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Hydride-Mediated Controlled Growth of a Bimetallic (Pd@Au₈)²⁺ Superatom to a Hydride-Doped (HPd@Au₁₀)³⁺ Superatom

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Structure and Properties of the Hydride-Containing Cluster Ion Pt(H)(PPh₃)(AuPPh₃)₇²⁺

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INTRODUCTION:

- Atomically precise synthesis of the ligand-protected metal clusters is the foundation of the research and has been mainly based on top-down approaches (e.g., size focusing via chemical etching) and high-resolution separation techniques.
- In contrast, precise synthesis by a bottom-up approach has been limited to a few examples due to the difficulty in controlling the kinetic balance between the fast clustering of the metal (0) atoms and the surface passivation by the ligands.
- Recently, a hydride doped gold cluster [HAu₉(PPh₃)₈]²⁺, was selectively converted to [Au₁₁(PPh₃)₈Cl₂]⁺ by the addition of two AuCl units.
- Hydride affects not only the chemical properties of the clusters toward the controlled growth but also the geometric and electronic structures of the clusters.

In this paper...

- They have focused on doping of H– into the oblate (Pd@Au₈)²⁺ superatomic core of [PdAu₈(PPh₃)₈]²⁺ having a coordinatively unsaturated Pd atom at the center. The structure was studied by nuclear magnetic resonance (NMR) techniques and density functional theory (DFT) calculations.
- [HPdAu₁₀(PPh₃)₈Cl₂]⁺ was formed by the sequential addition of AuCl units and the H dopant survived during the growth which was confirmed by the Single-crystal X-ray diffraction (SCXRD) analysis.

Experimental method:

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Synthesis of [PdAu_8(PPh_3)_8](NO_3)_2 (1):
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Au(NO<sub>3</sub>)(PPh<sub>3</sub>)

(1.56 g; 3.00 mmol) in + \frac{Pd(PPh_3)_4}{433 mg (Au:Pd = 8:1)} → Dark purple solution

80 ml CH<sub>2</sub>Cl<sub>2</sub> → Dark purple solution

\downarrow ethanolic solution of

NaBH4 (76 mg in 60 mL)

After 10 min,

[PdAu<sub>8</sub>(PPh<sub>3</sub>)<sub>8</sub>](NO<sub>3</sub>)<sub>2</sub>
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Synthesis of $[HPdAu_{10}(PPh_3)_8Cl_2](Cl, NO_3)$ (4):



Results and discussion:



Fig. 1 Positive-ion ESI-MS of (a) **1** and (b) the reaction products with NaBH4. Insets compare the experimental and theoretical isotope patterns. 1H NMR charts (400 MHz, C2D5OD-THF*d*8, 288 K) of (c) **1** and (d) the reaction products with NaBH4 in C2D5OD.



Fig. 2 (a) 31P{1H} NMR charts of **1** (top) and the product obtained by the addition of 0.1 M C2D5OD solution of NaBH4 (1 mol equiv) (bottom). (b) 1H NMR chart of the product obtained by the addition of 0.1 M C2D5OD solution of NaBH4 to **1** (top, same as Figure 1(d)) and 1H{31P} NMR chart of the corresponding sample (bottom).



Fig. 3 Geometric and electronic structures of (a) **1m** and (b) two isomers of **2m** obtained by DFT calculations. Color codes: yellow (Au); dark green (Pd); blue (P); red (H). Methyl groups are depicted as sticks.



Fig. 4 Time-resolved ESI-MS during the growth reaction of **2**. Mass peaks #1 and #2 are assigned to [HPdAu9(PPh3)8]2+(BH4–) and [PdAu9(PPh3)7Cl2]+, respectively.



Fig. 5 Positive-ion ESI-MS spectra of (a) a CH3CN solution of **4** and (b) a CD3CN solution of **4**. ESI-MS spectrum of (c) a CH3CN solution of **4'** synthesized by using NaBD4 in C2D5OD.



Fig. 6 X-ray structures (left) and the core structures (right) of (a) **4** and (b) [Au11(PPh3)8Cl2]+. Phenyl rings are depicted as gray sticks and hydrogen atoms are omitted for clarity. (c) Optimized structures of two isomers of **4**. Methyl groups are depicted as sticks.



Fig. 7 (a) Photograph of the crystals of **4**. (b) UV-vis spectra of **4** (red) and [Au11(PPh3)8Cl2]Cl. (c) 1H (red) and 1H{31P} (blue) NMR charts of **4**. Inset shows a magnified view of the hydride region. (d) 31P{1H} NMR chart of **4**.



Fig. 8 (a) Calculated energy diagrams and selected orbitals of AuCl and **2m-b**. (b) Optimized structures and the 1Pz orbitals of two isomers of **3**. Methyl groups are depicted as sticks. The color codes are the same as those in Figure 4.

Conclusions:

- They have elucidated the hydride-mediated growth of the oblate (Pd@Au₈)²⁺ superatom to a novel hydride-doped (HPd@Au₁₀)³⁺ superatom.
- SCXRD analysis and DFT calculations showed that the (HPd@Au₁₀)³⁺ superatom was significantly distorted due to the presence of an interstitial H atom.
- This study provides an atomically precise bottom-up synthesis of new Au-based superatoms.

