

The Chemistry of Thietane Ligands in Polynuclear Metal Carbonyl Complexes

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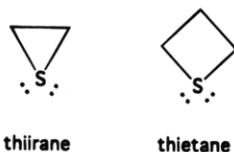
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1. Introduction

Small ring compounds can be valuable reagents because they contain a supply of energy as a result of their ring strain and thus can engage in a wide range of exothermic ring opening reactions.¹ Strained ring heterocycles are of particular interest because the heteroatoms can introduce useful functionality into the products.² There are two important families of saturated strained ring heterocycles that contain sulfur: thiiranes and thietanes.

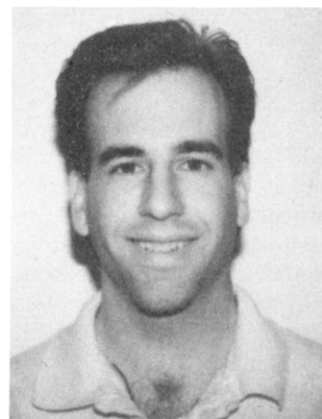


The thiiranes³ are based on three-membered rings and thietanes are based on four-membered rings.⁴ Thiiranes are readily polymerized both by Lewis acids and by Lewis bases.⁵ Thiiranes also undergo facile elimination of sulfur to yield the corresponding olefin.^{3,6} The desulfurization of thiiranes is promoted by metal atoms,⁷ and through this reaction these molecules have been found to serve as clean sources of monatomic sulfur for use in the synthesis of polynuclear metal complexes containing sulfido ligands.⁸

Interestingly, thietanes have only slightly less strain energy than thiiranes (80.3 kJ/mol versus 81.1 kJ/mol).⁹ On clean metal surfaces thietanes are readily desulfurized, even at low temperatures, with the formation of alkenes and cyclopropane.^{10, 11} Friend and co-workers have studied the reaction of thietane on the molybdenum(110) crystal surface.¹⁰ Three



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organic products; propene, propane, and cyclopropane, were formed; see Figure 1. Cyclopropane formation was proposed to occur by the direct cleavage of the two C–S bonds (pathway A). Propene and propane formation are believed to occur by stepwise or sequential cleavages of C–S bonds and involve interactions with adventitious hydrogen on the metal surface (pathways B–C and B–D).

Like thiiranes, thietanes are also readily polymerized by Lewis acids **A** and Lewis bases **B**: (Figure 2).^{4,12}

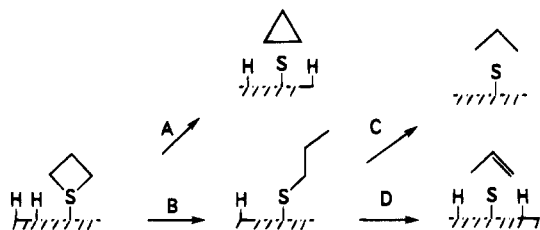


Figure 1. A schematic of the reactions of thietane on a molybdenum surface.

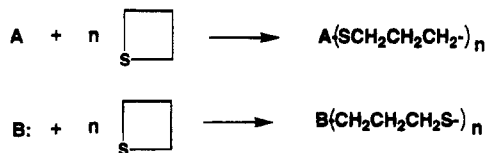
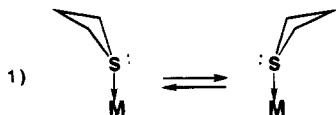


Figure 2. A representation of the general form polymerization reactions of thietane by Lewis acids **A** and Lewis bases **B**.

Unlike thiiranes, thietanes are sufficiently stable to serve as effective ligands in metal complexes through the coordination of one or both of the lone pairs of electrons on the sulfur atom. In the latter case the molecules are invariably found as bridging ligands between two metal atoms. In this review, the coordination chemistry of thietane ligands in polynuclear metal carbonyl complexes (also known as cluster compounds) in both the terminal coordination mode and the bridging coordination mode is discussed. This will include an extensive discussion of ring opening and cyclooligomerization transformations of these ligands. The review will conclude with a summary of recent studies of the coordination of thietane cyclooligomers (polythioether macrocycles) to metal cluster complexes.

2. Terminally Coordinated Thietane Ligands

The first thietane complexes were prepared by Abel et al.¹³ In most cases, thietane complexes are prepared by simple ligand substitution reactions. Spectral analyses indicate that thietane ligands have a pyramidal geometry at the sulfur atom with only one of the lone pairs of electrons on the sulfur being coordinated to the metal atom. These ligands readily undergo inversion of configuration at the sulfur atom at rates which are usually rapid on the NMR time scale at ambient temperatures (eq 1).¹⁴



The first structural characterization of a cluster complex containing a terminally coordinated thietane ligand was reported in 1990 for the complex, $\text{Os}_3(\text{CO})_{11}[\text{SCH}_2\text{CH}_2\text{CH}_2]$ (**1**, Figure 3).¹⁵ The thietane ligand is coordinated to only one of the three osmium atoms. The ligand is non-planar with a C-S-C/C-C-C dihedral angle of 28°. A terminally coordinated thietane ligand was recently characterized crystallographically in the mononuclear ruthenium complex $[\text{CpRu}(\text{PPh}_3)_2(\text{SCH}_2\text{CH}_2\text{CH}_2)][\text{O}_3\text{SCF}_3]$.¹⁶

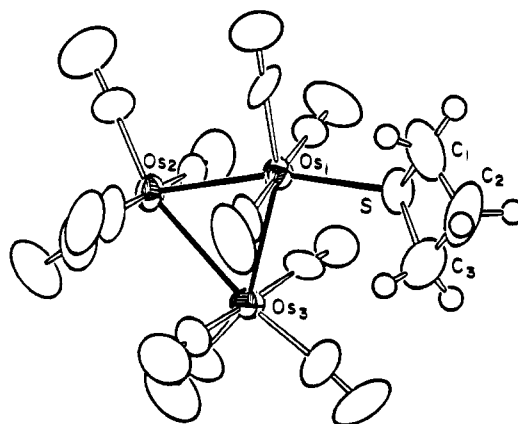


Figure 3. An ORTEP diagram of the molecular structure of $\text{Os}_3(\text{CO})_{11}[\text{SCH}_2\text{CH}_2\text{CH}_2]$ (**1**).

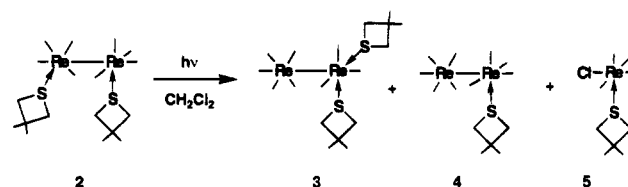
In this complex the dihedral angle of the thietane ligand is 29.4°. The structure of the thietane ligand does not differ significantly from that reported for the free molecule in the gas phase.¹⁷ In the free molecule the dihedral angle is 26° and the C-S distances are 1.85 Å. In the ligand the C-S distances are 1.83(2) and 1.85(2) Å¹⁵ and 1.823(8) and 1.828(9) Å.¹⁶

Thietane ligands undergo transformations involving C-H bond cleavage at the ring carbon atom at the 3-position. These transformations can be blocked by the placement of methyl groups at the 3-position. Thus, it has been possible to prepare a greater variety of thietane complexes by using 3,3-dimethylthietane (3,3-DMT). For example, the disubstituted complex

1,2- $\text{Re}_2(\text{CO})_8(\text{SCH}_2\text{CMe}_2\text{CH}_2)_2$ (**2**) was obtained from the reaction of 3,3-DMT with $\text{Re}_2(\text{CO})_8[\mu\text{-C}(\text{H})\text{-CBu}^n]$.¹⁸ In the presence of fluorescent room light, this compound was transformed and isomerized in methylene chloride solutions to three new compounds: 1,1- $\text{Re}_2(\text{CO})_8(\text{SCH}_2\text{CMe}_2\text{CH}_2)_2$ (**3**), $\text{Re}_2(\text{CO})_8(\text{SCH}_2\text{CMe}_2\text{CH}_2)$ (**4**), and *cis*- $\text{ReCl}(\text{CO})_4(\text{SCH}_2\text{CMe}_2\text{CH}_2)$ (**5**), the latter was obtained by reaction with the solvent; see Scheme 1. Each of these four complexes contains at least one terminally coordinated 3,3-DMT ligand. In compound **2** the thietane ligands are coordinated to different metal atoms, while in **3** they are both bonded to the same metal atom in coordination sites *cis* to the Re-Re bond. These thietane ligands are also nonplanar. The dihedral C-S-C/C-C-C angles in **2**, **3**, **4**, and **5** are 22.1°, 24.6°, 5.2°, and 25.6°, respectively. The structural analysis of **4** is of high quality; therefore, the small dihedral angle, 5.2°, is believed to be an accurate value. This could indicate that the energy well, related to ligand folding, is fairly shallow in this case and perhaps all cases.

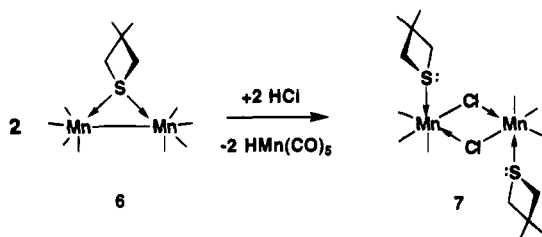
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Scheme 1



Treatment of the dinuclear complex $\text{Mn}_2(\text{CO})_8(\text{SCH}_2\text{CMe}_2\text{CH}_2)$ (**6**) with HCl yielded the thietane complex $[\text{Mn}(\text{CO})_3(\text{SCH}_2\text{CMe}_2\text{CH}_2)(\mu\text{-Cl})_2]$ (**7**) and $\text{HMn}(\text{CO})_5$ (Scheme 2).¹⁹

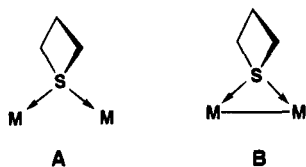
Scheme 2



Compound **6** contains a bridging 3,3-DMT ligand and will be described in the next section. Compound **7** contains two 3,3-DMT ligands, one on each metal atom. A *trans*-isomer which has the two 3,3-DMT ligands on opposite sides of the molecule was characterized crystallographically, but in solution it exists as a mixture of isomers. There is no metal-metal bond in **7**, $\text{Mn}\cdots\text{Mn} = 3.578(1)$ Å, and the metal atoms are held together by the bridging chloride ligands. The C-S-C/C-C-C dihedral angle in the 3,3-DMT ligands is 24.9° .

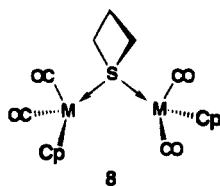
3. Bridging Thietane Ligands

By employing both of the lone pairs of electrons, thietane ligands can adopt a bridging coordination mode with simultaneous bonding to two metal atoms. The metal atoms can be separated, structure **A**, or mutually bonded as in structure **B**.



There are no known examples of thietane ligands bridging three or more atoms. Such a bonding situation may be unstable, since the sulfur atom has only two lone pairs of electrons and the coordinate bonds between the metal and sulfur atoms usually adopt a two-center two-electron type, but it is not impossible to imagine and examples may be found someday.

The first structurally characterized complex of the type **A** was $[\text{CpMn}(\text{CO})_2]_2[\mu\text{-SCH}_2\text{CMe}_2\text{CH}_2]$ (**8**) where each lone pair of electrons on the sulfur atom is coordinated to a different $\text{CpMn}(\text{CO})_2$ grouping.²⁰



The first cluster complex containing a bridging thietane ligand of the type **B** was $\text{Os}_3(\text{CO})_{10}$ -

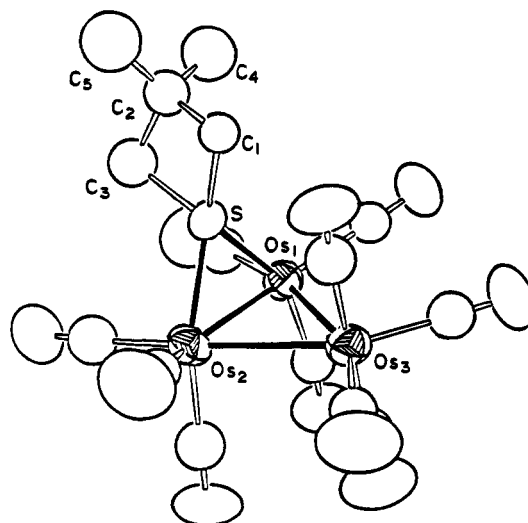
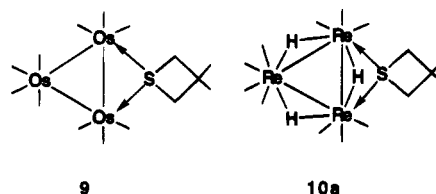


Figure 4. An ORTEP diagram of the molecular structure of $\text{Os}_3(\text{CO})_{10}[\mu\text{-SCH}_2\text{CMe}_2\text{CH}_2]$ (**9**).

$[\mu\text{-SCH}_2\text{CMe}_2\text{CH}_2]$ (**9**) which was obtained from the reaction of 3,3-DMT with $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$; see Figure 4.²¹

The complex was characterized crystallographically, and the C-S-C/C-C-C dihedral angle in the 3,3-DMT ligand at 20.6° is slightly smaller than that found for terminally coordinated 3,3-DMT ligands. The Os-S-Os angle is quite acute, $73.1(2)^\circ$, and may contain some strain from the bonding to the metal atoms.

The reactions of 3,3-DMT and thietane with $\text{Re}_3(\text{CO})_{10}(\text{NCMe})_2(\mu\text{-H})_3$ have yielded the new complexes $\text{Re}_3(\text{CO})_{10}[\mu\text{-SCH}_2\text{CMe}_2\text{CH}_2](\mu\text{-H})_3$ (**10a**) and $\text{Re}_3(\text{CO})_{10}[\mu\text{-SCH}_2\text{CH}_2\text{CH}_2](\mu\text{-H})_3$ (**10b**).²² Compound **10a** was

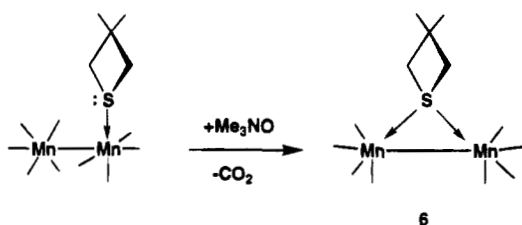


structurally characterized and was found to contain a closed trirhenium cluster and a bridging thietane ligand coordinated through its sulfur atom. The molecule is very similar to that of **9** but has three bridging hydride ligands, one across each of the Re-Re bonds to account for the fact that Re has one less electron than osmium. The C-S-C/C-C-C dihedral angle in the 3,3-DMT ligand is 12.4° .

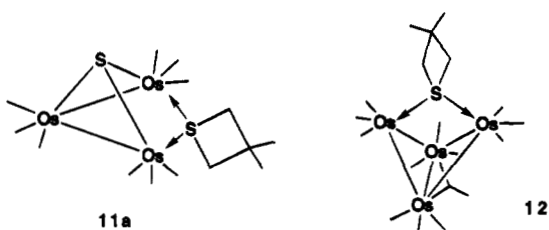
Decarbonylation of the complex $\text{Mn}_2(\text{CO})_9$ - $(\text{SCH}_2\text{CMe}_2\text{CH}_2)$ with Me_3NO yields the complex **6** (shown schematically in Scheme 3) by transformation of the terminal thietane ligand into a bridging ligand. There is a Mn-Mn single bond [$\text{Mn-Mn} = 2.8243(9)$ Å], but the M-S-M angle is significantly larger than that in found in **9** [$79.48(4)^\circ$]. The C-S-C/C-C-C dihedral angle of the 3,3-DMT ligand in **6** is 24.7° .¹⁹

The reactions of $\text{Os}_3(\text{CO})_{10}(\mu_3\text{-S})$ with 3,3-DMT or thietane in the presence of Me_3NO yielded the

Scheme 3



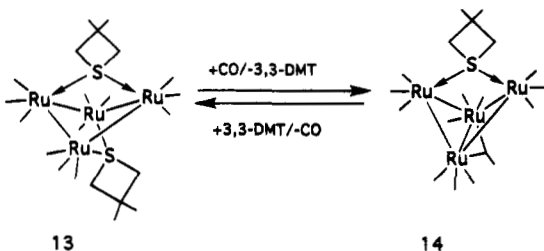
complexes $\text{Os}_3(\text{CO})_9(\mu_3\text{-S})[\mu\text{-SCH}_2\text{CMe}_2\text{CH}_2]$ (**11a**) and $\text{Os}_3(\text{CO})_9(\mu_3\text{-S})[\mu\text{-SCH}_2\text{CH}_2\text{CH}_2]$, (**11b**), respectively.²³ Compound **11a** was characterized structurally. In these compounds, the thietane ligands bridge two metal atoms that are not themselves mutually bonded. Thus, the Os–S–Os angle at the bridging sulfur atom of the thietane ligand at $99.8(1)^\circ$ is much larger than that in **9**.



$\text{Os}_4(\text{CO})_{12}(\mu\text{-CO})[\mu\text{-SCH}_2\text{CMe}_2\text{CH}_2]$ (**12**) was one of several products obtained from the pyrolysis of **9**.²⁴ The structure of this molecule consists of a butterfly tetrahedron of four osmium atoms with the thietane ligand situated as a bridge between the nonbonded wingtip metal atoms.²⁵ The pucker in the 3,3-DMT ligand is only 18.2° and the Os–S–Os angle is $104.3(1)^\circ$.

When $\text{Ru}_3(\text{CO})_{12}$ is allowed to react with 3,3-DMT, the tetraruthenium complex $\text{Ru}_4(\text{CO})_{12}[\mu\text{-SCH}_2\text{-CMe}_2\text{CH}_2]_2$, **13** is formed.²⁶ This complex contains a puckered square of four ruthenium atoms with two 3,3-DMT ligands bridging nonbonded pairs of ruthenium atoms across the cluster on opposite sides. Compound **13** reacts with CO by displacement of one of the DMT ligands to yield the butterfly cluster complex $\text{Ru}_4(\text{CO})_{13}[\mu\text{-SCH}_2\text{CMe}_2\text{CH}_2]$ (**14**) which is structurally analogous to **12**. This reaction is reversible; see Scheme 4.

Scheme 4

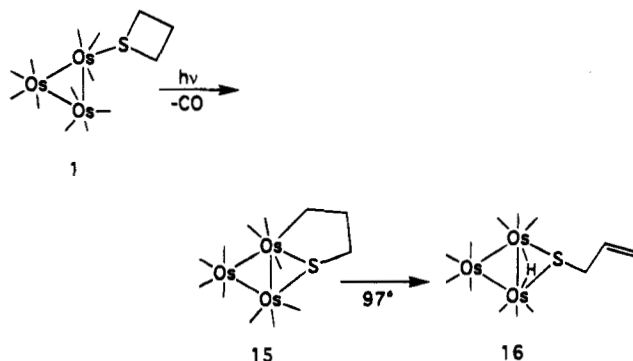


4. Ring-Opening Reactions—Thermal and Photochemical

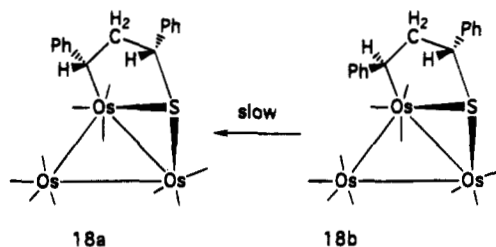
Compound **1** is decarbonylated when exposed to UV–vis irradiation to yield the complex $\text{Os}_3(\text{CO})_{10}(\mu\text{-$

$\text{SCH}_2\text{CH}_2\text{CH}_2)$ (**15**) which contains a thiametallacyclic ring formed by the insertion of one of the metal atoms into one of the S–C bonds of the thietane ligand. The propenethiolato complex $\text{Os}_3(\text{CO})_{10}(\mu\text{-SCH}_2\text{CH}=\text{CH}_2)(\mu\text{-H})$ (**16**) was also formed in small amounts, but this was shown to be a product derived from **15** by a thermal rearrangement involving an intramolecular $\beta\text{-CH}$ elimination reaction in **15**; see Scheme 5.^{15b}

Scheme 5

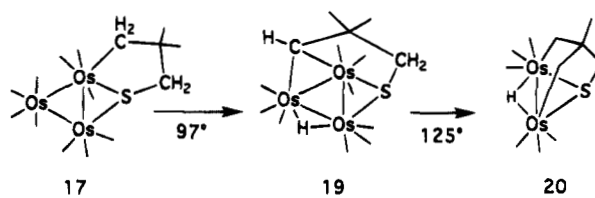


Photolysis of **8** yields the corresponding dimethyl homologue of **15**, $\text{Os}_3(\text{CO})_{10}(\mu\text{-SCH}_2\text{CMe}_2\text{CH}_2)$ (**17**).²⁴ Interestingly, the reaction of $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ with *trans*-2,4-diphenylthietane yielded the metallacyclic complex $\text{Os}_3(\text{CO})_{10}(\mu\text{-SC(H)PhCH}_2\text{C(H)Ph})$ as a mixture of *cis*- and *trans*-isomers **18a** and **18b** without irradiation.²⁷



The formation of isomers suggests the involvement of radical intermediates in the ring-opening process. This may be facilitated by the presence of the phenyl rings in this case. Interestingly, **18b** slowly isomerizes to **18a** in solution, presumably via homolysis of the Os–C bond. Compounds **18a,b** undergo facile intramolecular $\beta\text{-CH}$ elimination to yield triosmium clusters analogous to **16** containing 1,3-diphenylpropenethiolato ligands. Compound **17** cannot undergo C–H activation at the 3-position because of the presence of the methyl groups at this site. Instead, the thermal decarbonylation of **17** produces an $\alpha\text{-CH}$ cleavage to convert the metal-bound carbon atom into a bridging carbene ligand in the complex $\text{Os}_3(\text{CO})_{10}(\mu_3\text{-SCH}_2\text{CMe}_2\text{CH})(\mu\text{-H})$ (**19**, Scheme 6). Pyrolysis of

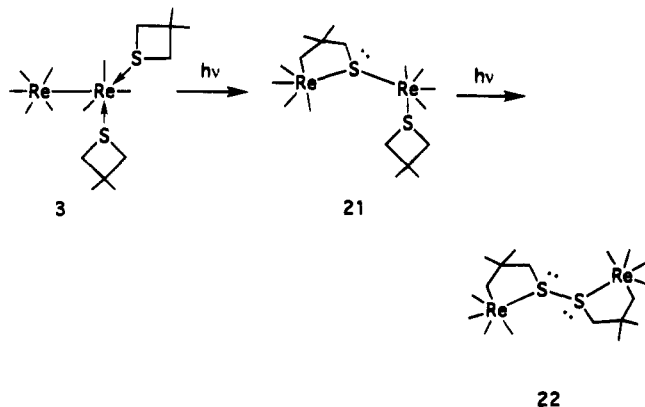
Scheme 6



complex **19** leads to an activation of a C–H bond on one of the methyl groups and an elimination of one of the osmium atoms to yield the diosmium complex $\text{Os}_2(\text{CO})_6[\mu\text{-SCH}_2\text{CMe}(\text{CH}_2)\text{CH}_2](\mu\text{-H})$ (**20**).

When solutions of **3** are exposed to fluorescent room light, the compound undergoes a series of ring-opening isomerizations to yield the complexes $\text{Re}_2(\text{CO})_8(\text{SCH}_2\text{CMe}_2\text{CH}_2)(\mu\text{-SCH}_2\text{CMe}_2\text{CH}_2)$ (**21**), and $[\text{Re}(\text{CO})_4(\mu\text{-SCH}_2\text{CMe}_2\text{CH}_2)]_2$ (**22**) that contain one and two thiametallacycles, respectively (Scheme 7).¹⁸

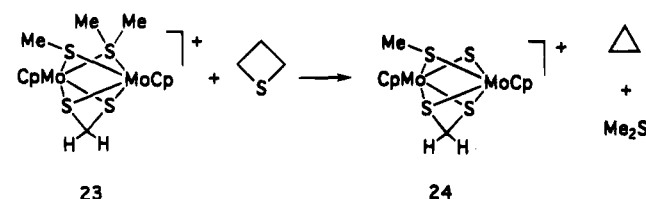
Scheme 7



Interestingly, the two thiametallacycles in **22** are joined by a sulfur–sulfur bond [S–S = 2.121(3) Å]. The sulfur atoms in the thiametallacyclic rings have one lone pair of electrons and pyramidal geometries.

Recently, Rakowski-DuBois and co-workers have reported that the cationic dimolybdenum complex $[\text{Cp}_2\text{Mo}_2(\mu\text{-SMe}_2)(\mu\text{-SMe})(\mu\text{-S}_2\text{CH}_2)]^+$ (**23**) reacts with thietane to form the sulfido complex $[\text{Cp}_2\text{Mo}_2(\mu\text{-S})(\mu\text{-SMe})(\mu\text{-S}_2\text{CH}_2)]^+$ (**24**) and cyclopropane by desulfurization of thietane, (Scheme 8).²⁸ Cyclopropane

Scheme 8



pane has been observed to form from the reaction of thietane on molybdenum surfaces,^{10,11} but this is the only example of cyclopropane formation from thietane produced by a metal complex.

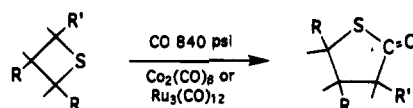
Interestingly, intramolecular ring-opening reactions have not yet been observed with the rhenium complexes, **10a,b**. Perhaps, the bridging hydride ligands in these complexes play some inhibitory role toward these transformations.

5. Ring-Opening Carbonylation of Thietanes

It has been shown that mononuclear metal complexes can promote the ring-opening expansion of thietane rings by the insertion of selected small molecules and ions into a carbon–sulfur bond.^{29–31} Alper and co-workers have shown that thietanes can be combined with CO catalytically to yield γ -thio-

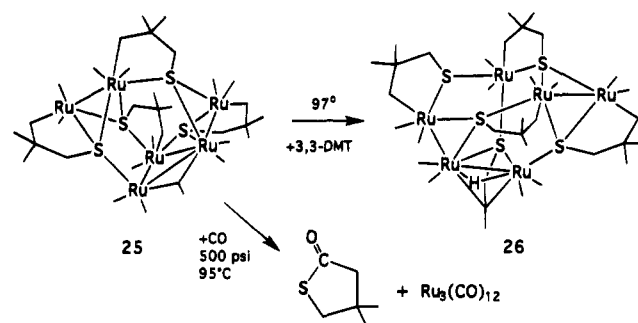
butyrolactones by using $\text{Co}_2(\text{CO})_8$ or $\text{Ru}_3(\text{CO})_{12}$ as catalyst precursors, (Scheme 9).³² No organometallic

Scheme 9



intermediates were identified or proposed in this report. However, in view of the results described in section 4 of this review, one could anticipate that metal-induced opening of the thietane rings is involved.³² In this regard, Adams et al. have shown that the pyrolysis of compound **13** yields two hexanuclear ruthenium complexes: $\text{Ru}_6(\text{CO})_{13}(\mu_3\text{-SCH}_2\text{CMe}_2\text{CH}_2)_4$ (**25**) and $\text{Ru}_6(\text{CO})_{12}(\mu_3\text{-SCH}_2\text{CMe}_2\text{CH}_2)_4(\mu_3\text{-S}(\text{CH}_2)_3\text{Me})$ (**26**) that contain four and five ring-opened thietane groupings, respectively.³³ Clearly, many steps were involved in the formation of these compounds and the mechanism of their formation has not been established, but it was shown that compound **26** can be obtained from **25** by a ring opening addition of 1 equiv of 3,3-DMT. There are no intact thietane ligands in compounds **25** or **26**. All of the thietane rings have been opened and transformed into thiametallacycles. Interestingly, when **25** was treated with CO at 500 psi/95 °C, 4,4-dimethylthiobutyrolactone and $\text{Ru}_3(\text{CO})_{12}$ was formed (Scheme 10).

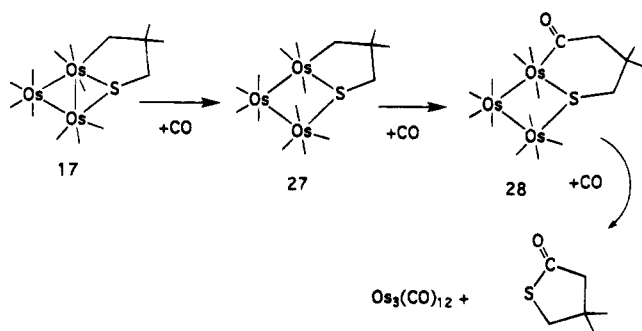
Scheme 10



It seems likely that the CO coupling process would occur by the traditional CO insertion mechanism into the metal–carbon bond in the thiametallacycles. Evidence to support this was obtained from another closely related system, the carbonylation of compound **17**.²⁴ The addition of CO to **17** proceeds first by an opening of the cluster by addition of a CO ligand to one of the metal atoms to yield the complex $\text{Os}_3(\text{CO})_{11}(\mu\text{-SCH}_2\text{CMe}_2\text{CH}_2)$ (**27**). In a second addition, a CO ligand is inserted into the metal–carbon bond of the thiametallacycle in **27** to form an acyl function in the complex $\text{Os}_3(\text{CO})_{11}(\mu\text{-SCH}_2\text{CMe}_2\text{CH}_2\text{C=O})$ (**28**, Scheme 11). Both **27** and **28** have been characterized structurally.

At a slightly higher temperature and higher pressure of CO, a bond is formed between the acyl carbon atom and the sulfur atom and the molecule 4,4-dimethylthiobutyrolactone is formed and expelled from the complex. The cluster is converted to $\text{Os}_3(\text{CO})_{12}$. Unfortunately, $\text{Os}_3(\text{CO})_{12}$ does not react with 3,3-DMT under sufficiently mild conditions to per-

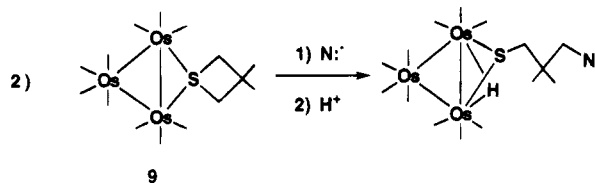
Scheme 11



form its carbonylation to 4,4-dimethylthiobutylolactone catalytically.³³

6. Nucleophilic Ring Opening of Thietane Ligands³⁴

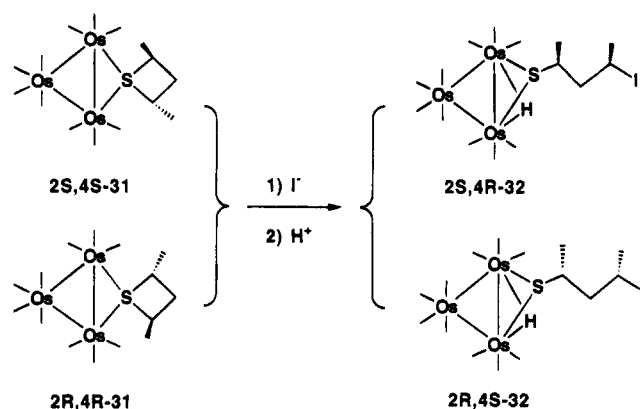
Most of the cluster complexes containing bridging thietane ligands were found to undergo surprisingly facile nucleophilic addition reactions that result in an opening of the thietane ring by cleavage of one of the carbon-sulfur bonds and the addition of the nucleophile to the carbon atom (e.g. eq 2, N^- = halide or OEt). The addition of negatively charged nucleophiles to neutral complexes produces negatively charged complexes which are often neutralized by treatment with H^+ to stabilize the complexes for easier handling.



Treatment of **9** with the nucleophiles F^- , Cl^- , Br^- , I^- , and EtO^- at 25 °C yielded after protonation the series of new complexes $Os_3(CO)_{10}[\mu-SCH_2CMe_2CH_2X](\mu-H)$ (**29a-e**, $X = F, Cl, Br, I, OEt$).³⁵ The yields increased in the order $F^- < Cl^- < Br^- < I^-$. The reaction of **9** with the nucleophilic secondary amines Et_2NH and $(CH_2)_3NH$ yielded the related complexes $Os_3(CO)_{10}[\mu-SCH_2CMe_2CH_2X](\mu-H)$ [**30a,b**, $X = NEt_2, N(CH_2)_3$] without a protonation step since the hydrogen atom on the nitrogen atom was shifted to the cluster. The mechanism of the addition was established by examining the stereochemistry of the addition of iodide to the related complex $Os_3(CO)_{10}[\mu-trans-SC(H)MeCH_2C(H)Me]$ (**31**) which was prepared as an equimolar mixture of *2R,4R*- and *2S,4S*-enantiomers. Two products *2S,4R*- and *2R,4S*- $Os_3(CO)_{10}[\mu-SC(H)MeCH_2C(H)Me(I)](\mu-H)$ (**32**) were obtained. The stereochemistry of the products indicates the occurrence of an inversion of configuration in the stereochemistry of the iodide containing carbon atom (Scheme 12) which is consistent with a nucleophilic backside addition mechanism.

Compounds **10a** and **10b** also undergo facile nucleophilic ring-opening additions reactions. Halide additions produce the anionic complexes $[Re_3(CO)_{10}(\mu-SCH_2CMe_2CH_2X)(\mu-H)_3]^-$ (**33a-d**, $X = F, Cl, Br, I$) and $[Re_3(CO)_{10}(\mu-SCH_2CH_2CH_2Cl)(\mu-H)_3]^-$ (**34b**).²²

Scheme 12



Interestingly, it was not possible to neutralize these anions by protonation with acetic acid. This may be a consequence of the presence of hydride ligands on each of the three Re-Re bonds. Surprisingly, even the very weak donor NMe_3 will add to **10a** and **10b** to yield the ring-opened complexes $Re_3(CO)_{10}(\mu-SCH_2CMe_2CH_2NMe_3)(\mu-H)_3$ (**35a**) and $Re_3(CO)_{10}(\mu-SCH_2CH_2CH_2NMe_3)(\mu-H)_3$ (**35b**). The latter is shown in Figure 5. These complexes are zwitterionic in character with a positive charge on the nitrogen atom and a negative charge on the thiolato sulfur atom.

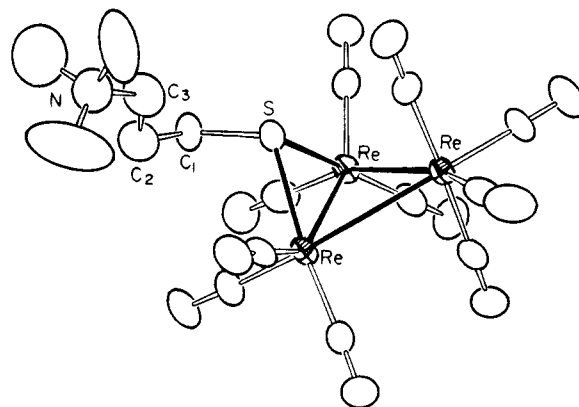
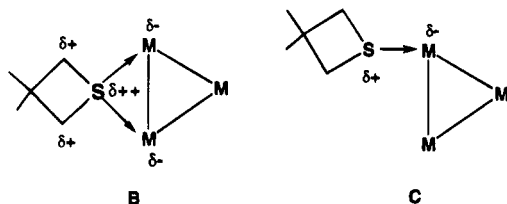


Figure 5. An ORTEP diagram of the molecular structure of $Re_3(CO)_{10}(\mu-SCH_2CH_2CH_2NMe_3)(\mu-H)_3$ (**34b**). The bridging hydride ligands are not shown.

Attempts to produce ring-opening additions to the bridging thietane ligand in **10b** by reaction with the tertiary phosphine, PMe_2Ph , yielded only $Re_3(CO)_{10}(PMe_2Ph)_2(\mu-H)_3$ by displacement of the thietane ligand.²² To date, ring opening additions of halides have been achieved *only* upon bridging thietane ligands. An attempt to produce a ring-opening addition of iodide to the terminally coordinated 3,3-DMT ligand in the complex $Re_3(CO)_{11}(SCH_2CMe_2CH_2)(\mu-H)_3$ yielded only the ligand substitution complex $[Re_3(CO)_{11}I(\mu-H)_3]^-$.

The mechanism of activation of the bridging thietane ligand to nucleophilic attack is a very simple one: the removal of electron density from the sulfur atom by the metal atoms; see structure **B**. This in turn leads to a loss of some electron density at the neighboring carbon atoms which is evidently sufficient to allow the addition of these simple nucleophiles under these mild conditions. This mechanism

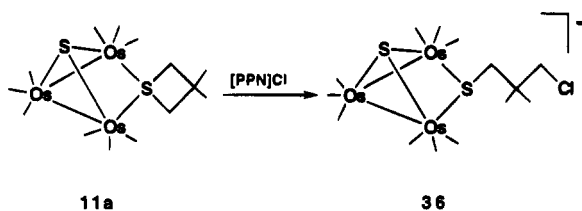
should also be operative for terminally coordinated thietane ligands **C**, but since the sulfur atom is coordinated to only one metal atom, the activation is evidently insufficient to allow the nucleophilic ring-opening reaction to occur.



It is believed that ring strain also plays an important role in the nucleophilic ring-opening additions that have been observed for thietane ligands, but ring strain is probably not a requirement since it has been reported recently that an unstrained bridging tetrahydrothiophene ligand (THT) in the complex $\text{Cl}_3\text{W}(\mu\text{-THT})_3\text{WCl}_3$ also undergoes ring-opening addition reactions with nucleophiles.³⁶

The reaction of the open cluster **11a** with bis-(triphenylphosphoranylidene)ammonium chloride ([PPN]Cl) also yielded the ring-opened chloride addition product $[\text{PPN}][\text{Os}_3(\text{CO})_9(\mu\text{-SCH}_2\text{CMe}_2\text{CH}_2\text{Cl})(\mu_3\text{-S})]$ (**36**, Scheme 13), but unlike the reaction of **9**,

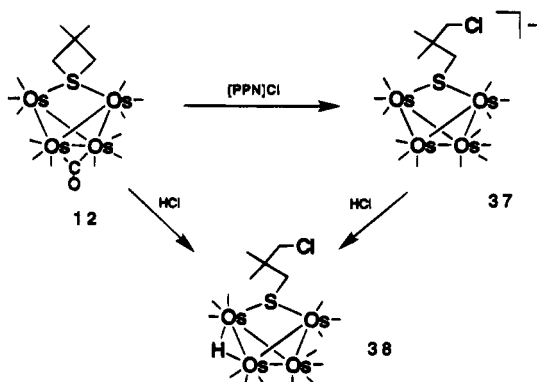
Scheme 13



attempts to open the ring of **11a** with Et_2NH were unsuccessful. The reason for this is not clear, but it could be related to the fact that the metal atoms bridged by the thietane ligand in **11a** are not mutually bonded.

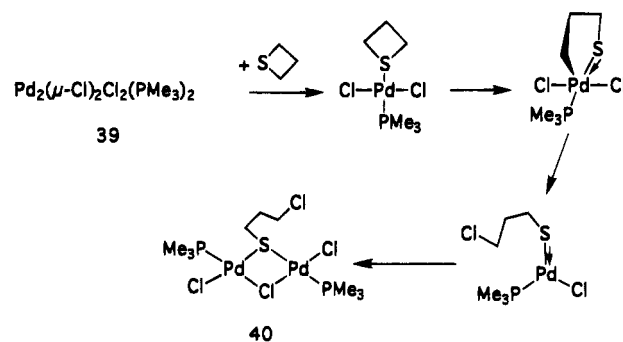
Similarly, the reaction of **12** with [PPN]Cl produced a ring-opening chloride addition to the thietane ligand to yield the salt $[\text{PPN}][\text{Os}_4(\text{CO})_{12}(\mu\text{-CO})(\mu\text{-SCH}_2\text{CMe}_2\text{CH}_2\text{Cl})]$ (**37**) which was structurally characterized in the form of the protonated neutral complex $\text{Os}_4(\text{CO})_{13}(\mu\text{-SCH}_2\text{CMe}_2\text{CH}_2\text{Cl})(\mu\text{-H})$ (**38**).²⁵ Compound **38** can be obtained in one step from the reaction of **12** with HCl (Scheme 14).

Scheme 14



A product formed by a ring-opening addition of chloride to thietane was obtained from the reaction of the dipalladium complex $[\text{Pd}(\mu\text{-Cl})\text{Cl}(\text{PMe}_3)_2]_2$ (**39**) with thietane.³⁷ A 3-chloropropanethiolato ligand was found in the product $\text{Pd}_2\text{Cl}_2(\text{PMe}_3)_2(\mu\text{-SCH}_2\text{CH}_2\text{CH}_2\text{Cl})(\mu\text{-Cl})$ (**40**) in which the sulfur atom bridges the two metal atoms. Interestingly, a mechanism involving mononuclear intermediates and a series of oxidative addition and reductive elimination transformations was proposed to explain the formation of this product (Scheme 15).

Scheme 15



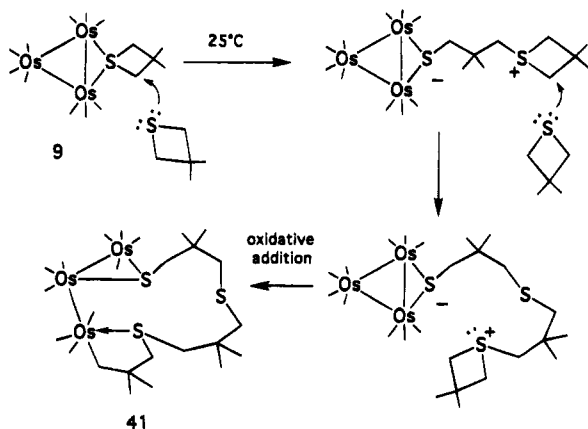
7. Ring-Opening Oligomerization and Cyclooligomerization of Thietanes by Cluster Complexes

In view of the tendency of coordinated thietanes to undergo ring-opening nucleophilic additions, it is not too surprising that oligomerizations, presumably as a result of ring-opening addition of thietane to thietane ligands, were observed fairly early in the study of the coordination chemistry of thietanes in polynuclear metal complexes. Indeed, the first example of a cluster-promoted oligomerization accompanied the report of the synthesis of complex **9** containing a bridging thietane ligand.²¹

The reaction of **9** with 3,3-DMT at 25 °C yielded the complex $\text{Os}_3(\text{CO})_{10}[(\mu\text{-SCH}_2\text{CMe}_2\text{CH}_2)_3]$ (**41**) which contains a 1-osmium-substituted 2,2,6,6,10,10-hexamethyl-4,8-dithiaundecanethiolato ligand. This ligand was formed by ring-opening head-to-tail addition of two 3,3-DMT molecules to **9**. The reaction is believed to proceed by a nucleophilic ring-opening addition of an uncoordinated 3,3-DMT molecule to one of the α -methylene groups of the bridging 3,3-DMT ligand in **9**. This would produce a positive charge at the sulfur atom (a thietanium grouping if one considers the entire four-membered ring of the added 3,3-DMT group). A negative charge will reside at the bridging thiolato sulfur atom. The thietanium ring should be sufficiently reactive to undergo a spontaneous ring-opening addition of second 3,3-DMT molecule to lengthen the chain and generate still another thietanium grouping. Polymerization could ensue, but the reaction evidently terminates itself through an oxidative addition of one of the S-C bonds in the ring to the cluster through a process that also results in the cleavage of one of the osmium-

osmium bonds. The ring strain is lost and the reaction is terminated; see Scheme 16. Cationic-ring

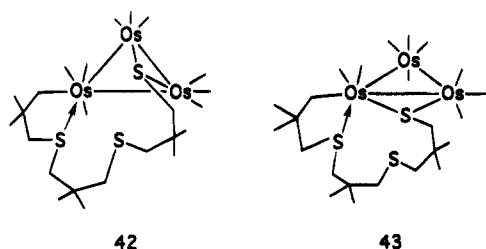
Scheme 16



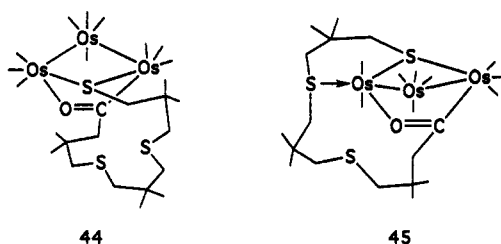
opening polymerization of thietanes via sulfonium intermediates is well known.³⁸

It occurred to us that if the two ends of the oligomer could be coupled by the formation of a carbon–sulfur bond then a trithioether macrocycle (thiacrown ether) would be formed. Conceivably, such a process could even be performed catalytically. Thiacrown ethers are emerging as an important new class of polydentate ligands.³⁹ If the thiacrown ether could be removed from the cluster, then perhaps a catalytic system could be designed for the formation of these molecules.

All attempts to connect the two ends of the thioether chain in this molecule were unsuccessful. When **41** was heated to 125°C in octane solvent, it was decarbonylated and two isomers $\text{Os}_3(\text{CO})_9[\mu\text{-SCH}_2\text{CMe}_2\text{CH}_2]_3$ (**42** and **43**) containing closed triosmium clusters were formed, but closure of the organic ring did not occur.²¹



Attempts were also made to expel the ligand from compounds **41** and **43** by carbonylation at 120°C and 650 psi of CO, but only carbonylation of the osmium–carbon terminus and the formation of the compounds **44** and **45** with bridging acyl groups occurred.²¹



Fortunately, the reaction of the bridging thietane ligand in **10b** with thietane took a different course.

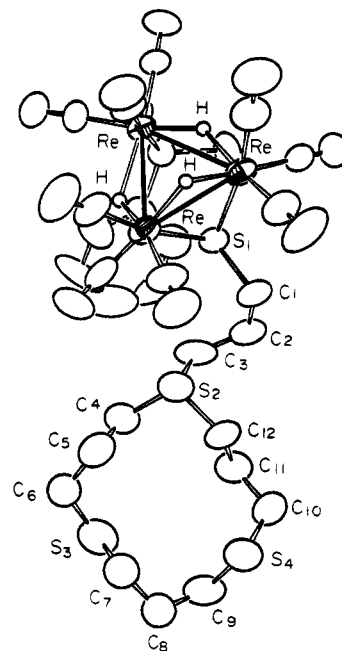
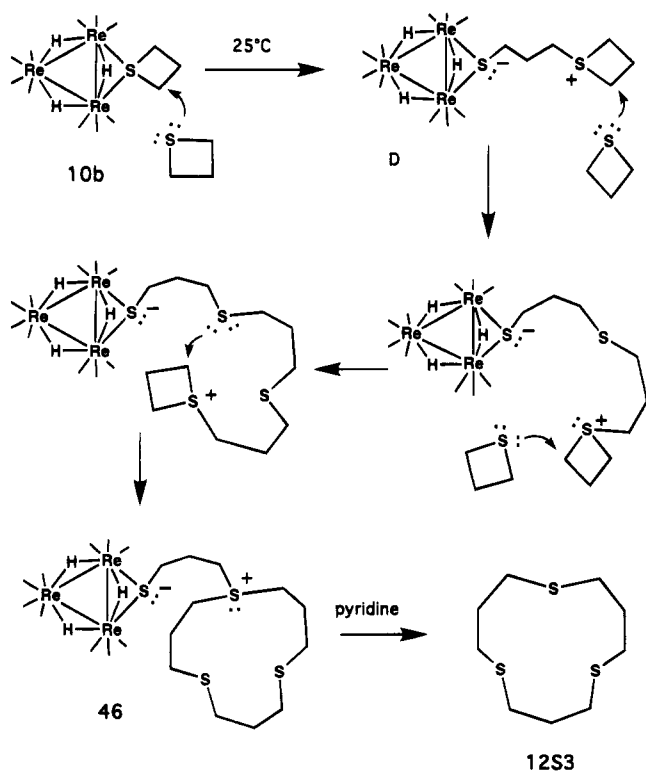


Figure 6. An ORTEP diagram of the molecular structure of $\text{Re}_3(\text{CO})_{10}[\mu\text{-SCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{CH}_2(\mu\text{-H})_3$ (**46**).

Three products were formed by the addition of thietane to **10b**, and they were formed by the addition of 3, 4, and 6 equiv of thietane, respectively. They have been identified as $\text{Re}_3(\text{CO})_{10}[\mu\text{-SCH}_2\text{CH}_2\text{CH}_2\text{-SCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{CH}_2(\mu\text{-H})_3$ (**46**), $\text{Re}_3(\text{CO})_{10}[\mu\text{-SCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{CH}_2(\text{SCH}_2\text{CH}_2\text{-CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{CH}_2)(\mu\text{-H})_3$ (**47**), and $\text{Re}_3(\text{CO})_{10}[\mu\text{-SCH}_2\text{-CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{CH}_2(\text{SCH}_2\text{CH}_2\text{CH}_2)_4\text{SCH}_2\text{CH}_2\text{CH}_2](\mu\text{-H})_3$ (**48**), respectively.⁴⁰ Compound **46** was characterized crystallographically in the form of its PMe_2Ph derivative, and an ORTEP drawing of its molecular structure is shown in Figure 6. The molecule consists of a closed cluster of three rhenium atoms with nine linear terminal carbonyl ligands and one PMe_2Ph ligand. Each metal–metal bond contains one bridging hydride ligand, but by far the most interesting ligand is the thiolato ligand. The thiolato sulfur bridges two of the rhenium atoms. It is connected to a trimethylene chain that is terminated with a 1,5,9-trithiacyclododecane (12S3) loop which is positively charged at the sulfur atom S(2). Compounds **47** and **48** are believed to be structurally similar with bridging thiolate chains terminated by 1,5,9,13-tetrathiacyclohexadecane (16S4) and 1,5,9,13,17,21-hexathiacyclotetacosane (24S6) loops. The mechanism of formation of **46** is believed to be similar to that of the formation of **41** except for the termination step; see Scheme 17. Instead of adding to the cluster via a ring-opening oxidative addition of one of the carbon–sulfur bonds of the thietanium ring, the thietanium ring is opened by the thioether sulfur atom that is positioned most closely to the thiolato sulfur atom. This results in the formation of the 12-membered ring and a sulfonium center. An important question is, “Why did the thietanium ring opening not occur at the trirhenium cluster?” We can

Scheme 17



only conclude that since each of the metal-metal bonds in this cluster are bridged by hydride ligands, these bridging hydride ligands somehow protect the cluster from attack by the thietanium grouping. A second important question is, "Why does ring formation preclude a simple polymerization reaction"? This may be related to the zwitterionic character of the intermediates. The ring-opening site is positively

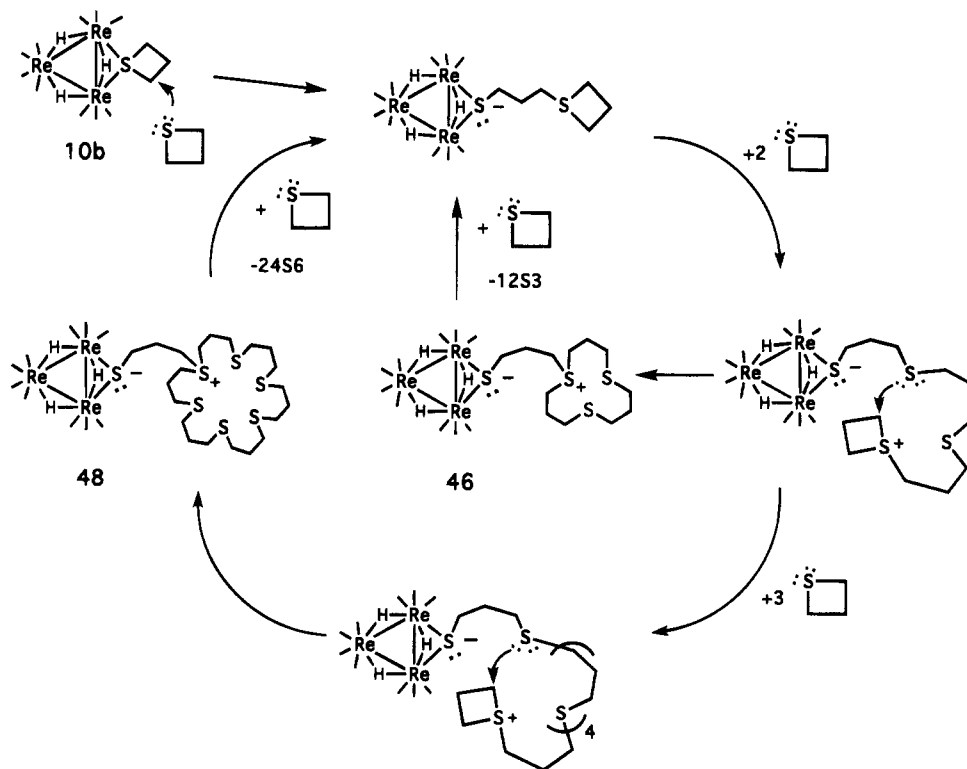
charged while the thiolato terminus is negatively charged. Presumably, the two ends of the chain remain proximate to one another as the chain grows. At certain chain lengths ring closure becomes favorable and cyclization then occurs.

8. The Catalytic Cyclooligomerization of Thietanes

The challenge remaining was to remove the macrocycle from the $\text{SCH}_2\text{CH}_2\text{CH}_2$ tether and if possible to try to develop that into a catalytic process. Removal of the ring was not difficult to achieve. A variety of bases (e.g. alkoxides and pyridine) were quite effective, but these bases then replaced the macrocycle at the terminal CH_2 site. They are strongly attached and all attempts to produce catalysis in their presence were unsuccessful. The breakthrough came when we finally attempted to cleave the macrocycle from the tether using thietane in a pure form. The complex was dissolved using the thietane as solvent, and when heated to reflux (94 °C) macrocycles were formed in large quantities. In a typical run, 1.179 of macrocycles were produced from a 17 mg quantity of **46** in 48 h. The mixture of macrocycles consisted mostly of 24S6, but there were also large amounts of 12S3. The mole ratio 24S6/12S3 was 1.78/1.⁴¹ 16S4 was a very minor component. There was no evidence for the formation of macrocycles produced by the cyclooligomerization of two, five, or more than six thietane molecules. Some insoluble material was formed which was assumed to be polymer. Catalytic cycles for the formation of 12S3 and 24S6 by this catalyst are shown in Scheme 18.

Much of the process is similar to that shown in Scheme 17 for the formation of **46**. A similar process

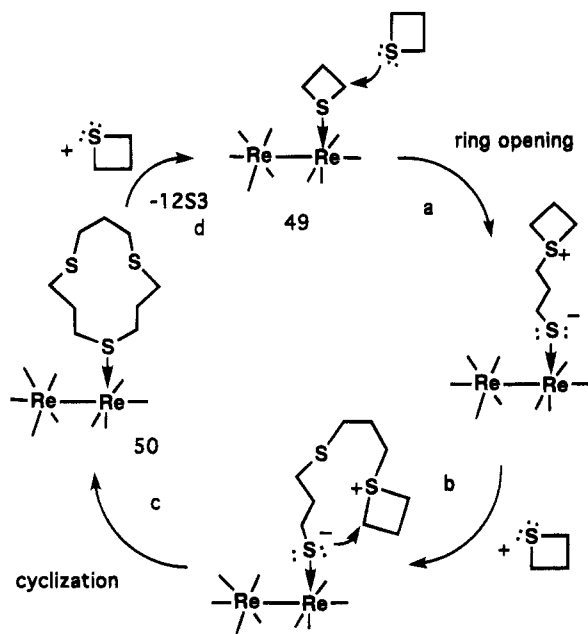
Scheme 18



to form **48** is anticipated. The slow steps in the processes are the cleavage of the macrocycles from the tether by a free molecule of thietane. These steps lead to the regeneration of the intermediate species **D** which then proceeds quickly to generate another molecule of **46** or **48** and so on. 3,3-DMT can be cyclooligomerized to 3,3,7,7,11,11,15,15,19,19,23,23-dodecamethyl-1,5,9,13,17,21-hexathiacyclotetrasane (Me_{12} -24S6) but there was no evidence for the formation of macrocyclic rings of any other sizes.

We have recently shown that the thietane containing dirhenium complex $\text{Re}_2(\text{CO})_9(\text{SCH}_2\text{CH}_2\text{CH}_2)$ (**49**) is also capable of producing the cyclooligomerization of thietane catalytically.⁴² As with **46**, the catalysis by **49** produces almost exclusively 12S3 and 24S6, but the selectivity for 12S3 formation is substantially higher. In fact, 12S3 is the major product and from a typical run a 12S3/24S6 product mole/mole ratio of 11.4/1 was obtained after 24 h of catalysis.⁴¹ The rate of formation of the macrocycles is comparable to that of **46**, and there is little or no competing polymer formation in this system. A kinetic analysis showed a linear first-order dependence on the concentration of **49**. The compound $\text{Re}_2(\text{CO})_9(12\text{S3})$ (**50**) is formed in the reaction and both compounds appear to be components in the catalytic cycle; see Scheme 19.

Scheme 19

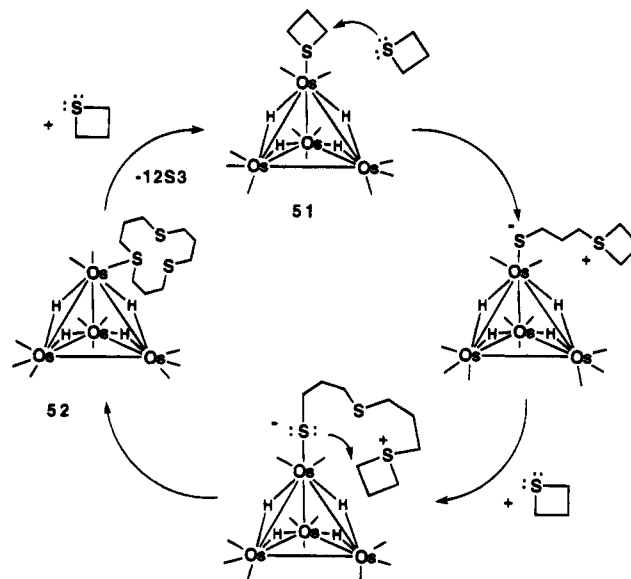


Unlike the catalysis initiated by **10b** and propagated by **46** and **48**, no bridging thietane ligands appear to be involved in this process. The terminally coordinated thietane ligand in **49** appears to be sufficiently activated to undergo a ring-opening addition of a free molecule of thietane, step **a**. The thietanium grouping so produced can react with additional thietane spontaneously, step **b**, and when a chain length favorable for the formation of certain rings is achieved (e.g. step **c**), cyclization occurs by a ring-opening coupling between the metal-bound

thiolato sulfur atom and a methylene group of the thietanium ring. The macrocycle that is formed is coordinated directly to one of the rhenium atoms in a terminal coordination mode. The product is released and the catalyst **49** is regenerated by a simple ligand substitution reaction, step **d**. Once again, the preference for cyclooligomerization over polymerization is believed to be due to the zwitterionic character of the intermediates.

We have also just found that the tetraosmium cluster $\text{Os}_4(\text{CO})_{11}(\text{SCH}_2\text{CH}_2\text{CH}_2)(\mu\text{-H})_4$ (**51**) produces the cyclooligomerization of thietanes catalytically with a preference for 12S3, but the selectivity for 12S3 (12S3/24S6 = 6/1) is not quite as high as that of the dirhenium system.⁴³ The 12S3 complex $\text{Os}_4(\text{CO})_{11}(12\text{S3})(\mu\text{-H})_4$ (**52**) is formed in the process and appears to be a component in the catalytic cycle; see Scheme 20. As in the dirhenium system, all sulfur-

Scheme 20



bound ligands appear to be terminally coordinated. The fact that all of the transformations in the catalytic processes of **49** and **51** occur at the site of a single metal atom is an important observation. It suggests that mononuclear metal complexes should be capable of performing this catalysis as well.

9. Coordination of Thietane Cyclooligomers to Metal Clusters

Although the coordination properties of polythioether macrocycles (thia crown ethers) to metal ions have been investigated considerably in recent years,³⁹ there have been very few reports on the coordination properties of these macrocycles to polynuclear metal carbonyl complexes.⁴⁴⁻⁴⁸ In this section, emphasis will be placed on polynuclear metal carbonyl complexes that contain macrocycles that can be produced by the cyclooligomerization of thietane.

It has recently been shown that 12S3 can be fully incorporated into the coordination sphere of Ru_3 -

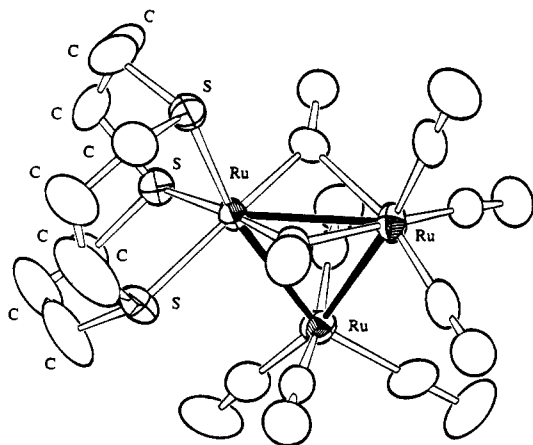
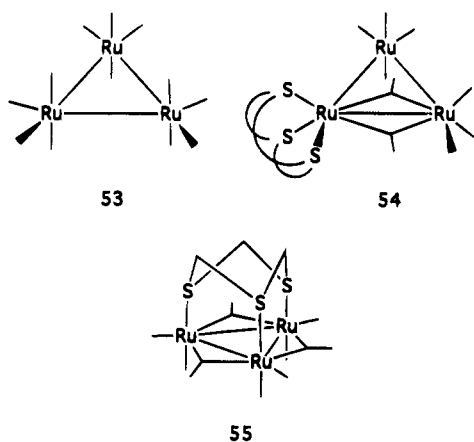


Figure 7. An ORTEP diagram of the molecular structure of $\text{Ru}_3(\text{CO})_7(\mu\text{-CO})_2(1,1,1\text{-}\eta^3\text{-12S3})$ (**54**).

(CO)₁₂ (**53**). This is shown in the complex $\text{Ru}_3(\text{CO})_7(\mu\text{-CO})_2(1,1,1\text{-}\eta^3\text{-12S3})$ (**54**); see Figure 7.⁴⁶



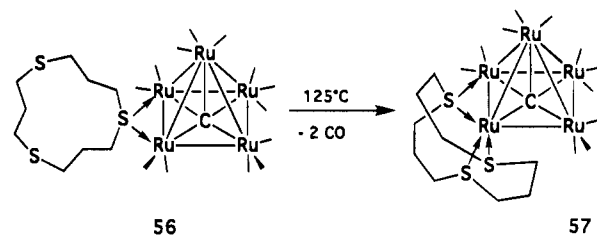
All three sulfur atoms are coordinated to just one metal atom. This differs from the structure of the small ring complex $\text{Ru}_3(\text{CO})_6(\mu\text{-CO})_3(\mu_3\text{-}\eta^3\text{-6S3})$ (**55**, $6\text{S3} = 1,3,5\text{-trithiacyclohexane}$ where each sulfur atom of the 6S3 ligand is coordinated to a different metal atom). The tendency of polydentate phosphine ligands to favor binding to a single metal atom is well known to increase as the chain length between the donor sites is increased.⁴⁹ As shown by the differences in **54** and **55**, this property also appears to extend to the coordination of polythioether macrocycles as well. Another interesting feature of the structure of **54** is the presence of two bridging carbonyl ligands across one metal-metal bond.

This type of structure has been observed previously for triiron carbonyl cluster complexes,⁵⁰ but has been observed only once before in a triruthenium complex and that was for a tetrasubstituted phosphine derivative of $\text{Ru}_3(\text{CO})_{12}$.⁵¹ It is believed that steric effects tend to force carbonyl ligands to assume bridging modes when otherwise they would prefer to be terminal,⁵² thus the formation of bridging CO ligands in **54** is attributed to the large steric effects produced by the bulky 12S3 ligand.

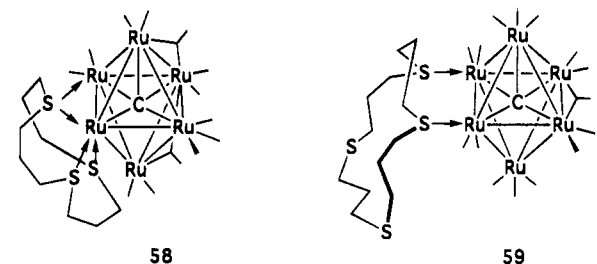
The addition of 12S3 to $\text{Ru}_5(\text{CO})_{15}(\mu_5\text{-C})$ proceeds in a stepwise fashion. The first product to be formed is $\text{Ru}_5(\text{CO})_{13}(\mu\text{-}\eta^1\text{-12S3})(\mu_5\text{-C})$, **56**. In **56** the 12S3 ligand bridges one edge of the square base of the $\text{Ru}_5(\mu_5\text{-C})$ cluster by using only one of its sulfur atoms.

The other two sulfur atoms are uncoordinated. A similar bridging 12S3 ligand was observed in the tetraosmium cluster complex $\text{Os}_4(\text{CO})_{13}(\mu\text{-}\eta^1\text{-12S3})(\mu_5\text{-C})$ where the sulfur atom bridges the wingtips of a butterfly tetrahedron of four osmium atoms.⁴⁴ When heated to 125°C , **56** is transformed into the new compound $\text{Ru}_5(\text{CO})_{11}(\mu\text{-}\eta^3\text{-12S3})(\mu_5\text{-C})$ (**57**) by the loss of two CO ligands and the incorporation of the two remaining sulfur atoms of the 12S3 ligand into the coordination sphere of the cluster. In **57** all three sulfur atoms of the 12S3 ligand are coordinated to one of the basal ruthenium atoms, but one of the sulfur atoms does remain as a bridge between two of the basal metal atoms, Scheme 21. A similarly coordinated 12S3 ligand was observed in the complex $\text{Ru}_6(\text{CO})_{15}(\mu_4\text{-}\eta^2\text{-CO})(\mu\text{-}\eta^3\text{-12S3})$.⁴⁴

Scheme 21



The reaction of $\text{Ru}_6(\text{CO})_{17}(\mu_6\text{-C})$ with 12S3 yielded the complex $\text{Ru}_6(\text{CO})_{13}(\mu\text{-}\eta^3\text{-12S3})(\mu_6\text{-C})$ (**58**), containing an octahedral cluster of six ruthenium atoms with a carbido ligand in the center.⁴⁸ The 12S3 ligand in **58** is coordinated to two metal atoms in a manner analogous to that found in **57**. In contrast, the 16S4 ligand in the complex $\text{Ru}_6(\text{CO})_{15}(\mu\text{-}\eta^2\text{-16S4})(\mu_6\text{-C})$ (**59**)



obtained from the reaction of 16S4 with $\text{Ru}_6(\text{CO})_{17}(\mu_6\text{-C})$ has only two of its sulfur atoms coordinated and these are terminally coordinated to different metal atoms. Efforts to bring the uncoordinated sulfur atoms in **59** into the coordination sphere of the metal atoms have not been successful.

Previous studies of the coordination chemistry of polythioether macrocycles have been inhibited by their lack of availability due to the difficult and low yield procedures for their synthesis. It is expected that the catalytic procedures that are now being developed by using the relatively low-cost reagent thietane will make at least some of these ligands more widely available and thus permit a greater exploration of their coordination chemistry.

10. Acknowledgments

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