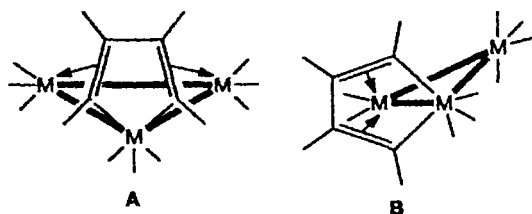


A novel intramolecular rearrangement of a metallacyclopentadiene derivative of triosmium cluster

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After we had recently obtained $\text{Os}_3(\text{CO})_9\{\mu_3\text{-}\eta^1\text{-}\eta^2\text{-}\eta^2\text{-}\text{C}(\text{SiMe}_3)\text{C}(\text{Me})\text{C}(\text{H})\text{C}(\text{R})\}$ ($\text{R} = \text{Ph}$ (1), Fc (2)) clusters with a novel type of coordination of the dienediyl ligand to the Os_3 framework (structure A),^{1,2} it was reasonable to assume that complexes of similar structure can be precursors of isomeric compounds that have structure B, i.e., the known and typical products of alkyne dimerization in the reactions with osmium carbonyl clusters. However, our attempts to induce thermal rearrangement of complexes 1 and 2 into isomers having the structure of type B resulted in their decarbonylation with the formation of hydride clusters $\text{Os}_3(\mu\text{-H})(\text{CO})_8\{\mu_3\text{-}\eta^1\text{-}\eta^1\text{-}\eta^4\text{-}\eta^1\text{-}\text{C}(\text{SiMe}_3)\text{C}(\text{Me})\text{C}(\text{H})\text{C}(\text{R}')\}$ (where $\text{R}' = \text{C}_6\text{H}_4$ (3), $\text{C}_5\text{H}_3\text{FeC}_5\text{H}_5$ (4)) containing an *ortho*-metallated phenyl¹ and ferrocenyl² moiety, respectively. Similar hydride clusters are also formed as a result of thermolysis of triosmium complexes of structure B, in which an aryl group is in the α -position of the osmacyclopentadiene ring.^{3–5} In these hydride clusters, the five-membered cycle is tilted with respect to the plane of the Os_3 triangle and is in intermediate position between those observed in the limiting cases (structures A and B).



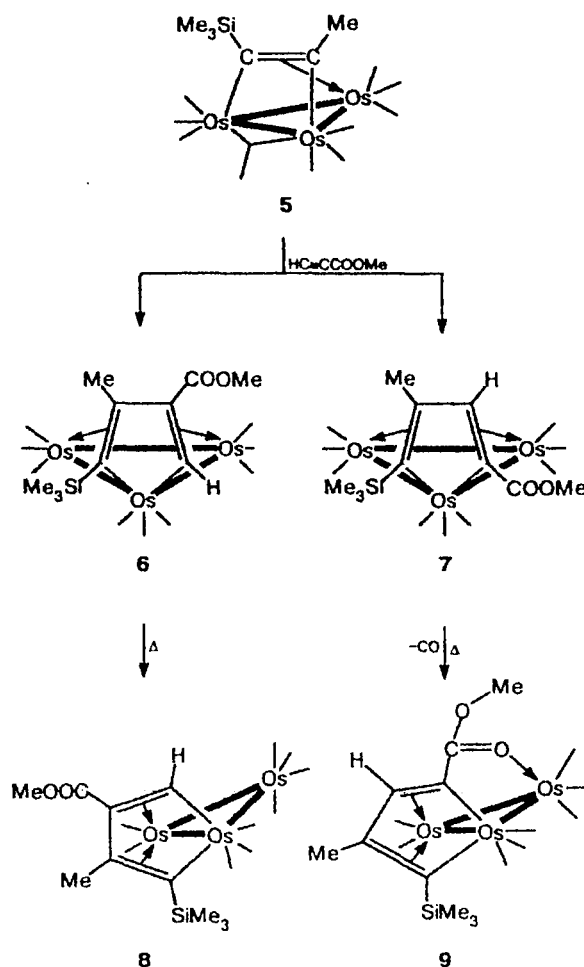
In a continuation of our studies of the heteroalkyne dimerization on the Os_3 cluster we synthesized a novel complex having structure A and were first to observe its $\text{A} \rightarrow \text{B}$ intramolecular rearrangement.

The reaction of the triosmium alkyne cluster $\text{Os}_3(\mu\text{-CO})(\text{CO})_9\{\mu_3\text{-}\eta^1\text{-}\eta^1\text{-}\eta^2\text{-}\text{Me}_3\text{SiC}_2\text{Me}\}$ (5) with $\text{HC}\equiv\text{CCOOMe}$ (benzene, 70 °C, 6 h) resulted in four complexes isolated chromatographically on a column with silica gel (Scheme 1). Compounds $\text{Os}_3(\text{CO})_9\{\mu_3\text{-}\eta^1\text{-}\eta^1\text{-}\eta^2\text{-}\text{C}(\text{SiMe}_3)\text{C}(\text{Me})\text{C}(\text{COOMe})\text{CH}\}$ (6), $\text{Os}_3(\text{CO})_9\{\mu_3\text{-}\eta^1\text{-}\eta^1\text{-}\eta^2\text{-}\text{C}(\text{SiMe}_3)\text{C}(\text{Me})\text{C}(\text{H})\text{C}(\text{COOMe})\}$ (7), $\text{Os}_3(\text{CO})_9\{\mu\text{-}\eta^1\text{-}\eta^1\text{-}\eta^4\text{-}\text{C}(\text{SiMe}_3)\text{C}(\text{Me})\text{C}(\text{COOMe})\text{CH}\}$ (8),

and $\text{Os}_3(\text{CO})_8\{\mu_3\text{-}\eta^1\text{-}\eta^1\text{-}\eta^4\text{-}\eta^1\text{-}\text{C}(\text{SiMe}_3)\text{C}(\text{Me})\text{CHC}(\text{COOMe})\}$ (9), obtained in yields of 16, 28.8, 40, and 9.4%, respectively, were characterized by IR and ^1H NMR spectroscopy. In addition, the structure of clusters 6 and 9 was confirmed by X-ray analysis (these results will be published elsewhere).

^1H NMR (CDCl_3 , 25 °C), δ : complex 6, 0.33 (s, 9 H, $\text{Si}(\text{CH}_3)_3$); 2.47 (s, 3 H, CH_3); 3.76 (s, 3 H, OCH_3);

Scheme 1



10.35 (s, 1 H, CH); **complex 7**, 0.35 (s, 9 H, Si(CH₃)₃); 2.32 (s, 3 H, CH₃); 3.79 (s, 3 H, OCH₃); 6.69 (s, 1 H, CH); **complex 8**, 0.37 (s, 9 H, Si(CH₃)₃); 2.80 (s, 3 H, CH₃); 3.85 (s, 3 H, OCH₃); 8.32 (s, 1 H, CH); **complex 9**, 0.33 (s, 9 H, Si(CH₃)₃); 2.67 (s, 3 H, CH₃); 3.83 (s, 3 H, OCH₃); 6.62 (s, 1 H, CH).

A special-purpose experiment showed that compound **9** is formed as a result of decarbonylation of cluster **7**, viz., thermolysis of the latter in benzene gave complex **9** as the only product.*

Unlike complexes **7**, or **1** and **2**, cluster **6** contains in the α -position of the osmacyclopentadiene ring neither a functional group that can be coordinated to the metal atom nor a substituent that can undergo *ortho*-metalation. Because of this, cluster **6** isomerizes into compound **8** under mild conditions (45–50 °C, CDCl₃ or C₆D₆, an NMR tube). The isomerization involves a $\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^2\text{:}\eta^2 \rightarrow \mu\text{-}\eta^1\text{:}\eta^1\text{:}\eta^4$ rearrangement of the hydrocarbon ligand and internuclear migration of one of the CO groups.

Thus, clusters of the type **B**, in which the hydrocarbon ligand forms a η^4 -diene bond with one of the osmium atoms, are thermodynamically more stable than

*An Os₃(CO)₈($\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^4\text{:}\eta^1\text{-C}_8\text{H}_4(\text{Ph})\text{COOMe}$) cluster synthesized using a complex procedure⁶ and related to compound **9** is known.

isomeric clusters of the type **A** containing two η^2 -olefin bonds. We believe this is the reason why the latter have remained "elusive" for such a long time.

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