Oxy-ligand derivatives of Os₃(CO)₁₂ represent an important and growing class of compounds. Most of these compounds are decacarbonyl species, for example HOs₃(CO)₁₀(OSiEt₂) [1] and HOs₃(CO)₁₀(O₂CH) [2], and are prepared by the oxidative addition of ROH to Os₃(CO)₁₂ (with loss of two CO ligands) or a "lightly stabilized" intermediate such as Os₃(CO)₁₀(NCCH₃)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. "HOs₃(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 H₂Os₃(CO)₉(OC₆H₅) [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 H₃Os₃(CO)₉CH (2) with neat sulfuric acid. During the course of reaction, methane was evolved. A similar attempt at direct reaction of H₃PO₄ with 2 failed to yield any isolable compounds. However, Keiter, et al. [6], were able to prepare the hydrogen phosphate cluster H₂Os₃(CO)₉(O₃POH) (3), analogous to 1, by an indirect method. This indirect method involved "dissolution" of 2 in neat F₃CSO₂H and addition of H₃PO₄ 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 arsenate clusters H₂Os₃(CO)₉(O₃ER) (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 ¹³C 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 [H₂Os₃(CO)₈(C(O)OMe)(O₃SO)]⁻.

We were successful in isolating the cluster H₂Os₃(CO)₉(O₃SCF₃)₂ (7) in high yield (76%) from the above triflic acid solutions generated by reaction of H₂Os₃-(CO)₉CH with neat F₃CSO₂H, and used in preparing the clusters 2 - 6. Containing as it does the generally labile trflate ligand [7], the utility of 7 as a synthetic precursor to other oxy-ligand triosmium clusters was exploited. Reaction of 7 with carboxylic acids gave compounds resulting from substitution of one trflate moiety (H₂Os₃(CC)₉(O₂CR)(O₃SCF₃), R = H, Me (8), CF₃) or two trflate moieties (H₂Os₃-(CO)₉(O₂CR)₂, R = H⁺(9), CF₃ (10). The coordination modes of the carboxylate ligands in the mono-substituted clusters were established as bridging bidentate. The trflate 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 trflate ligands in a "trans" axial configuration. Also prepared from 7 were the cluster cations [H₂Os₃(CO)₉(NCR)]⁻(O₃SCF₃)₂ (R = Me, Ph). The MeCN compound was studied by variable temperature ¹H NMR and E 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 $\text{Os}_2(\text{CO})_6(\text{O}_2\text{CCH}_3)_2$ could be isolated.

References