The Chemistry of Some Triosmium Alkylidene and Alkylidyne Cluster Complexes

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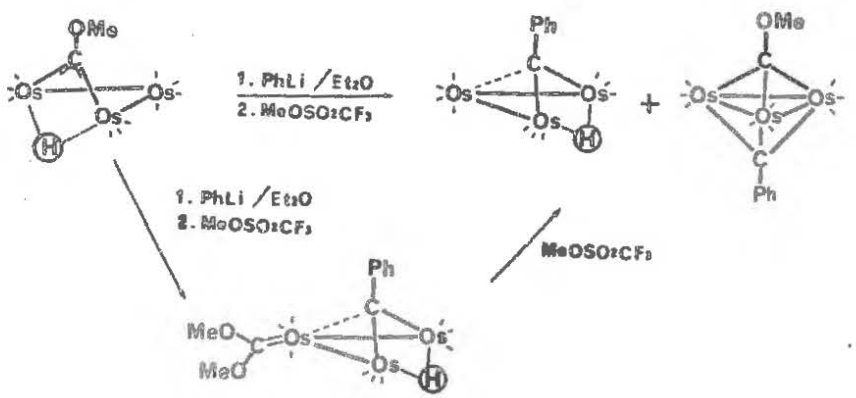
The chemistry of metal cluster complexes containing alkylidene ($=CR_2$) or alkylidyne ($\equiv CR$) ligands has been of interest for many years [1]. This interest has intensified due to the implication of surface-bound C_1 and C_2 units in some catalytic reaction mechanisms, such as alkyne (alkene) metathesis [2], alkyne (alkene) oligomerization [3], and Fischer-Tropsch synthesis [4].

Previous studies by Shapley and co-workers [5] established that sequential H^-/H^+ treatment of $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-COMe})$ affords $(\mu\text{-H})Os_3(CO)_{10}(\mu_3\text{-CH})$ via an alkylidene intermediate $[(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-CHOMe})^-]$. However, an analogous Ph^-/Me^+ treatment of $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-COMe})$, occurring at a carbonyl ligand, leads to formation of a mixed alkylidene-alkylidyne complex $(\mu\text{-H})Os_3(CO)_9(\eta^1\text{-}C(OMe)_2)(\mu_3\text{-CPh})$ [6]; furthermore, extended treatment of $(\mu\text{-H})Os_3(CO)_9(\eta^1\text{-}C(OMe)_2(\mu_3\text{-CPh})$ with $MeOSO_2CF_3$ gives the alkylidyne complexes, $(\mu\text{-H})Os_3(CO)_{10}(\mu_3\text{-CPh})$ [7] and $Os_3(CO)_9(\mu_3\text{-CPh})(\mu_3\text{-COMe})$ [8] (eq. 1). These compounds have been characterized by mass, IR, ^1H and ^{13}C NMR spectroscopies together with single-crystal X-ray diffraction analysis (by Churchill and coworkers).



(1)

Further studies of sequential Ph^-/Me^+ reactions with $(\mu\text{-H})Os_3(CO)_{10}(\mu_3\text{-CPh})$, $Os_3(CO)_9(\mu_3\text{-CPh})(\mu_3\text{-COMe})$, and $(\mu\text{-H})Os_3(CO)_9(\eta^1\text{-}C(OMe)_2)(\mu_3\text{-CPh})$ have been conducted. It appears that sequential Ph^-/Me^+ treatment is effective for the transformation of carbonyl ligands to alkylidene and alkylidyne moieties. Moreover, by repeating this two-step procedure, dialkylidyne and mixed alkylidene-alkylidyne complexes can be prepared. The overall predictability of this treatment, however, is low.

Several reactions of these compounds have been investigated, such as hydrogenation, pyrolysis, carbonylation, protonation, ligand substitution, and reactivity toward Lewis acids. The stereodynamics of fluxional cluster complexes have been studied by ^1H and ^{13}C NMR spectroscopy. The reactivity of alkylidyne and alkylidene ligands have been examined; examples include alkylidyne-alkylidyne coupling with $Os_3(CO)_9(\mu_3\text{-CPh})(\mu_3\text{-COMe})$, alkylidyne-carbonyl coupling with $(\mu\text{-H})Os_3(CO)_{10}(\mu_3\text{-CPh})$, alkylidyne-alkylidene coupling with $(\mu\text{-H})Os_3(CO)_9(\eta^1\text{-}C(OMe)_2(\mu_3\text{-CPh})$, alkylidyne-alkyne coupling with $(\mu\text{-H})Os_3(CO)_{10}(\mu_3\text{-CPh})$, and benzylidyne-tolyne interconversion with $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-CPh})$ and $(\mu\text{-H})_2Os_3(CO)_9(\mu_3,\eta^2\text{-}C_6H_3(CH_3))$.

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