

Alkyl, Alkylidene and Alkylidyne
Triosmium Chemistry

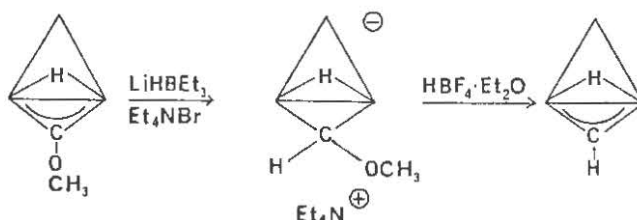
Michelle Cree-Uchiyama

Final Seminar

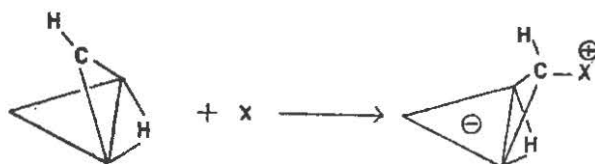
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Recent interest in the chemistry of polynuclear metal complexes results from proposals suggesting these clusters may serve as models for metal surfaces [1]. Cluster bound alkyl, alkylidene, and alkylidyne groups are of particular interest due to their implicated role in the hydrogenation of carbon monoxide and related processes catalyzed by metal surfaces [2].

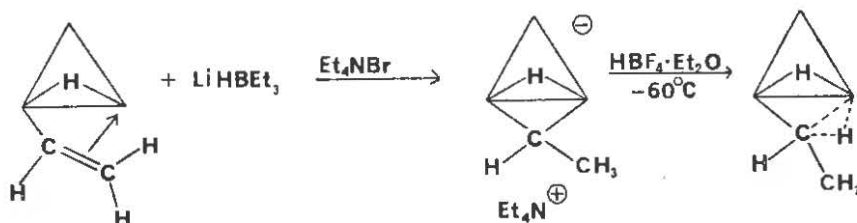
$\text{HOs}_3(\text{CO})_{10}\text{CH}$, a new complex with a triply bridging methylidyne has been prepared (eq. 1). In contrast with previous examples the methylidyne ligand in this complex interacts much more strongly with two of the metal centers than the third. $\text{HOs}_3(\text{CO})_{10}\text{CH}$ has been



characterized by an X-ray crystal structure by Churchill and Bueno [3]. ^{13}C NMR data for $\text{HOs}_3(\text{CO})_{10}\text{CH}$ in solution are fully consistent with the solid state structure. Bonding in the methylidyne complex may be regarded as two-electron donation from the formally saturated $\text{Os}(\text{CO})_4$ center to the electrophilic carbon atom of the bridging CH moiety. The facile reactions of $\text{HOs}_3(\text{CO})_{10}\text{CH}$ with various nucleophiles provide further evidence for the electrophilic nature of this methylidyne ligand.



Bridging alkyl derivatives of transition metal clusters are rare, yet their properties are potentially relevant to an understanding of Fischer-Tropsch and related processes involving C-H bond activation. Previously reported examples of μ -alkyl complexes have not included alkyl groups which contain β -hydrogens, consequently, the study of their reactivity has been limited [4]. We have prepared a series of triosmium alkyls containing both α and β hydrogens [5,6,7]. The synthesis of the simplest of these, the ethyl complex, is shown in equation 3.



The alkyl ligands contain α -C-H-Os three-center two-electron bonds. ^{13}C NMR spectra of the ethyl complex, $\text{HOs}_3(\text{CO})_{10}(\text{CH}_2\text{CH}_3)$, indicate the diastereotopic methylene hydrogens are equilibrated via a symmetric unsaturated intermediate, electronically analogous to $\text{H}_2\text{Os}_3(\text{CO})_{10}$. The alkyl ligands are subject to both α and β elimination processes, the latter of which predominates at higher temperature. The addition of nucleophiles induces reductive elimination of the alkane.

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