AIIM

Association for Information and Image Management

1100 Wayne Avenue, Suite 1100
Silver Spring, Maryland 20910
301/587-8202

Centimeter

Inches

MANUFACTURED TO AIIM STANDARDS
BY APPLIED IMAGE, INC.

1 of 1

The Transformation of Organic Amines by Transition Metal Cluster Compounds

Progress Report
1992-1993

Dr. Richard D. Adams
Professor of Chemistry

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF SOUTH CAROLINA
COLUMBIA, SC 29208

January 1993

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

PREPARED FOR THE U.S. DEPARTMENT OF ENERGY
UNDER GRANT DE-FG09-84ER13296

MASTER *de*
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

**The Transformation of Organic Amines by
Transition Metal Cluster Compounds**

**Progress Report
1992-1993**

**Dr. Richard D. Adams
Professor of Chemistry**

**DEPARTMENT OF CHEMISTRY
UNIVERSITY OF SOUTH CAROLINA
COLUMBIA, SC 29208**

January 1993

**PREPARED FOR THE U.S. DEPARTMENT OF ENERGY
UNDER GRANT DE-FG09-84ER13296**

--Contents of Progress Report--

- 1) The Activation of Tertiary Amines by Osmium Cluster Complexes.
- 2) Nucleophilic Ring Opening of Thietane Ligand in Metal Carbonyl Cluster Complexes.
- 3) Ring Opening of a Nitrogen Containing Strained Ring Heterocycle by an Osmium Cluster Complex.
- 4) Insertion of an Alkynes into a Metal-Metal Bond. Evidence for an Intramolecular Insertion with a *Trans*-Stereochemistry.
- 5) Cyclobutyne - The Ligand.

1) The Activation of Triethylamine by Triosmium Cluster Complexes.

In 1992, we completed our reinvestigation of the reactions of $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ with NEt_3 . Two new products $\text{Os}_3(\text{CO})_{10}(\mu\text{-CH}_2\text{C(H)=NEt}_2)(\mu\text{-H})$, **2** and $\text{Os}_3(\text{CO})_{10}(\text{syn-}\mu\text{-}\eta^1\text{-CHCHNEt}_2)(\mu\text{-H})$, **3** were obtained in low yields, 4% and 7%, in addition to the previously reported compound $\text{Os}_3(\text{CO})_{10}(\text{anti-}\mu\text{-}\eta^1\text{-CHCHNEt}_2)(\mu\text{-H})$, **1**, 20% when the reaction was conducted at 25°C using $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$. Compounds **2** and **3** were 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 $\text{Os}_3(\text{CO})_9(\mu_3\text{-CC(H)=NEt}_2)(\mu\text{-H})_2$, **4** (58% yield) by an additional CH activation to form a triply bridging η^1 -diethylaminovinylidene ligand. Compound **4** isomerizes to the compound $\text{Os}_3(\text{CO})_9(\mu_3\text{-HCCNEt}_2)(\mu\text{-H})_2$, **5** (70% yield) 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 are shown in Scheme 1.

Scheme 1

2) Nucleophilic Ring Opening of Thietane Ligand In Metal Carbonyl Cluster Complexes.

In recent studies we have been investigating the reactivity of thietane ligands **A** in metal carbonyl cluster complexes. We have synthesized a number of new complexes in which the thietane ligands bridge two metal atoms through the coordination of the two lone pairs of electrons on the sulfur atom, **B**.

In most cases it has been found that the complexes are more stable when alkyl groups are substituted for the hydrogen atoms at the methylene group in the 3-position of the thietane ring (i. e. opposite to the sulfur atom). We have found that bridging thietane ligands in cluster complexes with metal atoms from the third transition series are susceptible to 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 $\text{Os}_3(\text{CO})_{10}[\mu\text{-SCH}_2\text{CMe}_2\text{CH}_2]$, **6** was obtained from the reaction of 3,3-dimethylthietane (3,3-DMT) with $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$. The complex was characterized crystallographically and was found that the 3,3-DMT ligand bridged two of the metal atoms through the sulfur atom. The thietane ring is puckered, the dihedral angle is 20.6° , but this is less than that observed for terminally coordinated 3,3-DMT ligands (e.g. $\text{Os}_3(\text{CO})_{11}(\text{SCH}_2\text{CMe}_2\text{CH}_2)$, 28.0°).

The reaction of **6** with the nucleophiles F^- , Cl^- , Br^- , I^- , EtO^- at 25° yielded after protonation the series of new complexes $\text{Os}_3(\text{CO})_{10}[\mu\text{-SCH}_2\text{CMe}_2\text{CH}_2\text{X}](\mu\text{-H})$, $\text{X} = \text{F}; \text{Cl}; \text{Br}; \text{I}; \text{or EtO}$, Scheme 2. The yields increased in the order $\text{F}^- < \text{Cl}^- < \text{Br}^- < \text{I}^-$.

Scheme 2

The reaction of **6** with the nucleophilic secondary amines Et_2NH , and $(\text{CH}_2)_3\text{NH}$ yielded the related complexes $\text{Os}_3(\text{CO})_{10}[\mu\text{-SCH}_2\text{CMe}_2\text{CH}_2\text{X}](\mu\text{-H})$, $\text{X} = \text{NEt}_2$, **7**; $\text{N}(\text{CH}_2)_3$, **8** without a protonation step since the hydrogen atom on the nitrogen atom was shifted to the cluster.

The complex $\text{Os}_3(\text{CO})_{10}[\mu\text{-SCH}_2\text{CMe}_2\text{CH}_2\text{Cl}](\mu\text{-H})$ was characterized crystallographically and was found to contain a bridging chloroneopentylthiolato ligand formed by the ring opening addition of chloride to one of the methylene groups of the thietane ligand, Figure 1. To ascertain information about the mechanism of the addition step, the complex $\text{Os}_3(\text{CO})_{10}[\mu\text{-trans-SC}(\text{H})\text{MeCH}_2\text{C}(\text{H})\text{Me}]$, **9** (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 $\text{Os}_3(\text{CO})_{10}[\mu\text{-SC}(\text{H})\text{MeCH}_2\text{C}(\text{H})\text{Me}(\text{I})](\mu\text{-H})$, **10** by the addition of I^- , Scheme 3.

Figure 1

Scheme 3

Compound **10** 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 attack mechanism.

The reaction of chloride with the complex $\text{Os}_3(\text{CO})_{11}[\text{SCH}_2\text{CMe}_2\text{CH}_2]$, **11** in which the sulfur atom of the thietane ligand is coordinated to only one metal atom yielded only the known anion $[\text{Os}_3(\text{CO})_{11}\text{Cl}]^-$ by ligand substitution. The absence of a ring opening addition reaction with **11** suggests that a bridging coordination is necessary to activate the thietane molecule sufficiently to permit the ring opening reaction to occur. This observation has led us to propose the following activation process for this reaction, Scheme 4.

Scheme 4

The coordination of both lone pairs of electrons on the sulfur atom leads the formation of a partial positive charge $\delta++$ on the sulfur atom. This in turn produces a partial but smaller positive charge $\delta+$ on the neighboring carbon atoms **C**. This mechanism should also be operative for terminally coordinated thietane ligands **D** but since the sulfur atom is coordinated to only one metal atom the activation is evidently insufficient to allow the nucleophilic ring opening reaction to occur.

We have found that the thietane ring of **6** can be opened photolytically to yield the complex $\text{Os}_3(\text{CO})_{10}(\mu\text{-SCH}_2\text{CMe}_2\text{CH}_2)$, **12** that contains a thiametallacycle. This complex will add chloride ion when treated with $[\text{Et}_4\text{N}]\text{Cl}$, but the chloride ion is added to the metal atoms instead of the carbon atom to yield the salt $[\text{Et}_4\text{N}][\text{Os}_3(\text{CO})_{10}(\mu\text{-SCH}_2\text{CMe}_2\text{CH}_2)(\mu\text{-Cl})]$, **13** containing the complex cluster anion $[\text{Os}_3(\text{CO})_{10}(\mu\text{-SCH}_2\text{CMe}_2\text{CH}_2)(\mu\text{-Cl})]$ in which the chloride ligand bridges two of the metal atoms, Scheme 5.

Scheme 5

The absence of an addition to a carbon atom provides still further evidence that such additions occur only upon the unopened thietane ligand. It suggests that release of ring strain in the four membered ring may also play an important role in the addition of the nucleophiles to the carbon atoms.

The reactions of 3,3-DMT and thietane, $\text{SCH}_2\text{CH}_2\text{CH}_2$, with $\text{Re}_3(\text{CO})_{10}(\text{NCMe})_2(\mu_3\text{-H})_3$, **14** have yielded the new complexes $\text{Re}_3(\text{CO})_{10}[\mu\text{-SCH}_2\text{CMe}_2\text{CH}_2](\mu_3\text{-H})_3$, **15a** and $\text{Re}_3(\text{CO})_{10}[\mu\text{-SCH}_2\text{CH}_2\text{CH}_2](\mu_3\text{-H})_3$, **15b**, respectively. Compound **15a** was characterized crystallographically and was found to consist of a trirhenium cluster with three bridging hydride ligands and a bridging thietane ligand coordinated through its sulfur atom in a manner analogous to that of **6**. The 3,3-DMT ligand is significantly less puckered than that in **1**, 12.4° . Compounds **15a** and **15b** also react readily with halide ions by ring opening additions to yield the complex anions $[\text{Re}_3(\text{CO})_{10}(\mu\text{-SCH}_2\text{CMe}_2\text{CH}_2\text{X})(\mu\text{-H})_3]^-$, **16a** - **19a**, $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$, and $[\text{Re}_3(\text{CO})_{10}(\mu\text{-SCH}_2\text{CH}_2\text{CH}_2\text{Cl})(\mu\text{-H})_3]^-$, **17b**, see Scheme 6. It was not possible to neutralize these anions by protonation and with acetic acid.

Scheme 6

The trirhenium complex **15a** seems to be slightly more reactive than the osmium complex **1**, and the unsubstituted thietane complex **15b** is even more reactive than **15a**. Even the very weak donor NMe_3 will add to **15a** and **15b** to yield the ring opened zwitterionic complexes $\text{Re}_3(\text{CO})_{10}(\mu\text{-SCH}_2\text{CMe}_2\text{CH}_2\text{NMe}_3)(\mu\text{-H})_3$, **20a**, and $\text{Re}_3(\text{CO})_{10}(\mu\text{-SCH}_2\text{CH}_2\text{CH}_2\text{NMe}_3)(\mu\text{-H})_3$, **20b**, Figure 2. The zwitterions **20a-b** are positively charged at the nitrogen atoms. The negative charge is delocalized about the trirhenium centers.

The reactions of $\text{Os}_3(\text{CO})_{10}(\mu_3\text{-S})$ with 3,3-dimethylthietane (DMT) or thietane in the presence of Me_3NO at -42°C yielded the complexes $\text{Os}_3(\text{CO})_9(\mu_3\text{-S})[\mu\text{-}\overline{\text{SCH}_2\text{CMe}_2\text{CH}_2}]$, **21** and $\text{Os}_3(\text{CO})_9(\mu_3\text{-S})[\mu\text{-}\overline{\text{SCH}_2\text{CH}_2\text{CH}_2}]$, **22**, respectively. The most interesting feature about these compounds is that they 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 much larger, $99.8(1)^\circ$, than the very acute and presumably strained Os - S - Os angle found in **6**, $73.1(2)^\circ$. It was of interest to see if compound **21** would also nucleophiles to undergo a ring opening addition. The reaction of **21** with bis(triphenylphosphine)iminium chloride ([PPN]Cl) at 25°C did yield the salt $[\text{PPN}][\text{Os}_3(\text{CO})_9(\mu\text{-SCH}_2\text{CMe}_2\text{CH}_2\text{Cl})(\mu_3\text{-S})]$, **23** by a ring opening addition of the chloride ion to one of the methylene groups of the 3,3-DMT ligand, Scheme 7.

Figure 2

Scheme 7

In **23** a 4-chloro-3,3-dimethylpropanethiolato ligand bridges an open edge of the anionic triosmium cluster complex. Compound **23** was converted to the neutral complex $\text{Os}_3(\text{CO})_9[\mu\text{-SCH}_2\text{CMe}_2\text{CH}_2\text{Cl}](\mu_3\text{-S})(\mu\text{-H})$, **24** by protonation with HCl at 25°C. Compound **24** is structurally similar to **23** except that it contains a hydride ligand bridging one of the two metal-metal bonds. Interestingly, NEt_2H did not produce a ring opening addition to **21** in two days in solution at 25°C. Also, **21** does not react with 3,3-DMT at 25°C. This contrasts with the reactions of **6** in which NEt_2H and 3,3-DMT both give good yields of ring opened addition products in 12 h at 25°C. This result suggests that the thietane ligand in **6** is *slightly* more susceptible to ring opening than the one in **21**, but at this time we cannot be sure if the difference in reactivity is due to the presence or absence of the metal-metal bond or perhaps due to some electronic effect produced by the presence of the additional sulfido ligand in **21**.

The complex $\text{Os}_4(\text{CO})_{12}(\mu\text{-CO})[\mu\text{-SCH}_2\text{CMe}_2\text{CH}_2]$, **25** was obtained as a minor product from the pyrolysis of **6** 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, at 25°C in a ring opening

addition to one of the methylene groups of the thietane ligand to yield the salt $[\text{PPN}][\text{Os}_4(\mu\text{-CO})(\text{CO})_{12}(\mu\text{-SCH}_2\text{CMe}_2\text{CH}_2\text{Cl})]$ **26**, see Scheme 8.

Scheme 8

Compound **26** can be converted to the neutral complex $\text{Os}_4(\text{CO})_{13}(\mu\text{-SCH}_2\text{CMe}_2\text{CH}_2\text{Cl})(\mu\text{-H})$, **27**, by protonation with HCl . Complex **27** was characterized crystallographically and was found to contain a 4-chloro-3,3-dimethylpropanethiolato ligand bridging the wingtip metal atoms of a butterfly tetrahedral cluster of four osmium atoms. The hydride ligand bridges one of the edge-positioned metal-metal bonds of the cluster. Compound **27** was also obtained in a good yield in one step by the reaction of **25** with HCl . At 97°C , **27** is decarbonylated to form the complex $\text{Os}_4(\text{CO})_{12}(\mu_3\text{-SCH}_2\text{CMe}_2\text{CH}_2\text{Cl})(\mu\text{-H})$, **28** contains a triply bridging 4-

chloro-3,3-dimethylpropanethiolato ligand serving as a five-electron donor.

3) Ring Opening of a Nitrogen Containing Strained Ring Heterocycle by an Osmium Cluster Complex

The cluster complex $\text{Os}_3(\text{CO})_{10}(\mu\text{-}\overline{\text{NCH}_2\text{CH}_2\text{CH}_2})(\mu\text{-H})$, **29** was obtained in 34% yield from the reaction of $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ with azetidine. Complex **29** was shown to contain a four membered $\overline{\text{NCH}_2\text{CH}_2\text{CH}_2}$ ring bridging two of the metal atoms via the nitrogen atom. When heated to 125°C, **29** was transformed into two new triosmium complexes $\text{Os}_3(\text{CO})_{10}[\mu\text{-N}=\text{C}(\text{H})\text{Et}](\mu\text{-H})$, **30** (27% yield) and $\text{Os}_3(\text{CO})_9(\mu_3\text{-}\overline{\text{NCH}_2\text{CH}_2\text{C}})(\mu\text{-H})$, **31** (15% yield). A small amount of a pentaosmium cluster complex $\text{Os}_5(\text{CO})_{14}(\mu\text{-}\overline{\text{NCH}_2\text{CH}_2\text{C}})(\mu\text{-H})_3$, **32** was obtained in 3% yield. A summary of the reactions in this study is shown in the Scheme 9. The ligand in complex **30** was clearly formed by a ring opening process involving a cleavage of one of the carbon-nitrogen bond in the azetidine ligand and a shift of one of the hydrogen atoms of one of the methylene group that was not involved in the C-N cleavage to the methylene group that was involved in the C-N cleavage. This shift resulted in the formation of the C - N double bond and the ethyl group. Efforts to obtain evidence for metal-mediated C-H activation processes were performed by labeling the hydride site in **29** with ^2H prior to transformation to **30**, but these results were inconclusive due to lack of specificity and evidence for rapid H/D exchange processes that were apparently unrelated to the H-shift leading to **30**. The low yield of **30** combined with CH activation steps in

competing reactions (e.g. formation of **31**) and cluster fragmentation processes may have contributed to this.

Scheme 9

The formation of **31** 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 $\text{NCH}_2\text{CH}_2\text{C}$.

Compound **32** contains a capped butterfly cluster of five osmium atoms with the same heterocyclic ligand $\text{NCH}_2\text{CH}_2\text{C}$ but it bridges in a different manner between the wingtips of the butterfly. The isolation of compound **32** shows that the four-membered heterocycle $\text{NCH}_2\text{CH}_2\text{C}$ can also adopt an alternative bridging mode in which the carbon and nitrogen atoms are coordinated principally through σ -bonding. The increased metal nuclearity of **32** demonstrates that cluster fragmentation reactions are

also occurring under these conditions although the low yield indicates that these are not the dominant processes.

The formation of **30** at 125°C demonstrates that bridging coordination can promote the opening of the four membered nitrogen containing heterocycle $\overline{\text{NCH}_2\text{CH}_2\text{CH}_2}$ 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.

4) Insertion of an Alkynes Into a Metal-Metal Bond. Evidence for an Intramolecular Insertion with a *Trans*-Stereochemistry.

The reaction of the dirhenium complex $\text{Re}_2(\text{CO})_9(\text{NCMe})$, **33** with electrophilic alkynes, $\text{RC}\equiv\text{CCO}_2\text{R}'$, proceeds by displacement of the NCMe ligand and addition of the alkyne with insertion into the rhenium-rhenium bond to yield the dimetallated olefin complexes, $\text{Re}(\text{CO})_4[\text{trans-}\mu\text{-RC}=\text{C}(\text{CO}_2\text{R}')]\text{Re}(\text{CO})_5$, **34a**; $\text{R} = \text{H}$, $\text{R}' = \text{Me}$, **34a**; $\text{R} = \text{Me}$, $\text{R}' = \text{Me}$, **34b** and $\text{R} = \text{CO}_2\text{Et}$, $\text{R}' = \text{Et}$, **34c** that have a *trans*-stereochemistry at the C-C double bond. The carboxylate group is coordinated to one of the rhenium atoms through the ketonic oxygen atom to form a metallacycle. The reaction is insensitive to radical scavengers, solvent polarity and light. The absence of crossover in a reaction of a mixture of labeled and unlabeled **33** is consistent with the insertion of the alkyne into the metal-metal bond by an intramolecular mechanism. Compound **34a** was found to add CO (reversibly) to open the metallacycle and form the simple dimetallated olefin complex $\text{Re}(\text{CO})_5[\text{trans-}\mu\text{-HC}=\text{C}(\text{CO}_2\text{Me})]\text{Re}(\text{CO})_5$, **35**. When

irradiated, **34a** underwent a shift of the alkenyl hydrogen atom to the carboxylate-substituted carbon atom to form the carboxylate-substituted vinylidene complex $\text{Re}_2(\text{CO})_8[\mu\text{-C}=\text{CH}(\text{CO}_2\text{Me})]$, **36** in which the ketonic oxygen atom of the carboxylate group is coordinated to one of the metal atoms. The metal-metal bond in **36** was cleaved (reversibly) by addition of CO at 1 atm/25°C to yield the complex $\text{Re}_2(\text{CO})_9[\mu\text{-C}=\text{CH}(\text{CO}_2\text{Me})]$, **37**, and under a high pressure of CO (1000 psi/100°C), compound **37** underwent a CO insertion (reversible) into one of the Re - C bonds to form the complex $\text{Re}(\text{CO})_4[\mu\text{-O}=\text{C}-\text{C}=\text{CH}(\text{CO}_2\text{Me})]\text{Re}(\text{CO})_5$, **38**. A summary of these results are shown in scheme 10.

Scheme 10

5) Cyclobutyne - The 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. Accordingly, in 1992 we prepared and structurally characterized the first stabilized form of the molecule, cyclobutyne, $\overline{\text{C}=\text{C}}\text{CH}_2\text{CH}_2$. It was stabilized through complexation to a cluster of three metal atoms.

A cyclobutenyl grouping was introduced into a triosmium cluster complex by the reaction of $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ with 1-phenylthiocyclobutene. This yielded two products: $\text{Os}_2(\text{CO})_6(\mu-\eta^2-\overline{\text{C}=\text{CHCH}_2\text{CH}_2})(\mu\text{-SPh})$, **39** and $\text{Os}_3(\text{CO})_{10}(\mu-\eta^2-\overline{\text{C}=\text{CHCH}_2\text{CH}_2})(\mu\text{-SPh})$, **40** by the addition of the 1-phenylthiocyclobutene and cleavage of the carbon-sulfur bond to the cyclobutenyl group. The RS and cyclobutenyl groups are bridging ligands in both complexes. In **40** an η^2 -cyclobutenyl ligand and a benzenethiolato ligand bridge the two metal atoms that are not mutually bonded in an open triosmium cluster. The formation of **39** involved in addition a degradation of the cluster to two metal atoms.

The transformation of the cyclobutenyl ligand into the cyclobutyne ligand was accomplished by treatment of compound **40** with Me_3NO in CH_2Cl_2 and by heating to reflux for 30 hrs. Two products, **39** and the new complex $\text{Os}_3(\text{CO})_9(\mu\text{-SPh})(\mu_3-\eta^2-\overline{\text{C}_2\text{CH}_2\text{CH}_2})(\mu\text{-H})$ **41** were formed. Compound **41** was characterized crystallographically and an ORTEP diagram of its molecular structure is shown in Figure 3. This complex also consists of an open triosmium cluster with a benzenethiolato ligand bridging the open edge as in **40**, but also has a "cyclobutyne" ligand that serves as a four-electron donor coordinated to all three metal atoms. The

Figure 3

carbon atoms of the cyclobutyne ligand are labeled C(1) - C(4). The C₄ring is completely planar and is inclined 73.7° from the Os₃ plane. The ligand has adopted μ_3 -|| coordination mode that is characteristic of alkynes bonded to trimetallic centers. The length of unsaturated C - C bond, C(1) - C(2) is 1.37(2) and is also typical of alkynes coordinated to trimetallic sites. The other C - C bonds in the ligand are equal in length within experimental error, 1.51(2) - 1.54(2)Å, and are typical of C - C single bonds. The hydrogen atom that was shifted to the metal atoms bridges the elongated Os(1) - Os(3) bond, $\delta = -17.41$ ppm.

The bonding of alkynes to trimetallic centers can be viewed as a combination of the σ -donation and π -acceptance that leads to a substantial reduction of the C $\equiv$ C bond order. In the limit a resonance structure **C** can be drawn in which the cyclobutyne ligand in **41** is represented as a dimetallated cyclobutene with the C - C π bond acting as a donor to the third metal atom. It is believed that it is the stabilization provided by such coordination that has made the isolation of complex **41** possible. It is expected that studies of the complexed form of cyclobutyne will reveal some of its reactivity properties and might help to explain its curious absence in the free state. Further investigations are in progress.

B) Publications Under This Project In 1992.

1. R. D. Adams and J. T. Tanner, The Activation of Tertiary Amines by Osmium Cluster Complexes. Further Studies of the Reaction of $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ 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 $\text{Os}_3(\text{CO})_9[\mu_3\text{-C}(\text{Et})\text{N}(\text{Me})\text{CH}](\mu\text{-H})_2$ 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 $\text{Mn}_2(\text{CO})_8[\mu\text{-MeC}_2\text{N}(\text{Et})_2]$, $\text{Mn}_2(\text{CO})_8[\mu\text{-H}_4\text{CCC}(\text{H})\text{NEt}_2]$, $\text{Mn}_2(\text{CO})_8[\mu\text{-}\eta^2\text{-C}_3\text{H}_3\text{NEt}_2]$ and $\text{Mn}_2(\text{CO})_7[\mu\text{-}\eta^2\text{-C}_3\text{H}_3\text{NEt}_2]$, *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 $\text{Re}_2(\text{CO})_8[\mu\text{-H}_2\text{CCHCNMe}_2]$, $\text{Re}(\text{CO})_7[\mu\text{-H}_2\text{CCCNMe}_2](\mu\text{-H})$ and $\text{Re}_2(\text{CO})_8[\mu\text{-H}_2\text{C}=\text{CCNMe}_2](\mu\text{-H})$, *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 $\text{Os}_3(\text{CO})_{10}[\mu\text{-SCH}_2\text{CMe}_2\text{CH}_2]$ and $\text{Os}_3(\text{CO})_{10}[\mu\text{-trans-SC}(\text{H})\text{MeCH}_2\text{C}(\text{H})\text{Me}]$, *Organometallics*, **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 Transformation 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).
15. R. D. Adams*, G. Chen, X. Qu, W. Wu and J. H. Yamamoto, Cyclobutyne - The Ligand. The Synthesis and Molecular Structure of $\text{Os}_3(\text{CO})_9(\mu\text{-}\eta^2\text{-}\overline{\text{C}_2\text{CH}_2\text{CH}_2})(\mu\text{-SPh})(\mu\text{-H})$, *J. Am. Chem Soc.*, **114**, 10977 (1992).
16. R. D. Adams, Nucleophilic Ring Opening Transformations of Bridging Thietane Ligands in Metal Carbonyl Cluster Complexes, *J. Cluster Sci.*, in press.

(C) Proposed Research for the 1993 period.

(1) Studies of the Synthesis and Reactivity of Strained Ring Ligands in Metal Cluster Compounds.

As described in our most recent Progress Report we have recently prepared the first example of the molecule cyclobutyne, **A**, by the synthesis and complexation of it in the metal complex $\text{Os}_3(\text{CO})_{10}(\mu\text{-}\eta^2\text{-}\overline{\text{C=CHCH}_2\text{CH}_2})(\mu\text{-SPh})$, **1**. The free molecule has not yet been prepared and might never be due to the substantial ring strain, 90° , at the C - C triple bond. It is our plan to investigate the reactivity of our "cyclobutyne" complex **1**.

Cyclobutyne and Cyclobutyne Cluster Complex

In the coming year it is our plan to try to synthesize new examples of metal complexes containing the cyclobutyne ligand by using reagents similar to those that were used in the preparation of **1** (e. g. Cyclobutenylphenylthioether and $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$). We plan to investigate the reactivity of **1** for its tendency to undergo ring opening transformations that make help to explain the absence of this molecule in the free state. This may be achieved by simple pyrolysis of **1**. We also

intend to investigate the reactivity of **1** toward other small molecules, such as alkynes, to determine if the cyclobutyne ligand exhibits any anomalous reactivities. It should also be possible to expand upon the chemistry of **1** through its reactions with metal complexes. For example, reactions with simple mononuclear metal carbonyl complexes, such as $\text{Os}(\text{CO})_5$ or $\text{Pt}(\text{COD})_2$, should lead to enlargement of the cluster. I would be of interest to see how the added metal groupings interact, if at all, with the cyclobutyne ligand.

We have recently prepared the complex **2**, see below, that contains a four-membered heterocycle having one nitrogen atom, (i. e. azetidine). When heated to 125°C , two new complexes **3** and **4** were formed. Compound **3** contains an N-ethyliminyl ligand formed by the opening of the four membered ring in **2** while **4** contains a bridging ligand similar to the cyclobutyne in **1** but having a nitrogen atom.

It is planned to prepare new examples of cluster complexes similar to **2** and **4**. We propose to investigate the nature of the ring opening reaction, **2** to **3**, further and also to investigate the reactivity of complex **4** and any similar complexes that could be prepared in order to make comparisons with the corresponding reactivity of **1**.

(2) Studies of the Reactivity of Dimetallic Complexes with Alkynes.

In 1992 we discovered the first example of the insertion of an activated alkyne into a complex having metal-metal bond to yield a dimetallated olefin complex having a *trans*-stereochemistry of the metal atoms, see below. We plan to study this reaction further by using unactivated alkynes. Preliminary results indicate that there are some differences.

We have recently found that the product $(\text{OC})_4\text{Re}[\text{trans-}\mu\text{-HC}=\text{C}(\text{CO}_2\text{Me})]\text{Re}(\text{CO})_5$ can be transformed into an activated NCMethyl derivative $(\text{OC})_4\text{Re}[\text{trans-}\mu\text{-HC}=\text{C}(\text{CO}_2\text{Me})]\text{Re}(\text{CO})_4(\text{NCMe})$ by treatment with Me_3NO in NCMe solvent. This complex readily reacts with unsaturated hydrocarbons by insertions into the metal-carbon bond to yield new complexes through carbon-carbon bond forming reactions. Alkynes result in alkyne oligomerization. In 1993 it is proposed to investigate the scope and character of these reactions by performing reactions of the activated derivative with other unsaturated hydrocarbons, (e. g. $\text{RN}=\text{C}=\text{O}$, $\text{RN}=\text{C}=\text{S}$, $\text{S}=\text{C}=\text{S}$, $\text{H}_2\text{C}=\text{C}=\text{CH}_2$, etc.).

DATE
FILMED

6/15/94

END