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Significant effect of polyoxometalates on the molecular structures of phosphanegold cluster cations

Gold(I) cluster complexes have attracted much attention owing to their excellent catalytic activity in a broad range of organic reactions. We recently discovered that polyoxometalate (POM)-mediated clusterization of monomeric phosphanegold(I) complexes results in the formation of various intercluster compounds consisting of multinuclear phosphanegold(I) cluster cations and POM anions. This discovery was made during carboxylate elimination of [Au(*RS*-pyrrld)(PPh_3)] (*RS*-Hpyrrld = *RS*-2-pyrrolidone-5-carboxylic acid) in the presence of the free-acid form of the a-Keggin POM, H_3[a-$PW_{12}O_{40}$]·$7H_2O$. The formation of various phosphanegold(I) cluster cations depended strongly on the bulkiness, acidity, and charge density of the POMs and the substituent on the aryl groups of the phosphane ligands. The POM-mediated clusterization method provides effective synthetic routes to obtaining novel phosphanegold(I) cluster complexes by reactions between mononuclear [Au(carboxylate)(PR_3)] complexes and different POMs. In fact, the heptaphosphanegold(I) cluster has been isolated only by POM-mediated clusterization using [Au(*RS*-pyrrld)(PPh_3)] and H_3[a-$PW_{12}O_{40}$]·$7H_2O$.

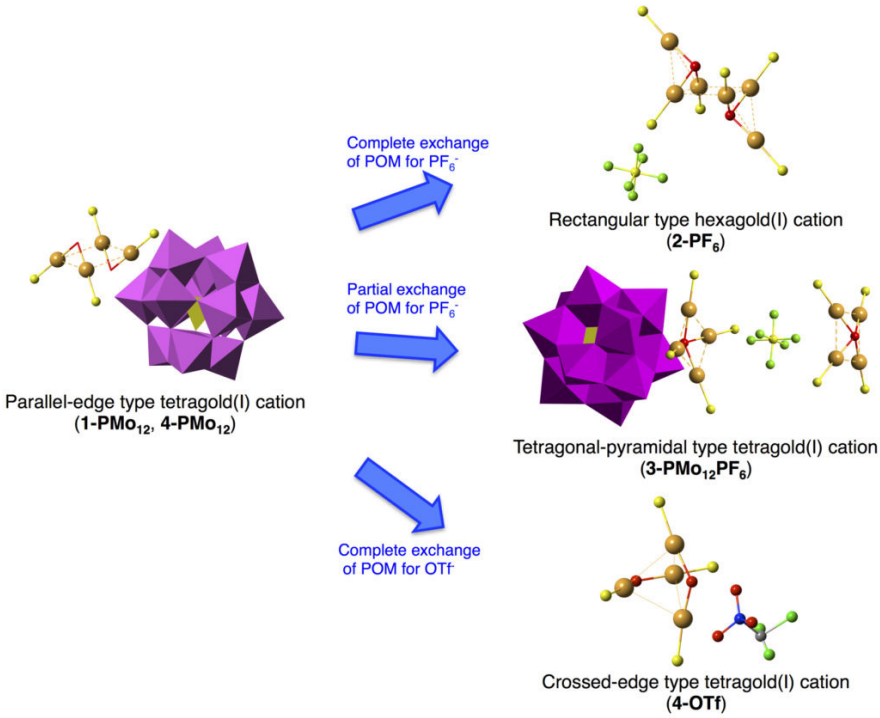

Fig. 1. Structures of gold(I) cluster complexes synthesized by POM-mediated clusterization and subsequent anion exchange. Phosphane ligands of gold(I) cluster complexes are omitted for clarity. Color code: Au, orange; C, gray; S, blue; F, light green; O, red; P, yellow; PO4, yellow polyhedron; MoO6, purple polyhedron.

To investigate the effect of counteranions on the molecular structures of phosphanegold(I) cluster complexes formed by POM-mediated clusterization, we prepared crystalline compounds of phosphanegold(I) cluster cations with and without POM anions and determined their molecular structures. For example,

tetraphosphanegold(I) cluster complexes with a parallel-edge arrangement, $[\{(AuL_x)_2(\mu\text{-}OH)\}_2]_3[\alpha\text{-}PMo_{12}O_{40}]_2\cdot 3EtOH$ (L_{Cl} = tris(4-chlorophenyl)phosphane, 1-PMo_{12}; L_F = tris(4- fluoro phenyl)phosphane, 4-PMo_{12}) were synthesized, and the POM anion of 1-PMo_{12} and 4-PMo_{12} was exchanged for smaller PF_6^- or trifluoromethanesulfonate (OTf^-) anions using an anion-exchange resin. Here, the abbreviations for the compounds are based on the combination of phosphanegold(I) cations and counteranions, where the composition of the phosphanegold(I) cations is indicated by a boldfaced number such as 1, 2, 3, and so on, and the Keggin POM $[PMo_{12}O_{40}]^{3-}$, PF_6^-, and OTf^- anions are abbreviated as PMo_{12}, PF_6, and OTf, respectively.

Exchanging the POM anion of 1-PMo_{12} for PF_6^- gave the fully exchanged compound ($[\{(AuL_{Cl})_3(\mu_3\text{-}O)\}_2](PF_6)_2\cdot 4CH_2Cl_2$; 2-$PF_6$) and the partially exchanged compound ($[\{(AuL_{Cl})_4(\mu_4\text{-}O)\}]_2[\alpha\text{-}PMo_{12}O_{40}]PF_6$; 3-$PMo_{12}PF_6$). The cation of 2-$PF_6$ was a dimeric form of the μ_3-O bridged pyramidal trigold(I) cations, i.e., the rectangular-type hexaphosphanegold(I) cluster complex. On the other hand, the partially exchanged compound 3-$PMo_{12}PF_6$ consisted of two tetraphosphanegold(I) cations, one POM anion, and one PF_6^- anion. The structure of cation of 3-$PMo_{12}PF_6$ consisted of the unusual tetragonal–pyramidal tetragold(I) cation with a μ_4-O atom occupying the apical position. The bonding mode can be described as an electron-deficient species with a bond order of 3/4 for four O–Au bonds and a μ_4-O ion with one lone pair. Interactions were observed between the tetraphosphanegold(I) cluster cation and the POM anion, which might be why the tetraphosphanegold(I) cation of 3-$PMo_{12}PF_6$ was first formed in the presence of both POM and PF_6^- anions.

The complex 4-PMo_{12} containing the tetraphosphanegold(I) cation with a parallel-edge arrangement was converted to the POM-free tetraphosphanegold(I) complex, i.e., $[\{(AuL_F)_2(\mu\text{-}OH)\}_2](OTf)_2\cdot 0.5Et_2O$ (4-OTf), by exchanging the POM anion for OTf^-. X-ray crystallography revealed that the parallel-edge arrangement of 4-PMo_{12} was converted to the crossed-edge arrangement of 4-OTf.

These results suggested that the counteranion plays an important role in determining the molecular structures of phosphanegold(I) cluster complexes and therefore that novel phosphanegold(I) cluster complexes can be synthesized by using various types of counteranions (single or mixed anions) as well as a combination of mononuclear [Au(carboxylate)(PR_3)] complexes and different POMs.

The POM-mediated clusterization and subsequent anion exchange presented in this research are applicable to other gold(I) complexes such as [Au(carboxylate)(NHC)] (NHC = N-heterocyclic carbene) in place of phosphane ligands. Synthesis of new gold(I) cluster complexes having unusual and novel structures and their catalytic behaviors will be studied as future work.

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