

**Studies of the Transformations of Sulfur  
Containing Heterocycles by Transition Metal  
Cluster Compounds**

**Final Report  
1995-1999**

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DOE Patent Clearance Granted

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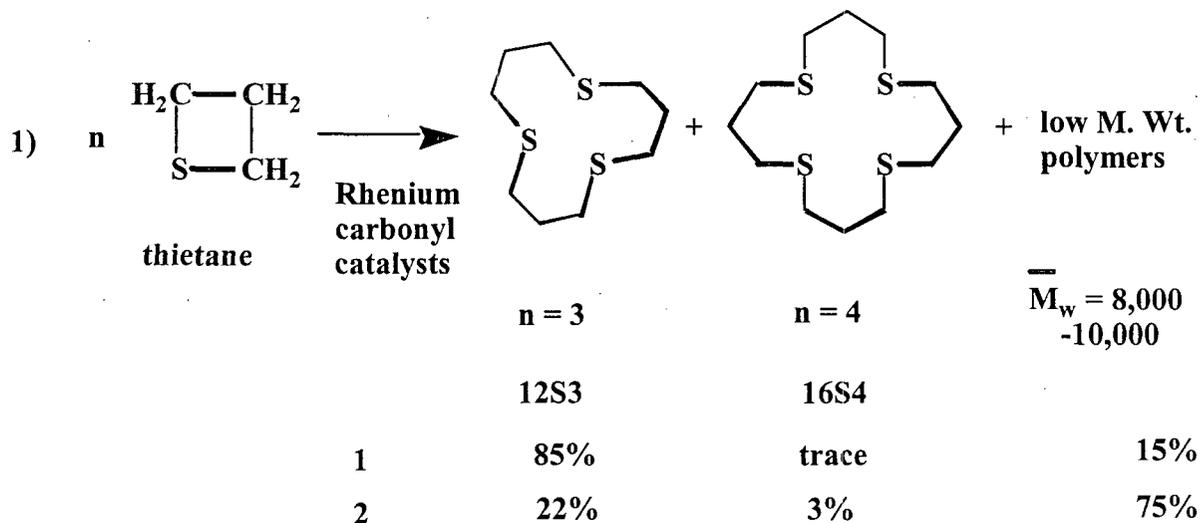
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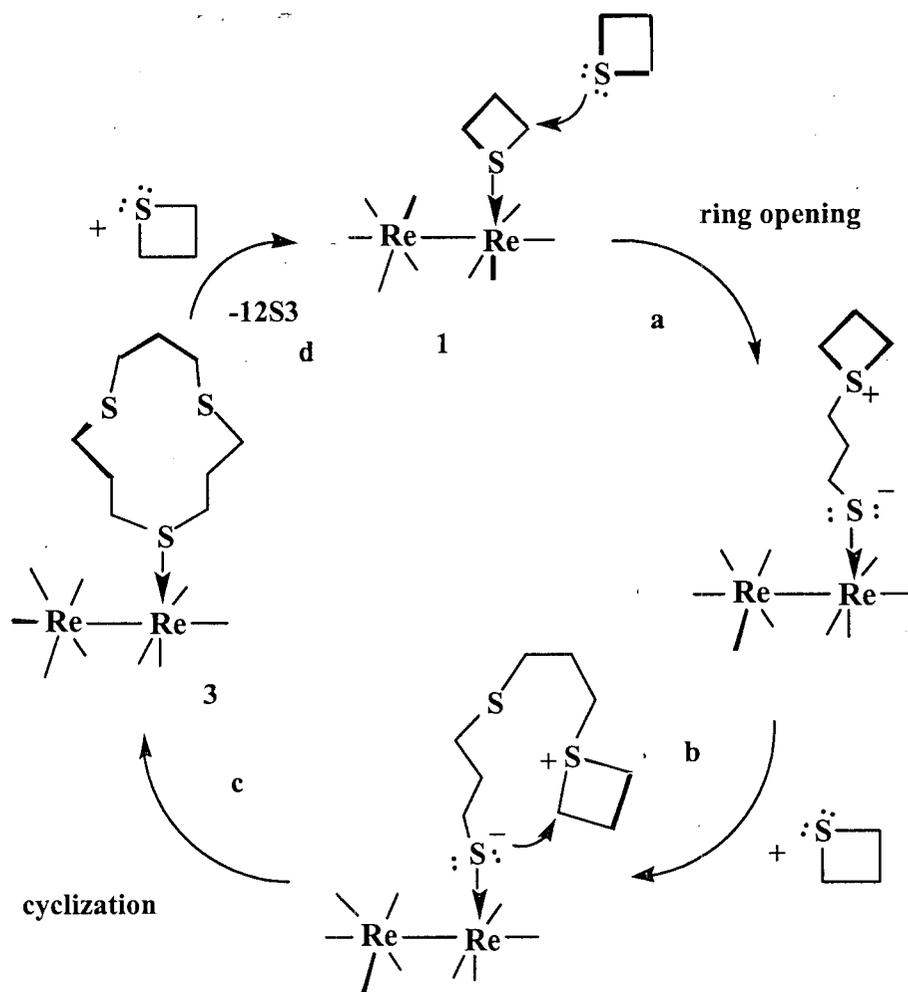
## A) Results 1995 - 99.

### 1) Ring Opening Macrocyclization of Thietane by Metal Carbonyl Complexes

In our studies through 1995 - 99 we have continued to develop our discovery of the catalytic ring opening macrocyclization (ROM) of thietane by transition metal carbonyl cluster complexes, Eq. (1).



We discovered that the dirhenium compound  $\text{Re}_2(\text{CO})_9(\overline{\text{SCH}_2\text{CH}_2\text{CH}_2})$ , **1**, is a much more effective catalyst for ROM of thietane than our original catalyst  $\text{H}_3\text{Re}_3(\text{CO})_{10}(\mu\text{-}\overline{\text{SCH}_2\text{CH}_2\text{CH}_2})$ , **2**. The macrocyclization by **1** produces 12S3 in high yield although small amounts of low molecular wt. oligomers are still present. The compound  $\text{Re}_2(\text{CO})_9(12\text{S3})$ , **3** is formed in the reaction and both compounds appear to be components in the catalytic cycle as shown in Scheme 1.

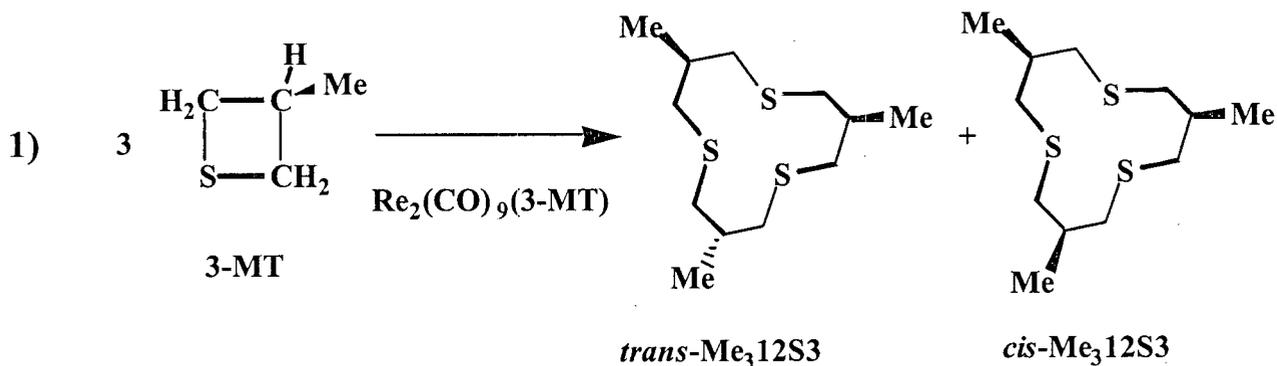


Scheme 1

We have also investigated the catalytic activity of the tetrametallic clusters  $\text{M}_4(\text{CO})_{11}(\overline{\text{SCH}_2\text{CH}_2\text{CH}_2})(\mu\text{-H})_4$ , **4**,  $\text{M} = \text{Os}$  and **5**,  $\text{M} = \text{Ru}$ . Compound **4** produces the macrocyclization of thietane catalytically with a strong preference for 12S3, but it is not quite as high as that of the dirhenium system. The 12S3 complex  $\text{Os}_4(\text{CO})_{11}(12\text{S3})(\mu\text{-H})_4$ , **5** is formed in the process and was established as a component in the catalytic cycle. As in the dirhenium system, all sulfur bound ligands are to be terminally coordinated. Compound **5** is not a good catalyst for the formation of 12S3. Studies have shown that the compound **5** decomposes very early in the reaction period. The fact that all of the transformations in the catalytic processes of **1** and **4** occur at the site of a single metal atom is an important observation. This suggests that mononuclear metal complexes should be capable of performing this catalysis as well. As a result we have prepared and shown that the tungsten complex,  $\text{W}(\text{CO})_5(\overline{\text{SCH}_2\text{CH}_2\text{CH}_2})$ , **6** also produces macrocyclization of thietane with the formation of 12S3 and low Mol. Wt. oligomers.

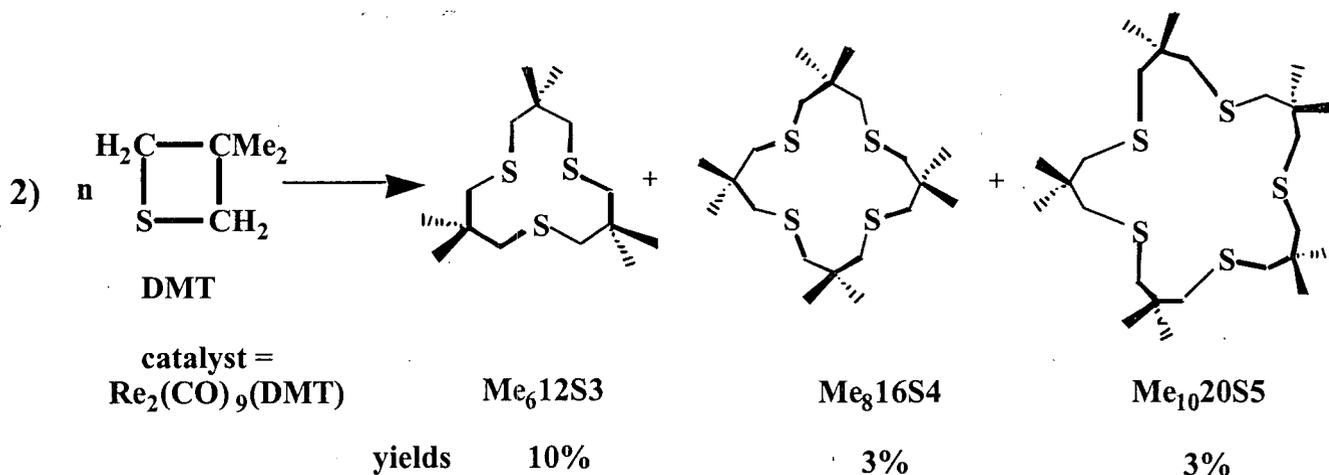
The activity of **6** is lower and the preference for 12S3 is much lower. The catalytic cycle appears to be similar to that of **1**. The complex  $\text{Cr}(\text{CO})_5(\overline{\text{SCH}_2\text{CH}_2\text{CH}_2})$ , **7** was also investigated. The catalytic activity of **7** was much lower than that of **6**, but some 12S3 was still formed. This might be explained by the strength of the metal - sulfur bond: the stronger the metal - sulfur bond is, the greater the activation of the thietane molecule should be, and the third - row transition metals should form stronger bonds to sulfur than those of the first row.

**2) Catalytic Macrocyclization of Substituted Thietanes.** Next, we showed the the process could be extended to substituted thietanes. The catalytic macrocyclization of 3-methylthietane (3-MT) by  $\text{Re}_2(\text{CO})_9(\overline{\text{SCH}_2\text{C}(\text{H})\text{MeCH}_2})$  yielded two isomers (*cis*- and *trans*-) of trimethyl-1,5,9-trithiacyclododecane,  $\text{Me}_3\text{12S3}$ , Eq. (1). The *trans*-isomer was the major product. It was characterized crystallographically. The minor *cis*-isomer was characterized crystallographically in the form of a  $\text{Re}_2(\text{CO})_9$  complex.

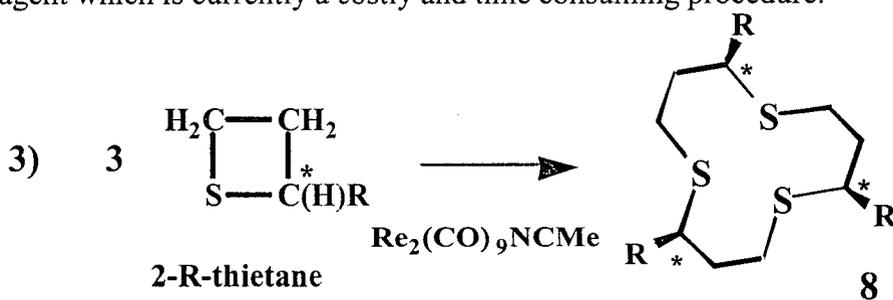


It was also discovered that the mononuclear tungsten complex  $\text{W}(\text{CO})_5(3\text{-MT})$  is also an effective catalyst for the macrocyclization of 3-MT to *cis*- and *trans*-  $\text{Me}_3\text{12S3}$ . A comparison of the two catalysts shows that the rhenium catalyst exhibits a higher activity and higher selectivity for the formation of  $\text{Me}_3\text{12S3}$  than the tungsten complex.

We have also demonstrated that macrocycles can be prepared catalytically from the disubstituted thietane, 3,3-methylthietane, DMT, Eq. (2). As expected this reaction is much slower than the previous ones due to the the increased steric crowding adjacent to the ring opening site. In addition, the yields are much lower and selectivity for one macrocycle relative to others is much lower too. Three macrocycles were isolated and structurally characterized.



By using chiral thietanes formed by placement of a methyl substituent at the 2-position of the thietane, we have been able to synthesize chiral macrocycles. This can be achieved if the thietane opens with a strong preference for addition to one or the other of the inequivalent sulfur-bound carbon atoms. This appears to be the case and we have prepared and isolated the first trichiral derivative of 12S3, **8**, (e.g. Eq. (3)). Absolute configuration tests on the product strongly indicate the ring opening occurs at the less crowded unsubstituted carbon atom. Unfortunately, the yield is very low, and the formation of pure chiral product requires the use of pure chiral reagent which is currently a costly and time consuming procedure.

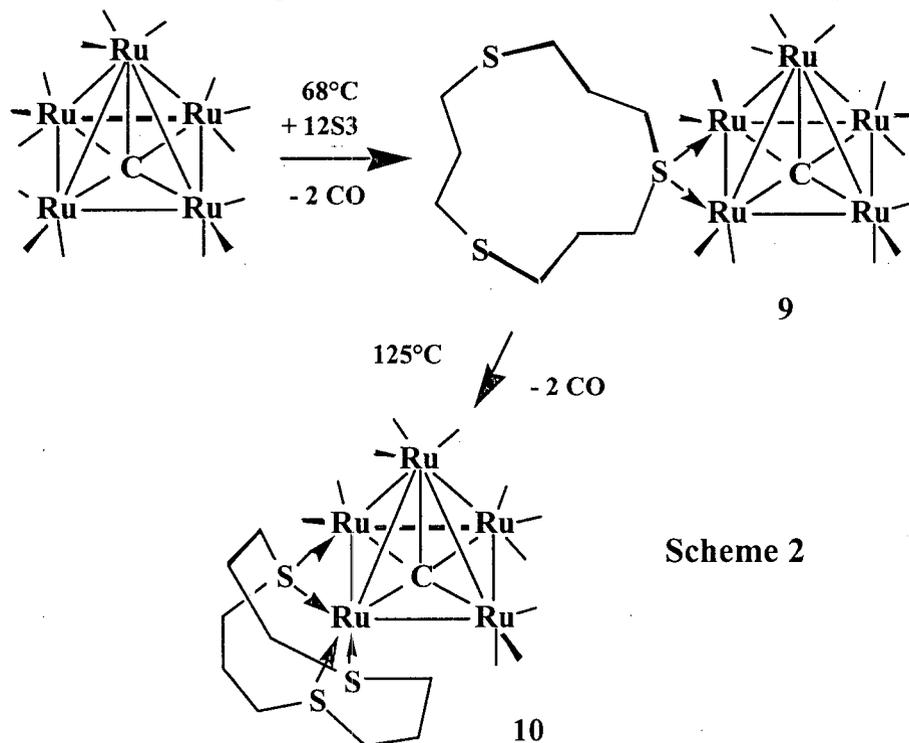


### 3) Complexes of Polythioether Macrocycles to Polynuclear Metal Carbonyl Complexes.

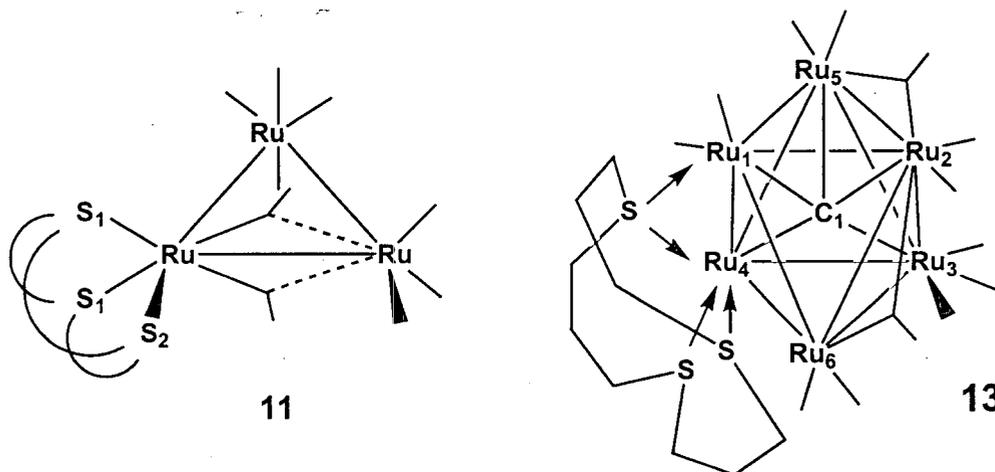
There is considerable interest in the use of polythioether macrocycles as ligands for the transition metals, but to date the complexation of these ligands to metal cluster complexes have been studied very little. Accordingly, we have investigated the reactions of some of the polythioether macrocycles that we have made with some metal carbonyl cluster complexes.

For example, we have prepared a series of two pentaruthenium complexes from the reaction of  $\text{Ru}_5(\text{CO})_{15}(\mu_5\text{-C})$  with 12S3. We showed that the ligand enters the coordination sphere of the cluster by the coordination of one of the three sulfur atoms as a bridge across two of the ruthenium atoms to form the complex  $\text{Ru}_5(\text{CO})_{13}(\mu_5\text{-C})(\mu\text{-}\eta^1\text{-12S3})$ , **9**, see scheme 2. When

heated to 125°C, the  $\text{Ru}_5(\text{CO})_{11}(\mu_5\text{-C})(\mu\text{-}\eta^3\text{-12S3})$ , **10** is formed by further loss of CO and incorporation of the two remaining sulfur atoms into coordination of the metal atoms.



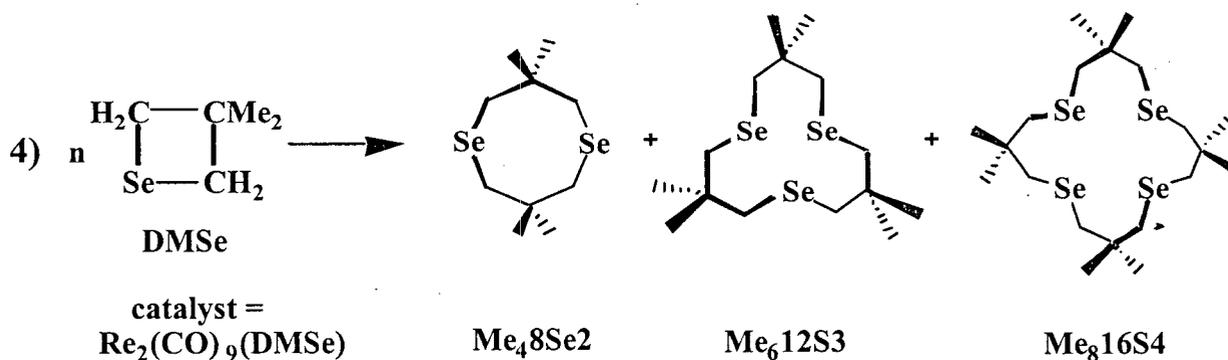
The compounds  $\text{Ru}_3(\text{CO})_7(\mu\text{-CO})_2(1,1,1\text{-}\eta^3\text{-12S3})$ , **11**, and  $\text{Ru}_3(\text{CO})_7(\mu\text{-CO})_2(1,1,1\text{-}\eta^3\text{-9S3})$ , **12**, 9S3 were obtained from the reactions of  $\text{Ru}_3(\text{CO})_{12}$  with 12S3 and 9S3, respectively. Both compounds were characterized crystallographically and were shown to possess  $\text{Fe}_3(\text{CO})_{12}$ -like structures having two bridging CO ligands across one of the Ru - Ru bonds and tridentate 12S3 and 9S3 ligands, respectively. Both compounds exhibit dynamical ligand activity on the NMR timescale that involves opening and closing rearrangements of the bridging CO ligands.



The reaction of 12S3 with  $\text{Ru}_6(\text{CO})_{17}$  yields a hexaruthenium product  $\text{Ru}_6(\text{CO})_{13}(\mu_6\text{-C})(\mu\text{-}\eta^3\text{-12S3})$ , **13** containing and bridging  $\eta^3$ -coordinated 12S3 ligand coordinated similarly to the  $\mu\text{-}\eta^3\text{-12S3}$  ligand observed in **10**.

#### 4) Catalytic Ring Opening Macrocyclization of Selenatanes by Metal Carbonyl Complexes.

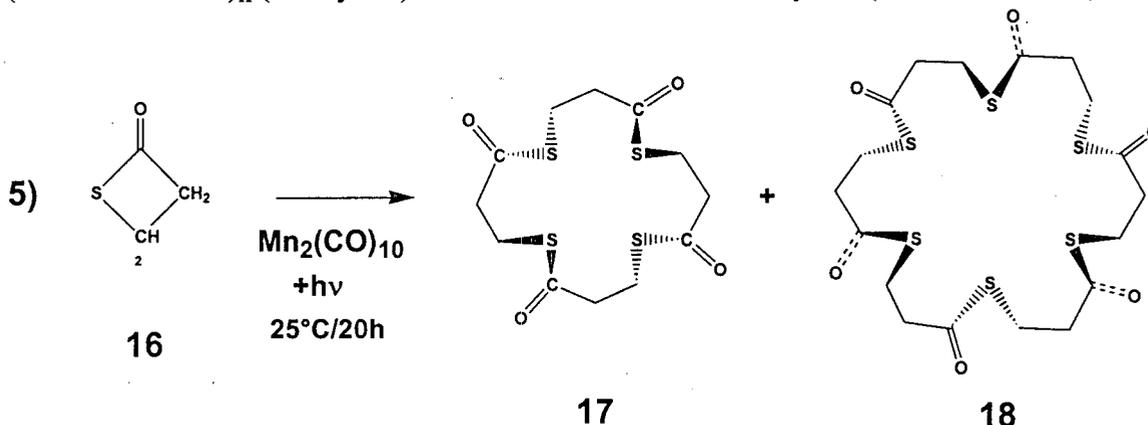
Our success in producing macrocyclization of thietanes has led us to investigate the possible macrocyclization of selenatanes. Selenatanes are the selenium analogs of thietanes. We have demonstrated that that 3,3-dimethylselenatane, DMSe, can be macrocyclized by the  $\text{Re}_2(\text{CO})_9$  grouping to yield new compounds tetramethyl-1,5-diselenacyclooctane,  $\text{Me}_4\text{8Se2}$ ; hexamethyl-1,5,9-triselenacyclododecane,  $\text{Me}_6\text{12Se3}$  and octamethyl-1,5,9,13-tetraselenacyclohexadecane,  $\text{Me}_8\text{16Se4}$ , by our catalytic procedure, Eq. (4).



All three macrocycles were isolated and characterized crystallographically. In addition two complexes of  $\text{Me}_6\text{12Se3}$ :  $\text{Re}_2(\text{CO})_9(\text{Me}_6\text{12Se3})$ , **14** and  $\text{Cu}_4\text{I}_4(\mu\text{-Me}_6\text{12Se3})_2$ , **15** were obtained from the reactions with  $\text{Re}_2(\text{CO})_9(\text{NCMe})$  and  $\text{CuI}$ , respectively. Compound **14** contains an  $\eta^1\text{-Me}_6\text{12Se3}$  ligand while compound **15** contains bridging  $\eta^2\text{-Me}_6\text{12Se3}$  ligands that link  $\text{Cu}_4\text{I}_4$  clusters into a 3-dimensional network in the solid state.

**5) Catalytic Ring Opening Macrocyclization of Strained Ring Thiolactones by Polynuclear Metal Carbonyl Complexes.** In 1996 we discovered a catalytic procedure for the synthesis of a

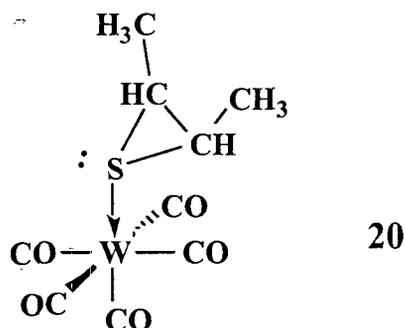
new family of macrocycles, polythiolactones. In the presence of  $\text{Mn}_2(\text{CO})_{10}$ ,  $\text{Mn}_2(\text{CO})_9(\text{NCMe})$  or  $\text{Re}_2(\text{CO})_9(\text{NCMe})$ ,  $\beta$ -propiothiolactone, **16** is catalytically transformed into polymer  $(\overline{\text{SCH}_2\text{CH}_2\text{C=O}})_n$  (55% yield) and a mixture of new macrocycles  $(\overline{\text{SCH}_2\text{CH}_2\text{C=O}})_n$ , Eq. (5).



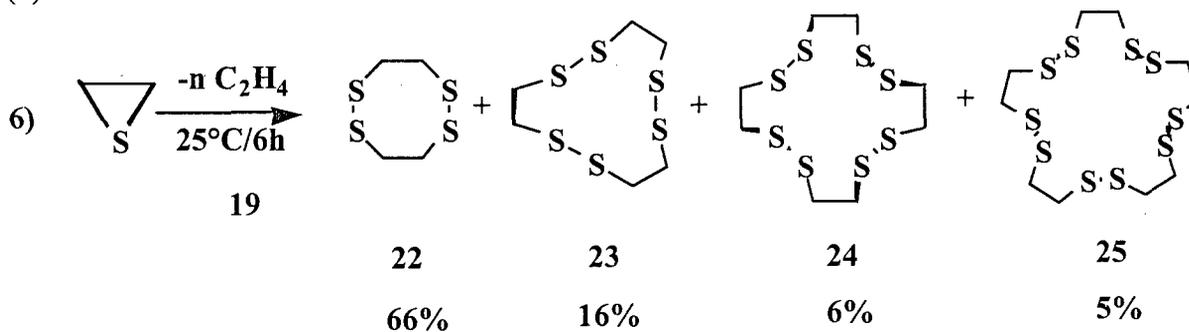
Two of these macrocycles have been isolated and characterized. The major macrocycle has been identified as 1,5,9,13-tetrathiacyclohexadecane-2,6,10,14-tetrone, **17**,  $n = 4$  (22% yield). One of the minor cyclooligomers has been identified as 1,5,9,13,17,21-hexathiacyclotetracosane-2,6,10,14,18,22-hexone, **18**,  $n = 6$ , (2% yield). These two macrocycles have been characterized crystallographically. The structure of the tetramer is unusual for a sulfur macrocycle because the sulfur atoms are turned toward the inside of the ring to form a tetrahedral cavity. The hexamer forms a large six-sided 24-membered ring and crystallizes from  $\text{CH}_2\text{Cl}_2$  solutions as an inclusion compound containing one equivalent of  $\text{CH}_2\text{Cl}_2$  in the center of the ring.

These catalytic reactions are promoted by light and inhibited by the radical scavenger TEMPO. It is concluded that these reactions involve radical intermediates formed by photolytic cleavage of the metal - metal bond of the dinuclear catalyst precursors.

**6) Catalytic Ring Opening Macrocyclization of Thiiranes by Metal Carbonyl Complexes.** In 1996 we discovered that thiiranes,  $\overline{\text{SCH}_2\text{CH}_2}$ , form stable complexes with the  $\text{W}(\text{CO})_5$  grouping, and we isolated the thiirane complexes,  $\text{W}(\text{CO})_5(\overline{\text{SCH}_2\text{CH}_2})$ , **19**,  $\text{W}(\text{CO})_5(\text{cis-}\overline{\text{SCHMeCHMe}})$ , **20** and  $\text{W}(\text{CO})_5(\text{trans-}\overline{\text{SCHMeCHMe}})$ , **21** have been isolated. Compound **22** was characterized crystallographically and shown to contain an S-coordinated dimethylthiirane ligand with a pyramidal sulfur atom.

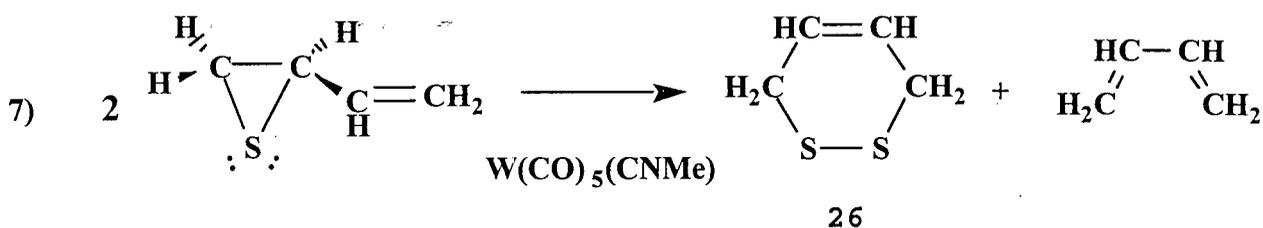


Most interestingly, compound **19** was found to be a catalyst for the transformation of thiirane into a mixture of macrocyclic polydisulfides  $(\text{CH}_2\text{CH}_2\text{SS})_n$ , **22** - **25**,  $n = 2, 3, 4,$  and  $5$  and ethylene, Eq. (6).

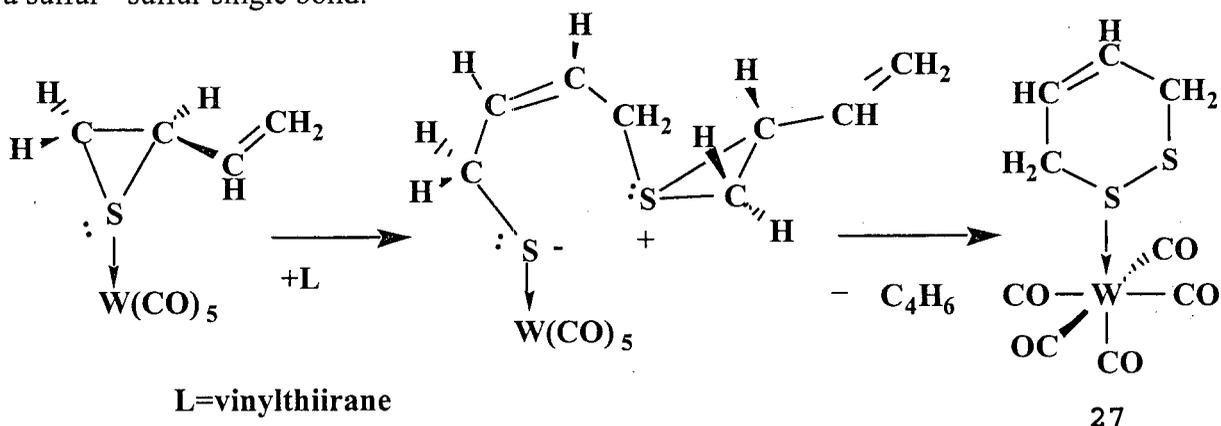


A mechanism involving the formation of  $\text{SCH}_2\text{CH}_2\text{S}$  groups by an opening of the thiirane ring by addition of the sulfur atom of a free molecule of thiirane to the carbon atom of a thiirane ligand in the complex was proposed to explain the formation of the cyclic polydisulfides, **22** - **25**. Evidence for formation of the transient intermediate  $\text{SCH}_2\text{CH}_2\text{S}$  was obtained by using  $(\text{MeO}_2\text{C})\text{C}=\text{C}(\text{CO}_2\text{Me})$  as a trapping agent to yield the heterocycle  $\overline{\text{SCH}_2\text{CH}_2\text{SC}(\text{CO}_2\text{Me})\text{C}(\text{CO}_2\text{Me})}$ .

We have also examined the catalytic transformation of vinylthiirane by  $\text{W}(\text{CO})_5(\text{NCMe})$ . This reaction produces the 1,2-dithiin, **26**, in 80% yield together with one equivalent of 1,3-butadiene at a rate of 14 turnovers/h at  $25^\circ\text{C}$ , eq. (7). A dithiin complex of the catalyst,  $\text{W}(\text{CO})_5(\overline{\text{SSCH}_2\text{CH}=\text{CHCH}_2})$ , **27** was isolated and characterized crystallographically. The dithiin was found to be coordinated to the tungsten atom through one of the two sulfur atoms.



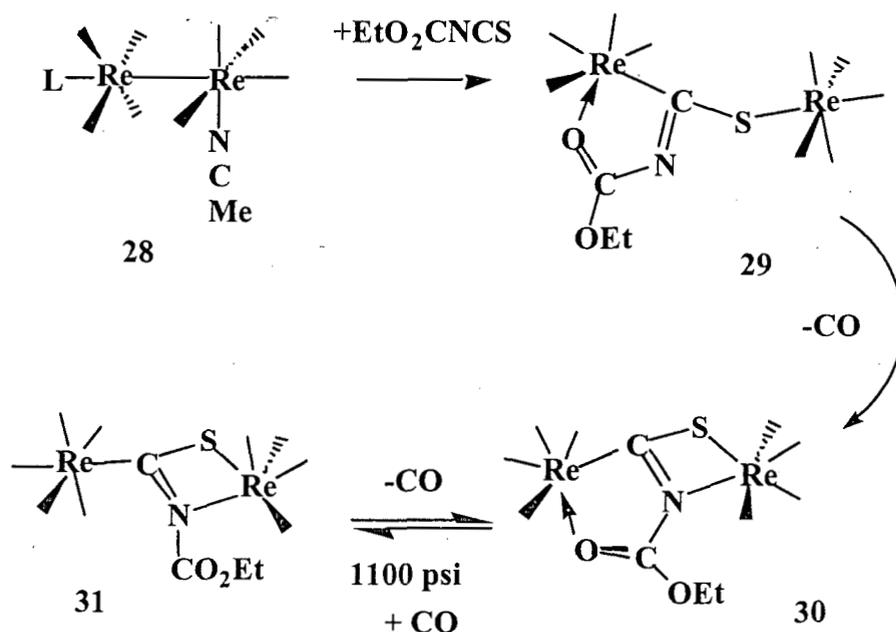
The formation of **26** can be explained by the mechanism shown in Scheme 2. The vinylthiirane is activated by coordination to a  $W(CO)_5$  group. A second thiirane then adds to the  $\beta$ -position of the vinyl substituent. This opens the ring of the coordinated thiirane and leads to the formation of a new C - C double bond between the carbon atoms at the 3 and 4 positions along ligand chain. The sulfur atom bonded to the tungsten atom develops a negative charge and the sulfur atom of the added thiirane develops a positive charge. 1,3-butadiene is eliminated from the positively charged sulfur atom and the charges on the sulfur atoms are neutralized by formation of a sulfur - sulfur single bond.



Scheme 3

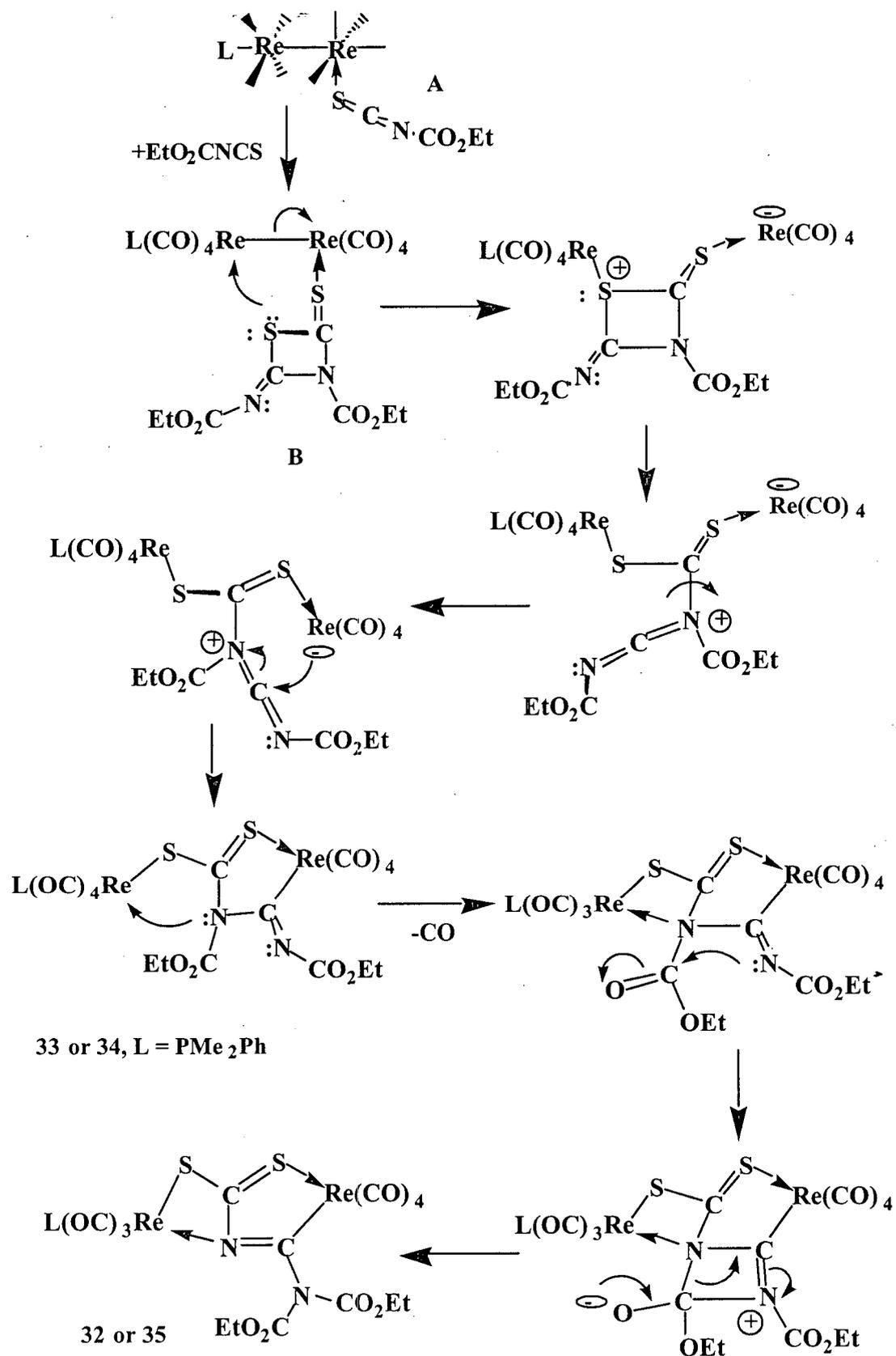
### 7) Other Reactions at Metal-Metal Single Bonds.

To investigate further the reactivity of dinuclear carbonyls of the manganese subgroup, we have examined the reactions of alkyl isothiocyanates with  $Re_2(CO)_9(NCMe)$ , **28**. The reaction of  $EtO_2CN=C=S$  with **28** proceeds with displacement of the  $NCMe$  ligand and insertion of the isothiocyanate into the rhenium - rhenium bond to yield the dirheniathioimidate complex **29**, see scheme 3. Compound **29** is thermally decarbonylated ( $68^\circ C$ ) to yield the complex **30** in which the iminyl nitrogen atom has become coordinated to one of the rhenium atoms. Interestingly, when  $CO$  is readded to **30** under pressure, it is not **29** that is reformed, but instead the new complex **31**.



### Scheme 3

A second product  $\text{Re}(\text{CO})_4[\mu\text{-C,N,S}_2\text{-(EtO}_2\text{C)}_2\text{NC=NCS}_2]\text{Re}(\text{CO})_4$ , **32** was also isolated from the reaction of **28** with  $\text{EtO}_2\text{CN=C=S}$ . Compound **32** contains a  $(\text{EtO}_2\text{C})_2\text{NC=NCS}_2$  ligand that was formed by an insertion and combination of two isothiocyanate molecules into the Re-Re bond of **28**. The reaction of  $\text{Re}(\text{CO})_4(\text{PMe}_2\text{Ph})\text{Re}(\text{CO})_4(\text{NCMe})$  with  $\text{EtO}_2\text{CN=C=S}$  yielded two isomeric products: *trans*- $\text{Re}(\text{CO})_4(\text{PMe}_2\text{Ph})[\mu\text{-(EtO}_2\text{C)N=CN(CO}_2\text{Et)CS}_2]\text{Re}(\text{CO})_4$ , **33** and *cis*- $\text{Re}(\text{CO})_4(\text{PMe}_2\text{Ph})[\mu\text{-(EtO}_2\text{C)N=CN(CO}_2\text{Et)CS}_2]\text{Re}(\text{CO})_4$ , **34**. Compound **33** and **34** contain a bridging  $(\text{EtO}_2\text{C)N=CN(CO}_2\text{Et)CS}_2$  ligand that was also formed by the coupling and rearrangement of two isothiocyanate molecules. This ligand is considered to be an intermediate en route to the  $(\text{EtO}_2\text{C})_2\text{NC=NCS}_2$  ligand as found in **32** since **28** and **29** can be transformed into the complex  $\text{Re}(\text{CO})_4[\mu\text{-C,N,S}_2\text{-(EtO}_2\text{C)}_2\text{NC=NCS}_2]\text{Re}(\text{CO})_3(\text{PMe}_2\text{Ph})$ , **30** a phosphine derivative of **27**. A multistep mechanism for the formation of the  $(\text{EtO}_2\text{C})_2\text{NC=NCS}_2$  ligand is shown in Scheme 4. This is supported by the isolation and structural characterization of the compounds **28** and **29** which are intermediates en route to **27** and **30**.



Scheme 5

## B) Publications Under This Project in 1995 - 99.

1. R. D. Adams and M. Huang, Reactions of Isocyanide Substituted Dimanganese Carbonyl Complexes with Alkynes. Alkyne-Isocyanide Coupling and the Synthesis of Metallated N-Substituted pyridines, *Organometallics*, **14**, 506 (1995).
2. R. D. Adams, L. Chen and J. H. Yamamoto, The Coordination and Fragmentation of 1,4-Dithiacyclohexane by a Triosmium Cluster, *Inorg. Chim. Acta*, **229**, 47 (1995).
3. R. D. Adams, L. Chen and M. Huang, Organic Reactions upon Dimetalated Olefins. Reactions of the Olefinic Group in the Dirhenium Complex  $(OC)_4Re[E-HC=C(CO_2Me)CS_2]Re(CO)_4$  with Amines, *J. Chin. Chem. Soc.*, **42**, 11 (1995).
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5. R. D. Adams, S. B. Falloon, K. T. McBride and J. H. Yamamoto, The Coordination of Polythiaether Macrocycles to Metal Cluster Complexes. 2. The Coordination of Polythiaether Macrocycles to Hexaruthenium Carbido Carbonyl Clusters, *Organometallics*, **14**, 1739 (1995).
6. R. D. Adams and S. B. Falloon, The Catalytic Cyclooligomerization of Thietane by Dirhenium Carbonyl Complexes, *Organometallics*, **14**, 1748 (1995).
7. R. D. Adams and J. E. Cortopassi, The Synthesis and Structural Characterization of  $Os_3(CO)_8[Si(OMe)_3][\mu-PMe_2(C_6H_4)](\mu-H)_2$ . An Unusual Unsaturated Triosmium Cluster Complex, *J. Cluster Sci.*, **6**, 437 (1995).
8. R. D. Adams and X. Qu, The Coordination and Transformations of Benzothienyl Ligands by Triosmium Cluster Complexes, *Organometallics*, **14**, 2238 (1995).
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10. R. D. Adams and J. H. Yamamoto, The Coordination of Polythiaether Macrocycles to Metal Cluster Complexes. 3. The Synthesis, Structures and Dynamical Activity of the Cluster Complexes  $Ru_3(CO)_7(\mu-CO)_2(1,1,1-\eta^3-12S3)$  and  $Ru_3(CO)_7(\mu-CO)_2(1,1,1-\eta^3-9S3)$ , *Organometallics*, **14**, 3704 (1995).
11. R. D. Adams and X. Qu, Carbon - Carbon Bond Cleavage by Osmium Clusters. The Ring Opening of a Cyclobutenyl Ligand by a Triosmium Cluster, *Organometallics* **14**, 4167 (1995).

12. R. D. Adams and M. Huang, Reactions of Heteronuclear Dimetalated Olefin Complexes. The Reactions of  $\text{CpFe}(\text{CO})_2[\mu\text{-(Z)-(MeO}_2\text{C)C=C(CO}_2\text{Me)]Re}(\text{CO})_4$  with CO and p-tolylisothiocyanate, *Organometallics*, **14**, 4535 (1995).
13. R. D. Adams and S. B. Falloon, Cluster Catalysis. The Catalytic Cyclooligomerization of Thietane by Tetraosmium and Tetraruthenium Tetrahydride Carbonyl Cluster Complexes, *Organometallics*, **14**, 4594 (1995).
14. R. D. Adams and S. B. Falloon, The Chemistry of Thietane Ligands in Polynuclear Metal Carbonyl Complexes, *Chem. Rev.*, **95**, 2587 (1995).
15. R. D. Adams, M. Huang, J. A. Yamamoto and L. Zhang, The Coordination and Transformation of a Thiourea Ligand in a Dirhenium Carbonyl Complex, *Chem. Ber.* **129**, 137 (1996).
16. R. D. Adams and X. Qu, The Chemistry of Cyclobutene and Cyclobutenyl Ligands in Metal Cluster Complexes, *Synlett.*, 493 (1996).
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18. R. D. Adams and M. Huang, The Synthesis of Stabilized Dimetalated Thioimide Complexes by the Insertion of Ethoxycarbonylisothiocyanate into a Rhenium - Rhenium Bond, *Chem. Ber.*, **129**, 485 (1996).
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