

Previous experimental and theoretical studies on bare gold clusters in gas phase have suggested that hydrogen atom can mimic the gold atom. Motivated by this interesting finding, I investigated structures and reactivities of hydride ( $\text{H}^-$ )-doped Au superatoms by using mass spectrometry, single crystal X-ray crystallography and density functional theory (DFT) calculations. The platforms I chose for this study were phosphine-protected Au-based clusters  $[\text{MAu}_8(\text{PPh}_3)_8]^{2+}$  ( $\text{MAu}_8$ ;  $\text{M} = \text{Au}^+, \text{Pd}, \text{Pt}$ ), that can be viewed as oblate-shaped Au superatoms with a semi-closed electronic configuration of  $(1\text{S})^2(1\text{P})^4$ .

*In situ* electrospray ionization mass spectrometry (ESI-MS) demonstrated the formation of hydride adducts  $[\text{HMAu}_8(\text{PPh}_3)_8]^+$  ( $\text{HMAu}_8$ ;  $\text{M} = \text{Au}^+, \text{Pd}, \text{Pt}$ ) upon the mixing of the solutions of  $\text{NaBH}_4$  and  $\text{MAu}_8$ . *In situ* NMR revealed that the conversion to  $\text{HMAu}_8$  proceeded almost quantitatively and the  $\text{H}^-$  was bound to the central M atom in  $\text{HMAu}_8$ . DFT optimized structures of the corresponding models  $[\text{HAu}_9(\text{PMe}_3)_8]^{2+}$  and  $[\text{HAu}_9(\text{PMe}_3)_8]^{2+}$  exhibited a nearly spherical shape and had a closed electron configuration of  $(1\text{S})^2(1\text{P})^6$ . The formal charge states of both H and peripheral Au atoms were neutral, indicating that the H atom acts as a dopant in Au superatom and that  $\text{HMAu}_8$  can be viewed as a hydride-doped 8e superatom. This is the first demonstration that the Au-H analogy proposed for model Au clusters in gas phase can be applied to ligand-protected Au superatoms.

Inspired by the previous reports that hydrogens on the Pd colloidal particles can reduce other metal ions, I studied the chemical properties of  $\text{HMAu}_8$  toward core-growth reactions. Addition of Au(I) complex to the  $\text{HAu}_9$  solution selectively yielded the well-know magic Au clusters,  $[\text{Au}_{11}(\text{PPh}_3)_8\text{Cl}_2]^+$  with 8 valence electrons. *In situ* ESI-MS revealed that  $[\text{Au}_{11}(\text{PPh}_3)_8\text{Cl}_2]^+$  was formed by sequential addition of two AuCl units while releasing a proton ( $\text{H}^+$ ). In case of  $\text{HPdAu}_8$ , in contrast, the sequential growth proceeded without  $\text{H}^+$  release to yield novel hydride-containing  $[\text{HPdAu}_{10}(\text{PPh}_3)_8\text{Cl}_2]^+$  with a good yield. DFT calculation suggested that this growth reaction is initiated by a nucleophilic attack of  $\text{HMAu}_8$  to AuCl via interaction with the sterically-exposed 1P orbital. This nucleophilic addition can be used for the doping of other metals. Actually, new trimetallic alloy clusters  $[\text{HPdAg}_2\text{Au}_8(\text{PPh}_3)_8\text{Cl}_2]^+$  and  $[\text{HPdCu}_2\text{Au}_8(\text{PPh}_3)_8\text{Cl}_2]^+$  could be synthesized by the regioselective doping of two Ag(I)Cl and Cu(I)Cl complexes, respectively, to  $\text{HPdAu}_8$ . Moreover, the target electrophiles can be extended to Au(I)L complexes (L represent thiolate or alkynyls) for surface modification. A general formula of  $\text{MAu}_{24}(\text{ligand})_{18}$  having an icosahedral  $\text{M@Au}_{12}$  superatomic core could be synthesized selectively in a large scale (~hundreds mg).

In summary, I demonstrate for the first time that (1) H acts as a dopant in Au superatoms rather than an electron withdrawing ligand as known in Ag and Cu clusters and (2) H-doped superatoms  $\text{HMAu}_8$  are highly reactive toward a variety of organometallic complexes. This work provides not only a new efficient bottom-up synthetic routes of ligand-protected superatoms, but also an opportunity to establish the structures-properties correlations for these artificial elements in nanoscale.