

# Catalytic Macrocyclizations of Thietanes and Thiiranes by Metal Carbonyl Complexes

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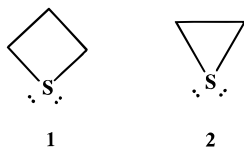
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## ABSTRACT

This Account summarizes our recent studies of the catalytic transformations of thietanes and thiiranes by metal carbonyl complexes of the third row of the transition elements. The goal of the work has been to prepare polythioether macrocycles (thiacrowns) catalytically. This has been achieved with high success for certain thietane reactions. Thiiranes, on the other hand, tend to yield macrocyclic polydisulfides, but it has recently been found that these reactions can be redirected toward the thiacrown products by using certain alkyne carboxylates as cocatalysts. Vinylthiiranes are transformed into 3,6-dihydro-1,2-dithiins catalytically in excellent yield via  $W(CO)_5$ (vinylthiirane) complexes.

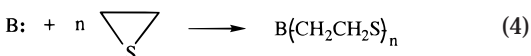
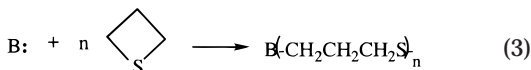
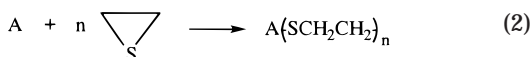
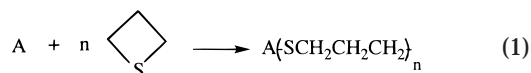
## A. Introduction

Thietanes **1** and thiiranes **2** are the two most important classes of small strained ring thioethers.<sup>1,2</sup> It has been

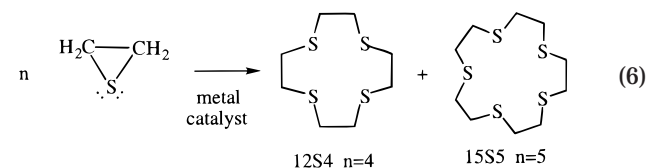
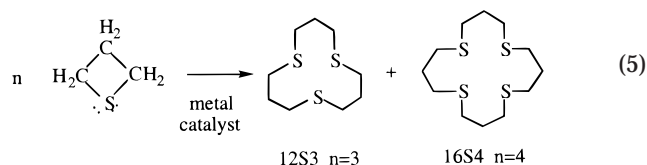


estimated that the parent compound of each class contains about 80 kJ/mol (19 kcal/mol) of strain energy.<sup>3</sup> These compounds are readily polymerized by Lewis acid catalysts including transition metal ions (eqs 1 and 2) and by Lewis base catalysts (eqs 3 and 4).<sup>4,5</sup> Thietanes are readily desulfurized upon exposure to clean metal surfaces.<sup>6</sup> Because the olefin is an excellent leaving group, thiiranes are desulfurized more easily than thietanes on metal surfaces<sup>7</sup> and are even desulfurized by many metal complexes. In fact, the desulfurization of thiiranes is so efficient that thiiranes have been used as reagents for the synthesis of metal sulfide complexes.<sup>8</sup>

Richard D. Adams received a B.S. degree in 1969 from the Pennsylvania State University and a Ph.D. in chemistry in 1973 from the Massachusetts Institute of Technology for research performed under the direction of F. A. Cotton. He was an assistant Professor of Chemistry at SUNY Buffalo, 1973–75, and Assistant and Associate Professor at Yale, 1975–84. In 1984 he moved to the University of South Carolina as Professor of Chemistry, and in 1995 was appointed as the Arthur S. Williams Professor of Chemistry. In 1999 he was the recipient of the American Chemical Society award in Inorganic Chemistry and the Charles H. Herty medal of the Georgia section of the American Chemical Society. He has received a Senior Scientist award of the Alexander von Humboldt Foundation (Germany) and was selected as a visiting scholar of the Institut Universitaire de France. He is the American Regional Editor of the Journal of Organometallic Chemistry and a coeditor of the Journal of Cluster Science. His research interests lie in the synthesis, structures, and catalytic properties of metal carbonyl cluster complexes. He is the author of over 380 research publications.



One goal of our recent research has been to try to gain control of the opening of the rings of these compounds for the purpose of synthesizing polythioether macrocycles or thiacrowns, as they are also called, through cyclooligomerization or “macrocyclization” reactions using transition metal catalysts (e.g., eqs 5 and 6). Thiacrowns have



recently attracted the attention of inorganic chemists because of their ability to serve as ligands for transition metal ions.<sup>9</sup> Unlike their oxygen-containing homologues, the crown ethers, many thiacrowns are difficult to synthesize in good yields.<sup>10</sup> Reactions 5 and 6 are thermodynamically favorable since the macrocycles have very little strain energy.

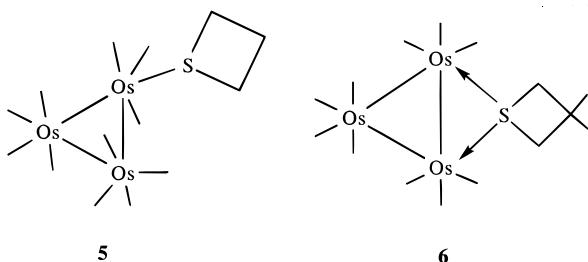
The terminology that will be used to define the thiacrowns herein will contain a number followed by an S and a second number. The first number will define the number of atoms in the ring. The second number will identify the number of sulfur atoms in the ring (e.g., 12S3 refers to the thiacrown 1,5,9-trithiacyclododecane). Our work began with the synthesis of metal complexes of the strained ring compounds for the purpose of studying their ring-opening reactions.

## B. Thietanes

The first thietane complexes were actually prepared by Abel et al., who studied their coordination properties in the late 1970s and early 1980s.<sup>11</sup> Thietane complexes have now been prepared in both terminal (**3**) and bridging<sup>12</sup> (**4**) coordination modes by using one or both of the lone pairs of electrons on the sulfur atom. The sulfur atom of the terminal thietane ligand has a pyramidal geometry due to the presence of a lone pair of electrons. The four-membered rings in both **3** and **4** are slightly puckered.

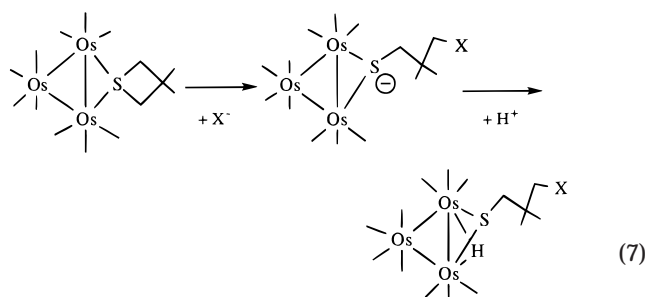


Proceeding on the assumption that polynuclear coordination can be more effective for the activation of small molecules than coordination to a single metal atom, our initial studies were focused on metal cluster complexes of thietanes. In the early 1990s, we reported the first examples of cluster complexes containing thietane ligands, e.g., **5** and **6**.<sup>13,14</sup> We found that these osmium complexes



readily underwent facile ring-opening transformations under mild conditions;<sup>15</sup> in fact, osmium complexes having bridging thietane ligands could be isolated only when alkyl substituents were present on the thietane ring to stabilize it.

It was found that complexes containing bridging thietane ligands would engage in nucleophilic ring-opening addition reactions that result in the cleavage of one of the carbon–sulfur bonds with nucleophiles as simple as the halide ions (eq 7, X = F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>).<sup>16</sup> An inversion of



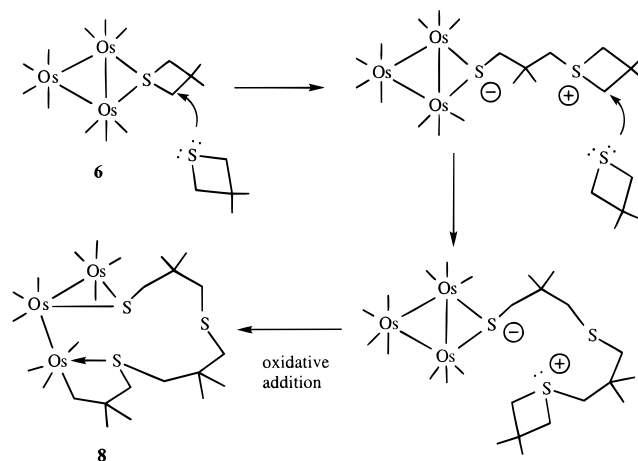
configuration of the stereochemistry at the carbon atom was found to accompany the addition of the nucleophile in the addition to *trans*-2,4-dimethylthietane. This is consistent with the backside addition mechanism.

The activation process is a very simple one. The donation of electron density from the sulfur atom to the metal atoms produces an increase in positive charge on the sulfur atom **7**. This in turn produces a smaller but still significant increase in positive charge on the adjacent carbon atoms that is sufficient to permit the ring-opening addition of the halide ions.

The first major step toward thiacycrown synthesis from thietanes was the discovery that **6** will selectively add 2 equiv of 3,3-dimethylthietane (3,3-DMT) to yield the

compound Os<sub>3</sub>(CO)<sub>10</sub>(SCH<sub>2</sub>CMe<sub>2</sub>CH<sub>2</sub>)<sub>3</sub> (**8**), which contains a ring-opened trimer of 3,3-DMT. It is believed that **8** was formed through a series of nucleophilic ring-opening additions that begins with a process analogous to that in eq 7, traverses a series of zwitterionic thietanium–thiolate intermediates, and finishes with an oxidative addition of one of the thietanium rings to the cluster. The addition to the cluster opens the ring and the cluster, and the reaction terminates (Scheme 1).<sup>14</sup> Thermal decarbonylation of **8** leads to closure of the cluster, but it was not possible to cyclize the hydrocarbon ring to form the thiacycrown Me<sub>6</sub>12S3 from this compound.

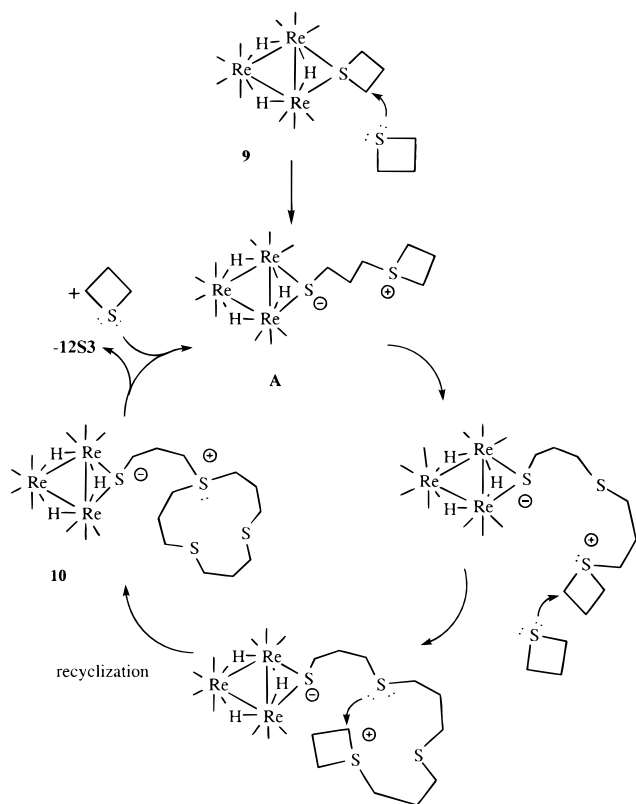
Scheme 1



The first successful construction of a 12S3 ring from a thietane was obtained from the reaction of the trirhenium–thietane complex Re<sub>3</sub>(CO)<sub>10</sub>(μ-SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)(μ-H)<sub>3</sub> (**9**) with thietane.<sup>17</sup> Compound **9** adds 3 equiv of thietane in a series of ring-opening steps involving zwitterionic intermediates and terminates with a recyclization that results in the formation of the compound Re<sub>3</sub>(CO)<sub>10</sub>(μ-SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>12S3)(μ-H)<sub>3</sub> (**10**). Compound **10** contains a 12S3 thiacycrown dangling from a SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub> tether that is linked to the cluster through the sulfur atom (see Scheme 2). This linkage produces a positive charge on that sulfur atom in the 12S3 ring.

The sulfur atom that is bonded to the cluster formally has a negative charge, so **10** is also a zwitterion. It was subsequently found that the 12S3 thiacycrown could be cleaved from the tether to the cluster by treatment with bases. In fact, thietane itself is sufficiently basic that it, too, can cleave the macrocycle from the tether when it is allowed to react with **10** in the absence of solvent at its boiling point (94 °C). This step regenerates the intermediate **A** and closes the cycle to provide the first example of a catalytic process for the formation of a thiacycrown (12S3)

Scheme 2

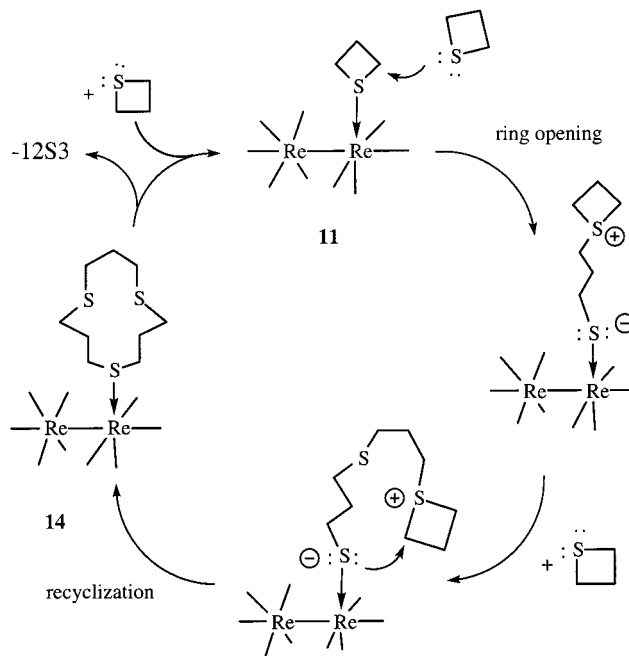


from a thietane (Scheme 2). The reaction yields considerable amounts of low-molecular-weight polymers that, in fact, exceed the amount of 12S3 on a per weight basis. Nevertheless, the reaction can provide useful quantities of 12S3 with a catalytic turnover frequency (TOF; number of moles of product per mole of catalyst per day) of 46. The reaction is successful in producing 12S3 largely because of the involvement of the zwitterionic intermediates that increase the probability for the recyclization step as opposed to simple polymerization.

It was subsequently discovered that third-row transition metal complexes containing terminally coordinated thietane ligands are also effective catalysts for the formation of 12S3 from thietane. The most efficient catalyst is  $\text{Re}_2(\text{CO})_9(\text{SCH}_2\text{CH}_2\text{CH}_2)$  (**11**), which produces 12S3 at a rate of 146 turnovers/day. The selectivity for 12S3 can be as high as 85%. A second product was initially thought to be 24S6,<sup>18</sup> but subsequent studies have shown that this is really a mixture of low-molecular-weight polymers, perhaps large cyclooligomers,  $M_w = 8700$ ,  $M_n = 5106$ , and polydispersity = 1.7.<sup>19</sup> The overall yields are usually less than 10% if the reaction is terminated within 24 h.<sup>18</sup> However, much unreacted thietane is recovered and can be recycled. The yield of 12S3 is approximately 40% based on the amount of consumed thietane. Small amounts of 16S4 are also formed in this reaction.  $\text{H}_4\text{Os}_4(\text{CO})_{11}(\text{SCH}_2\text{CH}_2\text{CH}_2)$  (**12**) produces 12S3 at a rate of 110 turnovers/day,<sup>20</sup> and  $\text{W}(\text{CO})_5(\text{SCH}_2\text{CH}_2\text{CH}_2)$  (**13**) produces 12S3 at 26 turnovers/day.<sup>21</sup>  $\text{H}_4\text{Ru}_4(\text{CO})_{11}(\text{SCH}_2\text{CH}_2\text{CH}_2)$  is significantly less active than **12** and also less selective, and  $\text{Cr}(\text{CO})_5(\text{SCH}_2\text{CH}_2\text{CH}_2)$  is significantly less effective than **13**.

The proposed mechanism for the formation of 12S3 by


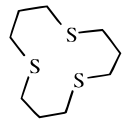

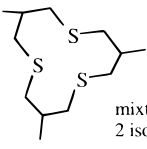

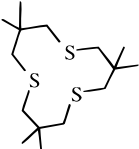

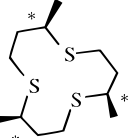

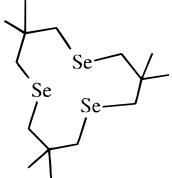
Scheme 3



**11** is shown in Scheme 3.<sup>18</sup> The rate of the reaction is first order in dirhenium, which argues against Re–Re bond-splitting processes. All transformations are proposed to occur at a single metal site. As with **10**, it is believed that the zwitterionic character of the intermediates promotes the formation of the macrocycle. This reaction is more effective than that of **10** because the recyclization occurs at the thiolate sulfur atom, which is more exposed than the bridging thiolate in **10** and more basic than the thioether sulfur in **10**, which is the actual site of recyclization. Recyclization at the thiolate sulfur atom in **10** can explain the higher selectivity for 12S3 formation. This recyclization produces the 12S3 as a sulfur-bound ligand in the complex **14**. Compound **14** was isolated and characterized crystallographically. It was observed spectroscopically in significant amounts in catalyst solutions, and it exhibits exactly the same activity as **11**, as it must if it is also a member of the catalytic cycle. More importantly, the catalytic cycle is completed simply by replacement of the 12S3 ligand by thietane, a simple ligand substitution process which is more facile than cleaving 12S3 from the  $\text{SCH}_2\text{CH}_2\text{CH}_2$  tether in **10**. This can explain the higher activity of this catalyst.

At this time our efforts were directed toward expanding the scope of the reaction and trying to prepare new polythioether macrocycles. The results of studies that used the  $\text{Re}_2(\text{CO})_9$  catalyst are shown in Table 1. By adding methyl substituents to the thietane ring, we were able to prepare 3,7,11-Me<sub>3</sub>-1,5,9-12S3, which exists as a mixture of *cis*- and *trans*-isomers, depending on the orientation of the methyl groups.<sup>22</sup> We have prepared 3,3,7,7,11,11-Me<sub>6</sub>-1,5,9-12S3 from 3,3-DMT,<sup>23</sup> and by using enantiomerically pure *R*-2-methylthietane it has been possible to prepare the macrocycle 2*R*,6*R*,10*R*-2,6,10-Me<sub>3</sub>-1,5,9-12S3, having three stereogenic centers all of the same configuration.<sup>24</sup>

**Table 1. Derivatives of 12S3 Obtained from Various Derivatives of Thietane**

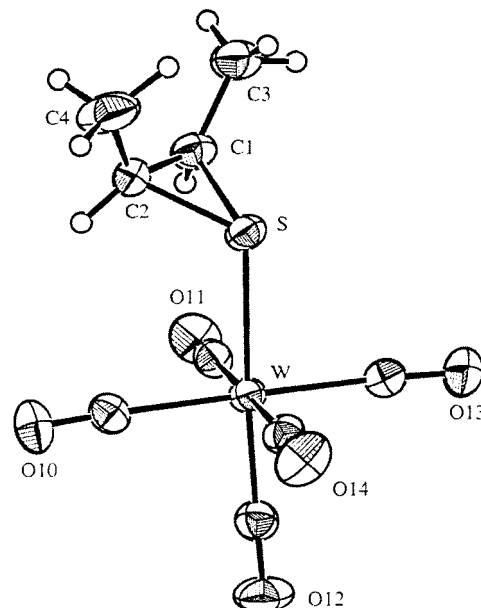
Starting Material	Product	Turnover Freq./h
		6.1
	 mixture of 2 isomers	2.0
		0.03
 R-isomer	 R,R,R-isomer	0.2
		1.5

As the substitution on the thietane ring increases, the rate of formation of the 12S3 products decreases. This is probably due to simple steric inhibition. In addition, the selectivity for the 12S3 rings also declines. For example, in the reaction of 3,3-DMT, the yield of the Me<sub>6</sub>12S3 is only about 10%, and the overall yield is very low, even after 72 h. There are significant quantities of 3,3,7,7,11,11,15,15-Me<sub>8</sub>-1,5,9,13-16S<sub>4</sub> and 3,3,7,7,11,11,15,15,19,19-Me<sub>10</sub>-1,5,9,13,17-20S<sub>5</sub>, but the polymers are the dominant products. The substituents retard not only the thietane ring-opening step but also the recyclization step.

We were even able to prepare polyselenaether macrocycles by replacing the sulfur atom in the thietane ring with a selenium atom. For the reaction of 3,3-dimethylselenatane we have obtained good yields of the new compound 3,3,7,7,11,11-Me<sub>6</sub>-1,5,9-12Se<sub>3</sub>, together with smaller amounts of 3,3,7,7-Me<sub>4</sub>-1,5,9-8Se<sub>2</sub> and 3,3,7,7,11,11,15,15-Me<sub>8</sub>-1,5,9,13-16Se<sub>4</sub>.<sup>24</sup>

### C. Thiiranes

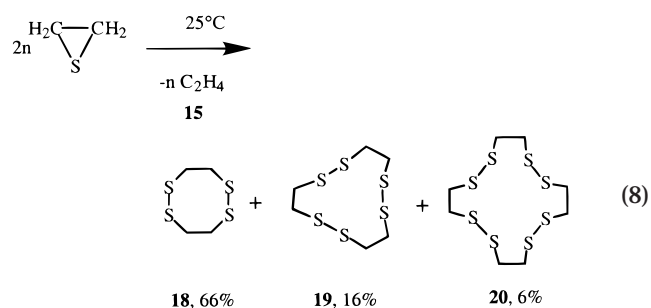
To perform ring-opening cyclooligomerization reactions of the thiiranes, it was necessary identify metal complexes that would not produce spontaneous polymerization or desulfurization reactions. There are very few examples of stable thiirane complexes. Abel et al. have reported the chromium complex Cr(CO)<sub>4</sub>(cis-1,4-cyclohexadienebis-


**FIGURE 1.** ORTEP diagram of the molecular structure of W(CO)<sub>5</sub>(*cis*-SCHMeCHMe) (**16**).

episulfide),<sup>26</sup> and Rauchfuss has prepared the ruthenium complex [Cp(PPh<sub>3</sub>)<sub>2</sub>Ru(SCH<sub>2</sub>CH<sub>2</sub>)] [O<sub>3</sub>SCF<sub>3</sub>].<sup>27</sup>

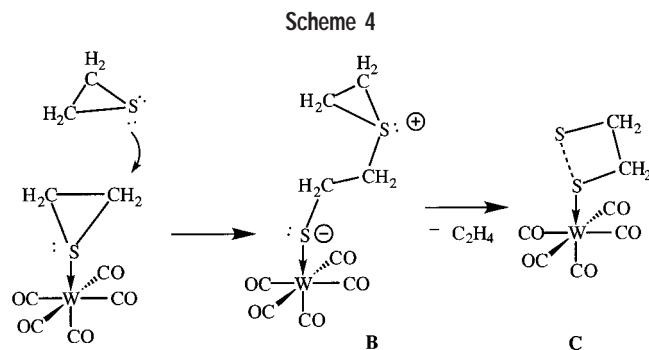
Our studies of the catalytic transformations of thiiranes began with the synthesis and characterization of the (thiirane)W(CO)<sub>5</sub> complexes: W(CO)<sub>5</sub>(SCH<sub>2</sub>CH<sub>2</sub>) (**15**), W(CO)<sub>5</sub>(*cis*-SCHMeCHMe) (**16**), and W(CO)<sub>5</sub>(*trans*-SCHMeCHMe) (**17**). Compound **16** was characterized crystallographically. A diagram of the molecular structure of **16** is shown in Figure 1. The *cis*-SCHMeCHMe ligand is coordinated to the tungsten atom through one of the lone pairs of electrons on the sulfur atom. In solution, this compound exists as a mixture of two isomers that differ by coordination to the two inequivalent lone pairs of electrons on the sulfur atom.

To our surprise, the reaction of the thiirane complexes with the thiiranes was significantly different than that of the thietanes. For example, the reaction of **15** with thiirane yielded the cyclic disulfides **18–20**, including a small amount of the pentadisulfide **21**, as the principal products (eq 8). Small amounts of the polythioethers 12S<sub>4</sub>, 15S<sub>5</sub>,



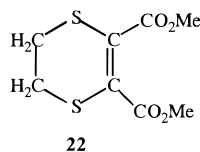
and 18S<sub>6</sub> are also obtained (see below), and there is also some competing desulfurization to yield elemental sul-





fur.<sup>28</sup> Interestingly, 1 equiv of ethylene is produced for each disulfide group that is formed. A mechanism involving backside ring-opening addition of a free molecule of thiirane to one of the methylene groups of the thiirane ligand was proposed (Scheme 4). This is supported by the observation that the products of the reactions of *R,S*-dimethylthiirane have only *R,R*- and *S,S*-stereochemistries at adjacent carbon atoms.

The zwitterion **B** then eliminates ethylene to yield a  $\text{SCH}_2\text{CH}_2\text{S}$  or "dithietane" grouping, as shown in **C**. It is believed that the dithietane groupings simply condense to yield the various cyclic disulfides. Evidence for the existence of a dithietane intermediate was obtained by trapping it with dimethylacetylene dicarboxylate (DMAD). When the reaction was performed in the presence of DMAD, the dithiacyclohexene **22** was formed catalytically at a rate of 1.5 turnovers/h. Compound **22** is not obtained

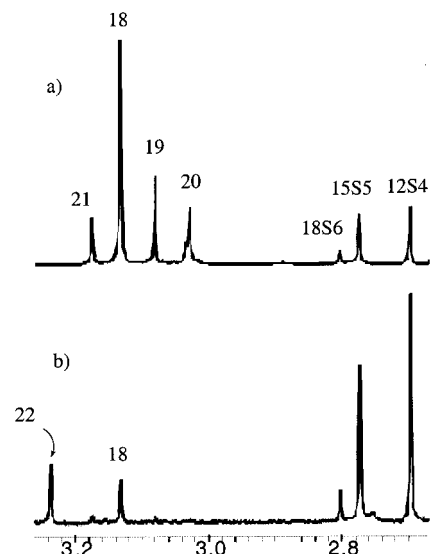


from mixtures of the cyclic disulfide products with DMAD and  $\text{W}(\text{CO})_5(\text{NCMe})$ .

No cyclic disulfides were obtained when **16** and **17** were allowed to react with *cis*- $\text{SCHMeCHMe}$  and *trans*- $\text{SCHMeCHMe}$ , respectively. Instead, isomerization of the thiiranes and desulfurization leading to a mixture of *cis*- and *trans*-2-butenes was observed.

Interestingly, the isomerization is completely suppressed when the reaction is performed in the presence of DMAD, and under these conditions cyclic disulfides are formed. Structural characterization of these disulfides showed that all adjacent carbon atoms always had the same stereochemistry, as observed in the structure of 3*S*,4*S*,7*R*,8*R*,11*S*,12*S*-hexamethyl-1,2,5,6,9,10-hexathia-cyclododecane.<sup>28a</sup>

In the presence of DMAD, the formation of the unsubstituted cyclic disulfides **18–21** is greatly suppressed, but the formation of the polythioethers is not, and under these conditions the polythioethers become the principal products. This is shown in Figure 2, which shows <sup>1</sup>H NMR spectra of reaction mixtures obtained in the absence (a) and presence (b) of DMAD. In the absence of DMAD, the



**FIGURE 2.** <sup>1</sup>H NMR spectra of reaction mixtures of **15** with thiirane in the  $\text{CH}_2$  region of the spectrum, (a) in the absence of DMAD and (b) in the presence of DMAD.

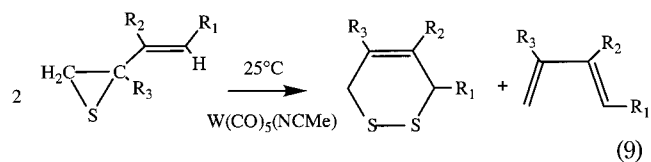
**Table 2. Results of Catalytic Transformations of Vinylthiiranes to Dihydrodithiins by  $\text{W}(\text{CO})_5(\text{NCMe})$**

reagent	product	yield (%) <sup>a</sup>	TON (24 h)	TOF
<b>23</b>	<b>28</b>	86	212	15
<b>24</b>	<b>29</b>	84	141	29
<b>25</b>	<b>30</b>	86	149	24
<b>26</b>	<b>31</b>	80	146	19
<b>27</b>	<b>29</b>	34	53	2

<sup>a</sup> Isolated yields after 24 h.

ratio of the total amount of thioethers to the total amount of cyclic disulfides is 0.26. In the presence of DMAD, this ratio is 7.7.

We have also found that the vinylthiiranes **23–27** can be effectively transformed into the 3,6-dihydro-1,2-dithiins **28–31** by use of tungsten carbonyl compounds such as  $\text{W}(\text{CO})_5(\text{NCMe})$  (eq 9).<sup>28</sup> These reactions are accompanied

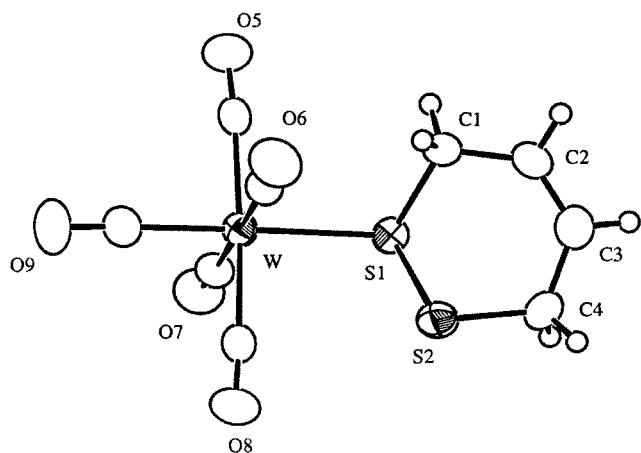
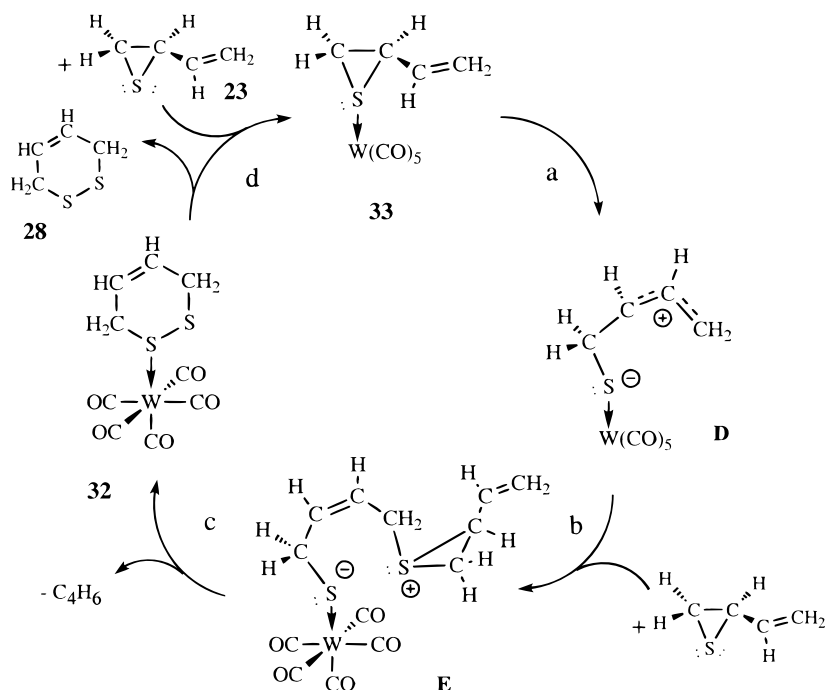


<b>23</b>	$\text{R}_1=\text{R}_2=\text{R}_3=\text{H}$	<b>28</b>	$\text{R}_1=\text{R}_2=\text{R}_3=\text{H}$
<b>24</b>	$\text{R}_1=\text{R}_3=\text{H}, \text{R}_2=\text{Me}$	<b>29</b>	$\text{R}_1=\text{R}_3=\text{H}, \text{R}_2=\text{Me}$
<b>25</b>	$\text{R}_1=\text{Me}, \text{R}_2=\text{R}_3=\text{H}$	<b>30</b>	$\text{R}_1=\text{Me}, \text{R}_2=\text{R}_3=\text{H}$
<b>26</b>	$\text{R}_1=\text{R}_2=\text{Me}, \text{R}_3=\text{H}$	<b>31</b>	$\text{R}_1=\text{R}_2=\text{Me}, \text{R}_3=\text{H}$
<b>27</b>	$\text{R}_1=\text{R}_2=\text{H}, \text{R}_3=\text{Me}$	<b>29</b>	$\text{R}_1=\text{R}_2=\text{H}, \text{R}_3=\text{Me}$

by the formation of the corresponding butadiene and proceed to essentially 100% conversion when they are performed at 25 °C. Interestingly, the reaction is inhibited by methyl groups on the thiirane ring but is accelerated when methyl groups are placed on the vinyl group. Turnover frequencies (TOFs) range from a low of 2  $\text{h}^{-1}$  to a high of 29  $\text{h}^{-1}$  for these compounds (see Table 2).

The reaction is insensitive to the atmosphere over it. For example, similar TOFs were obtained when the reactions were performed under nitrogen, in air, and even under CO. CO reacts only slowly with  $\text{W}(\text{CO})_5(\text{NCMe})$  to yield  $\text{W}(\text{CO})_6$ , which is catalytically inactive. The tungsten

Scheme 5



**FIGURE 3.** ORTEP diagram of the molecular structure of  $W(CO)_5$ - $(SSCH_2CH=CHCH_2)$  (**32**).

complex  $W(CO)_5(SSCH_2CH=CHCH_2)$  (**32**) was isolated from the vinylthiirane reaction and was structurally characterized.<sup>29</sup> This compound contains a dihydrodithiin ligand coordinated to the tungsten atom through one of the sulfur atoms. A structural diagram of **32** is shown in Figure 3. The W–S and S–S bond distances, 2.549(2) and 2.062(2) Å, are not unusual.

Compound **32** was shown to be a component in the catalytic cycle (see Scheme 5).  $W(CO)_5(NCMe)$  is a good catalyst precursor but is not a component in the catalytic cycle.  $^{13}C$  NMR studies of catalytically active solutions have shown that  $W(CO)_5(NCMe)$  and **32** are partially converted to vinylthiirane-containing tungsten complexes **33**, two isomers that differ depending on which of the two lone pairs of electrons on the sulfur atom is coordinated. Unlike the reactions of the simple thiiranes, it was proposed that the thiirane ring-opening occurs spontaneously in the

complexes **33** (step a), to give an allyl–thiolate intermediate **D**.<sup>29</sup> This could explain the enhancement of the rate of reaction by methyl substituents on the vinyl group. Intermediate **D** then rapidly adds a second equivalent of vinylthiirane (step b), to yield a thiranium–thiolate species **E** that eliminates butadiene (step c), to yield the stable dihydrodithiin complex **32**. Another equivalent of vinylthiirane then displaces the dihydrodithiin ligand to release the product **28** and complete the catalytic cycle (step d).

Interestingly, it has been shown that the catalysis is significantly increased when a phosphine ligand is substituted for CO on the tungsten atom. For example, the TOF for the catalytic formation of **28** from **23** by  $W(CO)_4(PPh_3)(NCMe)$  is  $47\text{ h}^{-1}$ , nearly 3 times the rate of that of  $W(CO)_5(NCMe)$ ! The increase can be attributed to steric crowding effects that promote the spontaneous ring-opening step (step a, Scheme 5).

Dihydrodithiins belong to the family of allyl disulfide compounds that are found naturally in allylium plant species including onions and garlic. They have been found to exhibit a range of antiviral, antifungal, and antibiotic properties.<sup>30</sup>

## D. Summary

The first generation of catalysts for the formation of thiocrowns both from thietanes and from thiiranes have now been prepared and characterized. Some of them are very efficient and could be used for large-scale synthesis of certain thiocrowns, such as 12S3. The most effective catalysts are derived from transition metals of the third row. The reason for this is not clear but may be related to the strength of the metal–sulfur bond of the thietane or thiirane complex; that is, the metal–sulfur bonds to the

third-row transition elements are stronger and thus produce greater activation for the ring-opening process.<sup>31</sup> The potential for preparing chiral thiocrowns catalytically is apparent. This cannot be done efficiently at this time. Also, at present we have little control of the size of the ring of the macrocycle that is obtained. It seems that the use of moderating agents or cocatalysts may be of value in achieving these goals.

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