Synthesis and Reactivity of μ_3-Alkylidyne Triosmium Cluster Compounds

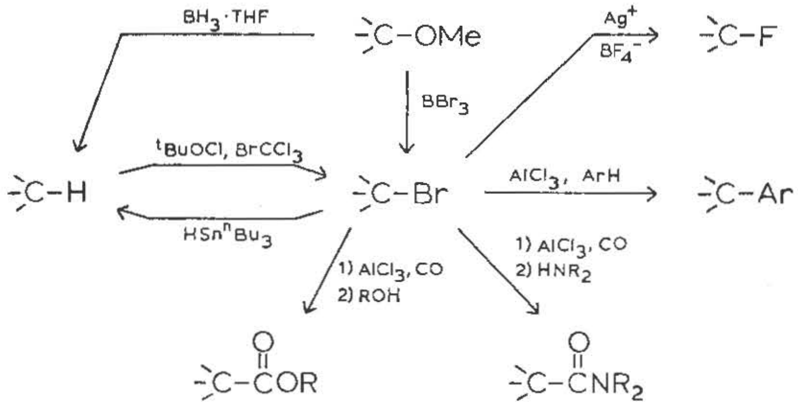
Debra S. Strickland Final Seminar January 27, 1983

The need to develop alternatives to oil as our major source of fuel and chemical feedstock is prompting a re-examination of the mechanisms of the Fischer-Tropsch synthesis reaction [1]. This synthesis converts hydrogen and carbon monoxide, available from coal, into mixtures of hydrocarbons, olefins, and oxygenated compounds, and is catalyzed by metal and metal oxide surfaces. Little is known about the mechanisms which lead to the various products but recent studies have shown that the first step can be dissociative chemisorption of carbon monoxide to give reactive surface carbon atoms [2]. In order to design new, selective catalyst systems an understanding of the key mechanistic steps is crucial.

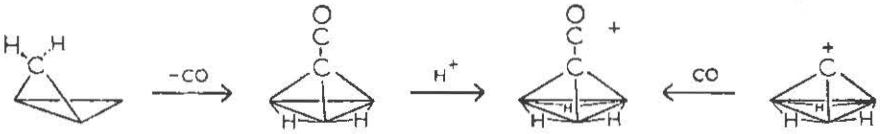
The complexity of the catalytic systems and the difficulties inherent in examining surface reactions has led some investigators to mimic possible surface reactions with soluble organometal clusters which, because of their multimetal sites, present attractive models for the structures and reactivities of small molecules chemisorbed to a metal surface [3]. The recent synthesis of several clusters with exposed carbon atoms [4,5] suggests that the reactivity of a cluster carbon atom will increase as its coordination number decreases.

Methods have been developed for the functionalization of the triosmium carbon unit at the carbon atom and the reactions imply the intermediacy of carbocationic and carbon radical cluster carbides. The reactivity of three carbonylmethylidyne clusters, $H_2Os_3(CO)_9(\mu_3\text{-CCO})$ and the related, and more reactive, acylium cation and acyl radical species, was investigated. Also examined were reactions which involve hydrogen migration from metal sites to alkylidyne carbon atoms.

The synthetically useful routes for the interconversion of $H_3Os_3(CO)_9(\mu_3\text{-CY})$ clusters are outlined below. The only previously known clusters in this group were those with Y=H [6], CH_3 [7], and OCH_3 [8].

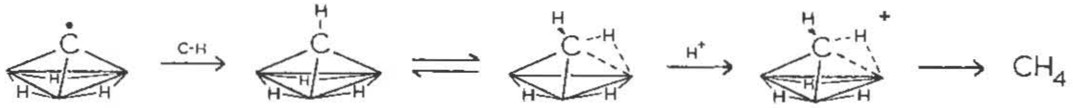


The bromomethylidyne cluster is reactive with Lewis acids as is the analogous $Co_3(CO)_9(\mu_3\text{-CCl})$ [9]. Notably, the triosmium carbocation can be generated with $AgBF_4$ and is reactive enough to abstract fluoride from the counterion, and to add to CO to give an acylium cation. The acylium is also available by protonation of $H_2Os_3(CO)_9$-(μ_3-CCO), which is the unexpected product obtained from thermolysis of $Os_3(CO)_{11}CH_2$ [10]. Hydrogenation of $H_2Os_3(CO)_9(\mu_3$-CCO) yields $H_3Os_3(CO)_9(\mu_3$-CH), demonstrating that the C-C coupling process is reversible. Nucleophiles attack $H_2Os_3(CO)_9(\mu_3$-CCO) at the methylidyne carbonyl carbon atom and the CCO ligand can be reduced to CCH_2 with $BH_3\cdot THF$.



The triosmium carbon radical, $H_3Os_3(CO)_9(\mu_3$-C•), can be generated under mild conditions from $H_3Os_3(CO)_9(\mu_3$-CBr) with photochemically-produced •Re$(CO)_5$ radicals. This method has permitted an exploration of the chemistry of this unusual carbide cluster, a chemistry which includes hydrogen abstraction from hydrocarbon C-H bonds and addition to aromatic rings. When generated in d^{12}-cyclohexane under CO, both the deuterium-substituted cluster and a bisalkylidyne diketone, which results from initial addition of CO to the cluster carbon radical, are isolated.

Slow intramolecular H/D exchange in $H_3Os_3(CO)_9(\mu_3$-CD) takes place at 25°C. Similar metal-to-carbon hydrogen migration processes are observed for μ_3-alkylidyne clusters in which an apical organic CO moiety can coordinate to a metal center, allowing isolation of the alkylidene isomers. Loss of methane from the methylidyne cluster is facilitated by protonation, and anion coordination has produced triosmium clusters with tridentate sulfate and phosphate ligands.



References

1. Rofer-DePoorter, C. K. Chem. Rev. 1981, 81, 447, and references therein.

2. (a) Bell, A. T. Catal. Rev.-Sci. Eng. 1981, 23, 203.
(b) Biloen, P.; Helle, J. N.; Sachtler, W. M. H. J. Catal. 1979, 58, 95.

3. (a) Muetterties, E. L.; Stein, J. Chem. Rev. 1979, 79, 479.
(b) Muetterties, E. L.; Rhodin, T. N.; Band, E.; Brucker, C. F.; Pretzer, W. R. Chem. Rev. 1979, 79, 91.

4. Tachikawa, M.; Muetterties, E. L. *Prog. Inorg. Chem.* **1981**, *28*, 203.

5. (a) Bradley, J. S.; Ansell, G. B.; Leonowicz, M. E.; Hill, E. W. *J. Am. Chem. Soc.* **1981**, *103*, 4968.
   (b) Tachikawa, M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1980**, *102*, 4541.
   (c) Holt, E. M.; Whitmore, K. H.; Shriver, D. F. *J. Organomet. Chem.* **1981**, *213*, 125.
   (d) Kolis, J. W.; Holt, E. M.; Drezdzon, M.; Whitmore, K. H.; Shriver, D. F. *J. Am. Chem. Soc.* **1982**, *104*, 6134.

6. Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 5225.

7. Deeming, A. J.; Underhill, M. *J. Chem. Soc., Chem. Comm.* **1973**, 277.

8. Keister, J. B. *J. Chem. Soc., Chem. Comm.* **1979**, 214.

9. Seyferth, D. *Adv. Organomet. Chem.* **1976**, *14*, 97.

10. Sievert, A. C.; Strickland, D. S.; Shapley, J. R.; Steinmetz, G. R.; Geoffroy, G. L. *Organometallics* **1982**, *1*, 214.