 then extracting a mixture, comprised primarily of the bis-complex, using acetone. For purification it is necessary to perform repeated crystallization's. It is noteworthy that subsequent characterization of **3** is hampered by the significant decrease of its solubility once purified. Characterization of **1**–**6** was accomplished by NMR spectrometry, elemental analyses, negative FAB-MS mass spectrometry or X-ray diffraction.

Assignment of NMR data was based on homonuclear decoupling, XH CORR, and COSY experiments. The NMR spectra of **1**–**3** reflect a highly symmetrical orientation of the three bridging thioether groups, that is, only one environment is detected for α , β , or γ nuclei (for labeling see Scheme 1). The NMR spectra of **4**–**6** resemble those of **1**–**3** but with an apparent doubling of all the resonances. This is consistent with one of the bridging thioethers having been replaced by a bridging chlorine atom. This would, for example, create two sets of magnetically equivalent α nuclei arising from the different orientations that they can adopt with respect to the bridging chloride. The apparent doubling is seen to decrease as one moves to nuclei located farther and farther away from the bridge where differing orientations are less pronounced. All ^1H NMR resonances are complicated by second-order effects. Chemical

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(11) *teXsan: Crystal Structure Analysis Package*; Molecular Structure Corporation: The Woodlands, TX, 1985 and 1992.

(12) Adams, R. D.; Falloon, S. B. *Chem. Rev.* **1995**, 95, 2587–98.

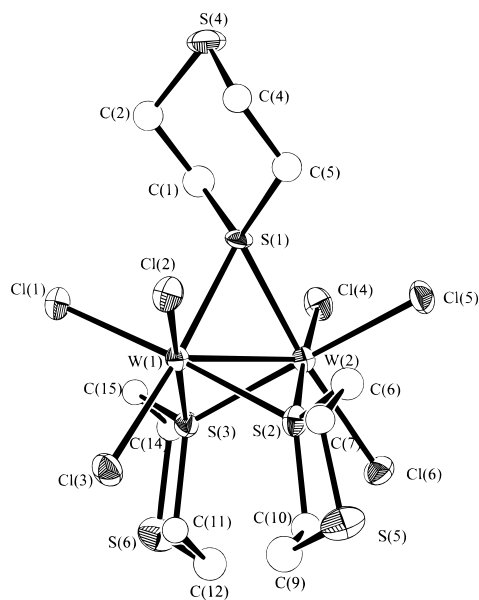


Figure 1. ORTEP representation and labeling scheme for $\text{Cl}_3\text{W}(\mu\text{-1,4-dithiane})_3\text{WCl}_3$ (**1**). Hydrogen atoms omitted for clarity.

shifts and chemical shift differences suggest that in **2** and **5** it is the sulfur and not the oxygen atom that is bridging.

Elemental analyses were not always consistent due to product mixtures, decomposition or the incorporation of solvent. For some, negative FAB-MS was useful for characterization. In the cases where both negative FAB-MS and elemental analyses were unclear, crystal structures were relied upon for definitive results.

As a metalloligand precursor it is the ring-opening of the tris complex which is of greatest interest for two reasons. An anionic nucleophile would be expected to react with a neutral species more favorably than with another anionic species, plus the creation of a dianionic metalloligand might not be expected to be as stable as a monoanionic one. When considering the viability of using the newly prepared tris-ring thioether bridged complexes in the syntheses of metalloligands, not only do these desired complexes have to be able to be synthesized, but they have to be synthesized in reasonable yields to be of any practical value. The disappointingly low yields of **1** and **2** prompted investigation into whether the bis complexes could be converted to the tris thereby potentially increasing the yields of desired species from 25 to 20% up to 50–100%, respectively.

Conversion of $[\text{Na}][\text{Cl}_3\text{W}(\mu\text{-L})_2(\mu\text{-Cl})\text{WCl}_3]$ to $\text{Cl}_3\text{W}(\mu\text{-L})_3\text{WCl}_3$ was attempted by refluxing in the presence of excess L (L = 1,4-dithiane, 1,4-thioxane). The best percent conversions observed were 50% and 20%, respectively, after reaction times of 6 h, when toluene was used as a solvent.

Molecular Structures. The structures of **1**, **2**, **3**, and **7**, and **8** are shown in Figures 1–5, respectively. They strongly support the validity of assignments made using NMR studies. Important bond lengths and angles are given in Tables 3–5. They are the first reported crystal structures of ditungsten(III) cyclic tris-thioether-bridged complexes. The X-ray crystal structure of **5** proves unequivocally that 1,4-thioxane bridges two ditungsten(III) centers using only its sulfur atom. All the complexes adopt the expected confacial bioctahedral framework. All possess acute WSW bond angles from 61 to 63° and short W–W bonds observed between 2.49 and 2.53 Å. Though the angles are similar to the isostructural $\text{W}_2\text{Cl}_9^{3-}$ ion, which is generally accepted to possess a triple bond, the W–W bond lengths are some of the longest observed for $\text{W}^{\text{III}}\text{--}\text{W}^{\text{III}}$ complexes approaching those of $\text{W}^{\text{III}}\text{--}$

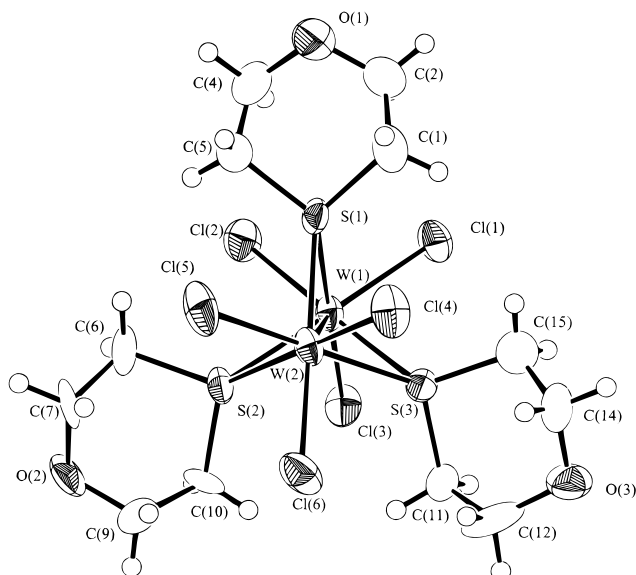


Figure 2. ORTEP representation and labeling scheme for $\text{Cl}_3\text{W}(\mu\text{-1,4-thioxane})_3\text{WCl}_3$ (**2**).

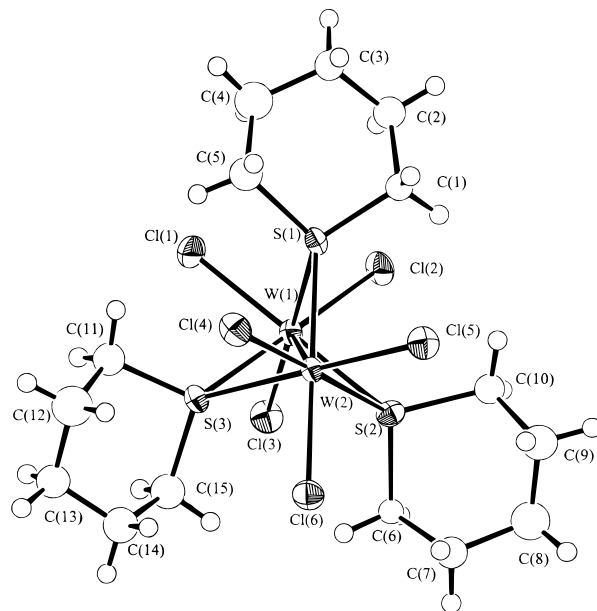


Figure 3. ORTEP representation and labeling scheme for $\text{Cl}_3\text{W}(\mu\text{-pms})_3\text{WCl}_3$ (**3**).

W^{IV} .¹³ The thioether rings are oriented perpendicular to the W–W bond and adopt staggered chair conformations with respect to one another. Unlike their tht analogue, $\text{Cl}_3\text{W}(\mu\text{-tht})_3\text{WCl}_3$ (**12**),¹⁴ the rings exhibited no disorder probably due to the chair conformation being involved in the stabilization of packing. All complexes were solvates. In the case of dithiane or thioxane there was no significant interaction between the solvent and the heteroatom in the ring. The S–C bond distances for all are comparable to those in $\text{Cl}_3\text{W}(\mu\text{-SEt}_2)_3\text{WCl}_3$ (**14**).¹ Interestingly, for the dithiane complexes, there is no appreciable difference between the $\mu\text{-S--C}$ bonds (1.79(2)–1.83(2) Å) and the nonbridging S–C bonds (1.79(2)–1.86(2) Å), however, the C–S–C angles are greater for the bridging S atoms (101.7(8)–104.1(8)°) as opposed to the nonbridging (96.8(9)–99.6(8)°). The authors have been able to find only one other

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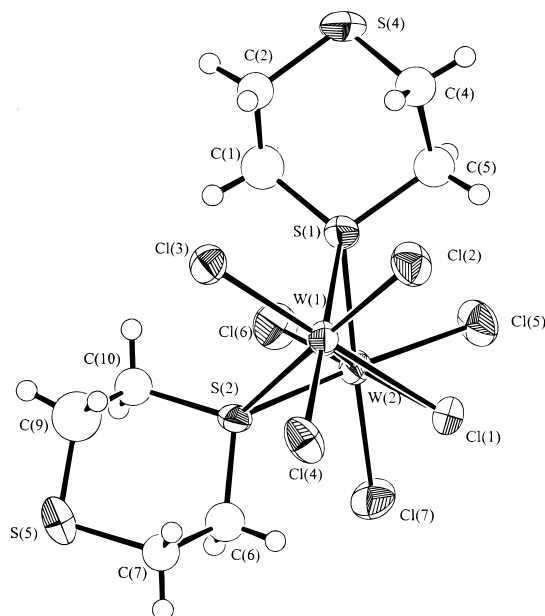


Figure 4. ORTEP representation and labeling scheme for the anionic portion of $[\text{PPh}_4][\text{Cl}_3\text{W}(\mu\text{-1,4-dithiane})_2(\mu\text{-Cl})\text{WCl}_3]$ (**7**).

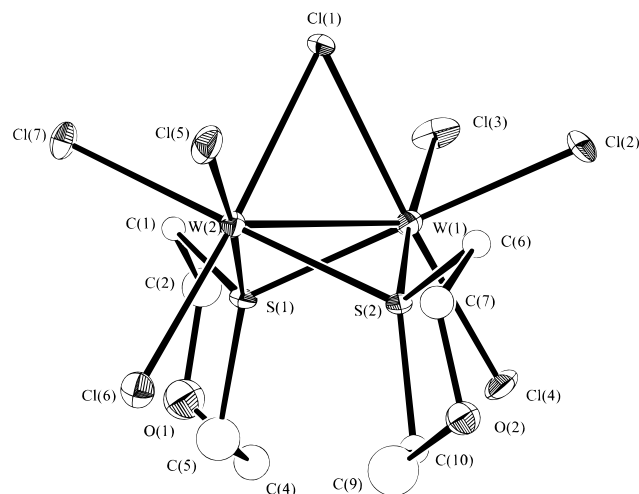


Figure 5. ORTEP representation and labeling scheme for the anionic portion of $[\text{PPh}_4][\text{Cl}_3\text{W}(\mu\text{-1,4-thioxane})_2(\mu\text{-Cl})\text{WCl}_3]$ (**8**). Hydrogen atoms omitted for clarity.

transition-metal dithiane bridged complex, where the sulfur atoms of the dithiane are unoxidized, $(\text{CO})_2\text{CpMo}(\mu\text{-S}(\text{CH}_2\text{-CH}_2)\text{S})\text{MoCp}(\text{CO})_2$.¹⁵ The dithiane ring in this structure also lies perpendicular to the metal–metal bond and adopts a chair conformation. Several structures of transition-metal thioxane bridged complexes have been found in the literature.^{16a–c} All are late transition-metal complexes (Cu(I), Ag(I), and Pt(II)) and bridging occurs via either both the S and O atoms or only the S atom.

Reactions with $[\text{PPh}_4][\text{Sptol}]$. Once synthesized, nucleophilic attack with $[\text{PPh}_4][\text{Sptol}]$ was examined to see if **1–3** were suitable candidates for ring-opening. When reacted with 1 equiv of $[\text{PPh}_4][\text{Sptol}]$, all resulted in the desired ring-opening

Table 3. Selected Bond Lengths (Å) for $\text{Cl}_3\text{W}(\mu\text{-L})_3\text{WCl}_3$ [L = 1,4-Dithiane (**1**), 1,4-Thioxane (**2**), pms (**3**)], $[\text{PPh}_4][\text{Cl}_3\text{W}(\mu\text{-1,4-dithiane})_2(\mu\text{-Cl})\text{WCl}_3]$ (**7**), and $[\text{PPh}_4][\text{Cl}_3\text{W}(\mu\text{-1,4-thioxane})_2(\mu\text{-Cl})\text{WCl}_3]$ (**8**)^a

	1	2	3	7	8
W(1)–W(2)	2.507(1)	2.529(1)	2.506(2)	2.481(2)	2.496(4)
W(1)–S(1)	2.413(4)	2.428(5)	2.418(6)	2.375(6)	2.38(2)
W(1)–S(2)	2.437(5)	2.419(5)	2.405(6)	2.406(6)	2.38(2)
W(1)–S(3)	2.420(5)	2.413(5)	2.414(6)	—	—
W(2)–S(1)	2.404(4)	2.415(6)	2.406(6)	2.378(7)	2.38(2)
W(2)–S(2)	2.431(5)	2.431(5)	2.401(6)	2.394(6)	2.39(2)
W(2)–S(3)	2.429(5)	2.425(5)	2.410(6)	—	—
S(1)–C(1)	1.81(2)	1.84(2)	1.79(2)	1.80(3)	1.80(8)
S(1)–C(5)	1.81(2)	1.82(2)	1.83(2)	1.87(3)	1.81(10)
S(2)–C(6)	1.79(2)	1.83(2)	1.83(2)	1.74(3)	1.84(8)
S(2)–C(10)	1.85(2)	1.79(2)	1.84(2)	1.80(3)	1.82(8)
S(3)–C(11)	1.83(2)	1.81(2)	1.80(3)	—	—
S(3)–C(15)	1.82(2)	1.82(2)	1.81(3)	—	—
X ₁ –C(2)	1.79(2)	1.44(3)	1.50(3)	1.81(2)	1.39(11)
X ₁ –C(4)	1.81(2)	1.44(3)	1.50(3)	1.78(2)	1.41(10)
X ₂ –C(7)	1.83(2)	1.39(3)	1.52(3)	1.86(3)	1.46(10)
X ₂ –C(9)	1.76(2)	1.46(3)	1.51(3)	1.76(3)	1.35(12)
X ₃ –C(12)	1.81(2)	1.48(3)	1.51(3)	—	—
X ₃ –C(14)	1.86(2)	1.44(3)	1.46(3)	—	—

^a X₁ = S(4) (**1**, **7**); O(1) (**2**, **8**); C(3) (**3**). X₂ = S(5) (**1**, **7**); O(2) (**2**, **8**); C(8) (**3**). X₃ = S(6) (**1**); O(3) (**2**); C(13) (**3**).

Table 4. Selected Bond Angles (deg) for $\text{Cl}_3\text{W}(\mu\text{-L})_3\text{WCl}_3$ [L = 1,4-Dithiane (**1**), 1,4-Thioxane (**2**), pms (**3**)], $[\text{PPh}_4][\text{Cl}_3\text{W}(\mu\text{-1,4-dithiane})_2(\mu\text{-Cl})\text{WCl}_3]$ (**7**), and $[\text{PPh}_4][\text{Cl}_3\text{W}(\mu\text{-1,4-thioxane})_2(\mu\text{-Cl})\text{WCl}_3]$ (**8**)^a

	1	2	3	7	8
W(1)–S(1)–W(2)	62.7(1)	62.9(1)	62.6(2)	62.9(2)	63.3(5)
W(1)–S(2)–W(2)	62.0(1)	62.8(1)	62.9(2)	62.2(2)	63.1(6)
W(1)–S(3)–W(2)	62.3(1)	63.0(1)	62.6(1)	—	—
C(1)–S(1)–C(5)	102.9(8)	99(1)	102(1)	104(1)	101(4)
C(6)–S(2)–C(10)	104.1(8)	99(1)	102(1)	104(1)	103(4)
C(11)–S(3)–C(15)	101.7(8)	99(1)	100(1)	—	—
C(2)–X ₁ –C(4)	98.0(8)	111(2)	112(2)	99(1)	115(7)
C(7)–X ₂ –C(9)	96.8(9)	112(2)	113(2)	98(1)	110(7)
C(12)–X ₃ –C(14)	99.6(8)	108(2)	112(2)	—	—

^a X₁ = S(4) (**1**, **7**); O(1) (**2**, **8**); C(3) (**3**). X₂ = S(5) (**1**, **7**); O(2) (**2**, **8**); C(8) (**3**). X₃ = S(6) (**1**); O(3) (**2**); C(13) (**3**).

via $\mu\text{-S-C}$ bond cleavage to produce **9–11**. The reactions producing **9** and **10** occurred at room temperature, that with **11** required refluxing conditions perhaps due to its insolubility once purified. The NMR spectra of **9–11** show resonances for two intact rings and the desired $\text{S}(\text{CH}_2)_2\text{E}(\text{CH}_2)_2\text{Sptol}$ moiety (E = S, O, CH₂). Assignment was based on comparison of the chemical shift changes observed for the Sptol ring-opened tht analogue, $[\text{PPh}_4][\text{Cl}_3\text{W}(\mu\text{-tht})_2(\mu\text{-S}(\text{CH}_2)_4\text{Sptol})\text{WCl}_3]$ (**15**),² COSY, and XHCORR experiments.

Electrochemical Studies. The extreme insolubility of **3** once purified and the difficulty in isolating **6** have resulted in unsuccessful studies on these species. Cyclic voltammetric studies of **1**, **2**, **4**, **5**, **7**, and **8** were performed in CH₂Cl₂ by employing $[\text{Bu}_4\text{N}][\text{PF}_6]$ as the supporting electrolyte and a graphite electrode with SCE reference electrode. **4** and **5** underwent cation exchange with the supporting electrolyte to produce $[\text{Bu}_4\text{N}][\text{Cl}_3\text{W}(\mu\text{-L})_2(\mu\text{-Cl})\text{WCl}_3]$ (L = 1,4-dithiane (**16**), 1,4-thioxane (**17**)). All exhibit reversible waves representative of a one-electron reduction. Within experimental error there is no significant difference between the potentials exhibited for the neutral heteroatom containing tris-thioethers, **1** and **2** (–0.62 V); however, they do differ significantly from the analogous hydrocarbon thioethers, **12** and **14** (–0.72 V).¹ The anionic

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Table 5. Comparison of Selected Structural Data for $\text{Cl}_3\text{W}(\mu\text{-L})_3\text{WCl}_3$ [$\text{L} = 1,4\text{-Dithiane (1), 1,4-Thioxane (2), pms (3)}$], $[\text{PPh}_4][\text{Cl}_3\text{W}(\mu\text{-1,4-dithiane})_2(\mu\text{-Cl})\text{WCl}_3]$ (**7**), and $[\text{PPh}_4][\text{Cl}_3\text{W}(\mu\text{-1,4-thioxane})_2(\mu\text{-Cl})\text{WCl}_3]$ (**8**)

	1	2	3	7	8
W–W (Å)	2.507(1)	2.529(1)	2.506(2)	2.481(2)	2.496(4)
min–max W–S–W (deg)	62.0(1)–62.7(1)	62.8(1)–63.0(1)	62.6(1)–62.9(2)	62.2(2)–62.9(2)	63.1(6)–63.3(5)
min–max W–S (Å)	2.404(4)–2.437(4)	2.413(5)–2.431(5)	2.401(6)–2.418(6)	2.375(6)–2.406(6)	2.38(2)–2.39(2)

bis-thioethers **7**, **8**, and **15** have a similar reduction wave occurring at a more negative reduction potential (–1.17 to –1.23 V). The peak to peak separations observed were from 120 to 140 mV. The reversible reduction of the anionic bis-thioethers suggests that similar behavior should be observed for the ring-opened species (**9–11**).

Conclusions

The preparation of an analogue of $\text{Cl}_3\text{W}(\mu\text{-tht})_3\text{WCl}_3$ (**12**) using the four-membered thietane ring is not possible using our thermally based synthetic procedure. The preparation of the six-membered ring analogues $\text{Cl}_3\text{W}(\mu\text{-L})_3\text{WCl}_3$ ($\text{L} = 1,4\text{-dithiane (1), 1,4-thioxane (2), pms (3)}$) has been achieved and is accompanied by the synthesis of $[\text{Na}][\text{Cl}_3\text{W}(\mu\text{-L})_2(\mu\text{-Cl})\text{WCl}_3]$ ($\text{L} = 1,4\text{-dithiane (4), 1,4-thioxane (5), pms (6)}$). Overall product yields were lowered when using a solid thioether. Incorporation of heteroatoms into the thioether ring resulted in

a significant change in the tris:bis product distribution ratio. Nucleophilic ring-opening was initiated in $\text{Cl}_3\text{W}(\mu\text{-L})_3\text{WCl}_3$ but could not be achieved for $[\text{Na}][\text{Cl}_3\text{W}(\mu\text{-L})_2(\mu\text{-Cl})\text{WCl}_3]$. The bis-thioether bridged complexes were converted to the tris- in low yields. Electrochemical results for the anionic bis-complexes suggest that ring-opened ditungsten (III) complexes could behave as electron reservoirs.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for complexes **1**, **2**, **3**, **7**, and **8** are available on the Internet only. Access information is given on any current masthead page.

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