Organometallic Chemistry of Tungsten-Triosmium Cluster Compounds

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The chemistry of transition metal cluster compounds has emerged over the last decade as one of the most rapidly expanding areas of organometallic chemistry [1]. This is in part due to a prospect that discrete cluster molecules may mimic metal surfaces in the processes of chemisorption and catalysis. Currently, mixed metal cluster compounds are under intense scrutiny since they have a number of advantages over their homonuclear counterparts [2]. The present study involves the synthesis, structure, and reactivity of several new tungsten-triosmium (WO₃)₃ cluster compounds. The presence of a tungsten atom in the cluster framework imparts a considerably different reactivity pattern than that observed in triosmium chemistry.

Since the unsaturated osmium cluster H₂Os₃(CO)₁₀ and the "lightly stabilized" osmium complex Os₃(CO)₁₀(NCMe)₂ were reported, their reaction chemistry has been extensively examined. In particular, it has been shown that H₂Os₃(CO)₁₀ undergoes facile insertion reactions with many alkynes (RC=CR) to form alkenyl derivatives [3] (equation (1)), while Os₃(CO)₁₀(NCMe)₂ also reacts with alkynes to provide alkyne triosmium complexes [4] (equation (2)). Stone and coworkers have utilized the isolobal relationships between alkynes and metal alkylidyne complexes (Ln⁻CR⁻M⁻L') to prepare a series of mixed-metal μ-alkylidyne species [5] (equation (3)). The success of this idea has prompted a study of the two reactive triosmium clusters with a tungsten alkylidyne to form WO₃₃ cluster compounds.

\[ \text{H}_2\text{Os}_3(\text{CO})_{10} + \text{RC} \equiv \text{CR} \rightarrow \text{HOS}_3(\text{CO})_{10}(\mu-\eta^2-\text{CR}=\text{CHR}) \]  \hspace{1cm} (1)

\[ \text{Os}_3(\text{CO})_{10}(\text{NCMe})_2 + \text{RC} \equiv \text{CR} \rightarrow \text{Os}_3(\text{CO})_{10}(\mu_3-\eta^2-\text{C}_2\text{R}_2) \]  \hspace{1cm} (2)

\[ \text{M}'\text{L}_n + \text{L}_m\text{M} \equiv \text{CR} \rightarrow \text{L}_x\text{M}'(\mu-\text{CR}) \]  \hspace{1cm} (3)

In contrast to the reaction with alkynes, however, a remarkably facile Os-Os bond cleavage has been observed in the reaction of H₂Os₃(CO)₁₀ with Cp(CO)₂W≡CTol (Cp = η⁵-C₅H₅, Tol = η-C₆H₃Me), giving three products by three parallel pathways: CpWO₃₃(CO)₁₁(μ₃-η²-C(0)CH₂Tol) (1), Cp₂W₂Os(CO)₇(μ₃-η²-C₂Tol₂) (2), and CpWO₃₃(CO)₁₀(μ₃-C₄Tol)₂H (3) [6]. Interestingly, the reaction of Os₃(CO)₁₀(NCMe)₂ with Cp(CO)₂W≡CTol gave a major product, CpWO₃₃(CO)₁₁(μ₃-CTol) (4), in which the Os₃ skeleton remains intact.


