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The Transformation of Organic Amines by Transition Metal Cluster Compounds

Progress Report

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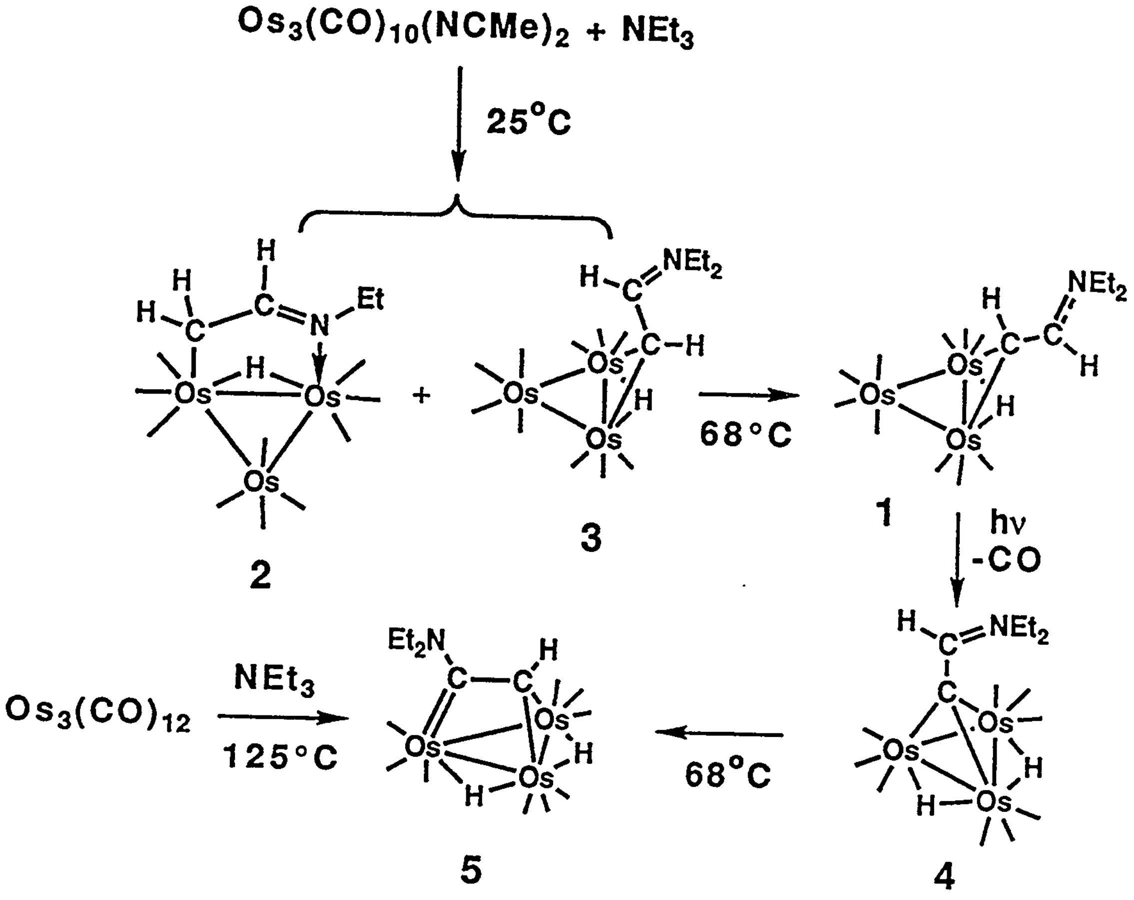
Our research during the current award period has covered several related topics which have emerged and grown as a consequence of the various discoveries that have been made during this award period. They have been divided into subsections as listed in the contents (see preceding page) for clarity and emphasis. A summary of the results of these studies is given in the following sections of this report. These studies have resulted in **50** scientific publications over the last three years and details of our studies beyond that given in the following sections can be found in those reports. All of these reports are listed in the final section of this report by the author's names, title and journal citation.

1) The Activation of Tertiary Amines by Osmium Cluster Complexes.

During the 3-year period of this award, we completed our studies of the reactions of $Os_3(CO)_{10}(NCMe)_2$ with NEt_3. Two new products $Os_3(CO)_{10}(\mu\text{-}CH_2C(H){=}NEt_2)(\mu\text{-}H)$, **2** and $Os_3(CO)_{10}(\mathit{syn}\text{-}\mu\text{-}\eta^1\text{-}CHCHNEt_2)(\mu\text{-}H)$, **3** were obtained, in addition to the previously reported compound $Os_3(CO)_{10}(\mathit{anti}\text{-}\mu\text{-}\eta^1\text{-}CHCHNEt_2)(\mu\text{-}H)$, **1** when the reaction was conducted at 25°C. Compounds **2** and **3** were both characterized by single-crystal x-ray diffraction analyses. Compound **2** contains a bridging methyl-metallated N-ethylimine ligand formed by the cleavage of one ethyl group from the NEt_3. Compound **3** is an isomer of **1** in which the bridging ligand has a *syn*-conformation with respect to the cluster as compared to the *anti*-conformation in **1**. Compound **3** slowly isomerizes to **1**. Compound **3** is decarbonylated by exposure to UV radiation and is transformed to the new compound $Os_3(CO)_9(\mu_3\text{-}CC(H){=}NEt_2)(\mu\text{-}H)_2$, **4** (58% yield) by an additional CH activation to form a triply bridging η^1-diethylaminovinylidene ligand. Compound **4** isomerizes to the compound

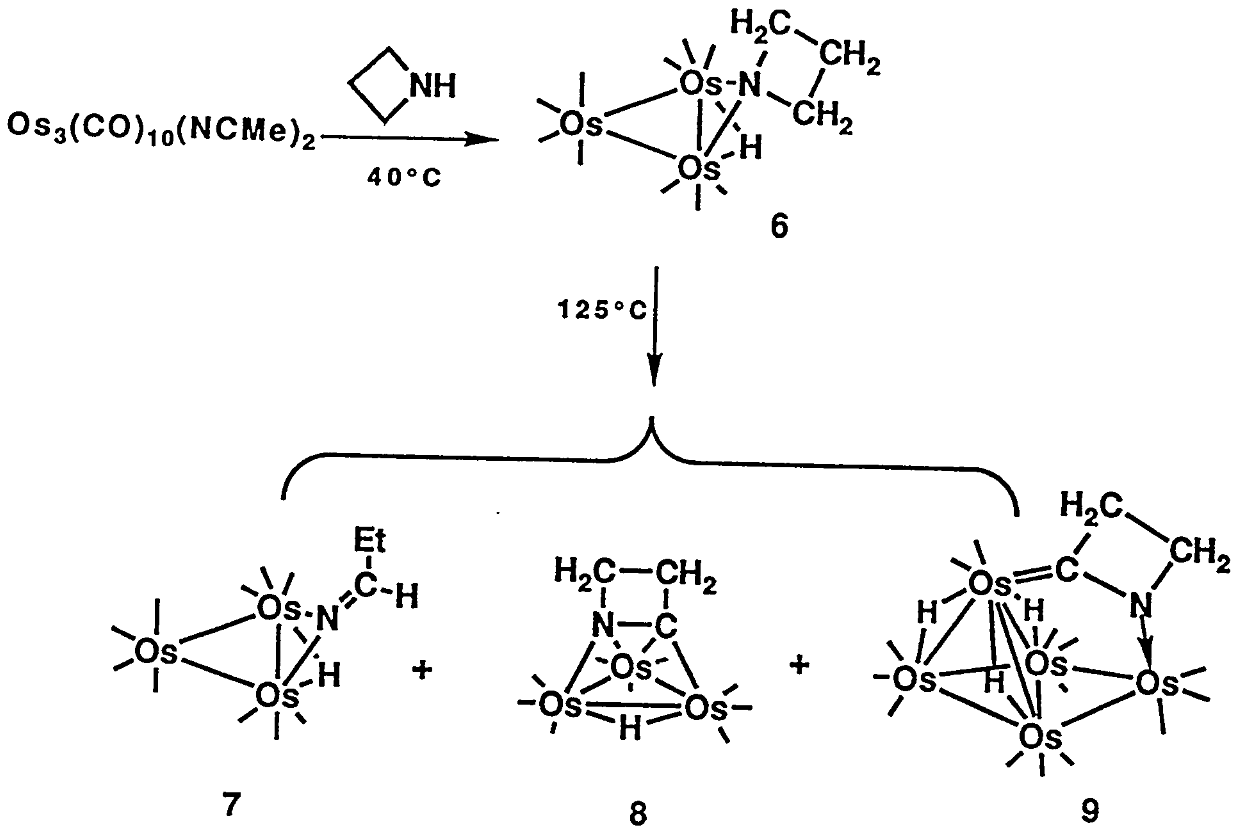
$Os_3(CO)_9(\mu_3\text{-}HCCNEt_2)(\mu\text{-}H)_2$, **5** at 68°C. Compounds **4** and **5** were also characterized by single-crystal x-ray diffraction analyses. The latter product contains a triply bridging ynamine ligand that exhibits structural and reactivity features that are characteristic of a carbene ligand at the amine substituted carbon atom. A summary of these results is shown in Scheme 1.



Scheme 1

2) CH Bond Activation and Ring Opening of a Nitrogen Containing Strained Ring Heterocycle by an Osmium Cluster Complex.

In an extension of our studies of tertiary amines we next directed our attention to the nitrogen containing strained ring heterocycles known as azetidines. We prepared the new cluster complex $Os_3(CO)_{10}(\mu\text{-}\overline{NCH_2CH_2C}H_2)(\mu\text{-}H)$, **6** from the reaction of $Os_3(CO)_{10}(NCMe)_2$ with azetidine. Complex **6** was shown by an x-ray crystallographic analysis to contain a four membered $\overline{NCH_2CH_2C}H_2$ ring bridging two of the metal atoms via the nitrogen atom. When heated, **6** was transformed into two new triosmium complexes $Os_3(CO)_{10}[\mu\text{-}N{=}C(H)Et](\mu\text{-}H)$, **7** and $Os_3(CO)_9(\mu_3\text{-}\overline{NCH_2CH_2C})(\mu\text{-}H)$, **8**. A small amount of a pentaosmium cluster complex $Os_5(CO)_{14}(\mu\text{-}\overline{NCH_2CH_2C})(\mu\text{-}H)_3$, **9** was also obtained. A summary of the results is shown in the Scheme 2. The ligand in complex **7** was clearly formed by an opening of the azetidine ring by a cleavage of one of the carbon-nitrogen bonds and a shift of one of the hydrogen atoms of one of the methylene groups to the other methylene group. This shift resulted in the formation of the C - N double bond and the ethyl group.



Scheme 2

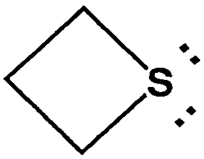
The formation of **8** occurred by the cleavage of both C-H bonds at one of the nitrogen bonded methylene groups and resulted in the formation of the triply bridging four-membered heterocycle $\overline{NCH_2CH_2C}$.

The formation of **7** at 125°C demonstrates that bridging coordination can promote the opening of the four membered nitrogen containing heterocycle $\overline{NCH_2CH_2CH_2}$ by carbon-nitrogen bond cleavage, a key step in the hydrodenitrogenation process. Metal promoted ring opening transformations of azetidines could also provide new ways for developing the organic chemistry of these molecules.

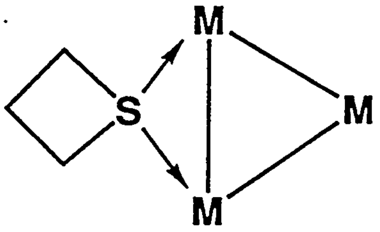
3) Ring Opening of Thietane Ligand in Metal Carbonyl Cluster Complexes.

In combination with our studies of ring opening of strained ring heterocycles containing nitrogen we began an investigation the ring opening reactions of the sulfur containing analogs known as thietanes, **A** by metal cluster complexes. The cleavage of carbon - sulfur bonds is a key step in the removal of sulfur from the sulfur containing heterocycles commonly found in fossil fuels.

We have synthesized a number of new complexes in which the thietane ligands bridge two of the metal atoms in cluster complexes through the coordination of the two lone pairs of electrons on the sulfur atom, **B**.



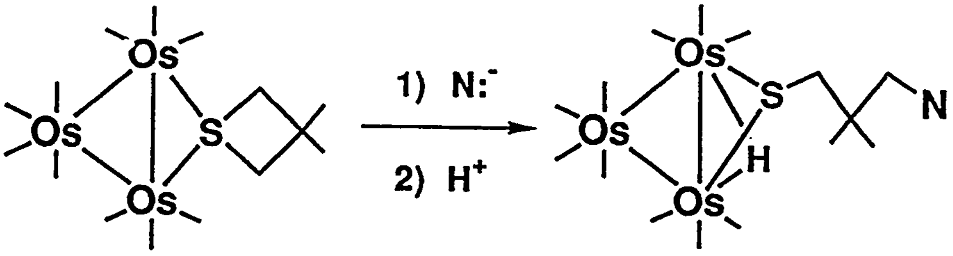
A



B

We have found that bridging thietane ligands in these cluster complexes are significantly activated toward the addition of nucleophiles at the carbon atoms that are bonded to the sulfur atom. This addition induces a cleavage in the carbon-sulfur bond and an opening of the four membered ring of the thietane ligand.

The complex $Os_3(CO)_{10}[\mu\text{-}\overline{SCH_2CMe_2CH_2}]$, **10** was prepared from the reaction of 3,3-dimethylthietane (3,3-DMT) with $Os_3(CO)_{10}(NCMe)_2$. The reaction of **10** with the nucleophiles F^-, Cl^-, Br^-, I^-, EtO^- yielded the series of new complexes $Os_3(CO)_{10}[\mu\text{-}SCH_2CMe_2CH_2X](\mu\text{-}H)$, X = F; Cl; Br; I; or OEt, after protonation, see Scheme 3.



1 0 N:⁻ = halide, OEt

Scheme 3

The reaction of **10** with the secondary amines Et_2NH, and $(CH_2)_3NH$ yielded the related complexes $Os_3(CO)_{10}[\mu\text{-}SCH_2CMe_2CH_2X](\mu\text{-}H)$, X = NEt_2, **11**; $N(CH_2)_3$, **12** without a protonation step since the hydrogen atom on the nitrogen atom was shifted to the cluster.

The complex $Os_3(CO)_{10}[\mu\text{-}SCH_2CMe_2CH_2Cl](\mu\text{-}H)$ was characterized crystallographically and was found to contain a bridging chloroneopentylthiolato ligand, Figure 1. To establish the mechanism of the addition step, the complex $Os_3(CO)_{10}[\mu\text{-}trans\text{-}\overline{SC(H)MeCH_2C}(H)Me]$, **1 3** (in the form of an equimolar mixture of *2R,4R*- and *2S,4S*-enantiomers of the thietane ligand) was synthesized and converted to the ring opened iodide substituted thiolato complex $Os_3(CO)_{10}[\mu\text{-}SC(H)MeCH_2C(H)Me(I)](\mu\text{-}H)$, **14**, (see Figure 2) by the addition of I^-, Scheme 4.

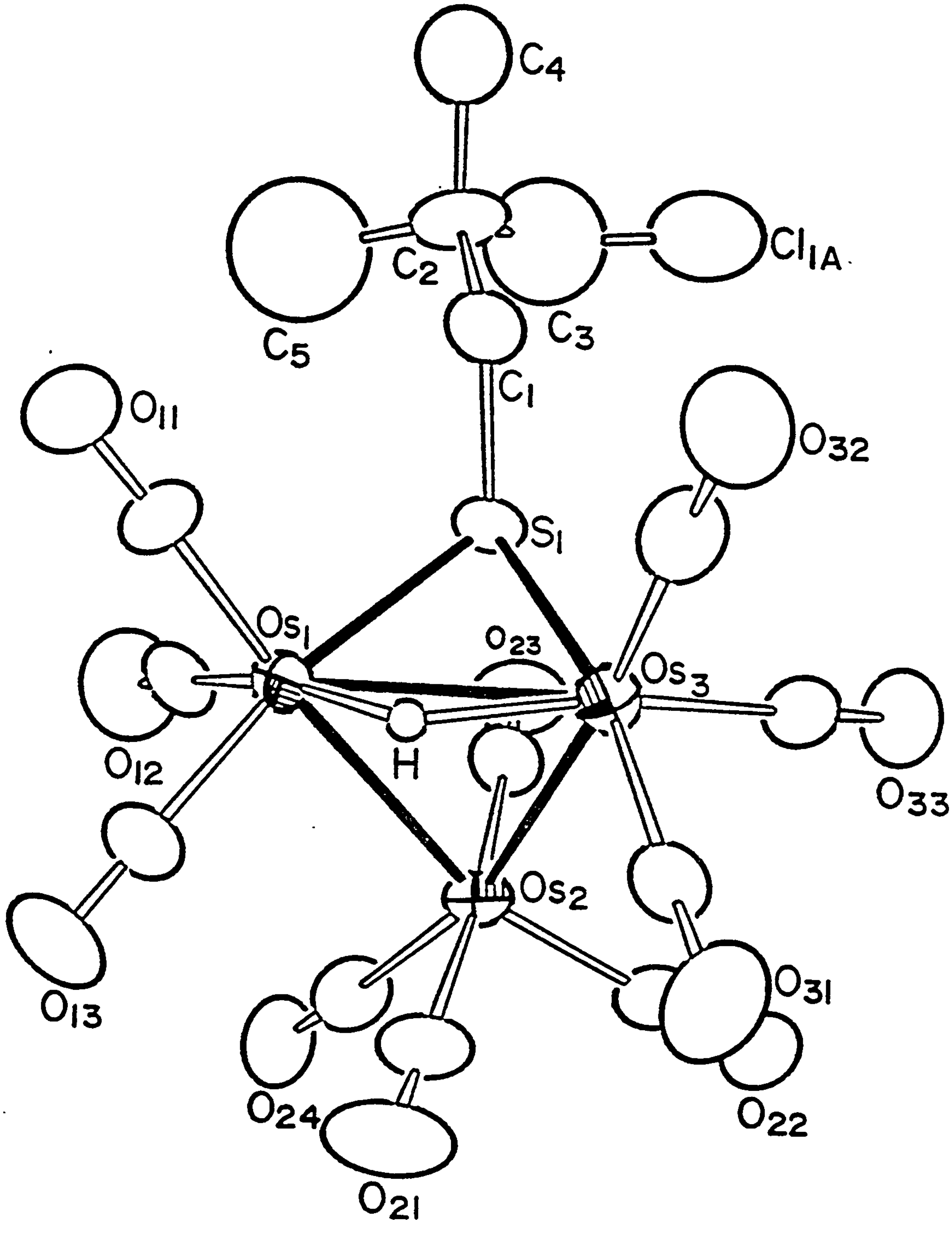

C4
C2
Cl1A
C5
C3
C1
O11
O32
S1
Os1
O23
Os3
O12
H
O33
Os2
O13
O31
O24
O22
O21

Figure 1

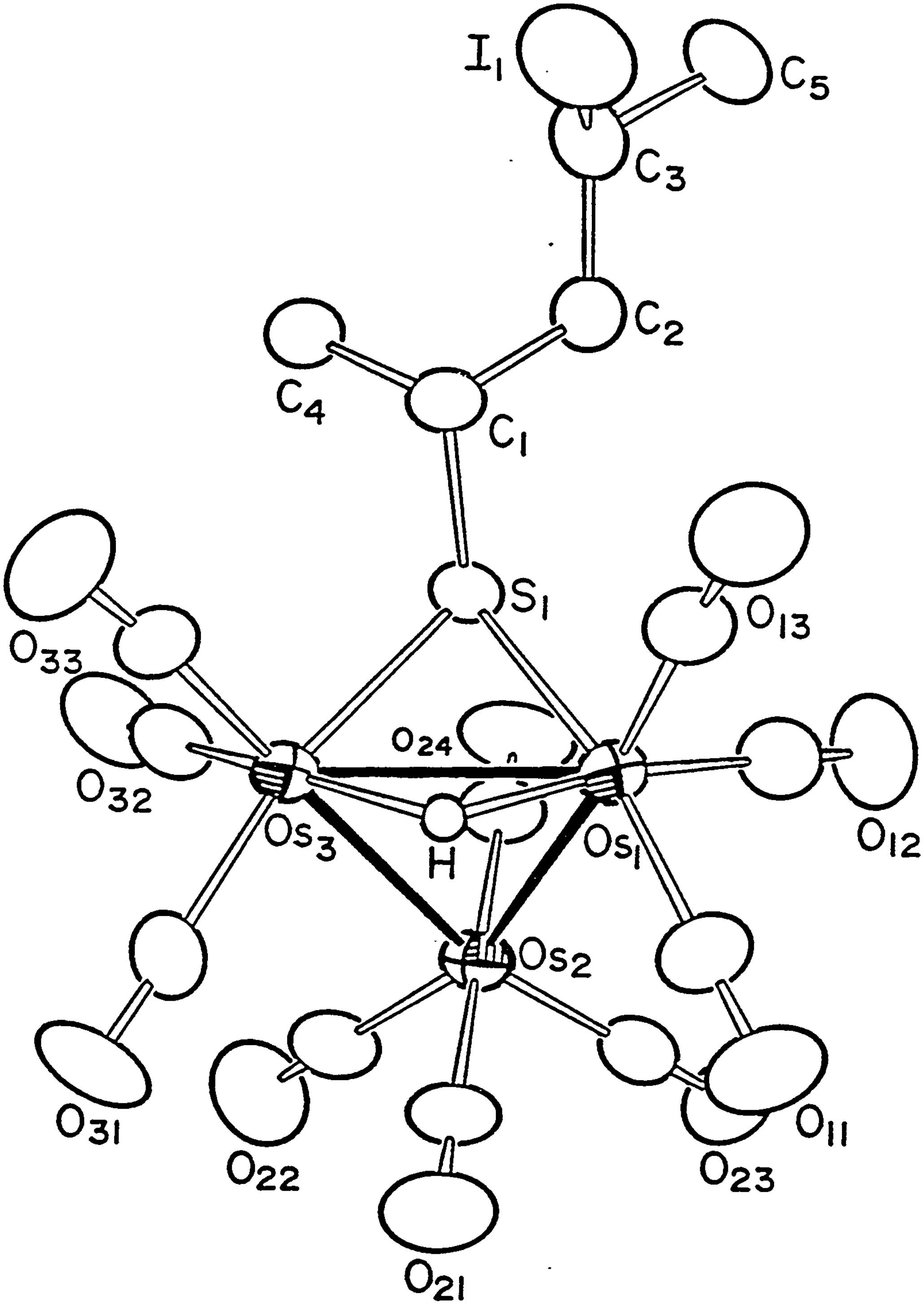
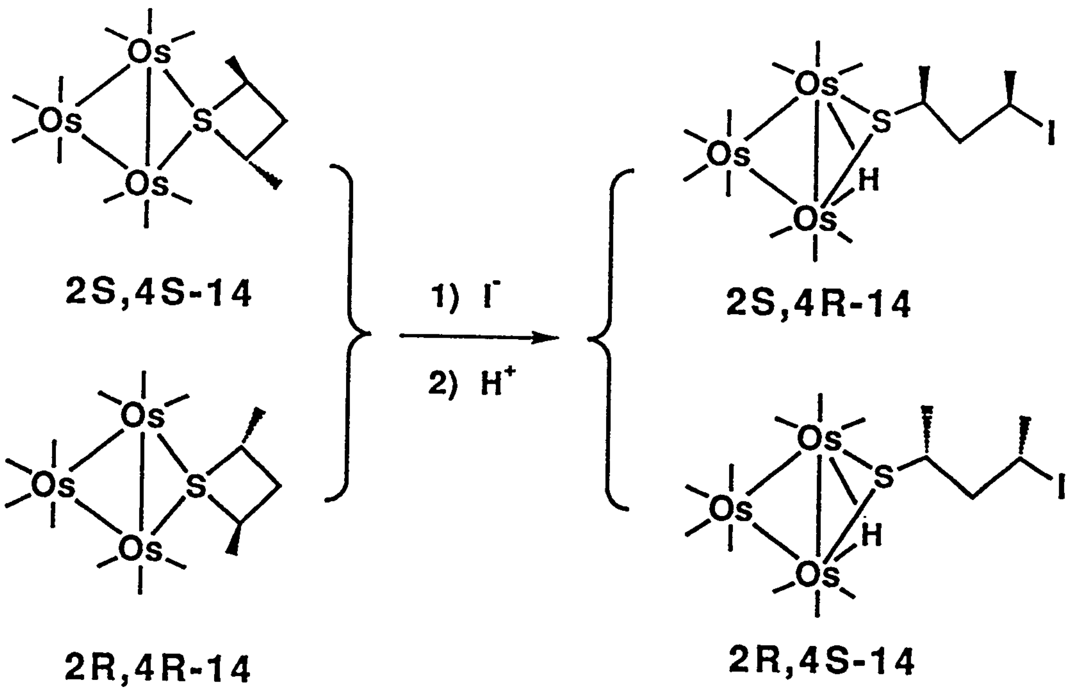
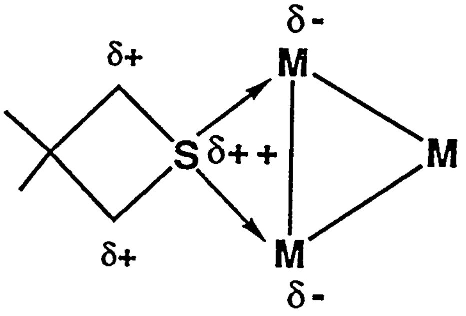

I1
C5
C3
C2
C4
C1
S1
O13
O33
O24
O12
O32
Os3
H
Os1
Os2
O31
O22
O21
O23
O11

Figure 2



Scheme 4

Compound **14** was found to be an equimolar mixture of enantiomers containing the *2R,4S*- and *2S,4R*-2-methyl-4-iodo-butanethiolato ligand. The stereochemistry of both products requires the occurrence of an inversion of configuration at the iodine-substituted carbon atom. This is most consistent with the conventional backside nucleophilic attack mechanism.



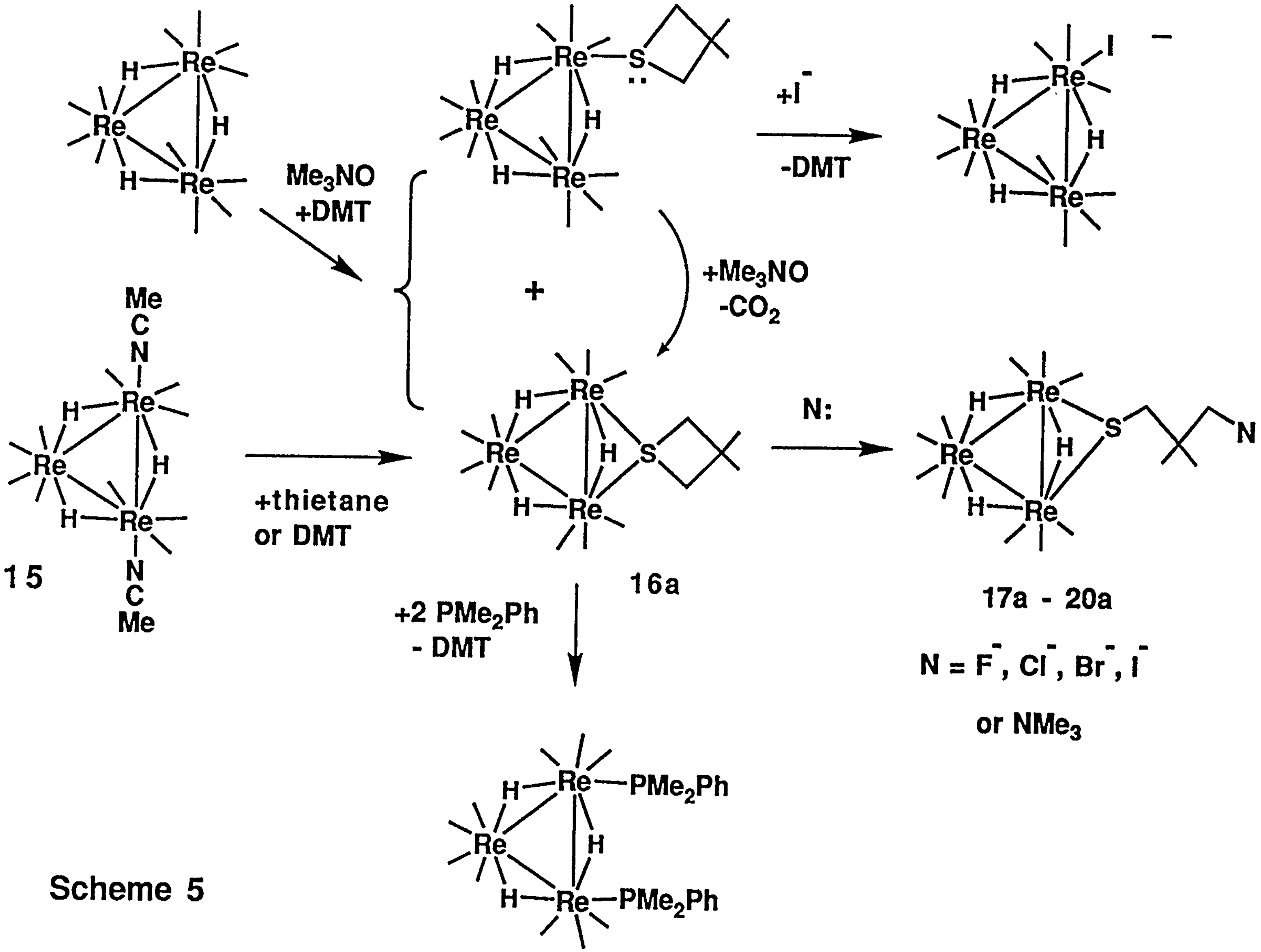
It is proposed that the activation mechanism occurs by the formation of a partial positive charge δ+ on the sulfur atom produced by the withdrawl of electron density through the coordination of lone pairs of electrons on the sulfur atom. This, in turn, produces a partial positive charge δ+ on the neighboring carbon atoms which are the sites of the nucleophilic additions.

The reactions of 3,3-DMT and thietane, $\overline{SCH_2CH_2CH_2}$, with $Re_3(CO)_{10}(NCMe)_2(\mu_3\text{-}H)_3$, **15** have yielded the new complexes $Re_3(CO)_{10}[\mu\text{-}\overline{SCH_2CMe_2CH_2}](\mu_3\text{-}H)_3$, **16a** and $Re_3(CO)_{10}[\mu\text{-}\overline{SCH_2CH_2CH_2}](\mu_3\text{-}H)_3$, **16b**, respectively that also contain bridging thietane ligands. Compounds **16a** and **16b** also react readily with halide ions by ring opening additions to yield the complex anions $[Re_3(CO)_{10}(\mu\text{-}SCH_2CMe_2CH_2X)(\mu\text{-}H)_3]^-$, **17a** - **20a**, X = F, Cl, Br, I, and $[Re_3(CO)_{10}(\mu\text{-}SCH_2CH_2CH_2Cl)(\mu\text{-}H)_3]^-$, **18b** , see Scheme 5. It was not possible to neutralize these anions by protonation with acetic acid.

Scheme 5 (see next page)

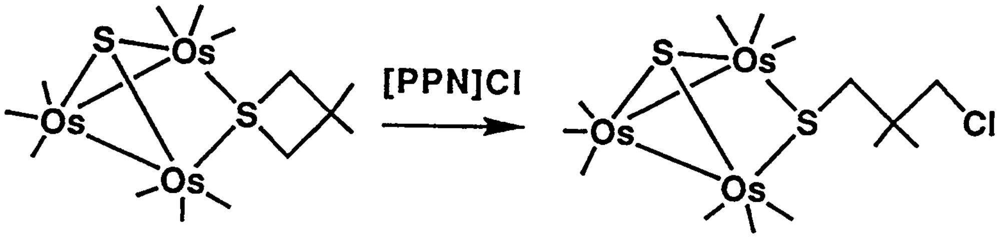
The trirhenium complex **16a** seems to be slightly more reactive than the osmium complexes, and the unsubstituted thietane complex **16b** is even more reactive than **16a**. Even very weak donors, such as NMe_3, will add to **16a** and **16b** to yield the ring opened zwitterionic complexes $Re_3(CO)_{10}(\mu\text{-}SCH_2CMe_2CH_2NMe_3)(\mu\text{-}H)_3$, **21a**, and $Re_3(CO)_{10}(\mu\text{-}SCH_2CH_2CH_2NMe_3)(\mu\text{-}H)_3$, **21b**. The zwitterions **21a-b** are positively charged at the nitrogen atoms with the negative charge delocalized about the trirhenium clusters.

The reactions of $Os_3(CO)_{10}(\mu_3\text{-}S)$ with 3,3-dimethylthietane (DMT) or thietane in the presence of Me_3NO at -42 °C yielded the complexes $Os_3(CO)_9(\mu_3\text{-}S)[\mu\text{-}\overline{SCH_2CMe_2CH_2}]$, **22** and $Os_3(CO)_9(\mu_3\text{-}S)[\mu\text{-}\overline{SCH_2CH_2CH_2}]$ **23**, respectively. These compounds both contain a thietane ligand bridging two metal atoms that are not themselves mutually bonded. Thus, the Os - S - Os angle at the bridging sulfur atom of the thietane ligand is


Me$_3$NO
+DMT
+I$^-$
-DMT
+Me$_3$NO
-CO$_2$
+thietane
or DMT
N:
+2 PMe$_2$Ph
- DMT
15
16a
17a - 20a
N = F$^-$, Cl$^-$, Br$^-$, I$^-$
or NMe$_3$

Scheme 5

much larger, 99.8(1), than the very acute and presumably strained Os - S - Os angle found in **10**, 73.1(2)°. Interestingly, compound **22** also undergoes a ring opening additions of nucleophiles. The reaction of **22** with bis(triphenylphosphine)iminium chloride ([PPN]Cl) yielded the salt [PPN][$Os_3(CO)_9(\mu\text{-}SCH_2CMe_2CH_2Cl)(\mu_3\text{-}S)$], **24** by a ring opening addition of the chloride ion to one of the methylene groups of the 3,3-DMT ligand, Scheme 6.



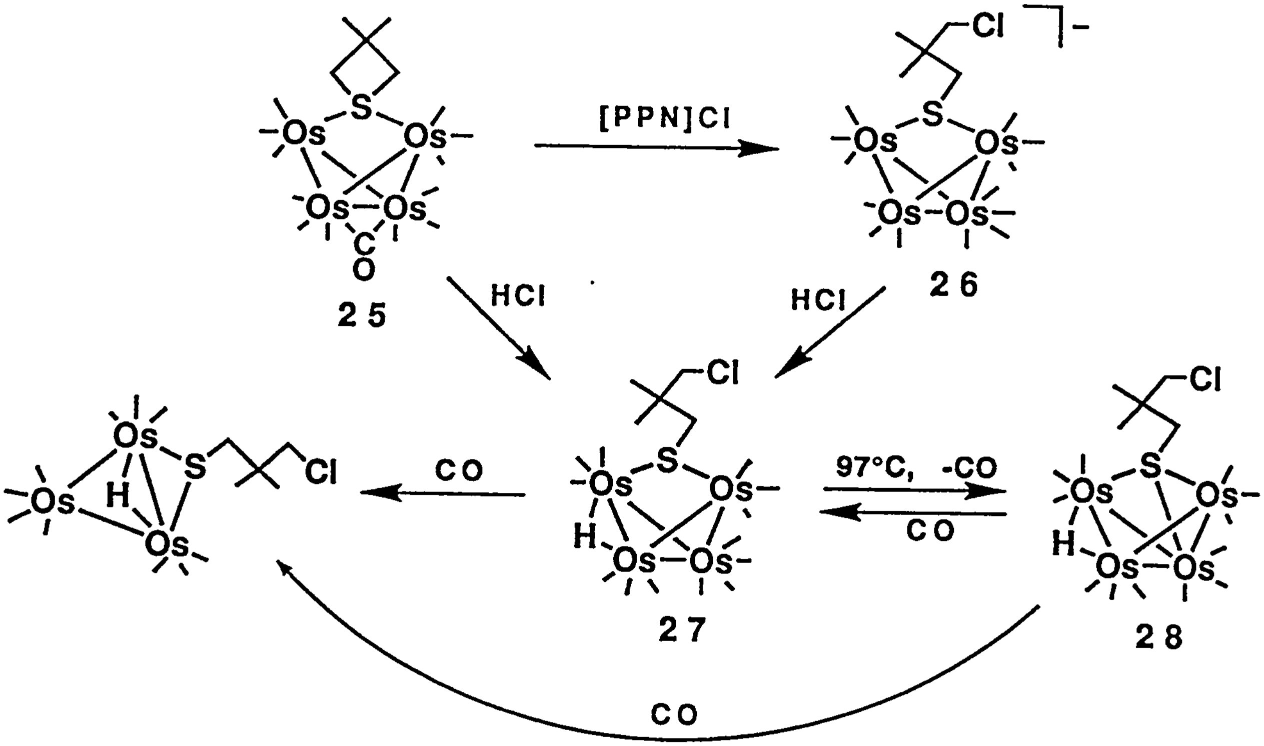
22

24

Scheme 6

However, NEt_2H did not produce a ring opening addition to **22** in two days in solution at 25°C. This contrasts with the reactions of **10** in which NEt_2H gave a good yield of the ring opened addition products. This result suggests that the thietane ligand in **10** is *slightly* more susceptible to ring opening than the one in **22.**

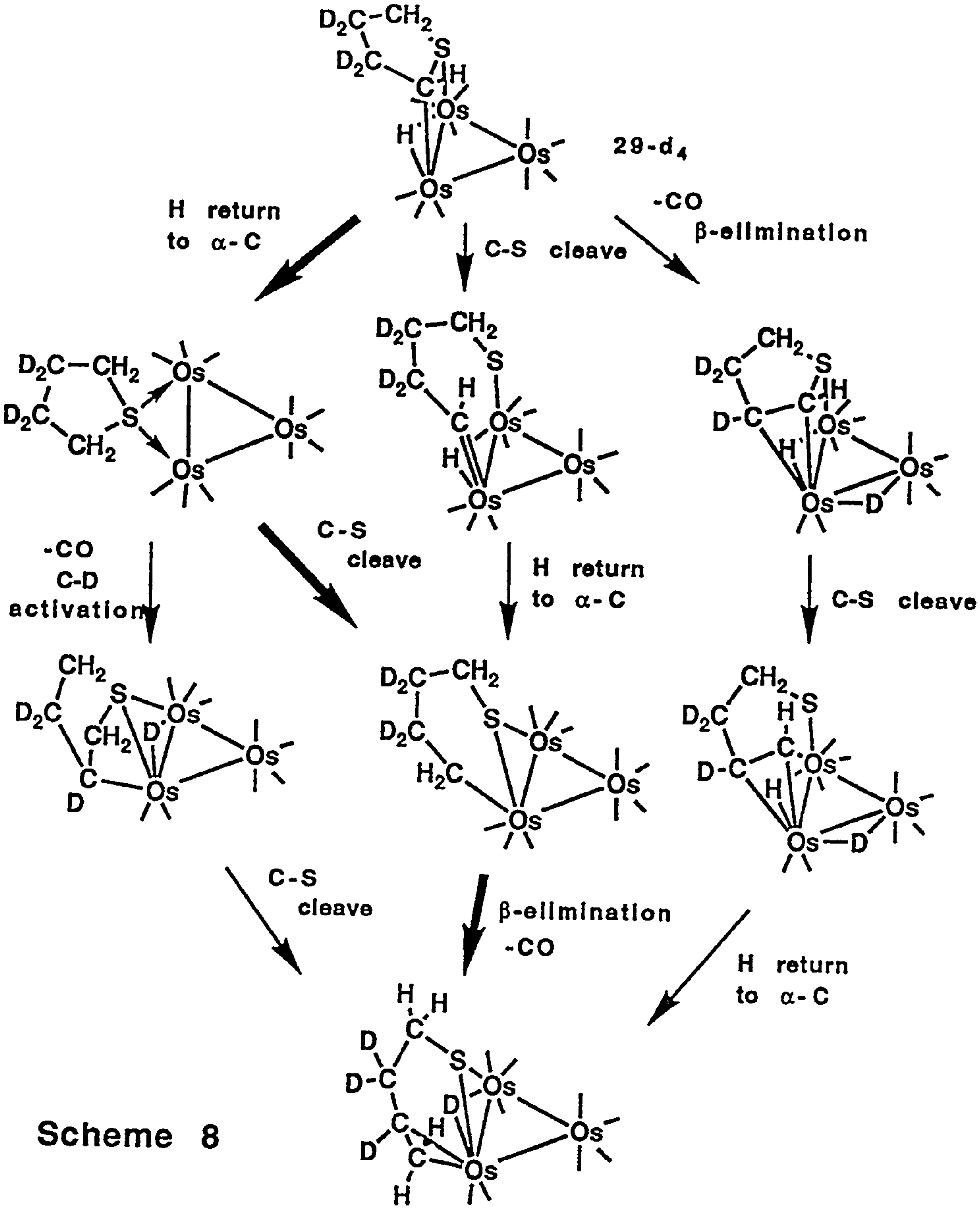
The tetraosmium complex $Os_4(CO)_{12}(\mu\text{-}CO)[\mu\text{-}\overline{SCH_2CMe_2CH_2}]$, **25** was obtained as a minor product from the pyrolysis of **10** at 125°C. This compound contains a butterfly cluster of four osmium atoms with a 3,3-DMT ligand bridging the wingtips of the cluster. Compound **25** was found to react with bis(triphenylphosphine)iminium chloride, [PPN]Cl, in a ring opening addition to one of the methylene groups of the thietane ligand to yield the salt [PPN][$Os_4(\mu\text{-}CO)(CO)_{12}(\mu\text{-}SCH_2CMe_2CH_2Cl)$ **26**, see Scheme 7.



Scheme 7

Compound **26** can be converted to the neutral complex $Os_4(CO)_{13}(\mu\text{-}SCH_2CMe_2CH_2Cl)(\mu\text{-}H)$, **27**, by protonation with HCl. At 97°C, **27** is decarbonylated to form the complex $Os_4(CO)_{12}(\mu_3\text{-}SCH_2CMe_2CH_2Cl)(\mu\text{-}H)$, **28** contains a triply bridging 4-chloro-3,3-dimethylpropanethiolato ligand serving as a five-electron donor.

To compare with the results of our studies ring opening reactions of strained ring heterocycles containing sulfur, we extended our studies to include the unstrained five- and six-memebered cyclic thioethers: tetrahydrothiophene (THT) $(\overline{SCH_2CH_2CH_2CH_2})$ and thiacyclohexane (TCH). We prepared the complex $Os_3(CO)_{10}(\overline{SCH_2CH_2CH_2CH_2})_2$, **28** by the reaction of $Os_3(CO)_{10}(NCMe)_2$ with tetrahydrothiophene (THT). Complex **28** was transformed to the complex $Os_3(CO)_{10}[\mu\text{-}\eta^2\text{-}(\overline{SCH_2CH_2CH_2CH})](\mu\text{-}H)$, **29** by loss of one THT ligand and the activation of a C-H bond on one of the methylene groups bonded to the sulfur atom. Most interestingly, we found that **29** was decarbonylated and transformed into the new compound $Os_3(CO)_9[\mu\text{-}\eta^3\text{-}S(CH_2)_2CH{=}CH_2](\mu\text{-}H)$, **30** by a ring opening cleavage of one of the C-S bonds at 125° C. Compound **30** contains a 3-butene thiolate ligand in which the sulfur atoms bridges one of the metal - metal bonds and the double bond is π-coordinated to one of the sulfur bridged metal atoms. An investigation of the transformation of $Os_3(CO)_{10}[\mu\text{-}(\overline{SCH_2CD_2CD_2C}H)](\mu\text{-}H)$, **29**-$d_4$ to $Os_3(CO)_9[\mu\text{-}\eta^3\text{-}SCH_2CD_2CD{=}CH_2](\mu\text{-}D)$, **30**-$d_4$ showed that the hydride ligand was returned to the carbon atom from which it was initially cleaved and deuterium was shifted to the metal atoms. Although several mechanisms are possible for this transformation, the one considered most likely involves the insertion of one of the metal atoms into the carbon - sulfur bond of a sulfur coordinated bridging THT molecule is shown in Scheme 8.



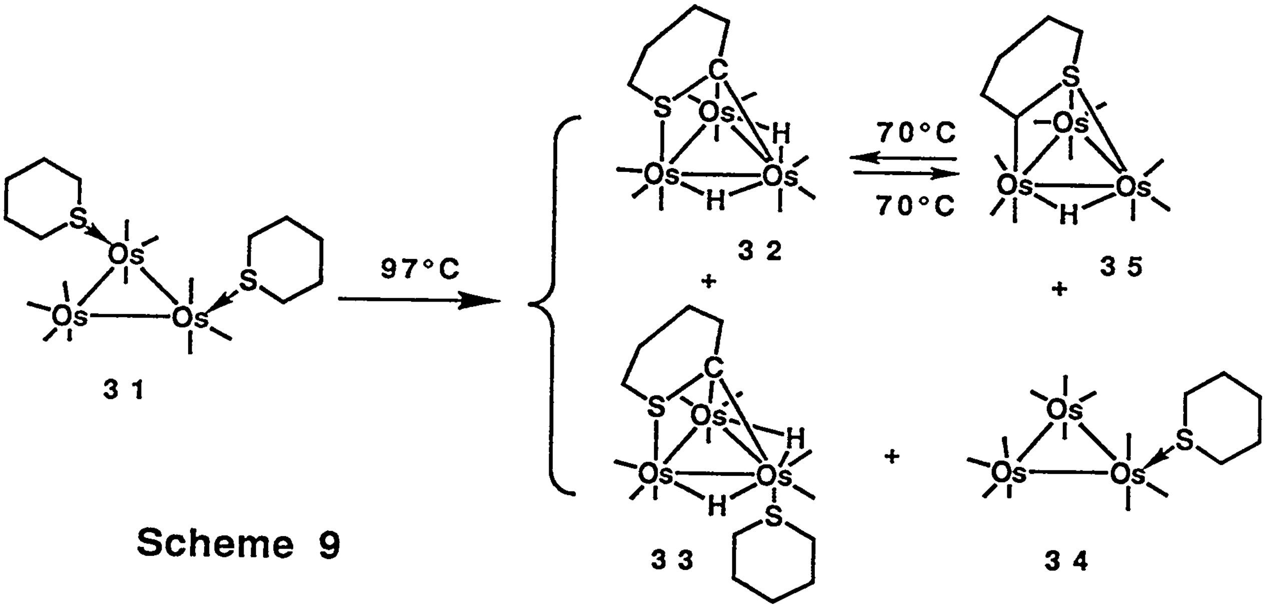
29-d$_4$

Scheme 8

30-d$_4$

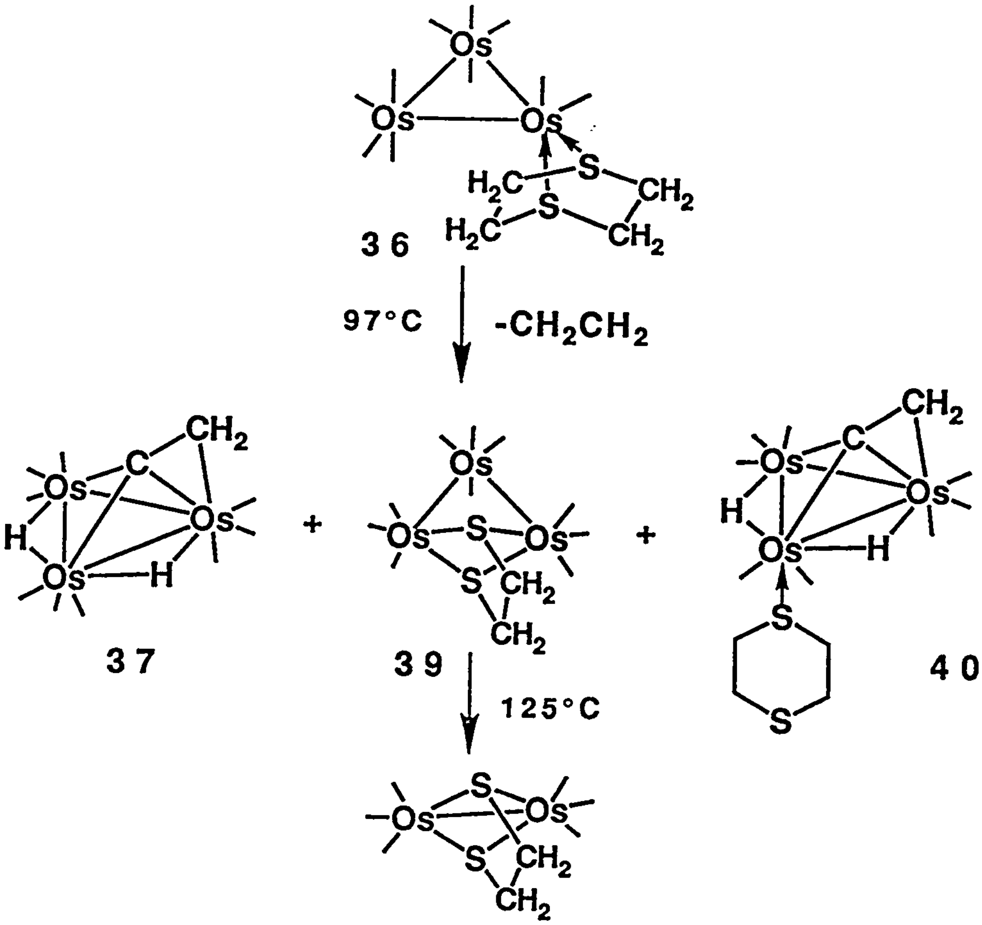
The reaction of thiacyclohexane (TCH) with $Os_3(CO)_{10}(NCMe)_2$ has yielded the disubstituted complex $Os_3(CO)_{10}(TCH)_2$, **31** which was transformed into four new compounds: $Os_3(CO)_9(\mu\text{-}\overline{SCH_2CH_2CH_2CH_2C})(\mu\text{-}H)_2$, **32**, $Os_3(CO)_8(\mu\text{-}\overline{SCH_2CH_2CH_2CH_2C})[S(CH_2)_5](\mu\text{-}H)_2$, **33**,

$Os_3(CO)_{11}(SCH_2CH_2CH_2CH_2CH_2)$, **34**, $Os_3(CO)_9(\mu\text{-}SCH_2CH_2CH_2CH_2CH)(\mu\text{-}H)$, **35** by heating to 97°C. Compounds **32**, **34** and **35** were formed by the loss of one TCH ligand. In compounds **32** and **35** the remaining TCH ligand has undergone activation of two and one of the CH bonds, respectively, α to the sulfur atom, and the TCH ligand was transformed into a metallated triply bridging ligand. Compounds **32** and **35** are interconvertible isomers. The structures and interrelationships of these compounds are shown in Scheme 9. In contrast to our previous investigations, we have found no evidence for ring opening transformations in the TCH ligand. This may be due to the lack of strain in the larger TCH molecule.



Scheme 9

In contrast our studies of the reactions of 1,4-dithiacyclohexane (1,4-DTCH) with triosmium clusters revealed a pattern of facile C - S bond cleavage reactions. The reaction of 1,4-DTCH with $Os_3(CO)_{10}(NCMe)_2$ at 25°C yielded $Os_3(CO)_{10}(SCH_2CH_2SCH_2CH_2)$, **36** that was characterized by a single crystal x-ray diffraction analysis. This molecule consists of a triangular triosmium cluster with a 1,4-DTCH ligand coordinated as a chelate to only one of the metal atoms. When compound **36** was heated to 80°C, four compounds were obtained: $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{=}CH_2)(\mu\text{-}H)_2$ **37**, $Os_2(CO)_6(\mu\text{-}SCH_2CH_2S)$, **38**, $Os_3(CO)_{10}(\mu\text{-}SCH_2CH_2S)$, **39**, $Os_3(CO)_8(\mu_3\text{-}\eta^2\text{-}C{=}CH_2)(\overline{SCH_2CH_2SCH_2C}H_2)(\mu\text{-}H)_2$, **40**. The formation of ethylene as a coproduct was observed by NMR spectroscopy when the reaction was performed in an NMR tube. The same cluster complexes were obtained from the direct reaction of 1,4-DTCH with $Os_3(CO)_{12}$ at 125°C. Compounds **38** and **39** were characterized by single crystal x-ray diffraction analysis. Both compounds contain a bridging, chelating ethanedithiolato, SCH_2CH_2S, ligand. Compound **38** can be obtained from **39** in good yield by heating to 125°C. Compound **37** has been reported previously. Compound **40** is a simple 1,4-DTCH derivative of **37**. The interrelationships among these compounds are shown in Scheme 10. The most important observation in this study is the facile elimination of ethylene from the 1,4-DTCH ligand by the cleavage of two C - S bonds. This is undoubtedly facilitated by the formation of the stable molecule ethylene, and implies that carbon - sulfur bond cleavage processes may be facile in other molecular systems containing sulfur heterocycles when the elimination of stable small molecules can occur.

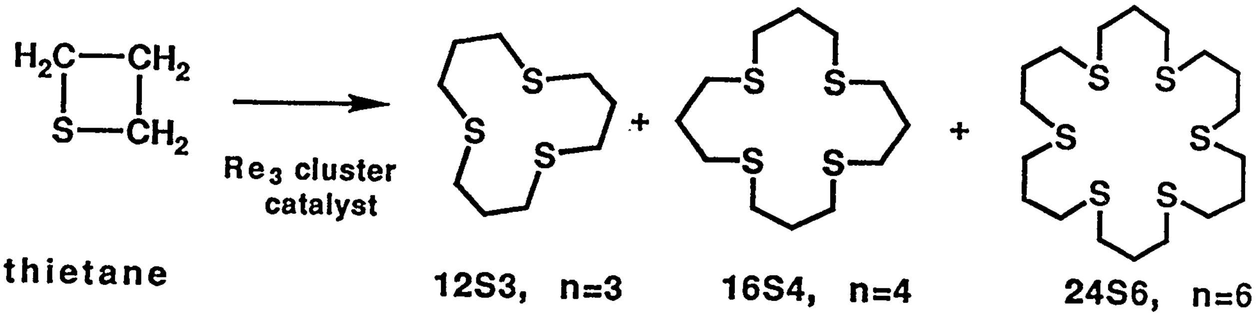


Scheme 10

3 8

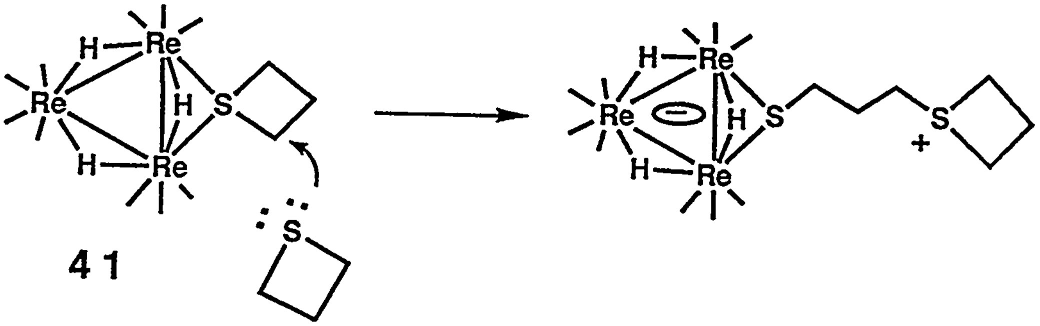
4) Cyclooligomerization of Thietanes.

In 1994 we discovered an important new catalytic process based on our previous studies of the ring opening reactions of thietanes by metal clusters, see above. This was the development of a catalytic process for the cyclooligomerization of thietanes and is the first example of a catalytic procedure for the synthesis of polythiaether macrocycles. It uses thietanes as the reagents, see Eq. (1).

1) n 

12S3 = 1,5,9-trithiacyclododecane
16S4 = 1,5,9,13-tetrathiacyclohexadecane
24S6 = 1,5,9,13,17,21-hexathiacyclotetracosane

We have found that the trirhenium cluster complex $Re_3(CO)_{10}[\mu\text{-}\overline{SCH_2CH_2CH_2}](\mu\text{-}H)_3$, **41** is an effective **catalyst** for this process, Eq. (1). 24S6 is the major product but large amounts of 12S3 are also formed. 16S4 is a minor product. Apparently, the lone pairs of electrons on the sulfur atom of thietane, itself, are also sufficiently nucleophilic to produce ring opening of a coordinated thietane, eq. (2).

2) 

However, unlike the simple nucleophilic addition, the thietane addition sets off a chain reaction of ring opening additions at the molecule of thietane that was added because that sulfur atom is positively charged and the thietane ring has not yet been opened. The ensuing reactions could result in the formation of a polymer and evidently does produce small amounts of polymer, but the dominant reactions are amounts of polymer, but the dominant reactions are instead cyclooligomerizations. That is, instead, of polymerization, the reaction spontaneously terminates itself in very early stages by internal cyclization processes which result in the formation of the macrocycles. We have even isolated and structurally characterized a phosphine derivative of one of the intermediates in the catalytic cycle that contains a positively charged 12S3 macrocycle dangling from the cluster on an $SCH_2CH_2CH_2$ tether, see figure 3.

A catalytic cycle for the formation of 12S3 is shown in scheme 11. After the first addition to form intermediate **C**, two more thietane molecules are added and opened, but the opening of the third thietane occurs at the thiaether sulfur in the chain that lies closest to the cluster. The macrocycle is formed (see cyclization step in the scheme), and chain growth is terminated. The species **E** that is formed may lie dormant for a period of time. Fortunately, however, the thietane monomer itself also appears to be sufficiently nucleophilic to cleave the macrocycle from the zwitterionic complex. That process regenerates **C** and the cycle repeats itself. Under typical conditions we have been able

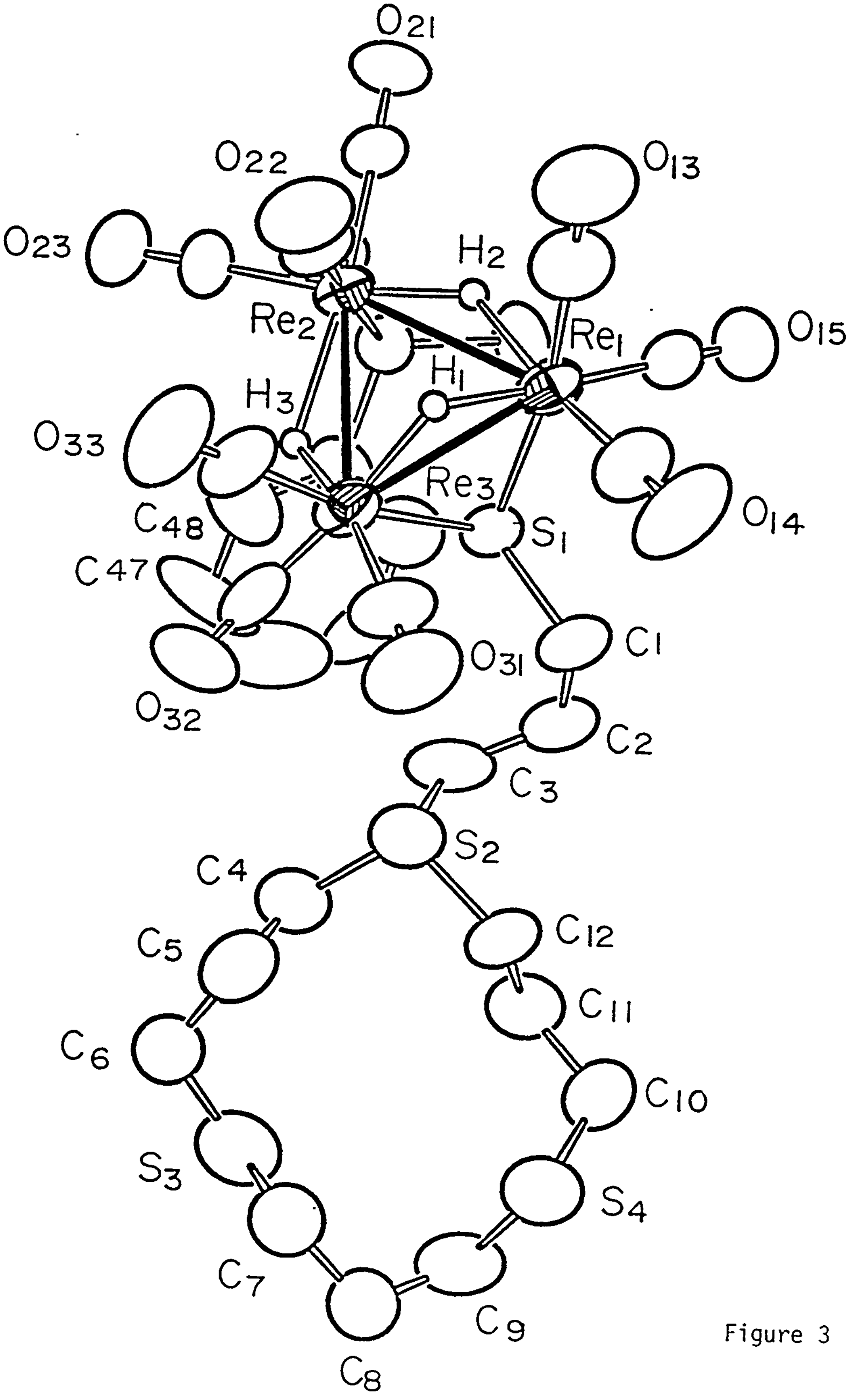
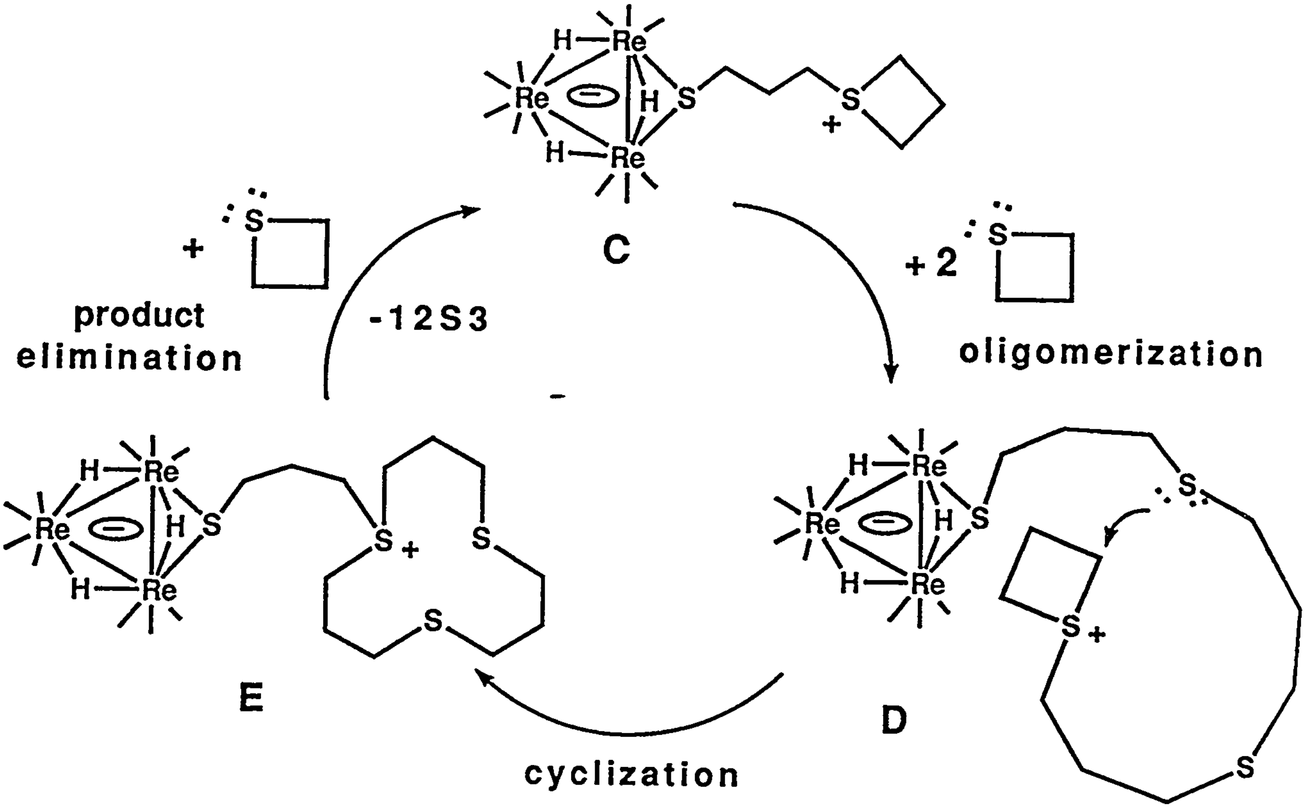

O21
O22
O13
O23
H2
Re2
Re1
O15
H1
H3
O33
Re3
C48
S1
O14
C47
C1
O31
O32
C2
C3
S2
C4
C12
C5
C11
C6
C10
S3
S4
C7
C9
C8

Figure 3

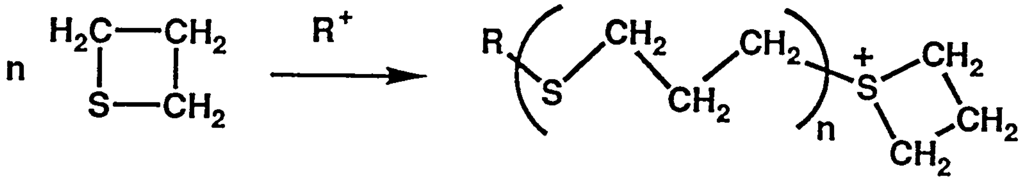


Scheme 11

to convert up to **450** equivalents of the thietane monomer into cyclooligomers in a 24 h period at 90°C. An additional quantity (less than 10% of the total) is believed to be polymer.

The reactions of thietanes with cations are well known to produce polymers by similar ring opening processes known as Cationic Ring Opening Polymerization (CROP reactions for short), see eq. (3).

3)

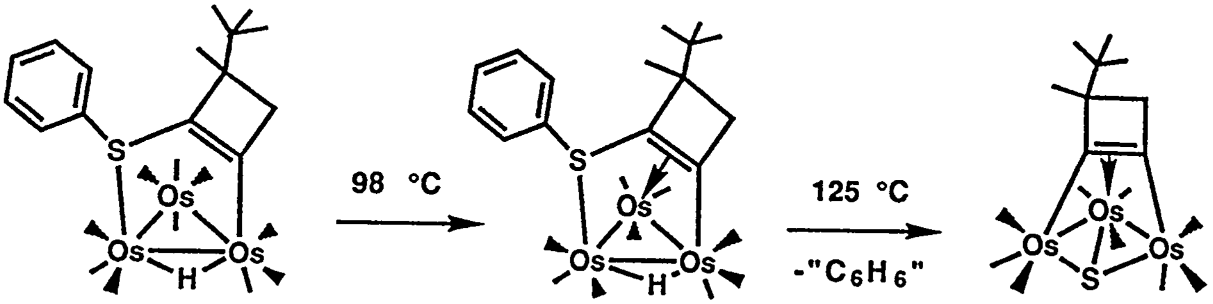


The question which arises then is "Why is our process so selective for the formation of cyclooligomers?" We think this is related to the intrinsic "zwitterionic" character of the intermediates. The chain grows at the positively charged sulfur atoms. However, the other end of the chain is terminated by the cluster which is negatively charged. As a result, the head and tail of the chain should remain proximate to one another as the chains grows, that is the polymer grows as a **"loop"** and not a linear chain, see species **D** in the scheme. When the loop attains the lengths appropriate for the formation of the more stable of the macrocyclic rings (e. g. 12S3 and 24S6), the sulfonium center reacts at the thiaether sulfur atom that lies closest to the cluster and the macrocycle is formed. In contrast, in the process of cationic ring opening polymerization one terminus of the chain is uncharged. As a result, there is a lower tendency for it to associate with the chain growth end. It tends to drift away from the chain growth site and a polymer is formed instead.

All previous procedures for the synthesis of polythiaether macrocycles were stoichiometric displacement reactions between dithiols or dithiolates with organic dihalides or displacement reactions similar to these. Polythiaether "crown" macrocycles have recently attracted considerable attention for their potential to serve as ligands for heavy metals. They have been found to be effective for the selective extraction of certain heavy metals from mixtures and have also been considered for use as ligands in complexes used in nuclear medicine. Polydentate thiaether macrocycles may also prove to be useful ligands for homogeneous transition metal catalysts.

5) Studies of the Cyclobutyne Ligand.

In order to expand upon our understanding of the transformations of strained ring heterocycles in metal cluster complexes, we decided that it would be necessary to investigate the chemistry of the corresponding carbocycles that do not contain heteroatoms. In 1992 we prepared and structurally characterized the first stabilized form of the molecule, cyclobutyne, $\overline{C{\equiv}CCH_2C}H_2$ through complexation to three osmium atoms atoms in a triosmium cluster. In 1993 we had great success in preparing new examples of these ligands and in studying the chemical and physical properties. In particular, we prepared the first dialkyl substituted cyclobutyne ligand $\overline{C_2CH_2C}(Me)^tBu$ in the complex $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}\overline{C_2CH_2C}(Me)^tBu)(\mu_3\text{-}S)$, **42**. The formation of **42** was the result of a series of reactions which began with the synthesis of $Os_3(CO)_{10}[\mu\text{-}PhS\overline{C_2CH_2C}(Me)^tBu](\mu\text{-}H)$, **43** by the reaction of 4-t-butyl-4-methyl-1-phenylthio-cyclobutene with $Os_3(CO)_{10}(NCMe)_2$. Compound **43** was decarbonylated to yield the new compound $Os_3(CO)_9[\mu_3\text{-}SPh\overline{C_2CH_2C}(Me)^tBu](\mu\text{-}H)$, **44** in which the alkenyl double bond of the metallated cyclobutenyl ligand has become coordinated to the cluster. At 125°C, compound **44** was transformed to the new complex $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}\overline{C_2CH_2C}(Me)^tBu)(\mu_3\text{-}S)$, **42** which contains a triply bridging 3,3-methyl-t-butylcyclobutyne ligand formed by cleavage from the sulfur atom from the cyclobutenyl ring in **44**. The phenyl group was also cleaved from the sulfur atom resulting in formation of a triply bridging sulfido ligand. The phenyl group and hydride ligand were eliminated, presumably as benzene. All of these products were characterized crystallographically and the structures and interrelationships of the compounds are shown in Scheme 12.

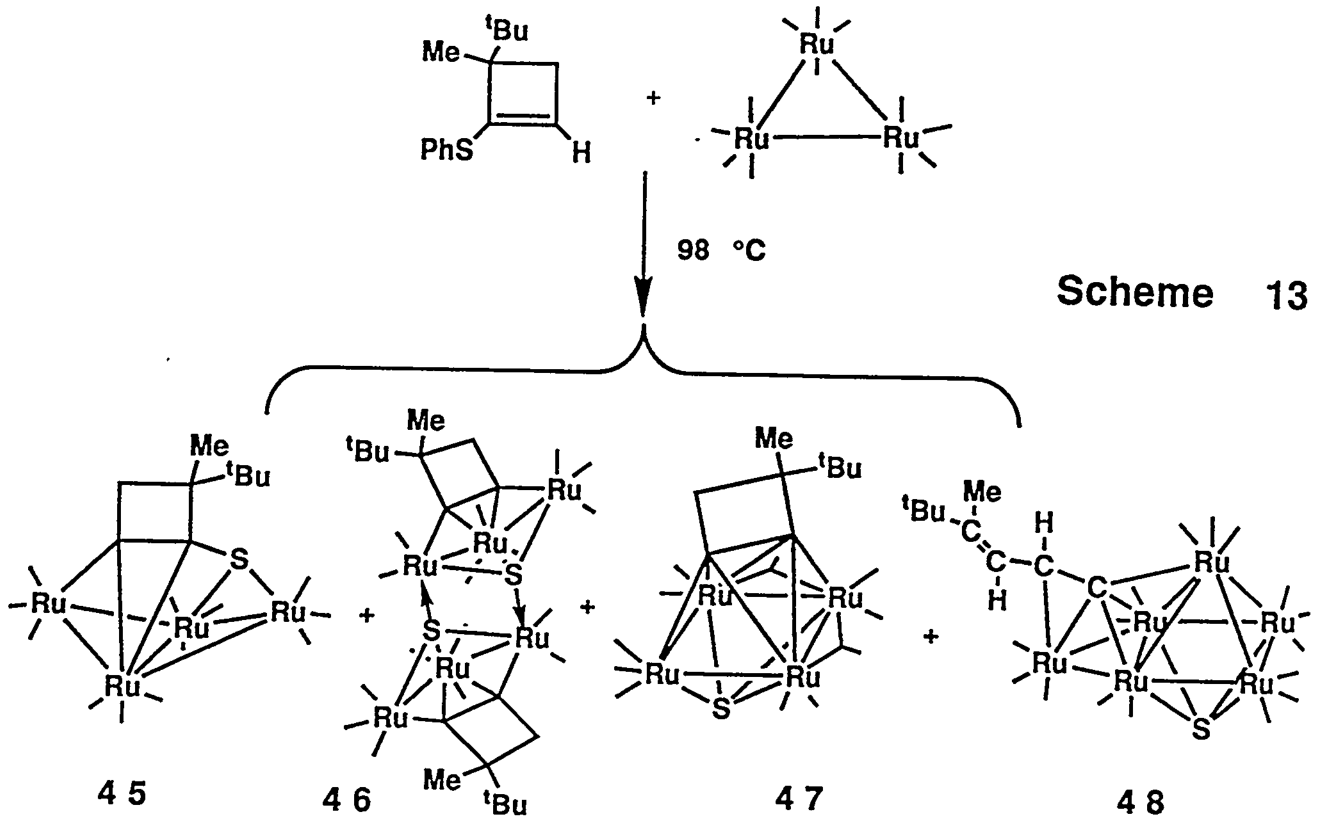


43 **44** **42**

Scheme 12

In 1994 we reported the first example of a quadruply bridging cyclobutyne ligand from the reaction $Ru_3(CO)_{12}$ with 4-t-butyl-4-methyl-1-phenylthio-cyclobutene. This reaction actually yielded four new complexes: $Ru_4(CO)_{12}[\mu_4\text{-}S\overline{C_2CH_2C}(Me)^tBu]$, **45**; $\{Ru_3(CO)_8[\mu_3\text{-}\eta^2\text{-}\overline{C_2CH_2C}(Me)^tBu](\mu_4\text{-}S)\}_2$, **46**; $Ru_4(CO)_{11}[\mu_4\text{-}\eta^2\text{-}\overline{C_2CH_2C}(Me)^tBu](\mu_4\text{-}S)$, **47**, and a trace of the hexanuclear complex $Ru_6(CO)_{16}[\mu_4\text{-}CCHCH{=}C(Me)^tBu](\mu_4\text{-}S)$, **48**. All four products were characterized by single crystal x-ray diffraction analyses. Compounds **46** and **47** contain the disubstituted cyclobutyne ligand $\overline{C_2CH_2C}(Me)^tBu$ formed by the cleavage of the hydrogen atom and the phenylthio group from the cyclobutene ring. Compound **45** contains a quadruply bridging metalated cyclobutenylthiolato group. It was transformed to compound **47** which contains the first example of a quadruply bridging cyclobutyne ligand. Compound **48** contains six ruthenium atoms arranged in the shape of an edge bridged square pyramidal cluster. A sulfido ligand bridges the square base and a $CH{=}C(Me)^tBu$ substituted vinylidene ligand bridges one triangle of the square pyramid and the edge bridging ruthenium atom. Compound **46** is a dimer that can be split by reaction with CO to yield two of the monomeric triruthenium cluster complexes $Ru_3(CO)_9[\mu_3\text{-}\eta^2\text{-}\overline{C_2CH_2C}(Me)^tBu](\mu_3\text{-}S)$.

The structures and interrelationships among these compounds are shown in Scheme 13.



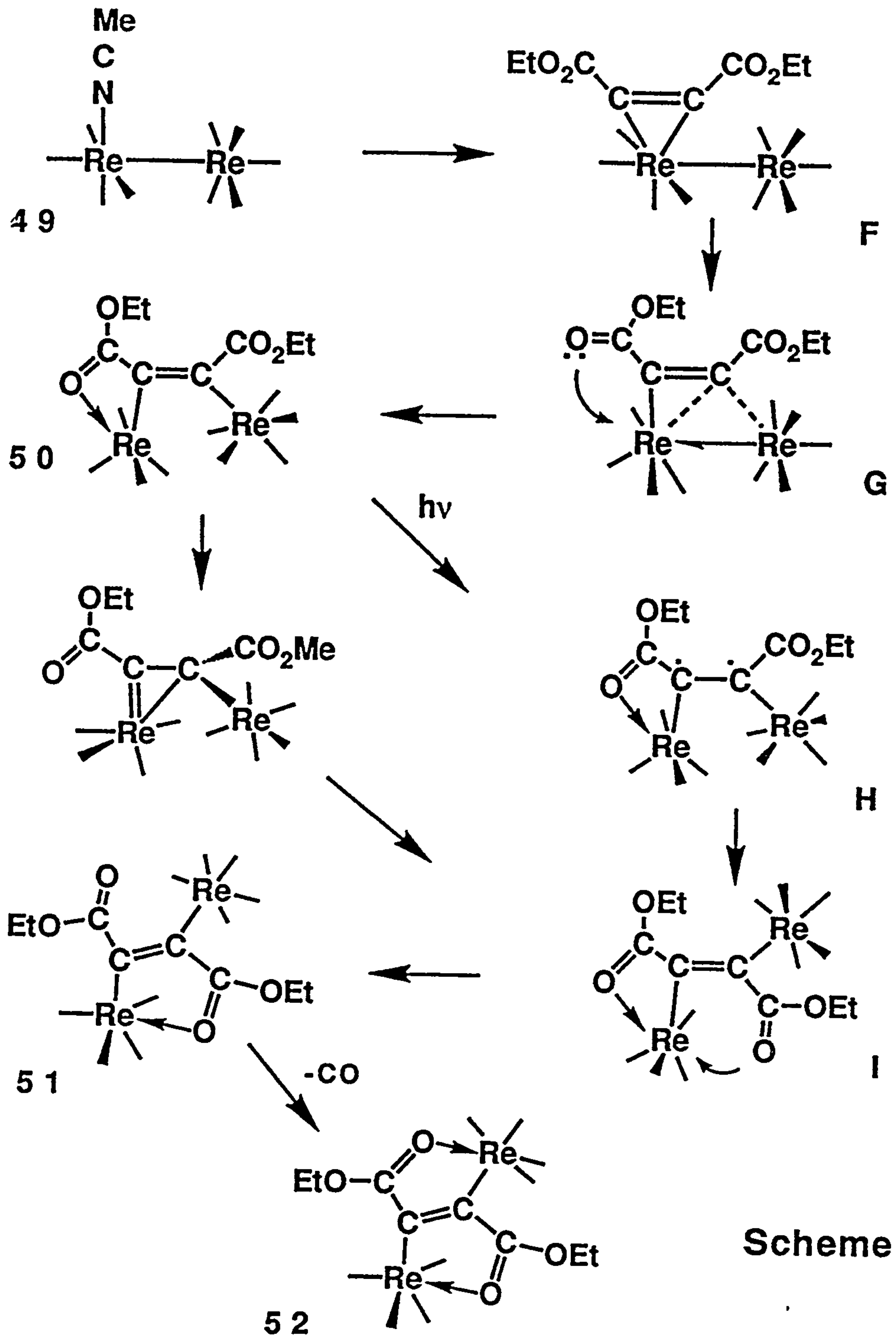
Scheme 13

6) Insertion of an Alkynes into Metal-Metal Bonds.

In section 1 of this report was described the results of some our studies of the transformations of saturated tertiary amines. Prior to these studies we had also investigated the chemistry of unsaturated tertiary amines. A summary of those results is given in the Progress Report on this project for the preceding award period, DOE report number, DOE/ER/13296-8. During this award period we continued to develop some of the important concepts that emerged from those studies. The most important these was focused on the interaction of alkyne functionality with metal - metal bonds. Our latest results are as follows:

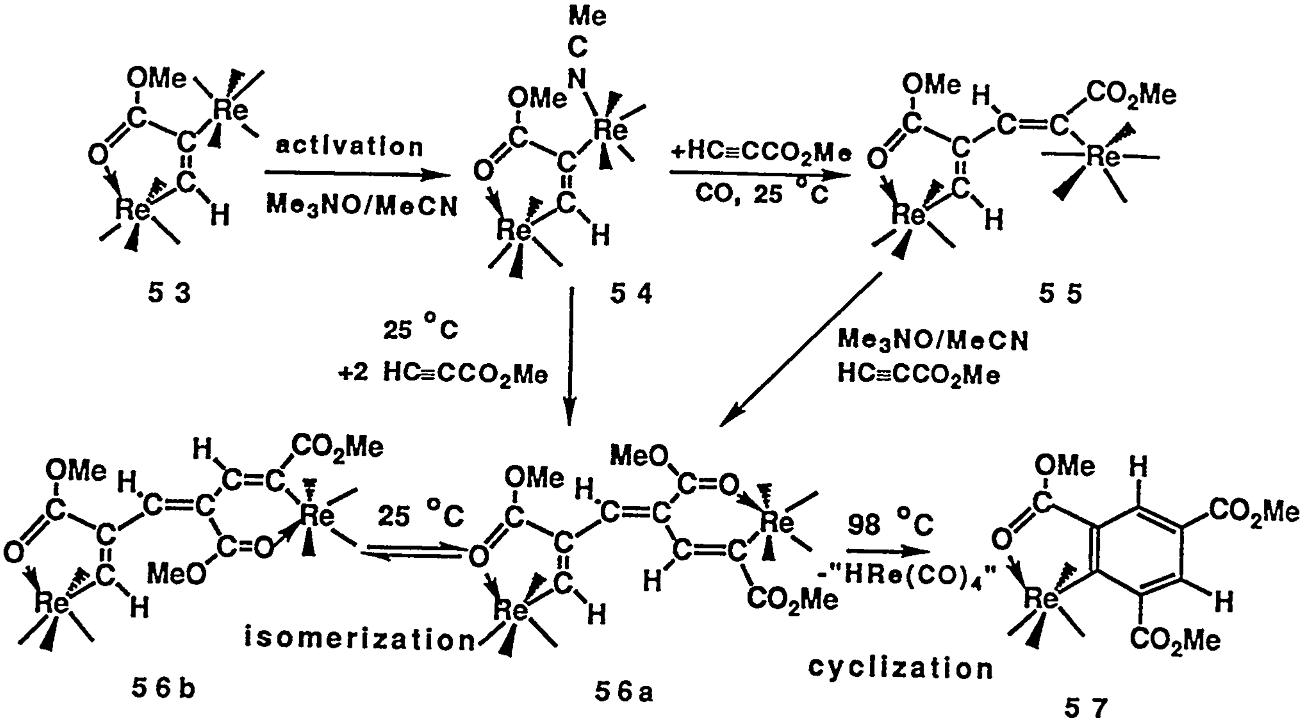
In 1992 we discovered the first example of the insertion of an alkyne into a metal-metal bond in the reaction of $HC{\equiv}CCO_2Me$ with $Re_2(CO)_9(NCMe)$, **49**. Interestingly, the dimetalated olefin product exhibited a *trans-* or *E*-stereochemistry. In 1993 we extended our investigations into the nature of these insertion reactions by investigating the reaction of the dicarboxylate acetylene, $EtO_2CC{\equiv}CCO_2Et$ with **49**. The new complex $Re(CO)_4[\mu\text{-}Z\text{-}(EtO_2C)C{=}C(CO_2Et)]Re(CO)_5$, **50** was the initial product. It was found to be a *cis-* or*Z*-dimetalated olefin complex formed by the insertion of the alkyne into the rhenium-rhenium bond. One of the carboxylate groups is coordinated to one of the rhenium atoms through the carbonyl oxygen atom to form a four membered metallacyclic ring. When irradiated, compound **50** was isomerized to the *trans* or *E*-complex $Re(CO)_4[\mu\text{-}E\text{-}(EtO_2C)C{=}C(CO_2Et)]Re(CO)_5$, **51** and the carbonyl oxygen atom of the carboxylate group became coordinated to the other rhenium atom to form a five membered metallacyclic ring. Decarbonylation of **51** by irradiation yielded the new complex $Re(CO)_4[\mu\text{-}E\text{-}(EtO_2C)C{=}C(CO_2Et)]Re(CO)_4$, **52** by coordination of the oxygen atom of the second carboxylate group. All complexes were characterized by single crystal x-ray diffraction analyses.

The mechanism that interrelates the alkyne insertion products in this study is shown in Scheme 14. In the first step the alkyne simply displaces the NCMe ligand to form an intermediate species such as **F**, which has not yet been observed, in which the alkyne is simply π-bonded to one metal atom. As the alkyne ligand begins to form a bonding interaction with the second metal atom, the metal - metal bond begins to develop a heteropolar character, species **G**. The carbonyl oxygen atom of one of the carboxylate groups is coordinated to the first metal atom to form the four membered metallacyclic ring and induce the cleavage of the metal - metal bond to yield **50**. A species similar to **50** might also be traversed in the course of the insertion of $HC{\equiv}CCO_2Me$ into the Re - Re bond of **49**, but that species can not be stablized by interaction with the CO_2Me group since the carbon containing that group must be bonded to the $Re(CO)_5$ grouping. The conversion **50** to **51** occurs photolytically. This could occur via a diradical intermediate such as **H** formed as a result of excitation of the π-electrons in the C - C double bond. Once a species with the *E*-geometry such as **I** is formed, the formation of **51** is occurs since the five membered metallacyclic ring will be much more stable than a strained four membered metallacyclic ring. The decarbonylation of **51** to **52** is a simple process of CO loss followed by the formation of a second five membered metallacyclic ring by using the second carboxylate group of the alkyne. The *cis*-insertion of alkynes into metal - metal bonds may resemble the important insertion of alkynes into metal - carbon and metal - hydrogen bonds. Further studies are in progress.



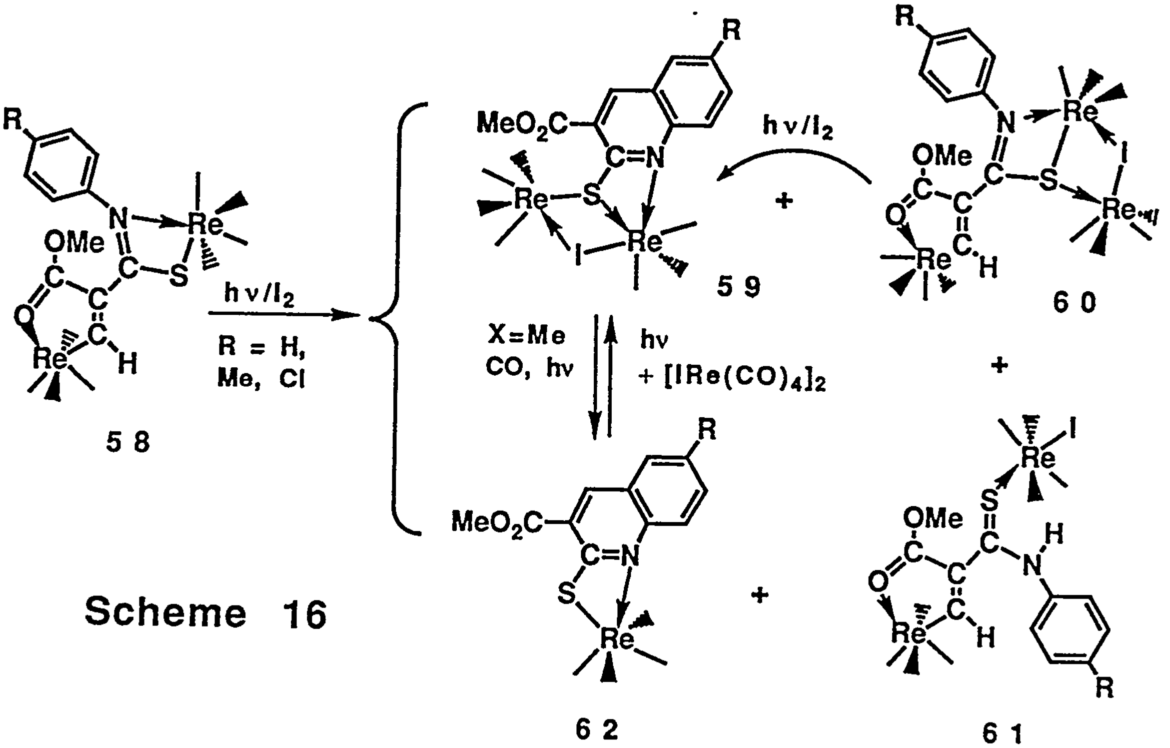
Scheme 14

We have also investigated some aspects of the organic chemistry of the complex $(OC)_4Re[\textit{trans}\text{-}\mu\text{-}HC{=}C(CO_2Me)]Re(CO)_5$, **53**, through its conversion to the reactive acetonitrile complex $(OC)_4Re[\text{trans-}\mu\text{-}HC{=}C(CO_2Me)Re(CO)_4(NCMe)$, **54**. Under an atmosphere of CO, complex **54** reacts with $HC{\equiv}CCO_2Me$ to yield the new complexes $(OC)_4Re[\mu\text{-}C(H){=}C(CO_2Me)C(H){=}C(CO_2Me)]Re(CO)_5$, **55**, and $(OC)_4Re[C(H){=}C(CO_2Me)C(H){=}C(CO_2Me)C(H){=}C(CO_2Me)]Re(CO)_4$, **56a-b** that exists in solution as a mixture of isomers formed by the head - to - tail coupling of two and three $HC{\equiv}CCO_2Me$ molecules, respectively. In complex **55** the two linked $HC{\equiv}CCO_2Me$ groups form a four carbon chain between the metal containing groups. At 98°C, **56** was transformed into **57**. One of the carboxylate substituents is also coordinated to form a five-membered metallacyclic ring. In complex **56a** the metal containing groups are joined by a six carbon chain formed from the three alkynes, and two of the carboxylate groups are coordinated to form five and six-membered metallacyclic rings. The six carbon chain in **57** was cyclized to form a 2,4,6-tri(methyloxycarbonyl)phenyl group that is σ-coordinated to the metal atom and also has one of its carboxylate groups coordinated to the metal. These results are summarized in Scheme 15.



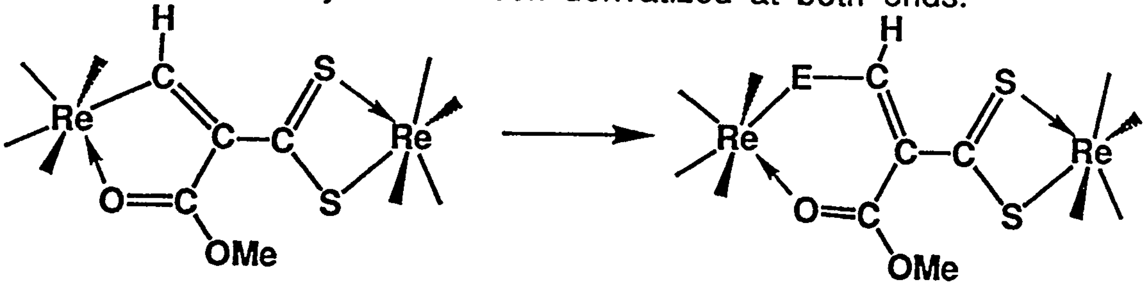
Scheme 15

Complex **54** reacts with arylisothiocyanates to yield a series of complexes having the general formula $Re(CO)_4[\textit{E}\text{-}HC{=}C(CO_2Me)CN(Ar){=}S]Re(CO)_4$, **58a**, Ar = p-tolyl; **58b**, Ar = Ph; **58c**, Ar = p-chlorophenyl formed by the loss of NCMe and the addition and insertion of one isothiocyanate molecule into one of the metal - carbon bonds to form a thioamido group that is chelated to one of the rhenium atoms. Irradiation of the complexes $Re(CO)_4[\textit{E}\text{-}HC{=}C(CO_2Me)C{=}N(C_6H_4\text{-p-}R)S]Re(CO)_4$, **58a-c** in the presence of iodine yielded a mixture of four products $Re_2(CO)_7[\mu\text{-}2\text{-}S,3\text{-}CO_2Me,6\text{-}R,NC_9H_4](\mu\text{-}I)$, **59a-c**, R = H, Me, Cl; $Re(CO)_4[\textit{E}\text{-}HC{=}C(CO_2Me)C{=}N(C_6H_4\text{-p-}R)S]Re_2(CO)_7(\mu\text{-}I)$, **60a-c**, R = H, Me, Cl; $Re(CO)_4[\textit{E}\text{-}HC{=}C(CO_2Me)C(NHC_6H_4\text{-p-}R){=}S]Re(CO)_4(I)$, **61a-c**, R = H, Me, Cl; and $Re(CO)_4(2\text{-}S,3\text{-}CO_2Me,6\text{-}R,NC_9H_4)$, **62a-c**, R = H, Me, Cl with the compounds **62** being the major products. UV irradiation of **58b** in the absence of iodine also yielded **62b**, as the major product. Compounds **59** and **62** contain substituted quinoline-2-thiolate ligands formed by a cyclization reaction involving one of the carbon atoms of the aryl ring and the hydrogen-substituted carbon atom of the alkenyl group. The structures and interrelationships of these complexes are shown in Scheme 16.



Scheme 16

We also found that compound **54** reacts CS_2 by an insertion process analogous to that of the isothiocyanates to yield the compound $(OC)_4Re[E\text{-}HC{=}C(CO_2Me)CS_2]Re(CO)_4$, **63** which is structurally analogous to **58**. In 1994 we reported a series of unusual reaction with pyridine oxide or ethylene sulfide with compound **63** in which the oxygen or sulfur atom is transferred and inserted into the remaining metal - carbon bond to yield the compounds $(OC)_4Re[EC(H)C(CO_2Me)C(S)S]Re(CO)_4$, **64**, E = O and **65**, E = S. Compound **65** was characterized crystallographically. The result of the sequence of two reactions, CS_2 plus pyridine oxide or ethylene sulfide, with **63** is that the alkyne has been derivatized at both ends.

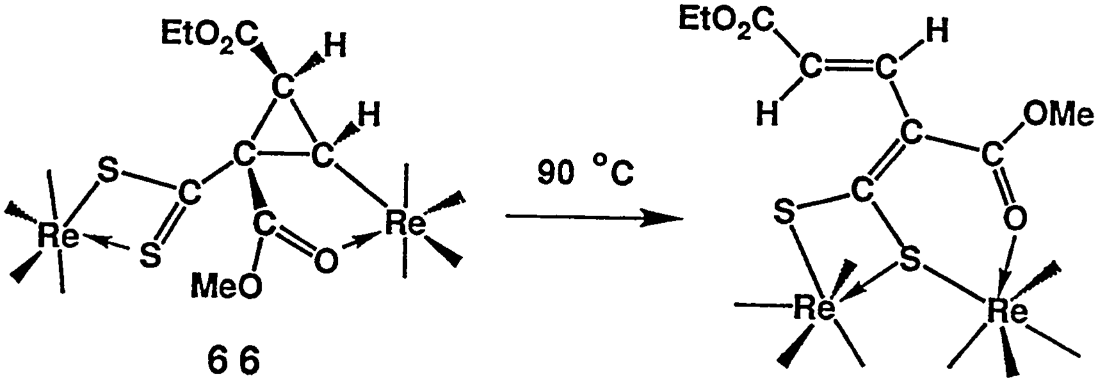


63

64, 65 E = O, S

Curiously, the compounds **58** do not engage in such a reaction with pyridine oxide or ethylene sulfide.

Ethyldiazoacetate reacts with compound **63** by transfer of a carbene grouping to the olefinic site. Two compounds: the metallated cyclopropane complex $(OC)_4Re[C_3H_2(CO_2Me)(CO_2Et)C(S)S]Re(CO)_4$, **66** and $Re_2(CO)_8[SC(S)C(CHCHCO_2Et)C(OMe)O]$, **67** were formed. The cyclopropane ring is opened when the compound **66** is heated and compound **67** is formed, Scheme 17.

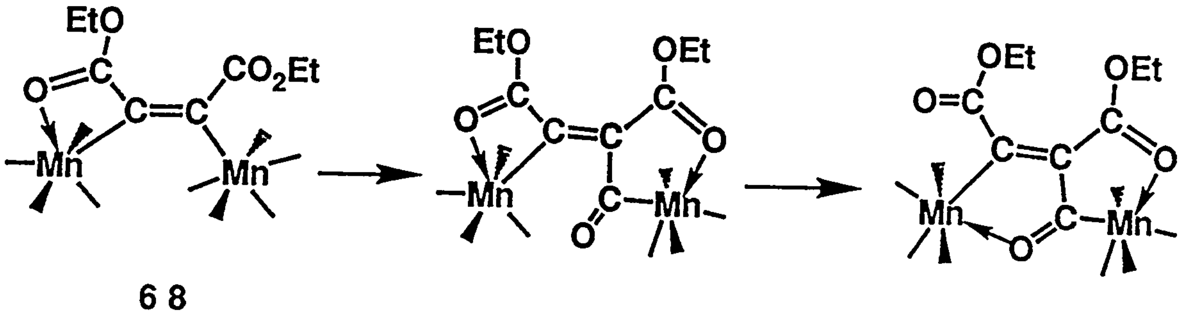


66

67

Scheme 17

In 1994 we reported on our studies of the reactions of $Mn_2(CO)_{10}$ with $EtO_2CC{\equiv}CCO_2Et$ in the presence of UV irradiation. This reaction yields the compound $Mn(CO)_4[\mu$-Z-$(EtO_2C)C{=}C(CO_2Et)]Mn(CO)_5$, **68**. Interestingly, compound **68** slowly isomerizes to the compound $Mn_2(CO)_8[\mu$-$(EtO_2C)C{=}C(CO_2Et)C{=}O]$, **69**, by an insertion of a CO ligand into the metal - carbon bond of the $Mn(CO)_5$ group, see Scheme 18.

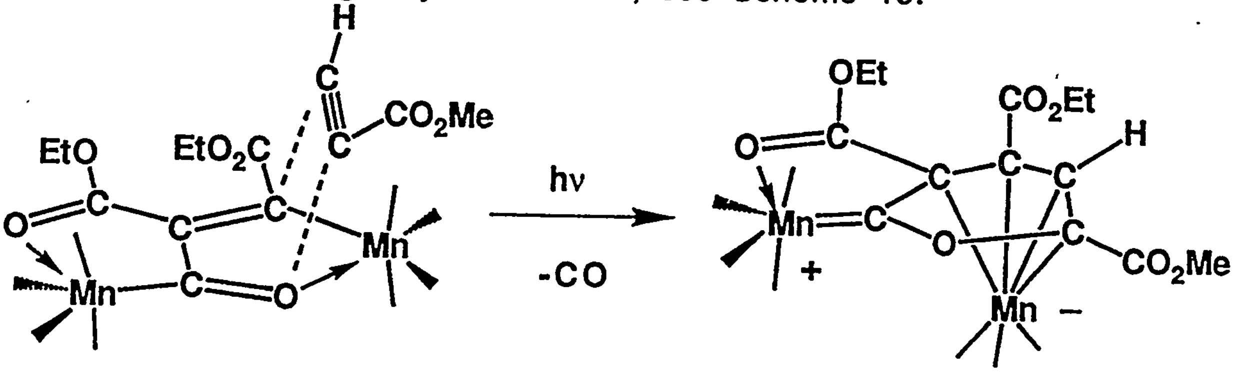


68

69

Scheme 18

The oxygen atoms of the inserted CO grouping and one of the carboxylate groupings are coordinated to the manganese atoms to form two five membered rings. The reaction of $Mn_2(CO)_9(NCMe)$ with $EtO_2CC{\equiv}CCO_2Et$ proceeds slowly to yield **69** directly, presumably via the intermediacy of **68**. CO coupling to the alkynes is an important difference between the chemistry of the rhenium and manganese dimetalated olefins. In further studies, we have found that the CO coupled alkyne ligand in the complex **69** engages in a novel coupling reaction with additional alkyne in the presence of UV-vis irradiation. The products $Mn_2(CO)_7[\mu$-η^4-$OCC(CO_2Et)C(CO_2Et)C(H)C(CO_2Me)]$, **70a**, and $Mn_2(CO)_7[\mu$-η^4-$OCC(CO_2Et)C(CO_2Et)C(CO_2Et)C(CO_2Et)]$, **70b**, and $Mn_2(CO)_7[\mu$-η^4-$OCC(CO_2Et)C(CO_2Et)CHCH]$, **70c**, were formed by that addition of the alkynes $HC{\equiv}CCO_2Me$, $EtO_2CC{\equiv}CCO_2Et$ and $HC{\equiv}CH$ to **69**. These compounds contain a six membered pyran ring that is metalated by one of the manganese atoms. The second metal atom is π-bonded to four of the carbon atoms of the pyran ring. The formation of the pyran ring is equivalent to a hetero Diels-Alder reaction between the enone grouping in 69 with the incoming alkyne molecule, see Scheme 19.

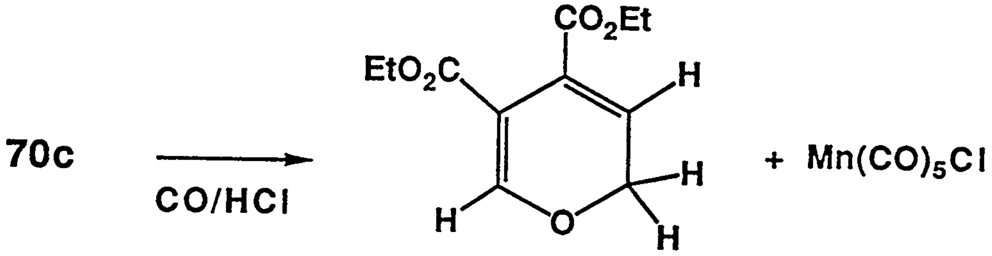


69 + **alkyne**

70a

Scheme 19

The role of the irradiation in this process has not been established, but may be required to induce the loss of CO from **69** to clear a pathway for the addition of the alkyne to the enone grouping. It is also possible that the alkyne may add to the decarbonylated metal atom prior to its coupling to the enone grouping. Treatment of the compounds **70** with a mixture of CO and HCl gases results in removal of the metal atoms and formation of the free pyran molecules which possess the α-structure as established for the pyran **71c** obtained from **70c**, Scheme 20.



71c

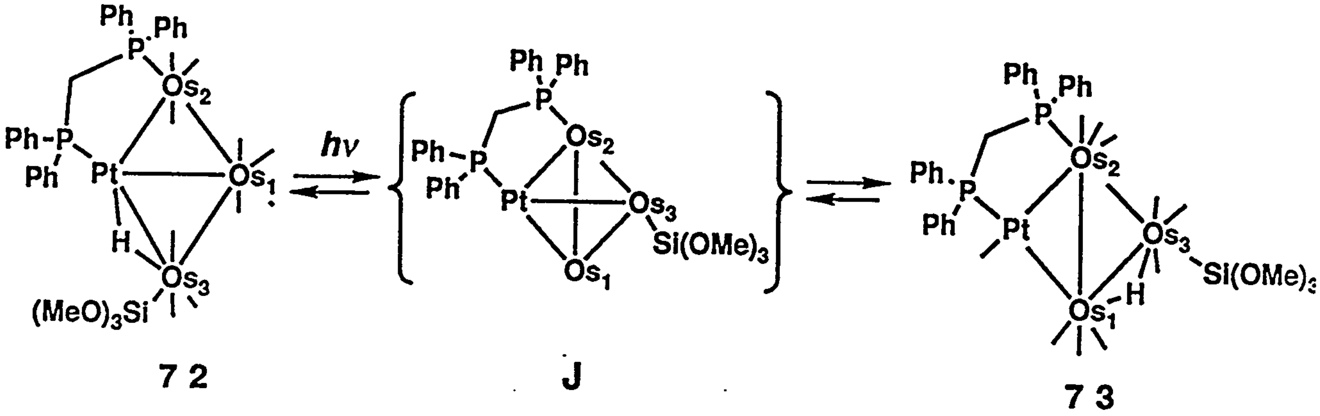
Scheme 20

The coupling of alkynes to CO generally leads to the formation of cyclopentadieneone rings. The formation of pyrans in this manganese system appears to be a novel result and may be related to the fact that the oxygen atom of the enone grouping is coordinated to one of the metal atoms which enforces the s-cis-geometry of the C - C and C - O double bonds that is required for the hetero Diels-Alder coupling. Pyran rings are important functional groupings that are found in a wide variety of natural products.

7) Energy Storage by Metal Clusters.

In 1993 we discovered a new energy capture and storage process that involves a photo transformation of a metal cluster complex. UV-vis irradiation of the cluster complex $PtOs_3(CO)_{10}(\mu\text{-}\eta^2\text{-dppm})[Si(OMe)_3](\mu\text{-}H)$, **72**, dppm = bis(diphenylphosphino)methane, produced a metastable energy-rich complex that released its energy over a period of hours by returning to the ground state. Since the process is reversible, it could be repeated by reirradiation. Both the original metal complex and its metastable isomer were stable enough to be fully characterized by single crystal x-ray diffraction analyses. Complex **72** was found to consist of a planar butterfly cluster of four metal atoms with the platinum atom located in one of the "hinge" sites. Its isomer **73** was formed by irradiation for 6 h. Compound **73** only slowly converts back to **72** thermally, $\Delta H^* = 24.3$ kcal/mol, $\Delta S^* = 6.0$ eu. Its half-life is 4.6 h at 47°C. The structure of **73** also consists of a planar $PtOs_3$ butterfly cluster of four metal atoms, but in contrast to **72** the platinum atom lies in a wingtip site of the cluster.

The transformation of **72** to **73** occurred by a rearrangement of the metal - metal bonding. This is believed to have occurred by a transition through a tetrahedral-like intermediate **J** by the formation of a bond between the wingtip metal atoms Os(2) and Os(3) in **72**, see Scheme 21. In **J** all of the metal atoms would obey the 18 electron rule. Although the transformation produces almost no side products, the quantum yield for the transformation of **72** to **73** measured at 345 nm is unfortunately very low, 0.003.



Scheme 21

The most important feature of this study is that it demonstrates for the first time that a metal cluster complex can capture and store energy by undergoing a transformation to a metastable species. Materials that can efficiently capture photon energy and then release it thermally after a significant time delay could, in principle, be of value in energy conversion and solar energy storage processes.

8) Publications for the period 1992-94.

1. R. D. Adams and J. T. Tanner, The Activation of Tertiary Amines by Osmium Cluster Complexes. Further Studies of the Reaction of $Os_3(CO)_{10}(NCMe)_2$ with Triethylamine, *Appl. Organomet. Chem.*, **6**, 449 (1992).

2. R. D. Adams and G. Chen, Clusters Containing Carbene Ligands. 14. Further Studies of the Reactivity of the Carbene Centers in the Dicarbene Cluster Complex $Os_3(CO)_9[\mu_3\text{-}C(Et)N(Me)CH](\mu\text{-}H)_2$ with Diphenylacetylene, *Organometallics*, **11**, 837 (1992).

3. R. D. Adams, G. Chen and Y. Chi, Clusters Containing Ynamine Ligands. 5. The Coordination and Transformations of an Ynamine Ligand in a Dimanganese Complex. The Synthesis and Structural Characterizations of $Mn_2CO)_8[\mu\text{-}MeC_2NEt_2]$, $Mn_2(CO)_8[\mu\text{-}H_4CCC(H)NEt_2]$, $Mn_2(CO)_8[\mu\text{-}\eta^2\text{-}C_3H_3NEt_2]$ and $Mn_2(CO)_7[\mu\text{-}\eta^2\text{-}C_3H_3NEt_2]$, *Organometallics*, **11**, 1473 (1992).

4. R. D. Adams, G. Chen, Y. Chi, W. Wu, and J. Yin, Clusters Containing Ynamine Ligands. 6. Transformations of an Ynamine Ligand in a Dirhenium Complex. The Synthesis and Structural Characterizations of $Re_2(CO)_8[\mu\text{-}H_2CCHCNMe_2]$, $Re(CO)_7[\mu\text{-}H_2CCCNMe_2](\mu\text{-}H)$ and $Re_2(CO)_8[\mu\text{-}H_2C{=}CCNMe_2](\mu\text{-}H)$, *Organometallics*, **11**, 1480 (1992).

5. R. D. Adams and M. P. Pompeo, Promotion of Ring-Opening Nucleophilic Addition to Thietane Ligands by the Bridging Coordination of the Sulfur Atom in the Complexes $Os_3(CO)_{10}[\mu\text{-}SCH_2CMe_2CH_2]$ and $Os_3(CO)_{10}[\mu\text{-}trans\text{-}SC(H)MeCH_2C(H)Me]$, *Organmetallics*, **11**, 1460 (1992).

6. R. D. Adams and G. Chen, Ring Opening of a Nitrogen Containing Strained Ring Heterocycle in an Osmium Cluster Complex, *Organometallics.*, **11**, 3510 (1992).

7. R. D. Adams, J. A. Belinski and M. P. Pompeo, The Transformations of 3,3-Dimethylthietane in Triosmium Cluster Complexes, *Organometallics*, **11**, 2016 (1992).

8. R. D. Adams and M. P. Pompeo, The Thermal and Photo-assisted Ring Opening of Thietane in a Triosmium Cluster Complex, *Organometallics*, **11**, 2281 (1992).

9. R. D. Adams and J. A. Belinski, The Nucleophilic Ring Opening of Bridging Thietanes in Open Triosmium Cluster Complexes, *Organometallics*, **11**, 2488 (1992).

10. R. D. Adams, J. A. Belinski and M. P. Pompeo, The Nucleophilic Ring Opening of a Bridging Thietane Ligand in an Open Tetraosmium Carbonyl Cluster Complex, *Organometallics*, **11**, 3129 (1992).

11. R. D. Adams, G. Chen, L. Chen, and M. P. Pompeo, Reversible Formation of an Intramolecular Agostic CH Interaction in a Dimanganese Complex, *J. Cluster Sci.*, **11**, 103 (1992).

12. R D. Adams and J A. Belinski, The Ring Opening and Carbonylation of 3,3-Dimethylthietane Ligands in Ruthenium Carbonyl Cluster Complexes, *Organometallics*, **11**, 3422 (1992).

13. R. D. Adams, L. Chen and W. Wu, Insertion of an Alkynes into a Re-Re Bond. Evidence for an Intramolecular Insertion with a*Trans*-Stereochemistry, *Organometallics*, **11**, 3505 (1992).

14. R. D. Adams, J. E. Cortopassi, and S. B. Falloon, The Nucleophilic Ring Opening of Bridging Thietane Ligands in Trirhenium Carbonyl Cluster Complexes, *Organometallics*, **11**, 3794 (1992).

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