Creation of exposed surface on chemically modified gold superatom: selective removal of the ligand

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Ligand-protected gold clusters have attracted much attention as ideal platforms to investigate a structure-property correlation of superatoms which can be viewed as artificial elements at nanoscale.¹ Although numerous examples have been reported in the past decades, it is still a challenge to synthesize and determine the structure of ligand-protected Au clusters with exposed Au sites for catalytic usage. As a first step toward the rational development of partially exposed Au cluster catalysts, we herein report a method to removal of an alkynyl ligand from $[IrAu_{12}(dppe)_5(PA)_2]^+$ (1: dppe = $(Ph)_2PC_2H_4P(Ph)_2$; PA = PhC=C⁻) by the reaction with Brønsted acid.

Cluster 1 was synthesized by ligand exchange reaction from [IrAu₁₂(dppe)₅Cl₂]⁺ with

PA-H in the presence of base,^{2,3} and its structure and purity were determined by single-crystal Xray diffraction analysis, NMR spectroscopy, and electrospray ionization (ESI) mass spectrometry (Figure 1a). Then, slightly excess amount of trifuluoroacetic acid or tetrafluoroboric acid was added to the acetonitrile solution of **1**. As shown in Figure 1b, $[IrAu_{12}(dppe)_5(PA)]^{2+}$ (**2**) was formed by removal of one PA:

$$[IrAu_{12}(dppe)_{5}(PA)_{2}]^{+} \xrightarrow{+ H^{+}} [IrAu_{12}(dppe)_{5}(PA)]^{2+}$$

$$1 \qquad PA-H \qquad 2$$

The formation of an exposed surface site in 2 was tested by a trap experiment using 1adamantyl isocyanide (Adm-NC). [IrAu₁₂(dppe)₅(PA)(Adm-NC)]²⁺ (3)was observed as the dominant peak in the mass spectrum (Figure 1c), while the direct exchange reaction of 1 with Adm-NC partially proceeded. These results indicate that the PA of 1 was selectively removed by the reaction with Brønsted acid and one reactive surface site was formed. Further characterization and catalytic application of this exposed surface site are undergoing.



Figure 1. Positive mode ESI-mass spectra of (a) 1, (b) 2 and (c) 3. The crystal structure of 1 is shown in the inset of (a). Color code: Au; yellow, Ir; dark blue, P; orange and C; gray. Phenyl groups in dppe ligands and hydrogens are omitted for simplicity. The insets of (b) and (c) compare the experimental spectra and theoretical isotope patterns of 2 and 3.

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