

Oxy-Ligands in Triosmium Carbonyl Cluster Compounds

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Oxy-ligand derivatives of $\text{Os}_3(\text{CO})_{12}$ represent an important and growing class of compounds. Most of these compounds are decacarbonyl species, for example $\text{HOs}_3(\text{CO})_{10}(\text{OSiEt}_3)$ [1] and $\text{HOs}_3(\text{CO})_{10}(\text{O}_2\text{CH})$ [2], and are prepared by the oxidative addition of ROH to $\text{Os}_3(\text{CO})_{12}$ (with loss of two CO ligands) or a "lightly stabilized" intermediate such as $\text{Os}_3(\text{CO})_{10}(\text{NCCH}_3)_2$ [2,3]. This class of clusters has proven to be of utility as molecular models for species chemisorbed to metal surfaces (e.g. formate on Cu or Ag) [4] or for clusters chemisorbed to oxide supports (e.g. " $\text{HOs}_3(\text{CO})_{10}$ " on alumina) [5]. In these decacarbonyl derivatives the oxy-ligands are bound to two osmium atoms. Until recently, no triosmium carbonyl cluster in which all three metal centers participate in ligand binding were known. The first such cluster reported was $\text{H}_2\text{Os}_3(\text{CO})_9(\text{O}_3\text{SO})$ (1) [6].

Compound 1 contains a sulfate ligand bound in a triply bridging tridentate fashion to a trimetal framework and has been structurally characterized [6]. It was prepared by reaction of $\text{H}_3\text{Os}_3(\text{CO})_9\text{CH}$ (2) with neat sulfuric acid. During the course of reaction, methane was evolved. A similar attempt at direct reaction of H_3PO_4 with 2 failed to yield any isolable compounds. However, Keiter, *et al.* [6], were able to prepare the hydrogen phosphate cluster $\text{H}_2\text{Os}_3(\text{CO})_9(\text{O}_3\text{POH})$ (3), analogous to 1, by an indirect method. This indirect method involved "dissolution" of 2 in neat $\text{F}_3\text{CSO}_3\text{H}$ and addition of H_3PO_4 to the resulting solution. After water quench, the cluster 3 was obtained in 82% yield.

We have extended the methodology used to prepare 3 to the syntheses of the phosphonate and arsonate clusters $\text{H}_2\text{Os}_3(\text{CO})_9(\text{O}_3\text{ER})$ (E = P, R = Ph (4), Me (5); E = As, R = Ph (6)). These clusters were characterized by a variety of techniques, including an x-ray diffraction study of 4. The diffraction study of 4 clearly indicated that the phenylphosphonate ligand was bound in a triply bridging tridentate fashion. Further, comparison of the principle ligand vibrations in solid and solution phases by IR established that the tridentate coordination mode exists in solution as well. Variable temperature ^{13}C NMR of 4 established hydride migration as a low barrier dynamic process in this class of molecules. Reactions of these clusters with nucleophiles (such as methoxide) resulted in adduct formation giving species such as $[\text{H}_2\text{Os}_3(\text{CO})_8(\text{C}(\text{O})\text{OMe})(\text{O}_3\text{SO})]^-$.

We were successful in isolating the cluster $\text{H}_2\text{Os}_3(\text{CO})_9(\text{O}_3\text{SCF}_3)_2$ (7) in high yield (76%) from the above triflic acid solutions generated by reaction of $\text{H}_3\text{Os}_3(\text{CO})_9\text{CH}$ with neat $\text{F}_3\text{CSO}_3\text{H}$, and used in preparing the clusters 2 - 6. Containing as it does the generally labile triflate ligand [7], the utility of 7 as synthetic precursor to other oxy-ligand triosmium clusters was explored. Reaction of 7 with carboxylic acids gave compounds resulting from substitution of one triflate moiety ($\text{H}_2\text{Os}_3(\text{CO})_9(\text{O}_2\text{CR})(\text{O}_3\text{SCF}_3)$, R = H, Me (8), CF_3) or two triflate moieties ($\text{H}_2\text{Os}_3(\text{CO})_9(\text{O}_2\text{CR})_2$, R = H (9), CF_3 (10)). The coordination modes of the carboxylate ligands in the mono-substituted clusters were established as bridging bidentate. The triflate ligands were unidentate. For the bis carboxylate compounds, one carboxylate ligand is bridging bidentate and the other unidentate. An x-ray diffraction study of 8 showed the acetate and triflate ligands in a "trans" axial configuration. Also prepared from 7 were the cluster cations $[\text{H}_2\text{Os}_3(\text{CO})_9(\text{NCR})_3]_+ (\text{O}_3\text{SCF}_3)_2$ (R = Me, Ph). The MeCN compound was studied by variable temperature ^1H NMR and π structure proposed.

Compound 8 was rather unreactive toward neutral two electron donors (e.g. THF, MeCN, PhCN). It did react with halide anions, but the only products which could be isolated arose from substitution of both the acetate and triflate ligands. Attempts to prepare from 8 a bis acetate complex analogous to 9 and 10 gave a mixture believed to contain the expected product, but only the cluster degradation product $\text{Os}_2(\text{CO})_6(\text{O}_2\text{CH}_3)_2$ could be isolated.

References

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