JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
COMMUNICATION
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Organogold Clusters Protected by Phenylacetylene

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S *Supporting Information*

ABSTRACT: A new class of monolayer-protected Au clusters with Au—C covalent bonds (organogold clusters) was synthesized by ligating phenylacetylene (PhC≡CH) to PVP-stabilized Au clusters. Matrix-assisted laser desorption ionization mass spectrometry revealed for the first time a series of stable compositions of the organogold ($Au:C_2Ph$) clusters.

Gold clusters protected by ligands, such as thiolates,[1] phosphines,[2] and amines,[3] have attracted great interest since they are promising materials for both fundamental research and applications. Among others, the structure, bonding, and stability of the thiolate-protected Au clusters are now well understood.[4] They have the potential to be applied in a wide range of areas, such as catalysis, biosensing, drug delivery, molecular electronics, and surface patterning.[5] However, for practical application, their robustness needs to be enhanced and their electronic properties need to be modulated by chemical modification. The latter requirement is especially important for molecular electronic applications, and researchers are currently searching for conductive Au nanoparticles/clusters with suitable stabilizers.[6]

Organogold nanoparticles/clusters stabilized by covalent bonds with a carbon atom of conjugated aromatic molecules are potential candidates for this purpose. Several groups have recently prepared Au, Pt, Ru, and Pd nanoparticles protected by ligands that are linked by metal—carbon bonds (organometallic nanoparticles).[7−13] Their synthesis involves attachment of aryl radicals and alkynyl anions to preformed or growing metal nanoparticles; the aryl radicals are produced spontaneously from or by reduction of diazonium salts in a similar way employed for grafting a metal surface,[14] and alkynyl anions are produced by abstraction of the alkynyl proton by a strong base under a strictly inert atmosphere.[8b,c] However, these methods produce organometallic nanoparticles that are larger than ~2 nm, and nonuniform multilayers may be produced due to radical-mediated processes.[14b,c]

We developed a new synthesis method of smaller organometallic clusters with a well-defined monolayer, which are expected to exhibit novel properties. The method is based on direct ligation of preformed small Au clusters by Au-catalyzed activation of C—H bonds in the ligands.[15] This approach allows us to perform the synthesis under ambient atmosphere in contrast to the previous methods which require a strictly inert atmosphere for the usage of hazardous chemical *n*-BuLi.[8b,c] In this study, we used phenylacetylene (PhC≡CH) as protecting molecules since the aryl group weakens the acetylenic C—H bond, making metal-catalyzed C—H bond breaking feasible.[16] The resulting phenylacetylide is expected to form a strong covalent bond with gold via the $p\pi-d\pi$ interaction. Such a bonding mode will enhance both the stability of Au clusters and the electronic coupling between the Au core and the organic functionality.

Scheme 1. Synthesis of Phenylacetylene Protected Au Clusters

We prepared organogold clusters by reacting phenylacetylene with Au clusters weakly stabilized by PVP (Au:PVP) (Scheme 1). Three samples of Au:PVP with different average diameters were prepared according to the reported methods.[17] Au:PVP clusters prepared by micromixers at 273 and 313 K are respectively referred to as **1a** and **1c**, and those prepared by a batch process at 273 K are referred to as **1b**.[18] Au clusters **1a**, **1b**, and **1c** have average diameters of 1.2 ± 0.2, 1.4 ± 0.2, and 1.8 ± 0.3 nm, respectively.[18] Matrix-assisted laser desorption ionization (MALDI) mass analysis and optical spectroscopy confirmed that the average diameter increases in the order **1a** < **1b** < **1c**.[18] An aqueous dispersion of Au:PVP was then mixed with a toluene solution of phenylacetylene (**2**) by either batch or microfluidic mixing at 333 K for 2 h. The water phase became colorless, whereas the toluene phase turned deep brown, indicating the efficient formation of $Au:C_2Ph$ clusters.[18] The $Au:C_2Ph$ clusters thus extracted in toluene were precipitated and washed repeatedly with methanol and were dried under vacuum to obtain a black powder.

Comparison of UV—vis spectra of $Au:C_2Ph$ and the corresponding Au:PVP precursors revealed that the $Au:C_2Ph$ yield decreased with increasing Au:PVP diameter.[18] This result indicates that ligation of **2** occurs only in smaller Au clusters. Although the origin and mechanism of this size-specific reaction are currently unclear, we conjecture that this reaction proceeds via π-complexation between **2** and Au clusters, as has been proposed for the formation of organo-Au(I) compounds.[16] The

Received: September 30, 2011
Published: November 15, 2011

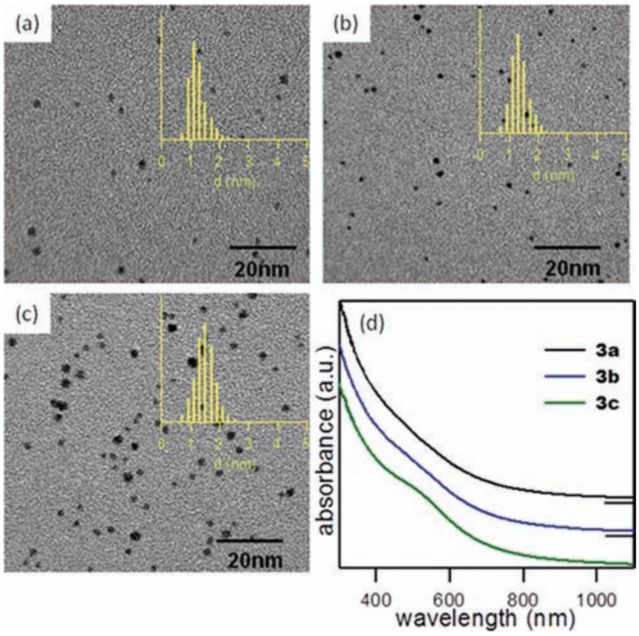

Figure 1. TEM images and particle size distributions of (a) **3a**, (b) **3b**, (c) **3c**, and (d) UV−vis spectra of **3a**−**3c**.

C−H bond of **2** is weakened by complexation with Au clusters, and a phenylacetylide is bound to Au clusters with simultaneous abstraction of acetylenic hydrogen. Formation of the C−Au bond is strongly suggested by the absence of the vibrational peak of acetylenic C−H in the Fourier-transformed infrared spectrum.[18] The acetylenic hydrogen of **2** may be abstracted by O_2 species coadsorbed on Au clusters, which has been proposed for the thiolation of Au:PVP.[19] However, this mechanism can be ruled out because the reaction proceeds even under anaerobic conditions. The Au:C_2Ph yields obtained using a micromixer were 20−30% higher than those of batch-prepared Au:C_2Ph.[18] This indicates that ligation proceeds more efficiently for microfluidic mixing than for batch mixing, probably because more homogeneous and rapid mixing of the two phases occurs in the former case. For further characterization, we used Au:C_2Ph (**3a, 3b**, and **3c**) prepared by the micromixer from **1a**, **1b**, and **1c**, respectively.

Figure 1a−c show TEM images and diameter distributions of Au:C_2Ph (**3a**−**3c**), respectively. Au:C_2Ph clusters (**3a**, **3b**, and **3c**) have average diameters of 1.3 ± 0.2, 1.4 ± 0.2, and 1.5 ± 0.4 nm, respectively. These diameters reflect those of the corresponding Au:PVP precursors. Figure 1d shows UV−vis spectra of Au:C_2Ph (**3a**−**3c**). Optical spectra have smooth profiles with a small surface plasmon band at ∼520 nm, which becomes more prominent with increasing diameter (i.e., **3a** < **3b** < **3c**). Powder X-ray diffraction and X-ray photoelectron spectroscopy confirmed the formation of Au(0) clusters.[18]

We further characterized Au:C_2Ph by MALDI−TOF mass spectrometry. Figure 2 shows representative mass spectra of **3a**−**3c** in the negative-ion mode recorded using low laser power to suppress fragmentation. Interestingly, the mass spectra contain a limited number of sharp peaks in the mass range 10−30 kDa, demonstrating that Au:C_2Ph with well-defined compositions are produced as stable species. The chemical compositions of these species were determined by comparing the mass spectra of Au clusters protected by $-C\equiv C-C_6H_5$ and $-C\equiv C-C_6H_4$-(*p*-CH_3). The numbers of ligands were determined from the mass difference between the corresponding clusters, and then the numbers of Au atoms were determined from the molecular weight of the clusters.[18] After careful analysis, the chemical compositions of the reproducible mass peaks were assigned to $Au_{43}L_{22}$, $Au_{46}L_{24}$, $Au_{52}L_{26}$, $Au_{54}L_{26}$, $Au_{59}L_{27}$, $Au_{71}L_{32}$, $Au_{90}L_{36}$, $Au_{94}L_{38}$, $Au_{101}L_{38}$, and $Au_{110}L_{40}$, where L represents the C_2Ph ligands.[18]

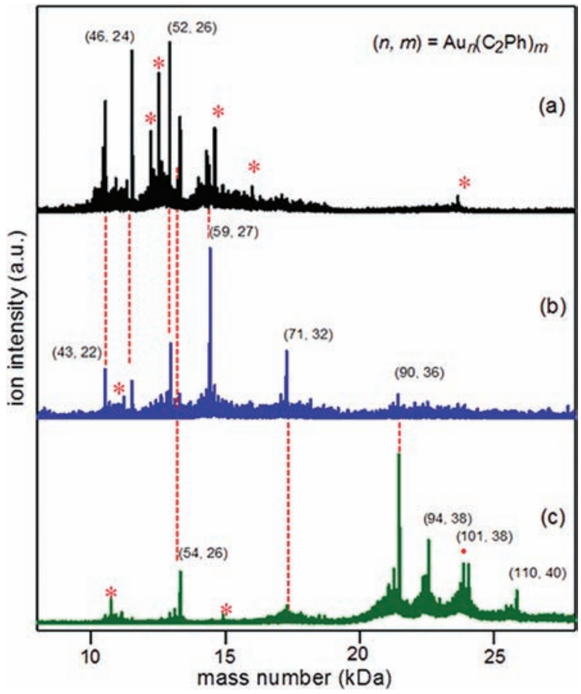

Figure 2. Negative-ion MALDI mass spectra of (a) **3a**, (b) **3b**, and (c) **3c**. Asterisks indicate peaks that were not reproducibly detected.

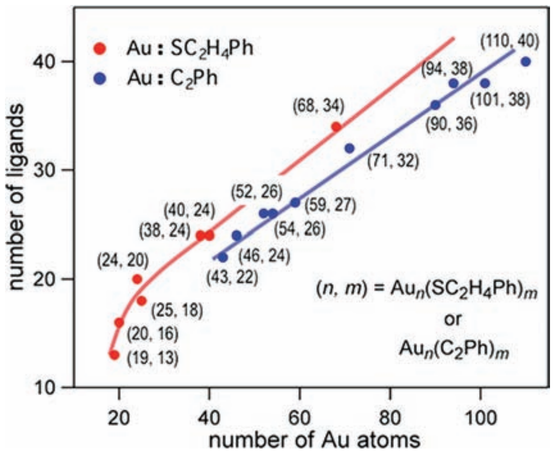

Figure 3. Plot of chemical compositions (number of ligands vs number of gold atoms) of Au:SC_2H_4Ph and Au:C_2Ph.

To clarify the structural properties of Au:C_2Ph, the compositions of Au:C_2Ph were compared with those of phenylethane thiolate-protected Au clusters (Au:SC_2H_4Ph) isolated so far.[20] Figure 3 shows a plot of the compositions of Au:SC_2H_4Ph and Au:C_2Ph as functions of the numbers of Au atoms and ligands. Au:C_2Ph clusters have smaller ligand-to-Au ratios than Au:SC_2H_4Ph. Since **2** and phenylethane thiolate have a similar bulkiness, this result suggests that the Au core of Au:C_2Ph has a smaller effective surface area than that of Au:SC_2H_4Ph. In Au:SR, it is well established that $-S(R)-[Au-S(R)-]_x$ oligomers are formed on the surface of the Au core;[20a,b,g] in other words, the Au atoms give rise to a rough surface. The smaller coverage for Au:C_2Ph implies that phenylacetylene forms a smooth interface with Au clusters, as crystallographically demonstrated for $[Au_{10}(C_6F_5)_4(PPh_3)_5]$.[21]

Selective formation of magic Au:C_2Ph clusters may be governed by their inherent stability and/or kinetics of the formation process. Thus, a high population of certain Au:C_2Ph clusters may reflect that in Au:PVP precursors. For example, the high abundance of $Au_{43}(C_2Ph)_{22}$ may be associated with that of Au_{43}:PVP.[17c,18] Alternatively, selective formation may be associated with the electronic and/or geometrical stability. However, the numbers of valence electrons for Au:C_2Ph calculated by the superatom formula[22] do not match with those required to close the electronic shell in a simple spherical potential. Further study is required to explain the origin of these magic compositions.

In summary, we synthesized a new class of organogold clusters protected by a monolayer of phenylacetylene by covalent Au−C bonds. The synthesis involves Au-catalyzed C−H bond breaking of the phenylacetylene. We also identified chemical compositions of a series of stable Au:C_2Ph clusters by nondestructive MALDI mass analysis.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Details of synthesis and characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

This research was financially supported by Funding Program for Next Generation World-Leading Researchers (NEXT Program) (GR-003). We thank Profs. M. Sawamura (Hokkaido University), H. Häkkinen (University of Jyväskylä), and T. Wakabayashi (Kinki University) for their valuable comments.

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