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The Transformation of Organic Amines by Transition Metal Cluster Compounds

Progress Report

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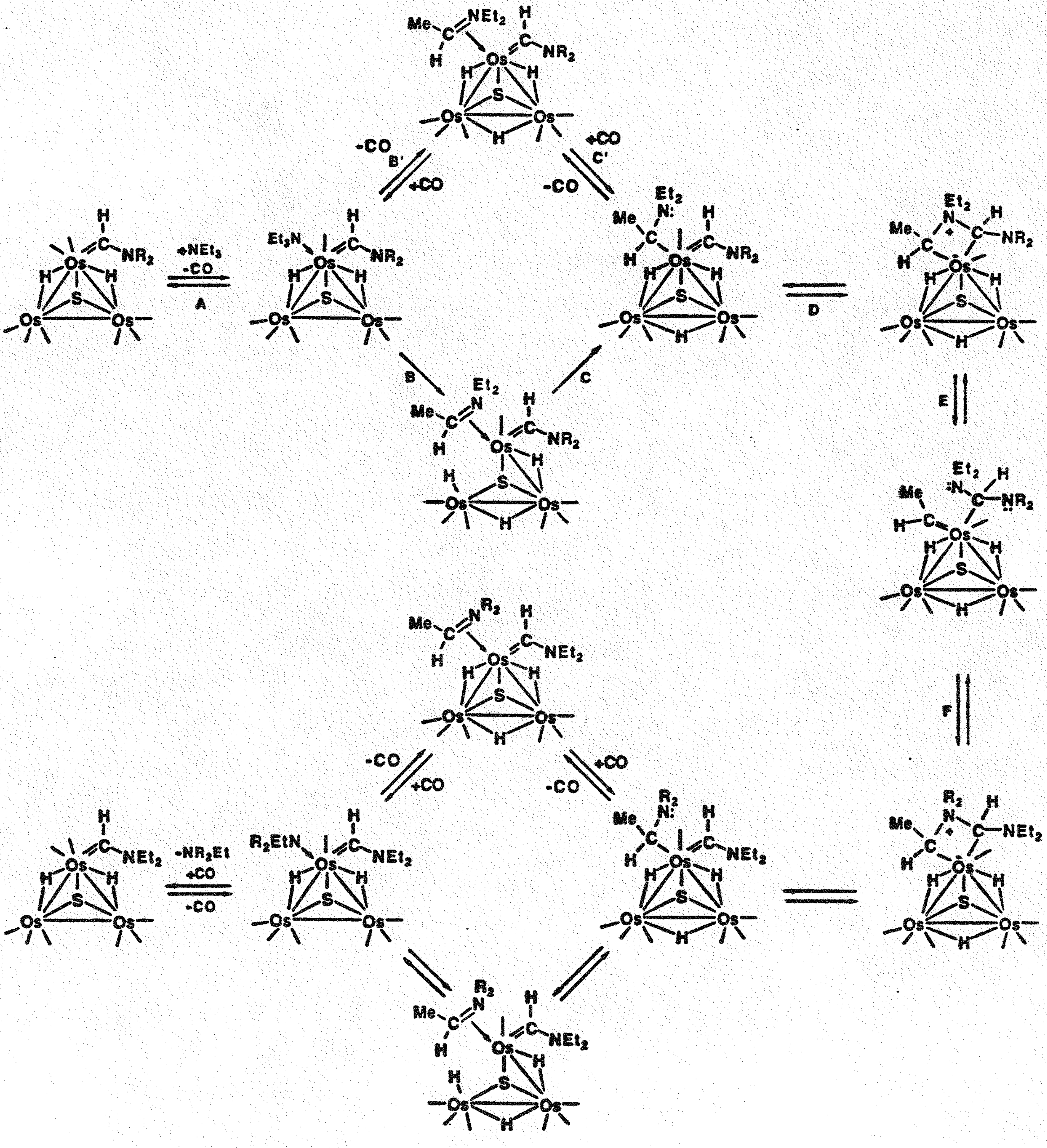
1) Studies of Metal Carbonyl Cluster Complexes Containing Amino Carbene Ligands.

A) Sulfido Osmium Carbonyl Clusters Containing Secondary Amino Carbene Ligands and Catalytic Tertiary Amine Metathesis.

$Os_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}S)$ and $Os_3(CO)_{10}(\mu\text{-}SPh)(\mu\text{-}H)$ were found to react with NMe_3 to yield the complex $Os_3(CO)_8[C(H)NMe_2](\mu_3\text{-}S)(\mu\text{-}H)_2$, **1a** in yields of 31% and 26%, respectively. $Os_3(CO)_{10}(\mu\text{-}CNMe_2)(\mu\text{-}H)$ was found to react with H_2S to yield **1a** in 36% yield. Compound **1a** was analyzed by a single-crystal x-ray diffraction analysis and was found to contain a secondary dimethylaminocarbene ligand terminally coordinated to a sulfur-bridged triosmium cluster. The amino group in the carbene ligand was exchanged by reactions of **1a** with NEt_2H and $NPr_2{}^nH$ at 56°C and 80°C and by reaction with NEt_3 or $NPr_3{}^n$ at 145°C in MeOH solvent. Significant amounts of $[Os_3(CO)_9(\mu_3\text{-}S)(\mu\text{-}H)]^-$, **3** were also formed in the latter reactions. The diamine $HN(Et)(CH_2)_2NMe_2$ reacted with **1a** at 80°C to yield $Os_3(CO)_8[C(H)N(Et)(CH_2)_2NMe_2](\mu_3\text{-}S)(\mu\text{-}H)_2$, **1e**, 42%. **1e** was decarbonylated at 145°C to yield $Os_3(CO)_7[C(H)N(Et)(CH_2)_2NMe_2](\mu_3\text{-}S)(\mu\text{-}H)_2$, **2e** in 41% yield. Compound **2e** was characterized by a single-crystal x-ray diffraction analysis and was found to contain a terminally coordinated $C(H)N(Et)(CH_2)_2NMe_2$ carbene ligand chelated to the cluster through coordination of the NMe_2 group. Labeling studies have shown that the reactions of the carbene complexes with tertiary amines involve C-H activation processes in the alkyl groups and exchange of the amino group of the carbene ligand. A mechanism is proposed that involves iminium ligand intermediates that couple to the carbene ligand to form a nitrogen containing metallacycle, see Scheme 1. Solutions of **1a** in methanol were found to catalyze the exchange of alkyl groups between NEt_3 and NPr_3^n, but analysis of the catalyst mixtures have shown that most of the catalysis was produced by 3, a decomposition product of the carbene containing cluster complexes.

B) Aminocarbene Ligands formed by the Hydrogenation of Ynamine Ligands.

The reaction of the complex $Os_3(CO)_9(\mu_3\text{-}MeC_2NMe_2)(\mu_3\text{-}S)$, 1 with hydrogen at 125°C/1atm yielded the two new compounds $Os_3(CO)_7[\mu\text{-}C(Et)N(Me)CH_2](\mu_3\text{-}S)(\mu\text{-}H)_3$, 3, 7% and $Os_3(CO)_8[C(Et)NMe_2](\mu_3\text{-}S)(\mu\text{-}H)_2$, 4, 9%. At 125°C/10atm of H_2 pressure the yield of 4 was increased to 33%, the yield of 3 decreased to essentially zero, and two new compounds $Os_3(CO)_8[C(Et)N(Me)CH_2](\mu_3\text{-}S)(\mu\text{-}H)$, 5 and $Os_3(CO)_8[\eta\text{-}H_2CC(H)C(H)NMe_2](\mu_3\text{-}S)(\mu\text{-}H)$, 6 were formed in very low yield. Compounds 3 and 4 can be interconverted by the addition and elimination of CO. Compounds 3-6 were characterized by IR, NMR and single-crystal x-ray diffraction analyses. Each compound consists of a sulfur-bridged triangular triosmium cluster. Compound 3 contains a bridging $EtCN(Me)CH_2$ ligand. The ethyl-substituted carbon is a carbene center. Compound 4 contains a terminally coordinated carbene, $EtC(NMe_2)$, and compound 5

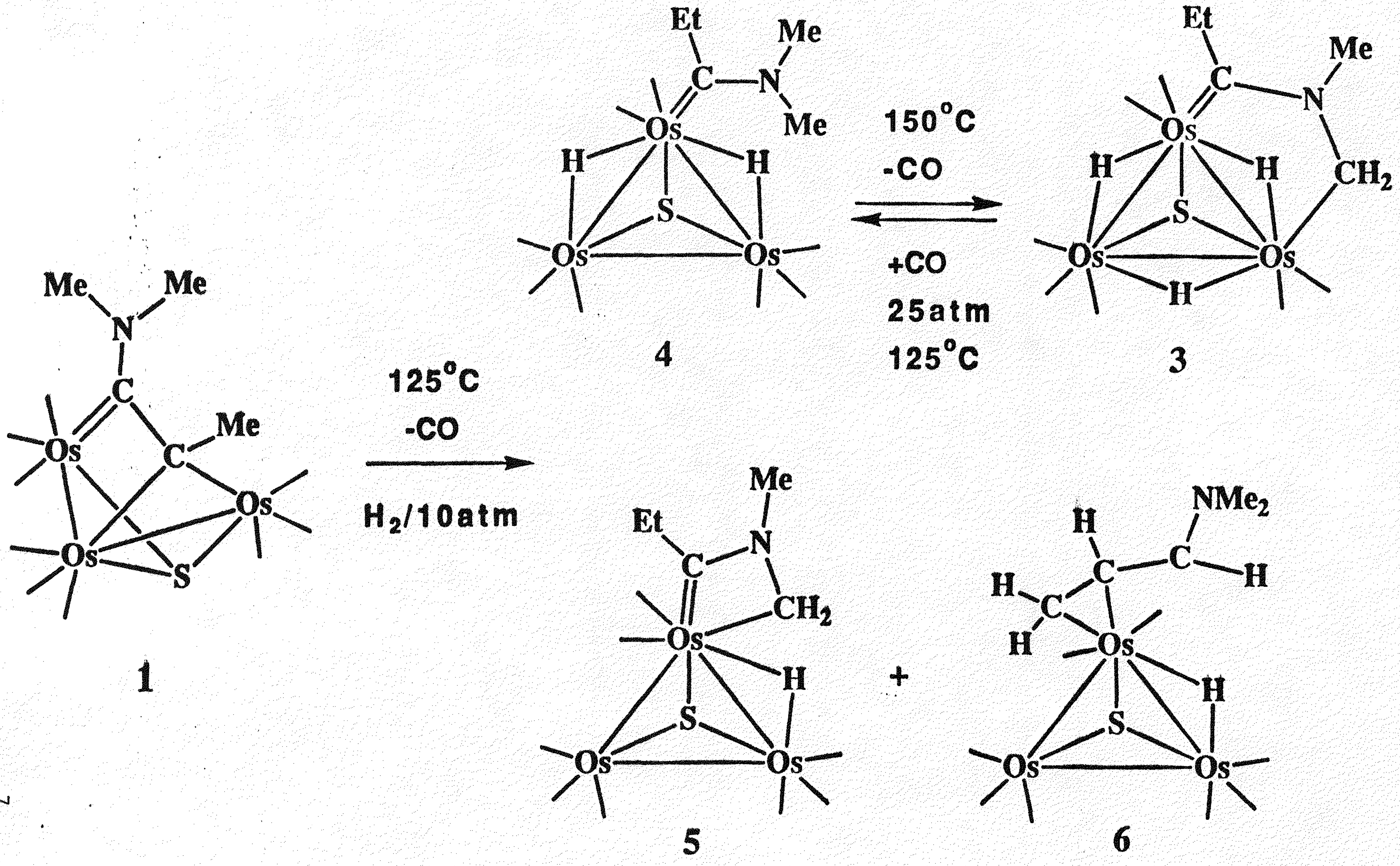


Scheme 1

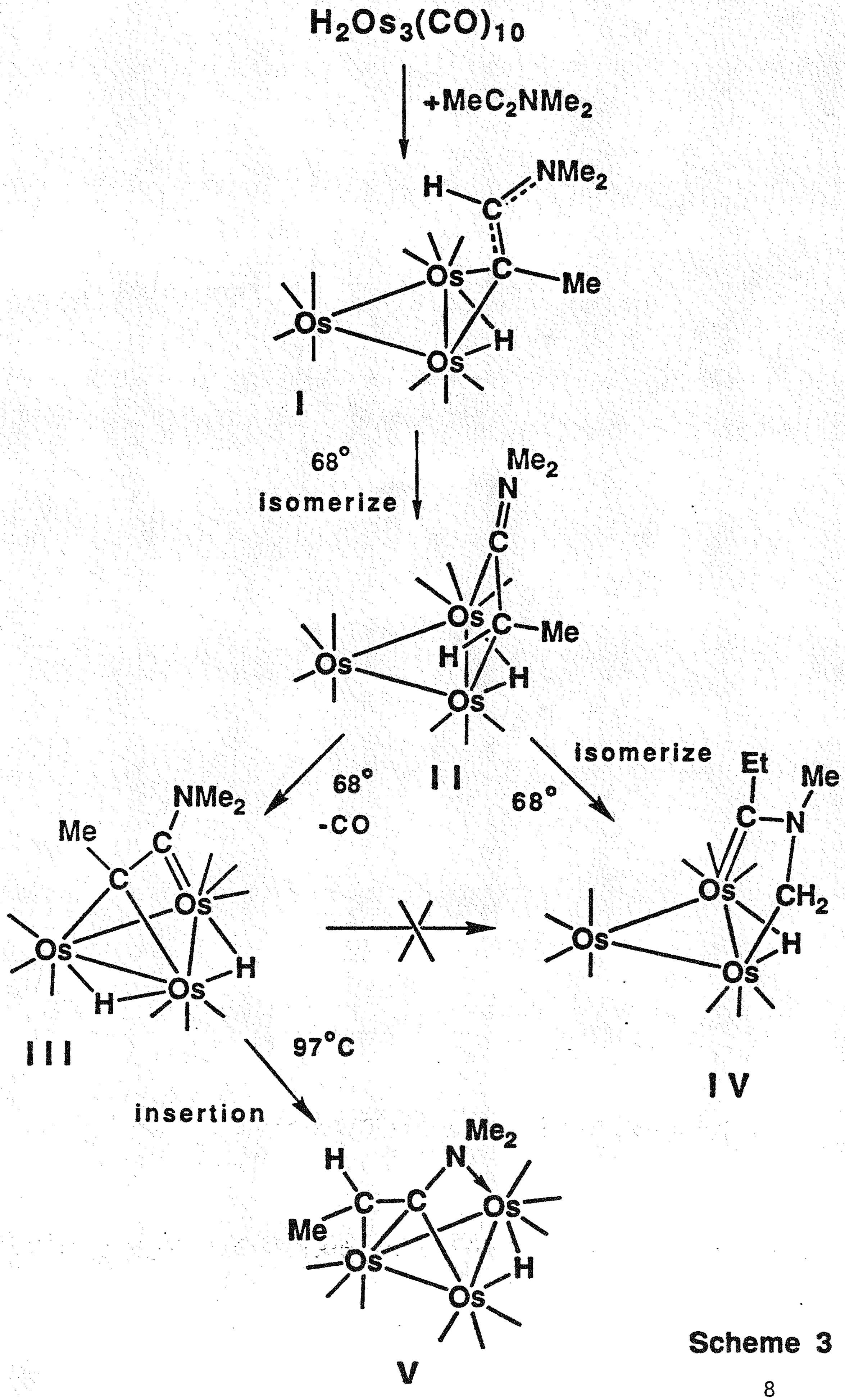
contains a chelating $EtCN(Me)CH_2$, in which the ethyl-substituted carbon is a carbene center. Compound **6** contains a η^2-$H_2CC(H)C(H)NMe_2$ ligand. The carbene centers in compounds **3-5** were formed by novel 1,1 hydrogenations at the methyl-substituted carbon atom of the ynamine ligand in **1**, see Scheme 2. In compounds **3** and **5** one of the N-methyl groups was metallated. The dimethylaminoallyl ligand in **6** was formed by a 1,2 dihydrogenation of the ynamine ligand in **1** plus a CH activation on the methyl group on the carbon atom.

C) Aminocarbene Ligands formed by the Reaction of $Os_3(CO)_{10}(\mu\text{-}H)_2$ with Ynamines.

The reaction of $Os_3(CO)_{10}(\mu\text{-}H)_2$ with $MeC{\equiv}CNMe_2$ at 25°C yielded the new complex $Os_3(CO)_{10}[\mu\text{-}C(Me)C(H)NMe_2](\mu\text{-}H)$, **1**, 68% by the addition and insertion of $MeC{\equiv}CNMe_2$ into one of the metal-hydrogen bonds. Compound **1** contains a bridging $C(Me)C(H)NMe_2$ ligand that is coordinated only by the methyl-substituted carbon atom. The hydride ligand was shifted to the NMe_2-substituted carbon atom. When heated to 68°C in hexane, **1** isomerized to the new complex $Os_3(CO)_{10}[\mu\text{-}CH(Me)CNMe_2](\mu\text{-}H)$, **2**, by a shift of the hydrogen atom from the NMe_2-substituted carbon atom to the methyl-substituted carbon atom, see scheme 3. At 68°C, **2** was slowly decarbonylated to yield the new compound $Os_3(CO)_9(\mu_3\text{-}MeC_2NMe_2)(\mu\text{-}H)_2$, **3**, which contains a triply bridging MeC_2NMe_2 ligand. In a competing reaction **2** was simultaneously isomerized to the new compound $Os_3(CO)_{10}[\mu\text{-}C(Et)N(Me)CH_2](\mu\text{-}H)$, **4** which contains an N-methyl metallated ethyldimethylaminocarbene ligand



Scheme 2


H₂Os₃(CO)₁₀
+MeC₂NMe₂
H
NMe₂
C
C
Me
Os
Os
Os
H
I
68°
isomerize
Me₂
N
C
C
Me
Os
Os
Os
H
H
II
68°
-CO
isomerize
68°
NMe₂
Me
C
C
Os
Os
Os
H
H
III
Et
Me
C
N
Os
CH₂
Os
Os
H
IV
97°C
insertion
Me₂
H
N
C
C
Me
Os
Os
Os
H
V

Scheme 3

that bridges an edge of the triosmium cluster. When heated to 97°C for 36 hrs., **3** was isomerized to the new compound $Os_3(CO)_9[\eta_3\text{-}CH(Me)C(H)NMe_2](\mu\text{-}H)$, **5** that exists in solution as a mixture of isomers. One of the isomers was crystallized and characterized structurally. It was shown to contain a triply bridging $MeC(H)CNMe_2$ ligand. The carbon atoms of the alkenyl group are σ-π coordinated to an edge of the cluster, while the nitrogen atom is coordinated to the third metal atom. The ligand contains a Z-stereochemistry. On the basis of NMR spectroscopy the other isomer is believed to contain a similarly coordinated ligand having an E-stereochemistry. Compounds **1-5** were all characterized by IR, NMR and single-crystal x-ray diffraction.

2) Studies of the Structure and Bonding of Ynamine Ligands in Metal Cluster Complexes.

A) Reactions of MeC_2NMe_2 with $Os_4(CO)_{12}(\mu_3\text{-}S)$.

The reaction of $Os_4(CO)_{12}(\mu_3\text{-}S)$, **1** with MeC_2NMe_2 yielded the complexes $Os_3(CO)_9(\mu_3\text{-}MeC_2NMe_2)(\mu_3\text{-}S)$, **2**; $Os_4(CO)_{11}(\mu_3\text{-}MeC_2NMe_2)(\mu\text{-}MeC_2NMe_2)(\mu_3\text{-}S)$, **3**; $Os_4(CO)_{11}[\mu\text{-}C(Me)C(NMe_2)C(NMe_2)CMe](\mu_3\text{-}S)$, **4**; $Os_4(CO)_{11}[\mu\text{-}C(NMe_2)C(Me)C(Me)C(NMe_2)](\mu_3\text{-}S)$, **5**; $Os_4(CO)_9(\mu\text{-}MeC_2NMe_2)[\mu\text{-}C(Me)C(NMe_2)C(Me)C(NMe_2)](\mu_3\text{-}S)$, **6** and $Os_3(CO)_7(\mu_3\text{-}MeC_2NMe_2)(\mu\text{-}MeC_2NMe_2)(\mu_3\text{-}S)$, **7** all in low yields. Compounds **3-7** are new and have been characterized by IR, ^1H NMR and single-crystal x-ray diffraction analyses. Compounds **3** contains a chain of four osmium atoms with two bridging ynamine ligands and a bridging sulfido ligand. Both ynamine ligands contain strong π-bonding interactions between the NMe_2 groups and the neighboring carbon atoms in the alkynyl group. These interactions alter the metal-carbon bonding and the ynamine ligands adopt structures that resemble aminocarbene ligands. Similar structures for the ynamine ligands were found for the ynamine ligands in 7. Compounds **4-6** contain spiked triangular clusters of four osmium atoms with a triply bridging sulfido ligand on the triangular grouping. Each of these compounds also contains a metallacyclopentadiene group formed by the coupling of two ynamine ligands. In each compound, the two ynamine ligands have been coupled in a different way. In **4**, they were coupled tail-to-tail. In **5** they were coupled head-to-head and in **6** they were coupled head-to-tail. There is structural evidence for significant, albeit weaker, π-bonding interactions between the amino-groups and the adjacent carbon atoms in these complexes. This seems to produce a weakening of the corresponding metal-carbon bonding.

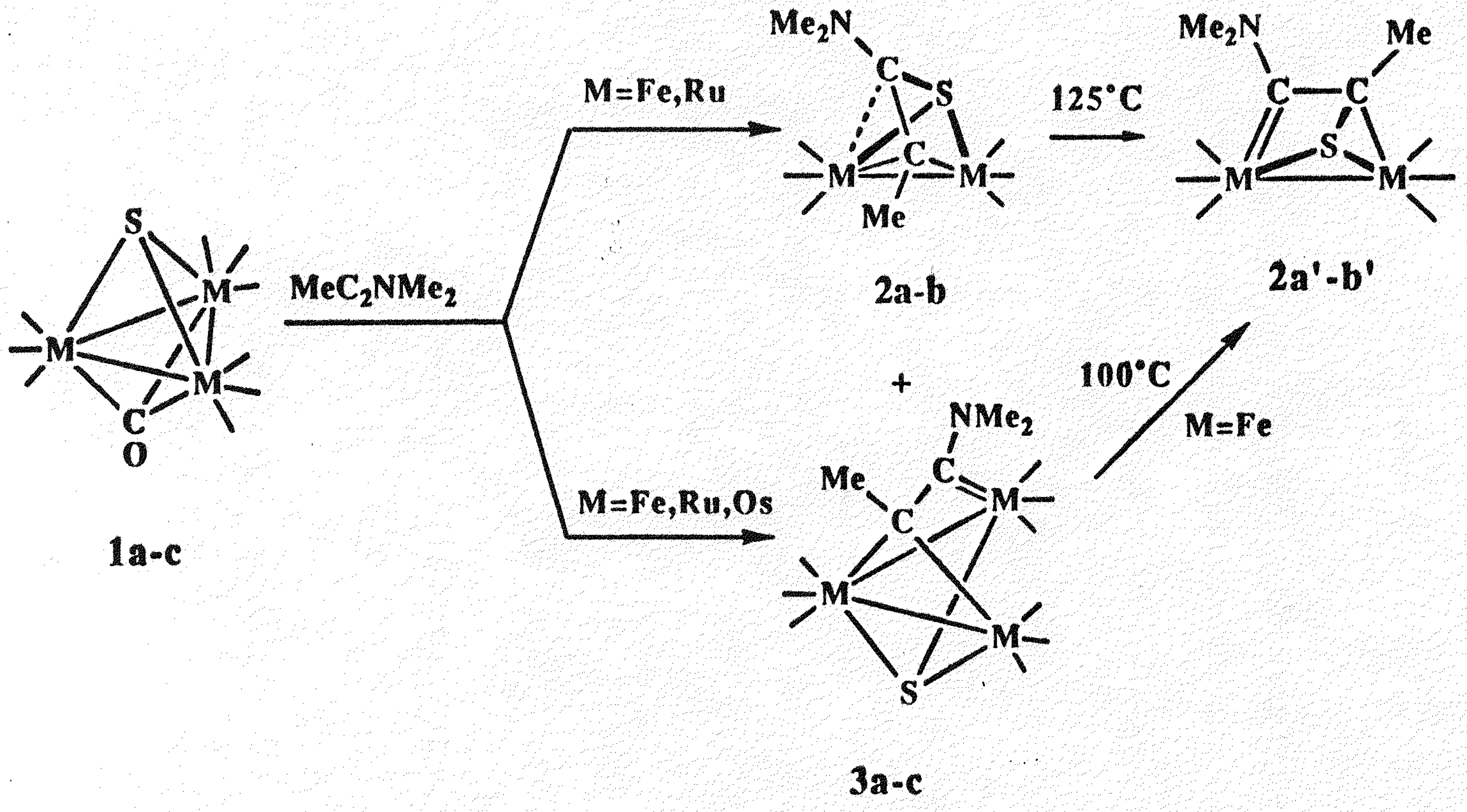
B) Reactions of MeC_2NMe_2 with the Molecules $M_3(CO)_{10}(\mu_3$-S), M = Fe, Ru, and Os.

The reactions of the compounds $M_3(CO)_{10}(\mu_3-S)$, **1a**, M = Fe, and **1b**, M = Ru with MeC_2NMe_2 yielded the products $M_2(CO)_6[\mu-SC(NMe_2)CMe]$, **2a**, M = Fe, 3%; **2b**, M = Ru, 36% and $M_3(CO)_9[\mu_3-MeC_2NMe_2](\mu_3-S)$, **3a**, M = Fe, 30%; **3b**, M = Ru, 14%. The reaction of $Os_3(CO)_{10}(\mu_3-S)$, **1c** with MeC_2NMe_2 yielded only the trinuclear product $Os_3(CO)_9[\mu_3-MeC_2NMe_2](\mu_3-S)$, **3c**, 87%. Compounds **2b** and **3c** were characterized by single-crystal x-ray diffraction analyses. Compound **2b** consists of a metal-metal bonded $Ru_2(CO)_6$

grouping bridged by a $SC(NMe_2)CMe$ ligand. The sulfur and C-methyl carbon atom are strongly bonded to both metal atoms. The NMe_2 substituted carbon atom is weakly bonded to one metal atom and not bonded to the other. Compound **3c** consists of an open triosmium cluster with a triply bridging sulfido ligand and a triply bridging MeC_2NMe_2 ligand. The C-methyl carbon atom is bonded to two metal atoms. The NMe_2-substituted carbon atom is coordinated only to the one remaining metal atom. Structurally, this grouping resembles an NMe_2-substituted carbene ligand. This is also supported by the ^{13}C NMR spectrum which shows a very low field resonance, +251.92 ppm for **3a** and +243.50 ppm for **3c**. It is proposed that the ynamine ligands in the compounds **3a-c** should be formulated as α,α dimetallioethyldimethylaminocarbene ligands. Compound **2b** isomerizes when heated to form the compound $Ru_2(CO)_6[\mu\text{-}SC(Me)CNMe_2]$, **2b′** in 38% yield, see scheme 4. Compound **2b′** was characterized structurally. The structure is similar to that of **2b** except that the methyl substituted carbon atom is bonded to the sulfur atom, and the NMe_2-substituted carbon atom is not a bridging atom, but is terminally coordinated to one of the metal atoms. The iron homolog of **2b′**, $Fe_2(CO)_6[\mu\text{-}SC(Me)CNMe_2]$, **2a′** was obtained (55% yield) by pyrolysis of **3a** at 100°.

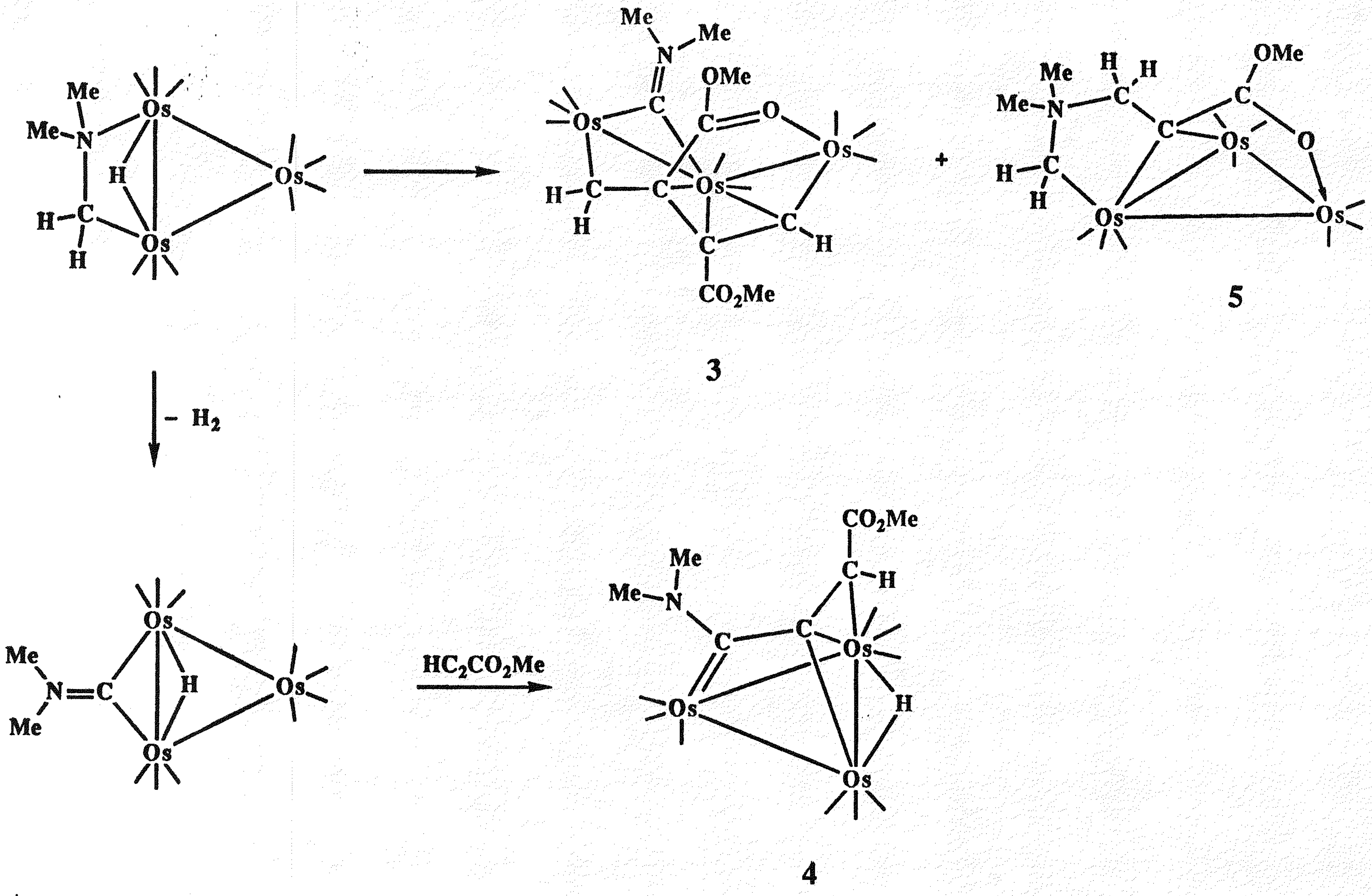
3) <u>Studies of the Reactions of Alkynes with Iminium Ligands.</u>

The reaction of $Os_3(CO)_{10}(\mu\text{-}H_2CNMe_2)(\mu\text{-}H)$, **1** with $HC{\equiv}CCO_2Me$ has yielded three new products $Os_3(CO)_8(\mu\text{-}CNMe_2)[\mu_3\text{-}CH_2C(CO_2Me)C(CO_2Me)CH]$, **3**, 7%; $Os_3(CO)_9[\mu_3\text{-}Me_2NCCC(H)(CO_2Me)](\mu\text{-}$



Scheme 4

H), 4, 20% and $Os_3(CO)_9[\mu_3-H_2CNMe_2CH_2CCO_2Me]$, 5, 6%. Compound 4 was also obtained in a slightly higher yield (28%) from the reaction of $Os_3(CO)_{10}(\mu-CNMe_2)(\mu-H)$, 2 and HC_2CO_2Me. Compounds 3-5 were characterized by IR, ^1H NMR and single-crystal x-ray diffraction analyses. Compound 3 consists of an open cluster of three osmium atoms with a bridging dimethylaminocarbyne ligand and a triply bridging $CH_2C(CO_2Me)C(CO_2Me)CH$ ligand. The former was formed by the removal of the two hydrogen atoms from the methylene group of the iminium ligand. The latter was formed by a tail-to-tail coupling of two $HC{\equiv}CCO_2Me$ molecules and the transfer of one hydrogen atom to one of the CH groups. Compound 4 contains a closed triangular cluster of metal atoms with a triply bridging $Me_2NCCC(H)CO_2Me$. This ligand was apparently formed by a C-C coupling of a rearranged $HC{\equiv}CCO_2Me$ ligand and a $CNMe_2$ group. Compound 5 contains a closed triangular cluster of metal atoms with a triply bridging $CH_2NMe_2CH_2CO_2Me$ ligand. This ligand was formed by a C-N coupling of the iminium ligand in 1 to a $HC{\equiv}CCO_2Me$ ligand that had been inserted into the metal-hydride bond in 1, see scheme 5.



Scheme 5

5) Publications under this Project. 1989 - 1990.

1. R. D. Adams,. J. T. Tanner, The Anomalous Coordination Behavior of Ynamine Ligands in Polynuclear Metal Complexes. The Synthesis and Structural Characterization of $\mathrm{Os_3(CO)_{10}[\mu\text{-}CH_3C_2N(CH_3)_2]}$ and $\mathrm{Os_3(CO)_9[\mu_3\text{-}\eta^3\text{-}H_2CC_2N(CH_3)_2]\text{-}(\mu\text{-}H)}$, Organometallics, 8, 563 (1989).
2. R. D. Adams, G. Chen, J. T. Tanner and J. Yin, Clusters Containing Carbene Ligands. A New Route to Alkyl(dialkylamino)carbene Ligands by a Novel 1,1-Hydrogenation of Ynamine Ligands, Organometallics, 8, 2493 (1989).
3. R. D. Adams and J. T. Tanner, Insertion of an Ynamine into the C-N Bond of a Dimethylaminocarbene Ligand, Organometallics, 8, 2276 (1989).
4. R. D. Adams, G. Chen, S. Sun, J. T. Tanner, and T. A. Wolfe, Cluster Complexes Containing Ynamine Ligands. 1. The Synthesis and Structural Characterizations of the Complexes $\mathrm{Os_4(CO)_{11}(\mu_3\text{-}MeC_2NMe_2)(\mu\text{-}MeC_2NMe_2)(\mu_3\text{-}S)}$, $\mathrm{Os_4(CO)_{11}[\mu\text{-}C(Me)\text{-}C(NMe_2)C(NMe_2)CMe](\mu_3\text{-}S)}$, $\mathrm{Os_4(CO)_{11}[\mu\text{-}C(NMe_2)C(Me)C(Me)C\text{-}(NMe_2)](\mu_3\text{-}S)}$, $\mathrm{Os_4(CO)_9(\mu\text{-}MeC_2NMe_2)[\mu\text{-}C(Me)C(NMe_2)C(Me)C(N\text{-}Me_2)(\mu_3\text{-}S)}$, Organometallics, 9, 251 (1990).
5. R. D. Adams, J. R. Babin and T. A. Wolfe, Reactions of Iminium Ligands with Alkynes. The Addition of $\mathrm{HC{\equiv}CO_2Me}$ to $\mathrm{Os_3(CO)_{10}(\mu\text{-}H_2CNMe_2)(\mu\text{-}H)}$, Organometallics, in press.

6. R. D. Adams, G. Chen, S. Sun and T. A. Wolfe, The Ring

6. R. D. Adams, G. Chen, S. Sun and T. A. Wolfe, The Ring Opening and Oligomerization of Thiirane by Hexaosmium Carbonyl Cluster Complexes, *J. Am. Chem. Soc.*, 112, 868 (1990).

7. Z. Nomikou, J. F. Halet, R. Hoffmann, J. T. Tanner and R. R. D. Adams, Electronic Structure of the Non-Classical Trimetallic Alkyne Cluster Complex $Os_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-}HC_2NEt_2)$, *Organometallics*, in press.

8. R. D. Adams, G. Chen, J. T. Tanner and J. Yin, Clusters Containing Ynamine Ligands. 2. The Reactions of $MeC{\equiv}CNMe_2$ with $M_3(CO)_{10}(\mu_3\text{-}S)$, M=Fe, Ru, and Os, Including the Structural Characterizations of $Ru_2(CO)_6[\mu\text{-}SC(NMe_2)CMe]$, $Ru_2(CO)_6[\mu\text{-}SCMeC(NMe_2)]$ and $Os_3(CO)_9[\mu_3\text{-}MeC_2NMe_2](\mu_3\text{-}S)$, *Organometallics*, in press.

9. R. D. Adams, J. E. Babin, H. S. Kim, J. T. Tanner and T. A. Wolfe, Clusters Containing Carbene Ligands. 7. The Preparation of $Os_3(CO)_8[C(H)NMe_2](\mu_3\text{-}S)(\mu\text{-}H)_2$ and the Nature of its Reactions with Secondary and Tertiary Amines, *J. Am. Chem. Soc.*, in press.

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11. R. H. Fish, H. S. Kim, R. H. Fong, and R., D. Adams, Facile Nucleophilic Addition of Methyl Ketone Enolates to Pentamethylcyclopentadienylrhodium(η^6-p-xylene) Dication, *Organometallics*, in press.

12. R. D. Adams, G. Chen and J. T. Tanner, Clusters Containing Carbene Ligands. 9. The Reaction of $MeC\equiv CNMe_2$ with $Os_3(CO)_{10}(\mu\text{-}H)_2$, *Organometallics*, in press.