

## Communication

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# Bidentate Phosphine–Assisted Synthesis of An All–Alkynyl– Protected Ag<sub>74</sub> Nanocluster

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Supporting Information Placeholder

**ABSTRACT:** Determining the total structure of metal nanoparticles is vital to understand their properties. In this work, the first all alkynyl protected Ag nanocluster,  $Ag_{74}(C=CPh)_{44}$ , was synthesized and structurally characterized by single crystal diffraction. Ag atoms are arranged in a  $Ag_4@Ag_{22}@Ag_{48}$ three shell structure and all 44 phenylethynyl ligands coordinated with Ag in a  $\mu_3$  mode. In spite of being absent in nanocluster, <sup>31</sup>P NMR study reveals that bidentate phosphine firstly reacts with Ag(1) to form a dinuclear complex, from which Ag atoms are then released to phenylethynyl ligands. This phosphine mediated strategy may find general application in synthesis of alkynyl protected Ag nanoclusters.

To fundamentally understand the nature and properties of metal nanoparticles, determining their total structures including metal-ligand interface is of paramount significance.<sup>1-3</sup> However, to realize such a goal is a daunting task even for the state-of-the-art transmission electron microscope (TEM) technology, which cannot directly image the stabilizers (usually organic) or the interfacial bonding. Fortunately, the past several years have witnessed significant progress in isolation of atomically precise metal nanoclusters as single crystals for X-ray crystallography.<sup>4</sup> One prominent example is the total structural determination of Au<sub>102</sub>(SR)<sub>44</sub> (SR=SPh-*p*-COOH), in which a fascinating "RS-Au-SR" staple surface bonding motif was revealed.<sup>5</sup> A family of atomically precise Au nanoclusters has since been discovered, <sup>6-8</sup> while the number of Ag nanoclusters is relatively small.<sup>9-14</sup>

Beyond the conventional thiolate and phosphine ligands, alkynyl-protected nanoclusters have begun to draw attention only very recently. Their structural features were exemplified in a series of Au<sub>8</sub>,<sup>15</sup> Au<sub>19</sub>,<sup>16</sup> Au<sub>23</sub>,<sup>17</sup> Au<sub>24</sub>,<sup>18</sup> and intermetallic Au<sub>7</sub>Ag<sub>8</sub>,<sup>19</sup> Au<sub>24</sub>Ag<sub>20</sub>,<sup>20</sup> Au<sub>34</sub>Ag<sub>28</sub>,<sup>21</sup> Au<sub>80</sub>Ag<sub>30</sub>,<sup>22</sup> nanoclusters. They exhibited interesting Au-alkynyl staple motifs, resembling that of thiolate protected Au nanoclusters. However, what is the bonding motif of alkynyl ligands on Ag nanoparticle remains elusive. This is actually highly unexpected, since alkynyl ligands are of strong affinity toward Ag and are versatile in coordination abilities (in both  $\sigma$  and  $\pi$  modes).<sup>23-26</sup> These features have already inspired the emergence of a large variety of Ag(I)-alkynyl structures ranging from simple complex, multinuclear clusters to supramolecular assemblies in the last decades.<sup>24-26</sup> This leaves how to access alkynyl-protected Ag(o) nanocluster an outstanding puzzle to be solved.

Herein, we propose a phosphine mediated approach for synthesis of the first all alkynyl-protected  $Ag_{74}(C=CPh)_{44}$  nanocluster ( $Ag_{74}$  for short). Its structural features including Ag-ligand interfacial bonding will be revealed in detail. Especially, the role of phosphine ligand during synthesis will be fully unraveled by <sup>31</sup>P NMR.



Figure 1. The overall structure of Ag<sub>74</sub>(C≡CPh)<sub>44</sub>.

The preparation of Ag74 involves reduction of Ag(I) in the presence of phenylacetylene (denoted as **PA**) and a bidentate phosphine. Typically, AgNO<sub>3</sub> was dissolved in ethanol before **PA** and dppp (1,3-Bis(diphenylphosphino)propane) were introduced. A fresh NaBH<sub>4</sub> solution was then added. The reaction was aged for 12 h during which the color gradually changed from pale-yellow to brown-red (supporting information). A black block crystal was obtained by diffusing hexane and ether into CH<sub>2</sub>Cl<sub>2</sub> containing **Ag74** (Figure S1).

Single crystal analysis revealed that  $Ag_{74}$  is a 1.2 nm Ag nanoparticle peripherally protected by a monolayer com-

posed of 44 PAs (Figure 1). It crystallized in R-3 space group (Figure S2). The metal core includes 74 Ag atoms that are arranged into a three-shell Russian doll architecture, i.e., Ag<sub>4</sub>@Ag<sub>22</sub>@Ag<sub>48</sub> (Figure 2a). Its anatomy is illustrated in Figure 2. The first inner shell is a Ag<sub>4</sub> tetrahedron (Figure 2b) which are surrounded by the second Ag<sub>22</sub> shell. A combination of the inner two shells can be viewed as a fusion of four centered Ag<sub>13</sub> icosahedrons by sharing the Ag<sub>4</sub> tetrahedron. Each Ag atom of Ag<sub>4</sub> is located at the center of one icosahedron (Figure 2c). The outermost shell consists of 48 Ag atoms which are enclosed into 12 pentagons and 56 triangles (Figure 2d). Every three pentagons (in orange) form a triad through an edge-sharing triangle (in green, Type A triangle). There are four triads that are tetrahedrally arranged on the Ag48 shell. The space between them is filled with the rest 52 triangles, which, for simplicity, are divided into another two categories. One is a super triangle composed of four triangles (Figure 2d, blue, Type B), and the other one is a saddleshaped subunit made up of six triangles (yellow, Type C). There are four super triangles and six saddles respectively. The average Ag-Ag bond length between inner shell 1 and shell 2 is 2.802 Å, close to that in bulk. Under the influence of peripheral ligands, the Ag-Ag bonds between shell 2 and 3 were significantly elongated to 2.980 Å.



**Figure 2.** The structure anatomy of  $Ag_{74}(C \equiv Ph)_{44}$ . (a)  $Ag_{74}$  metal core, (b)  $Ag_4$  shell. (c)  $Ag_4@Ag_{22}$  shells, the brown polyhedron indicated one of the four centered icosahedrons. (d)  $Ag_{48}$  shell. Color lables: orange, pentagon; green, Type **A** triangle; blue, Type **B**; yellow, Type **C** (e) The distribution of **PA** ligands on **Ag74** surface. The grey polyhedron is  $Ag_{22}$  shell. (f) An illustration of bonding motif of **PA** with surface Ag atoms.

The distribution of peripheral ligands is closely dependent on the arrangement of surface Ag atoms. A dozen **PA** ligands penetrate through twelve pentagons and bond to surface and

subsurface simultaneously (Figure 2e and S<sub>3</sub>). Therefore, there are totally twelve Ag atoms from Ag22 shell coordinating with **PA** through  $\sigma$  bonds. In addition, every Type **A** triangle is capped by a PA. For each Type B super triangle, a PA only coordinates with the centered triangle. For each Type C saddle, there are four PA ligands capping the four corner triangles (Figure S<sub>3</sub>). Altogether, there are 44 PA ligands forming a protective monolayer. On the other hand, the binding motif of PA on Ag74 seems dull. All 44 PA ligands employ a  $\mu_3$ -bridging mode (Figure 2f), with the only difference being the bond type ( $\sigma$  or  $\pi$ ). This sharply contrasts with the vivid coordination patterns in Ag(I) alkynyl complexes.<sup>26</sup> Also, the V-shaped PhC $\Xi$ -Au-C $\Xi$ (Ph)-Au-C $\Xi$ Ph or L-shaped PhC **₹**-Au-C **₹**Ph staple motifs in alkynyl stabilized Au nanoclusters was not observed in Ag74 either.<sup>16,18</sup> The results indicated that alkynyl does not necessarily take on the same coordination mode for all coinage metal nanoclusters. We did not observe the counterion by X-ray crystallography, possibly because the anions are not locked into place in the lattice. However, the electrospray ionization mass spectrometry (ESI-MS) showed a single peak corresponding to a molecular ion  $[Ag_{74}(C=CPh)_{44}]^{2+}$  (Figure S4). FT-IR of Ag<sub>74</sub> single crystal displayed a stretching absorption of NO<sub>3</sub><sup>-</sup> (Figure S5). The presence of NO<sub>3</sub><sup>-</sup> was further confirmed by ion chromatography (Figure S6). Thus, the electric neutrality was likely balanced by  $NO_3$ . Furthermore, Ag<sub>74</sub> shows two absorption peaks at 245 and 514 nm respectively. And stimulated by a 296 nm light, Ag<sub>74</sub> exhibited two sharp emission bands at 572 and 620 nm (Figure S7). These results are similar with that in references.<sup>4</sup>



**Figure 3.** Trace of phosphine ligands with <sup>31</sup>P NMR in CDCl<sub>3</sub>. (a) dppp. (b) Ag+dppp+**PA**. (c) Ag+dppp. Reaction for 2 hours (d) and 12 hours (e) after adding NaBH<sub>4</sub>.

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Our repeated attempts to stabilize Ag nanoclusters solely by **PA** proved to be futile, flocculent precipitate was always seen upon reduction. In the presence of phosphine, however, a gradual color change from pale-yellow to brown-red was observed during hours. The necessity of phosphine ligand in the synthesis and its absence on Ag74 surface proposed a question of particular interest: what is the role of it? <sup>31</sup>P NMR was used to trace its evolution. As shown in Figure 3a, dppp dissolved in CDCl<sub>2</sub> showed one peak at -17.61 ppm, representing the "free" bidentate phosphine.<sup>28</sup> The mixture formed after introduction of PA and dppp into AgNO<sub>3</sub> solution gave a distinct <sup>31</sup>P singlet at 8.44 ppm (Figure 3b). The change of the chemical environment is most likely due to the coordination of phosphine with Ag. To probe whether PA participates in the coordination, the same mixture but without PA was subjected to NMR test and a same signal was detected (Figure 3c). The possibility that the signal represents a Ag-dppp complex in both cases stimulated us to isolate it. And two same single crystals from Ag+dppp and Ag+dppp+PA solutions were successfully obtained, which turned out to be a known dinuclear Ag(I)complex, Bis-u-[1,3bis(diphenylphosphino)propane]-dinitratodisilver(I) (Figure 3c and S8).<sup>29</sup> Redissolving the crystals for <sup>31</sup>P NMR test confirmed the signal at 8.44 ppm originated from this complex. Furthermore, in the first two hours upon addition of NaBH<sub>4</sub>, an evident peak at 32.25 ppm revealed itself (Figure 3d). After 12 hours, it became the only phosphorus species in solution (Figure 3e). Considering the signal is at low field, one might suggest it is bonded with electron-withdrawing group, such as oxygen. In order to verify this, we synthesized oxide of dppp following a reported procedure.<sup>30</sup> A comparison of its <sup>31</sup>P NMR ( $\delta$ =32.21 ppm) with that in Figure 3e implies dppp ends up as dioxide. Thus, dppp functions more like a reservoir of Ag. Before adding NaBH<sub>4</sub>, it binds Ag in the form of dinuclear complex. During reduction, Ag atoms were gradually given away, while dppp was converted to oxide. Also of note, we obtained the same crystals of Ag74 by using either dppe (1,2-Bis-(diphenylphosphino)ethane) or dppb (1,4-Bis-(diphenylphosphino)butane) as auxiliary ligands, indicating this method might be general for bidentate phosphines.

**Ag74** is fairly stable. The as-prepared colloidal solution was stored at ambient conditions for at least ten days without deterioration (Figure S9). Also, immobilization of **Ag74** na-noparticles on activated carbon was realized by simply adding its solution into a dispersion of the support (Figure S10). As Figure S11 shows, monodispersed Ag nanoparticles with size of 1 nm were smoothly immobilized on the support. It is believed that hydrophobic **PA** surface ligands enhanced the interaction of the clusters with the support. These features should facilitate the applications of **Ag74** in catalysis in future.<sup>31</sup>

In conclusion, our finding here suggests that the ligands introduced in the synthesis of metal nanoclusters may play very different roles. Although bidentate phosphine did not directly involved in the protection of **Ag74**, it slowed down the reduction rate of Ag(I) by coordinating with and then releasing it. The strategy gave rise to an unprecedented all alkynyl protected Ag nanocluster. It is hoped this approach will pave the way for the synthesis of more alkynyl protected Ag nanoclusters.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on theACSPublicationswebsite.

Experimental details, photos, TEM images and crystallographic data (PDF) Detailed crystallographic structure and data (CIF)

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#### Notes

The authors declare no competing financial interests.

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