Alkynyl- and phosphine-ligated quaternary Au$_2$Ag$_2$ clusters featuring an Alkynyl-AuAg motif for multicomponent coupling

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The coordination motif of alkynyl with a metal atom is versatile and plays a pivotal role in tailoring the kernel configuration of the atomically precise metal nanoclusters. In this study, we synthesized a new mono-valent Au(I)$_2$Ag(I)$_2$(C$_6$H$_5$NO)$_4$(Ph$_3$P)$_2$ alloy cluster with a very high yield of >90%, which is well characterized by a serial of technologies, e.g. UV-vis, X-ray single crystal diffraction (SCXRD) and FT-IR. The SCXRD analysis shows the alloy cluster is composed of a quadrangular Au$_2$Ag$_2$ kernel protected by four alkynyl and two phosphine ligands. Intriguingly, a new divergent alkyne-metal coordination model is revealed in this cluster, the alkynyl ligands selectively bind to Au and Ag atoms via $\sigma$- and $\pi$-bond configurations and adopt a VI-shaped alkynyl-M motif. It is distinct from the convergent motif observed in big clusters featuring an IV- or V-shaped alkynyl-M motif due to the steric effect. Finally, the titanium oxide-supported Au$_2$Ag$_2$ cluster catalysts show good catalytic performance in the multicomponent coupling reaction of alkynes, aldehydes and amines.

Introduction

Metal nanoclusters protected by monolayer organic ligands have drawn increasing interest for their unique structures and properties which differ from those of metal atoms and bulk metal.1-14 Recently, it has been reported that nanoclusters show great potential application in fundamental studies: photoluminescence, bio-imaging, medicine and catalysis.15-19 But revealing their structure is not always possible in this field. With the developments in nanotechnology, some big molecule-like metal nanoclusters having different core structures and sizes have been determined by X-ray single crystal diffraction.19-23 For the application of newly discovered materials, there is no doubt that the insight into their nanostructure at the atomic level is helpful for the understanding of the relationship between structures and properties, which is an indispensable step for exploring the application of these nanomaterials.

Generally, the shapes, sizes and properties of metal nanoclusters will be affected deeply by the protecting ligands on the outmost surface, which not only enhances the stability against aggregation, but generates significant interfaces related to optical, catalytic, biological and sensing applications.15-19 To date, five types of ligands have been used as protecting ligands for the atomically precise metal nanoclusters, including thiolate, phosphine, halogen, alkynyl and carbene; the former three ligands are extensively studied for many years, and alkynyl and carbene ligands are used as an emerging ligands.20-24 Due to their special and different coordination models, the co-present of two or three of them is more efficient for the stability of nanoclusters. In details, thiolate may take a $\mu_2$-$\eta^1$-$\eta^1$ model coordinate with two metal atoms on the surface of core forming staple motifs.17 Carbene and phosphine take a $\mu_1$ coordination model via $\sigma$-bonds.25,26 A halide could coordinate with four metal atoms at most. The situation of alkynyl is very complex for the presence of $\pi$ electrons which will be the focus of present work. What’s more, in the alkynyl protected nanoclusters, the metal species in core will affect the coordination model in return.15 There are some possible coordination motifs in theory shown in Scheme 1. Far as we know, I- to V-shape occurred in homogeneous and heterogeneous clusters have been reported by Tsukuda and Wang successively.27,28 The VI-shape different from the five convergent motifs is a divergent motif which is not good for the formation of zero-dimension structures. Therefore, whether it is possible for the existence of motif VI in clusters still remained unknown yet.

Herein, we report a quaternary clusters Au$_4$Ag$_2$(L)$_4$(PPh$_3$)$_2$ (where L represents 2-(prop-2-ynyloxy)benzonitrile, short as Au$_4$Ag$_2$L, hereafter) ligated by alkynelate and phosphine ligands. The structure of the alloy cluster was revealed by X-ray single crystal diffraction analysis. The small Au$_4$Ag$_2$L clusters adopt a VI alkynelate motif, and it is constructed by two parallel L–(AgPPh$_3$)$_2$–Au–(AgPPPh$_3$)–L motif by sharing the silver atoms. The Au$_4$Ag$_2$L cluster, supported onto TiO$_2$, shows good catalytic performance in...
the multicomponent coupling reaction of alkynes, aldehydes and amines.

**Experimental**

**Chemicals and method**

All chemicals, including solvents, were commercially available as reagent grade and used as received without further purification. Me$_2$StensorCl (98%), AgBF$_4$ (99%), NaBH$_4$ (99%) 2-hydroxy- benzonitrile and 3-bromoprop-1-yne were purchased from Adamas-beta®. 2-(Prop-2-ynyloxy)benzonitrile was synthesized in our lab according to reported method. All chemicals, including solvents, were commercially available as reagent grade and used as received without further purification. Me$_2$StensorCl (98%), AgBF$_4$ (99%), NaBH$_4$ (99%) 2-hydroxy- benzonitrile and 3-bromoprop-1-yne were purchased from Adamas-beta®. 2-(Prop-2-ynyloxy)benzonitrile was synthesized in our lab according to reported method. Typical procedure for the multicomponent coupling reaction of alkynes, aldehydes and amines.

**Synthesis of Au$_2$Ag$_2$(L)$_4$(Ph$_3$P)$_2$ clusters**

The synthesis method of the Au$_2$Ag$_2$ clusters was designed according to a bottom-up strategy. L-Au of 20 mg and L-Ag of 20 mg were mixed in a mixture solution of 4 mL dichloromethane and methanol (v/v = 1 : 1) under rapid stirring for ~30 min, giving a yellow suspension. Ph$_3$P of 10 mg was then added slowly. Notably, the addition of phosphine ligands can largely improve the solubility of the alkynyl-Ag/Au complexes via a reaction (alkynyl-Ag/Au + PPh$_3$ → alkynyl-Ag(Au-PPh$_3$)) in the dichloromethane and methanol solutions, and the capped phosphine ligands on surface of metal clusters can facilitate crystallization. After ~24 h, a brown mixture was obtained. The solid was then removed by filtration, and the filtrate was diffused by ether in dark. A high yield of over 90%, based on the consumption of Me$_2$S tensorCl, is achieved. After two weeks, the yellow block crystals of Au$_2$Ag$_2$ cluster was obtained. IR (cm$^{-1}$): 2230 (vs., C≡N), 2122 (vw, C≡C). 1646 (s, H\_Ar).

**X-ray crystallographic analysis**

Data reduction, cell refinement and experimental absorption correction were performed with the software package of CrystalisPro. The structures were solved by intrinsic phasing correction were performed with the so...
metal clusters/oxide (100 mg), and 5 mL water were added to a 10 mL vial. The mixture was stirred under N₂ atmosphere at 80 °C for 16 h as indicated in Table 2. The catalysts were separated and collected by centrifugation, washed with water and EtOAc to remove salts and organic compounds, respectively, and dried under vacuum. The products were identified by \(^1\)H NMR using the CDCl₃ as solvent.

### Results and discussion

#### Synthesis of \( \text{Au}_2\text{Ag}_2 \) clusters

The alkynyl protected \( \text{Au}^1\text{Ag}^4 \) alloy nanoclusters were prepared by the simply self-assembly of alkynyl-Au\(^1\) and alkynyl-Ag\(^4\) complexes in the presence of phosphine in a dichloromethane and methanol solution. The prepared clusters only gave one optical peak at 326 nm (Fig. 1), which might be caused by the ligand–metal charge transformation (LMCT)\(^{13,14}\) assigned to the adsorption of the M–PPh₃ groups (where, M = Au or Ag). Further, the structures of \( \text{Au}_2\text{Ag}_2 \) cluster are determined by X-ray single-crystal diffraction, as shown in Fig. 2a. This small alloy cluster is crystallized in a triclinic system with a \( P\overline{1} \) group. SCXRD suggests that this cluster is composed by 2 Au atoms, 2 Ag atoms, 2 Ph\(_3\)P ligands and 4 L ligands. Intriguingly, the L ligands are coordinated with gold and silver atoms in an IV type (Scheme 1), and the phosphine ligands only bind with the silver atoms. It worthy to note that the preparation of the homologous \( \text{Au}^4\text{Ag}^1 \) is unsuccessful under the similar synthetic conditions. Thus, most part of Ag is selectively bind to Au and Ag atoms through \( \sigma \)-bonds, and \( \pi \)-bonds (more details are listed in Table 1). A pair of L ligands from different side of the place constructed by \( \text{Au}_2\text{Ag}_2 \) core coordinated with same Au atom via \( \sigma \)-bond (1.992(8) Å in average) to give an L–Au–L unit. Two L–Au–L units further linked by two Ag atoms in parallel forming a new plane via \( \pi \)-bonds which is ~2.624(6) Å, furnishing a dihedral angle of 35.547(9)° with \( \text{Au}_2\text{Ag}_2 \) core plane. Of note, the Ag atoms interact with L ligands via \( \sigma \)-bond give rise to two sides (VI-mode in Scheme 1), rather than one side (V-mode). This is different from the reported big metal clusters, which is caused by the steric effects of the bulky ligands (e.g. PPh\(_3\), –CC–A) on the surface of the metal clusters.\(^{15}\) In short, the alkynyl ligands selectively bind to Au and Ag atoms through \( \sigma \)- and \( \pi \)-bond, respectively, which may be the reason why the homologous \( \text{Au}^4\text{Ag}^1 \) clusters cannot be prepared under the similar synthetic conditions. Thus, most part of Ag

#### Crystal structure of \( \text{Au}_2\text{Ag}_2 \) clusters

The screening of the \( \text{Au}_2\text{Ag}_2 \) clusters is depicted in the Table 1. Interestingly, the two gold atoms and two silver atoms are located in a plane to give a parallelogram. In details, the two Au atoms interact with another two Ag atoms in the same plane via strong the Au–Ag bonds (length of 2.957(2) Å to 3.112(4) Å), forming a parallelogram where the Au and Ag atoms are arranged right on the diagonal, respectively (Fig. 2b). Of note, the distance of two Au atoms is 3.648 Å, which is much longer than the Au–Au bond (e.g. <2.8 Å).\(^{4,13}\) The angles constructed by

#### Table 1

| Entry | Lengths and angle | Average | Scope |
|-------|-------------------|---------|-------|
| 1     | Au–Au             | 3.648 Å | —     |
| 2     | Au–Ag             | 3.006 Å | 2.957–3.112 Å |
| 3     | Au–C₇             | 1.984 Å | 1.942–2.023 Å |
| 4     | Ag–C₇             | 2.386 Å | 2.337–2.438 Å |
| 5     | Ag–P              | 2.418 Å | 2.426 & 2.410 Å |
| 6     | Au–Ag–Au          | 73.876° | —     |
| 7     | Ag–Au–Ag          | 106.125° | —     |

Fig. 1 UV-vis spectrum of the prepared \( \text{Au}_2\text{Ag}_2(L)_4(\text{Ph}_3\text{P})_2 \) clusters (dissolved in a CH\(_2\)Cl\(_2\)/methanol solution).

Fig. 2 (a) The full structure of \( \text{Au}_2\text{Ag}_2(L)_4(\text{Ph}_3\text{P})_2 \) with 30% probably ellipsoids. (b) The core structure and coordination model in \( \text{Au}_2\text{Ag}_2 \) clusters. Color code: Au, gold; Ag, dark blue; P, pink; O, red; N, blue; C, grey. H atoms are omitted for clarity.
atoms are bare, which is a good chance for the coordination of \(\text{Ph}_3\text{P}\). And the \(\text{PPPh}_3\) ligand is very smart to catch this chance. Two \(\text{Ph}_3\text{P}\) ligands coordinate through \(\text{P} \cdots \text{Ag}\) bonds (2.418(9) Å) with the half-bare Ag atoms taking a typical top model. The presence of \(\text{Ph}_3\text{P}\) is very important for the formation of this cluster to restrict its size in space.

In each cell of crystal, there are about \(4 \times (2 \times 1/1 + 8 \times 1/8 + 4 \times 1/4)\) clusters contained, two in the centre of the cell \((2 \times 1 = 2)\) clusters, eight on the vertexes \((8 \times 1/8 = 1)\) cluster and four at the centre of edges \((4 \times 1/4 = 1)\) cluster, respectively, as shown in Fig. 3a. The two clusters in the centre of cell interact with each other through intermolecular force including \(\text{C} \cdots \text{C} \approx 3.3\) Å van der Waals’ force, \(\text{N} \cdots \text{Hphenyl}\) hydrogen bonds \((2.738\) Å) and unique \(\text{H} \cdots \text{πalkynyl} \approx 2.822\) Å interactions for which the special arrangement of \(\text{L}\) ligands in clusters should be responsible (Fig. 3b). The two clusters in cell further interact with outside cluster molecular through \(\text{N} \cdots \text{O} \approx 3.0\) Å van der Waals’ force and \(\text{H} \cdots \text{πphenyl} \approx 2.60\) Å in average) interactions form the three-dimensional framework (Fig. 3c).

We further suited the IR spectra of \(\text{Au}_2\text{Ag}_2\) cluster, which was then compared with IR of \(\text{HL}\), as depicted in Fig. 4, compared with \(\text{HL}\), the most representative peaks near 3286 cm\(^{-1}\) assigned to strong \(\text{H} \cdots \text{C} \equiv \text{C}\) stretching vibration almost disappeared in the FT-IR spectra of \(\text{Au}_2\text{Ag}_2\) clusters, indicating that the \(\text{H}\) atoms linked to the terminal carbon of \(\text{H} \cdots \text{L}\) was removed and bonded by metal atoms. Besides, the peak in the scale of 2220–2230 cm\(^{-1}\) assigned to the vibration of \(\text{C} \equiv \text{N}\) bonds remained unchanged basically, indicating that the \(\text{C} \equiv \text{N}\) group in \(\text{L}\) did not take part in the coordination with metal atoms, which is in good line with the SCXRD results as well. The strong peak near 1646 cm\(^{-1}\) should be assigned to the presence of \(\text{Ph}_3\text{P}\) ligands in \(\text{Au}_2\text{Ag}_2\). The two peaks near 2842 and 2922 cm\(^{-1}\) should be caused by the strong stretching vibration of \(\text{C} \cdots \text{H}\) bonds from \(\text{CH}_2\) group. In all, these FT-IR results highly match with the \(\text{Au}_2\text{Ag}_2(\text{L})_4(\text{Ph}_3\text{P})_2\) structure convinced by SCXRD.

In recent decade, the metal clusters have been utilized to be a novel and promising catalyst in the carbon–carbon coupling reaction, which generate new chemicals, such as alkaloids as well as in numerous biologically active parts of pharmaceutical and agrochemical specialties.\(^{35-38}\) The \(\text{Au}_2\text{Ag}_2\) nanoclusters, capped by alkyne ligand, can be a good catalyst to incur the activation of alkydes, which is the key step during the multicomponent-coupling reactions of benzaldehyde, pyridine and phenylacetylene. In our previous studies, we have found that the alkyne/phosphine capped \(\text{Au}_{25}(\text{PPPh}_3)_10(\text{C}_2\text{Ph})_5\text{X}_2\) clusters have showed promising catalytic performance in the multicomponent-coupling reactions.\(^{39}\) Therefore, we decided to investigate the catalytic performance of \(\text{Au}_2\text{Ag}_2\) clusters in the multicomponent coupling reactions to yield the product of

![Fig. 3](image_url)

(a) \(\text{Au}_2\text{Ag}_2\) clusters in one cell unit. (b) The intermolecular interactions between \(\text{Au}_2\text{Ag}_2\) clusters. (c) The packing model of \(\text{Au}_2\text{Ag}_2\) cluster along \(b\)-direction. The uncoordinated atoms in (a) are omitted for clarity.

![Fig. 4](image_url)

Comparison of the IR spectra of prepared \(\text{Au}_2\text{Ag}_2\) clusters (red line) and free \(\text{HL}\) ligands (black line).
propargylamine was achieved, Table 2, entry 2. For comparison, the yield of 45% was found when the multicomponent coupling reaction was catalyzed over the Au13/TiO2 catalysts (Table 2, entry 3). And a much lower yield of 62% was obtained (Table 2, entry 4). The prominent activity of the alloy clusters is mainly due to the steric effect; the small-sized particles can provide more catalytically active sites during the multicomponent coupling reactions. It is worthy to note that the plain TiO2 supports were inactivity during the multicomponent coupling reaction, which implies that the catalytic reactions should be occurred over the metal clusters.

Further we examined the catalytic activity of the reused Au2Ag2/TiO2 to evaluate the recyclability of the alloy clusters. A fresh reaction was carried out using the recycled catalyst with reactants in fresh water under the identical reaction conditions. It is found that recycled catalyst yields nearly the same activity as fresh catalyst (Table 2, entries 5 and 6). After three cycles, no appreciable loss of catalytic activity was observed; thus, Au2Ag2/TiO2 is deemed as a good recyclable catalyst for the multicomponent coupling reactions.

Conclusions

In summary, a new mono-valence Au2Ag2[(C14H11NO)]4(P3H)2 alloy cluster is prepared. Its nanostructure is well studied by SCXRD analysis, showing that this cluster is composed of an Au2Ag2 core protected by alkynyl and phosphine ligands forming a bimetal quaternary cluster. Notably, a new divergent alkyne-metal coordination model is revealed, which is different to the convergent motif found in big clusters. Besides, the selectivity of alkynyl show up in this case, which coordinate with Ag and Au via π bonds and σ binds respectively. The structural revealing of small clusters makes it possible for the further understanding of growth process from the small to big ones. The Au2Ag2 alloy clusters exhibit good catalytic performance in the carbon–carbon coupling reactions.

Conflicts of interest

There are no conflicts to declare.

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