Mechanistic insights into Ag\(^+\) induced size-growth from [Au\(_6\)(DPPP)\(_4\)]\(^{2+}\) to [Au\(_7\)(DPPP)\(_4\)]\(^{2+}\) clusters†

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The size conversion of atomically precise metal nanoclusters lays the foundation to elucidate the inherent structure–activity correlations on the nanometer scale. Herein, the mechanism of the Ag\(^+\)-induced size growth from [Au\(_6\)(dppp)\(_4\)]\(^{2+}\) to [Au\(_7\)(dppp)\(_4\)]\(^{3+}\) (dppp is short for 1,3-bis(diphenylphosphino)propane) is studied via density functional theory (DFT) calculations. In the absence of extra Au sources, the one Au\(^+\) addition was found to be regulated by the Ag\(^+\) doping induced Au-activation, i.e., the formation of formal Au\(_1\) blocks via the Ag\(^+\) alloying processes. The Au\(_1\) blocks could be extruded from the core structure in the formed Au–Ag alloy clusters, triggering a facile Au\(^+\) migration to the Au\(_6\) precursor to form the Au\(_7\) product. This study sheds light on the structural and stability changes of gold nanoclusters upon the addition of Ag\(^+\) and will hopefully benefit the development of more metal ion-induced size-conversion of metal nanoclusters.

Introduction

The stimuli response upon exposure to extra metal ions represents an attractive characteristic of metal nanoclusters.\(^1\)–\(^8\) The structural response may be reflected in the complexion of the metal ion(s) with the surface ligands,\(^9\)–\(^11\) the doping/exchange/addition of the metal ion(s) into the metallic framework of the cluster,\(^12\)–\(^15\) the slightly changed structure with a different charge state\(^16\) or the re-arrangement of the entire cluster structure.\(^17\)–\(^20\) Moreover, enhanced physicochemical properties (such as thermostability) and novel applications\(^21\)–\(^23\) could be achieved due to the synergistic effect.

Associated with the experimental outcomes, the atomic precision, spectroscopic characterization, and theoretical simulations have greatly improved our mechanistic understanding on these reactions. For example, the [M\(^+\)]\(^–\)Cl (M = Ag/Cu) interactions of the M\(^+\) with the vertex AuCl moiety of the rod-shaped Au\(_{24}\)(SR)\(_3\)(PR\(_3\))\(_{10}\)Cl\(_2\) were found to be a dominating effect to initiate the single atom addition, and thus, the formation of the rod-shaped Au\(_{25}\)M(SR)\(_3\)(PR\(_3\))\(_{10}\)Cl\(_2\) clusters.\(^24\) The Cs–S/O and cation–π interactions are pivotal to the Cs\(^+\) induced one-dimensional linear assembly of Ag\(_{20}\)(SSR)\(_{13}\)(PPh\(_3\))\(_4\).\(^25\) In addition, the anti-galvanic mechanism was proposed to account for the cation-stimulated alloying.\(^26\)–\(^28\) Nevertheless, the reported mechanistic study mainly focuses on the metal ion-induced alloying/assembly, while the mechanistic details on the ion “catalyzed” size conversion of nanoclusters (Ag\(^+\) induced [Au\(_6\)(dppp)\(_4\)]\(^{2+}\) to [Au\(_7\)(dppp)\(_4\)]\(^{3+}\) and Cu\(^+\) induced Au\(_{25}\)(PET)\(_{18}\) → Au\(_{44}\)(PET)\(_{18}\))\(^28\)–\(^31\) have been largely unknown.

Intrigued by the fantastic foreign metal effect,\(^29\)–\(^31\) we sought to perform a detailed mechanistic study on the Ag\(^+\) induced reaction of [Au\(_6\)(dppp)\(_4\)]\(^{2+}\) to [Au\(_7\)(dppp)\(_4\)]\(^{3+}\) with density functional theory (DFT) calculations. According to Konishi’s experiments,\(^18\) [Au\(_6\)(dppp)\(_4\)]\(^{2+}\) transformed into [Au\(_7\)(dppp)\(_4\)]\(^{3+}\) within one minute after 5 molars equivalent AgBF\(_4\) was added. According to single-crystal structure analysis, [Au\(_6\)(dppp)\(_4\)]\(^{3+}\) comprises a bi-capped tetrahedral skeleton. The tetrahedral Au atoms (Au\(^{1\text{-}4}\)) are each protected by one P hand of the dppp ligand, while the two-terminal Au atoms (Au\(^{5\text{-}6}\)) are each protected by two P hands from two dppp ligands. The framework of [Au\(_7\)(dppp)\(_4\)]\(^{3+}\) is similar to that of [Au\(_6\)(dppp)\(_4\)]\(^{2+}\), except for the addition of one formal Au\(^+\), and the re-arrangement of one dppp ligand (one P coordination on the Au\(^6\) atom migrates to coordinate to Au\(^7\)).

According to the DFT calculation results, the addition of Ag\(^+\) on clusters favorably generates the alloy structure with higher

![Scheme 1](https://doi.org/10.1039/d2na00301e)
nucleation (i.e. with more tetrahedral and triangular blocks in the core structure). The incorporated Ag⁺ induced activation of the exterior Au atoms in the metal framework, resulting in an easy structural tautomerization therein. This proposal correlates with the heavily doping-induced size-rearrangement of metal nanoclusters in recent studies²⁷,²³ and will be hopefully applicable to other alloying systems (Scheme 1).¹⁸

Results and discussion

Throughout this study, the experimentally used dppp ligands (i.e. bis(diphenylphosphino)propane) were simplified with dmpp (i.e. bis(dimethylphosphino)propane ligands) to reduce computational costs. Similar structural simplification has also been used in recent studies.²³,²⁴

The doping of Ag⁺ in Au₆P₈ clusters

The formula of Au₆P₈ is differentiated from Au₅P₈ by only one Au⁺, which is unlikely to be released directly from the Au₆P₈ precursor. To this end, the dissociation of Au⁺ is anticipated to be induced by the Ag⁺ doping of Au₆P₈. Given the high activity of the mono-nuclear, cationic Au⁺ species, the generation of Au⁺ from the gold cluster precursors is designated as the activation of the Au atom. Of note, the Ag⁺ alloying-induced activation of the “Au” site(s) correlates with the general concept of antigalvanic reduction.²⁵ Using Ag⁺ as a dopant, we considered the possible configurations and energy demands for successive doping procedures.

Considering the structural symmetry and the Fukui function analysis (f⁻, Fig. 1)³⁵ of the Au₆P₈ precursor, the terminal Au⁵/₆ atom, Au¹⁴-Au⁺ bond, and Au¹³/Au⁺ bond are the most labile sites for the electrophilic attack of the first Ag⁺. In this study, the isodesmic reaction of NC₃ fertil AgBF₄ → [NCAg⁴+(n⁻¹)⁺ + BF₄⁻] (NC denotes the reaction precursor for the Ag⁺ addition steps) was used to determine the reaction energy of the Ag⁺ addition steps. As shown in Fig. 1, the addition of the first Ag⁺ could possibly generate Au₅Ag₄P₈⁻¹ and Au₅Ag₄P₈⁻², and the suffix of −1/−2 denotes the isomeric products via adding Ag⁺ on different sites. Both two doping processes are thermodynamically highly feasible. Nevertheless, adding an exterior Ag⁺ makes little perturbation on the Au⁵ skeleton in the former case, but results in a stretched core structure in the latter case (Fig. 1 and S1†).

From Fig. 1, the Au⁴-Au³ bond insertion is significantly more feasible than the Au⁵ binding mode (−48.8 vs. −37.3 kcal mol⁻¹). Alternatively, Ag⁺ is more likely to be reduced by Au⁶⁺ that is, Ag⁺ is incorporated into the core sites to form a highly coordinated structure (the coordination number¹⁸ of Ag⁺ in Au₅Ag₄P₈⁻¹ and Au₅Ag₄P₈⁻² is 1 and 3; please see ESI† for more details), and thus Au₅Ag₄P₈⁻² is preferentially formed.

According to the Hirshfeld charge analysis, the charge state of the terminal Au⁵/₆ in Au₅P₈ (0.002/−0.009, Table S1†) is slightly higher than that of the tetrahedral Au (avg. −0.030). By contrast, the charge of Au⁵ in Au₅Ag₄P₈⁻¹ and Au₅Ag₄P₈⁻² (0.055 and 0.057) is significantly more positive than that of tetrahedral Au atoms (avg. −0.012) and becomes closer to the charge of Au in the Au₅(dppp)₂Cl₂⁷ complex (0.082). The results unambiguously demonstrate the improved positive charge of the Au⁵ atom after Ag⁺ incorporation, and thus the higher reactivity for bond dissociation (due to the increased electrostatic repulsion between the cationic metal centers). In other words, the incorporation of Ag⁺ activates the core Au atoms, particularly in the corner sites.¹⁸ Of note, compared to the aforementioned Ag⁺-addition processes, the metal exchange of Ag with Au in Au₅P₈ is thermodynamically much more disfavored (Scheme S1†). Therefore, the metal exchange pathways were not examined in the following section.

According to the Fukui function analysis, the most nucleophilic sites of Au₅Ag₄P₈⁻² are located in the region nearby Au⁵ and Au⁶ atoms (Fig. 2). Accordingly, we examined four possible binding modes of the second Ag⁺.

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Fig. 1. The isosurface of the f⁻ for Au₅P₈ using the width of Gaussian function of 0.01 au, and the energy (in kcal mol⁻¹) and structural change for the doping of first Ag⁺ into Au₅P₈. The Hirshfeld charge of Au⁵/₆ in the starting structure is given in blue and bold.

Fig. 2. The isosurface of the f⁻ for Au₅Ag₄P₈⁻², using the width of Gaussian function of 0.01 au and the energy (in kcal mol⁻¹) and structural changes for the doping of second Ag⁺ into Au₅Ag₄P₈⁻². The Hirshfeld charge of Au⁵/₆ in the starting structure is given in blue and bold.
As shown in Fig. 2, the activation of the terminal Au\(_5^+\) could occur via the addition of Ag\(_{2}^+\) on the site 1 of Au\(_5^+\) or site 2 of attacking the Au\(_5^–\)-Ag\(_3^+\) bond to form the isomeric Au\(_4\)Ag\(_2\)P\(_8\)-1 and Au\(_4\)Ag\(_2\)P\(_8\)-2, respectively. Similarly, the corner Au\(_5^+\) could be possibly activated via Ag\(_{2}^-\) insertion into the space behind (site 3) or in front (site 4) of the butterfly-like Au\(_{1}^{3+}\)-Au\(_2^+\)-Au\(_3^-\)-Au\(_6^-\) structure to form Au\(_4\)Ag\(_3\)P\(_8\)-3 or Au\(_4\)Ag\(_3\)P\(_8\)-4.

The results indicate that the binding of second Ag\(_{2}^+\) (i.e. Ag\(_{2}^+\)) directly on Au\(_5^+\) makes little perturbation on the framework, correlating with the results of Au\(_4\)P\(_8\) + AgBF\(_4\) → Au\(_4\)Ag\(_3\)P\(_8\)-1 + BF\(_4\)\(^-\) (Fig. 1). Nevertheless, the reaction energy is remarkably higher (−5.4 kcal mol\(^{-1}\) in Au\(_4\)Ag\(_3\)P\(_8\)-2 + AgBF\(_4\) → Au\(_4\)Ag\(_3\)P\(_8\)-1 vs. −37.3 kcal mol\(^{-1}\) in Au\(_4\)P\(_8\) + AgBF\(_4\) → Au\(_4\)Ag\(_3\)P\(_8\)-1 + BF\(_4\)\(^-\)), implying that the structure of the precursor is pivotal to the facilitation of alloying. Moreover, the attack of Ag\(_2^+\) to Ag\(_1^-\) resembles a synergistic bi-molecular electrophilic reaction mechanism as the Au\(_5^+\) atom migrates from cis-to trans-configuration (refer to Au\(_1^+\)) around the Au\(_5^-\)-Au\(_3^-\) bond spontaneously during the geometry optimization (see Fig. S2\(^†\) for the details). The formation of Au\(_4\)Ag\(_3\)P\(_8\)-2 from Au\(_4\)Ag\(_2\)P\(_8\)-2 is exothermic by 30.7 kcal mol\(^{-1}\). Besides, the approaching of Ag\(_{2}^+\) to either Au\(_1^-\)-Au\(_2^+\)-Au\(_3^-\)-Au\(_6^-\) or Au\(_4^-\)-Au\(_3^-\)-Au\(_3^-\)-Au\(_6^-\) results in a core-structure reorganization, predominantly via incorporating Ag\(_1^-\) into the tetrahedral blocks and forming the face-sharing tri-tetrahedral structure. Due to the meta-orientation of the two Ag\(_{2}^+\) and the symmetry of the tri-tetrahedral core structure, the relative energy and the M-P framework of the formed Au\(_4\)Ag\(_3\)P\(_8\)-3 are almost the same as those of Au\(_4\)Ag\(_3\)P\(_8\)-4. Both steps are highly exothermic (−44.8 and −45.1 kcal mol\(^{-1}\)). Through the structural re-organization, the reduced coordination number of Au\(_5^+\) and Au\(_6^-\) (compared to the related one in the precursor) is overwhelmed by the extra stability associated with the formation of a larger metallic core structure. Therefore, the formation of Au\(_4\)Ag\(_3\)P\(_8\)-3/4 is favored over that of Au\(_4\)Ag\(_3\)P\(_8\)-1/2.

Comparing the optimized geometries of Au\(_4\)Ag\(_3\)P\(_8\)-2 and Au\(_4\)Ag\(_3\)P\(_8\)-3/4, we found that the bond distance between the Au\(_5^+\)/Au\(_6^-\) and the core metal atoms is significantly lengthened after incorporating the second Ag\(_{2}^+\). Moreover, the charge on Au\(_5^+\)/Au\(_6^-\) atoms becomes more positive (Au\(_4\)Ag\(_3\)P\(_8\)-2: 0.057/0.035 → Au\(_4\)Ag\(_3\)P\(_8\)-2: 0.086/0.083, Table S1\(^†\)), and is comparable to that of the aforementioned Au(i) complex (0.082). The results indicate the formation of a formal Au(i) center on the cluster, and thus, the enhanced activity for the nucleophilic coordination and Au–Au dissociation (the charge of the other Au atoms also becomes more positive, Table S1\(^†\)). Nevertheless, the alloying with Ag\(_{2}^+\) remains thermodynamically feasible, and therefore, we examined the energetics for further doping of Ag\(_2^-\) in the target system.

In view of the preferential core expansion via Ag\(_2^-\) doping (over the Ag addition steps), we mainly examined the core-expansion pathways from Au\(_4\)Ag\(_3\)P\(_8\)-4. As shown in Fig. 3, the third Ag\(_2^-\) doping process leads to four possible Au\(_4\)Ag\(_3\)P\(_8\) isomers. The third Ag\(_2^-\) (i.e. Ag\(_3^-\)) could possibly attack site 1 of the Ag\(_2^-\)-Au\(_5^+\) bond, site 2 of the Au\(_1^-\)-Ag\(_3^-\) bond, site 3 of the Au\(_2^-\)-Ag\(_5^-\) bond, and site 4 of the Ag\(_2^-\)-Au\(_6^-\) bond, forming Au\(_4\)Ag\(_3\)P\(_8\)-1, Au\(_4\)Ag\(_3\)P\(_8\)-2, Au\(_4\)Ag\(_3\)P\(_8\)-3, and Au\(_4\)Ag\(_3\)P\(_8\)-4, respectively. The approaching of Ag\(_2^-\) into the Ag\(_2^-\)-Au\(_5^+\) bond internalizes Ag\(_3^-\) into the left tetrahedral \(\text{Ag}^{3+}\) block, forming a square pyramid (\(\text{Ag}^{2+}\)Au\(_5^+\)) therein. Moreover, the approaching of Ag\(_3^-\) to the Au\(_2^-\)-Ag\(_5^-\) bond results in the enlargement of the Au\(_2^-\)-Au\(_1^+\)-Ag\(_3^-\)/Au\(_1^-\) bond angle, and the incorporation of Ag\(_3^-\) to form two vertex-sharing tetrahedral blocks (see Fig. S3\(^†\) for the partial optimization energy profile). The approaching of Ag\(_2^-\) to the Au\(_2^-\)-Ag\(_3^-\) bond leads to the extrusion of the Au\(_1^-\)-Au\(_2^+\) bond from the metallic core structure, resulting in the formation of a face-sharing bi-tetrahedral block with a vertex-sharing triangular Au\(_1^+\)-Au\(_2^+\) unit (Au\(_4\)Ag\(_3\)P\(_8\)-3). The attack of Ag\(_3^-\) on the Ag\(_2^-\)-Au\(_3^-\) bond results in the formation of a distorted square-pyramid Au\(_3^-\)-Ag\(_2^-\)-Ag\(_3^-\) block, and the cleavage of the Au\(_1^+\)/Ag\(_2^-\)-Au\(_2^+\) bonds. In the formed Au\(_4\)Ag\(_3\)P\(_8\)-4, the new-formed square-pyramid shares one facet with the original left tetrahedron. According to the calculation results, the four types of Ag\(_{2}^-\) insertion steps are exothermic by 10.3, 12.0, 4.2, and 10.2 kcal mol\(^{-1}\), respectively.

The slightly higher energy of Au\(_4\)Ag\(_3\)P\(_8\)-3 than the other isomers is predominantly caused by the lower cohesive degree of the whole metal skeleton\(^\text{29}\) (the average coordination number of the metal atoms is 3.4/3.4/3.1/3.3 for Au\(_4\)Ag\(_3\)P\(_8\)-1/2/3/4, see details in Table S2\(^†\)).\(^\text{29}\) In addition, the comparable energies of Au\(_4\)Ag\(_3\)P\(_8\)-1, Au\(_4\)Ag\(_3\)P\(_8\)-2, and Au\(_4\)Ag\(_3\)P\(_8\)-4 indicate the competitive Ag\(_{2}^-\) doping sites. For clarity reasons, the following analysis and discussions mainly refer to the most stable intermediate Au\(_4\)Ag\(_3\)P\(_8\)-2.

According to Hirshfeld charge analysis, the doping with the third Ag\(_{2}^-\) further enhances the electron deficiency of the Au\(_5^+\)/Au\(_6^-\) atoms (with the charge of 0.114/0.109, compared to the charge of 0.086/0.083 in Au\(_4\)Ag\(_3\)P\(_8\)-2, Table S1\(^†\)). Moreover, the average charge of the Au\(_5^+\) (Au\(_5^+\) denotes the tetrahedral Au\(_5^+\) block in the Au\(_5^+\) reactant, and \(n = 1–4\)) blocks also significantly increases with the doping with the third Ag\(_{2}^-\) (Au\(_4\)Ag\(_3\)P\(_8\)-2: −0.012 → Au\(_4\)Ag\(_3\)P\(_8\)-4: 0.019 → Au\(_4\)Ag\(_3\)P\(_8\)-4: 0.070),
resulting in critically increased electrostatic repulsion within the metal skeleton and the reduced stability. This is also the reason why the Ag⁺ doping becomes less feasible after each doping process (the first, second, and third Ag⁺ doping steps are exothermic by −48.8, −45.1, and −12.0 kcal mol⁻¹).

Starting from Au₆Ag₃P₈⁻, the fourth Ag⁺ (i.e. Ag⁴⁺) could be capped on the Ag₁⁻³Au⁴⁺ facet as the maximum of f⁻ appears above the Ag₁⁻³Au⁴⁺ facet, and then the four-Ag⁺-doped product Au₆Ag₄P₈⁻1 was formed.

The incorporation of Ag⁴⁺ also resembles a synergistic bimolecular electrophilic reaction mechanism, similar to the reaction of Au₆Ag₃P₈⁻ + AgBF₄ → Au₆Ag₄P₈⁻. When the Ag⁴⁺ atom is capped on the bare Ag₁⁻³Au⁴⁺ facet, the Au³⁺ atom leaves the back capping site (on the Ag₁⁻³Au⁴⁺ facet) with the right part of the face-sharing bi-tetrahedron remaining. Distinct from the aforementioned exothermic doping processes in the 1–3 Ag⁺ incorporation steps, adding the fourth Ag⁺ via this pathway was endothermic by 3.8 kcal mol⁻¹ (Fig. 4). In other words, the incorporation of the fourth Ag⁺ is thermodynamically disfavored. The reason is mainly ascribed to the significantly enhanced electrostatic repulsion among the metal atoms (the average Hirshfeld charge of the metal atoms in the Au₆Ag₃ core is 0.112 for Au₆Ag₃P₈⁻1). Throughout the Ag-doping pathway, Ag⁺ favors the core site of Au₆Ag₃ and leads to the oxidation of Au atoms (i.e. Au⁵⁺). As shown in Scheme S2,† the contribution of Ag⁺ to the HOMO of Au₆Ag₃ (n = 0, 1, 2, and 3) increased remarkably with the increased doping number of Ag⁺ (Au₆Ag₃: 0.00%, Au₆Ag₄: 21.74%, Au₆Ag₅: 41.27%, and Au₆Ag₆: 43.05%). In combination with the Fukui function analysis (Fig. 1–4), the Au sites adjacent to Ag atoms are the active sites for the electrophilic attack of the incoming Ag⁺.

**Size-growth by the dimerization of Au₆Ag₃P₈⁻**

According to the aforementioned results and discussion, the successive addition of Ag⁺ on Au₆P₈ favorably generates the alloy structure with a higher degree of nucleation (i.e. with more tetrahedral and triangular blocks in the core structure). Mean⁰ Meanwhile, the most plausible doping number of Ag⁺ is 3 (Au₆P₈ + 3AgBF₄ → Au₆Ag₃P₈⁻ + 3BF₄⁻), wherein the metallic core has been largely activated due to the strong electrostatic repulsion therein (most Au atoms show Au(↓) character, Table S1†). In this context, the terminal Au⁵⁺ and Au⁶⁺ atoms are the most labile sites for the subsequent reactions because of the relatively lower steric hindrance and the higher electron deficiency (compared to all other metal sites). For this reason, the Au⁵⁺ (or Au⁶⁺) in Au₆Ag₃P₈⁻ is used as the [Au]⁺ source to react with the Au₆P₈ cluster precursor to form Au₆P₈⁻.

Of note, the direct approaching of Au₆Ag₃P₈⁻ to Au₆P₈ is precluded due to the high inter-cluster steric hindrance (see Fig. S4;† note: the steric hindrance would be much higher for the experimental dppp protected system). In this context, a prior Au⁵⁺–P dissociation on Au₆P₈ (Au₆P₈ → Au₆P₈⁻, see Fig. S5†) might occur first to release the steric hindrance. After that, the nucleophilic attack of P⁴⁻ to Au⁵⁺ occurs with the formation of Dimer-1 (Fig. 5), and this step is slightly endothermic by 5.2 kcal mol⁻¹. By contrast, the coordination of P⁴⁻ to the Au⁶⁺ atom is thermodynamically slightly less disfavored (6.7 kcal mol⁻¹, Scheme S3†); thus, its subsequent transformations were omitted for clarity reasons. The P–Au bonding makes no obvious influence on the framework of both cluster precursors. To this end, the endothermicity might be caused by the high steric hindrance around the over-protected Au⁵⁺ (coordination number: 4, with three P-coordination).

Given the high steric hindrance around Au⁵⁺, the adjacent bare Ag¹ in Dimer-1, and the easiness for 1,2 P migration in cluster systems,⁴¹–⁴³ we examined the possibility of a 1,2-P₂ migration from Au⁵⁺ to Ag¹. The kinetic analysis by partial optimization (via gradually shortening the P²⁻-Ag¹ bond distance; see Fig. S6† for details) demonstrates the gradual bond cleavage of Au⁵⁺–Ag²⁺ and Au¹⁺–Ag²⁺ bonds. As a result, the triangular bi-pyramidal block of Au¹⁺–Ag²⁺–Au¹⁺ (Fig. 6, inset) tautomerizes into a twisted square pyramid. The energy curve indicates a low energy barrier (12.4 kcal mol⁻¹, Fig. S6†), which could be easily overcome under the experimental condition (i.e. room temperature).⁴⁶ Meanwhile, due to the released steric...
hindrance around the Au$^+$ atom, the concerned P$^3$-migration from Dimer-1 to Dimer-2 is exothermic by 17.3 kcal mol$^{-1}$.

As the square pyramid block has been found to be less stable than the triangular bipyramid block (Au$_5$Ag$_3$P$_8$-1 vs. Au$_5$Ag$_3$P$_8$-2, Fig. 3), we further examined an isomerization of Dimer-2 via changing the square pyramidal block into a triangular bipyramidal one (Dimer-3 in Fig. 7). This isomerization was found to occur easily via lengthening the Au$^+$-Au$^+$ bond distance, with a barrier of 8.0 kcal mol$^{-1}$ (Fig. S7†). The relative energy of Dimer-3 is lower than that of Dimer-2 by 6.4 kcal mol$^{-1}$, demonstrating the thermodynamic facility of this step.

From Dimer-3, the approaching of the Au$^+$ atom to the Au$_6$ block is requisite to forming the target Au$_7$ structure, which could be regulated by a series of single bond rotation processes of the related dmpp ligand (Dimer-3 $\rightarrow$ Dimer-6 in Scheme 2; see Fig. S8† for the details). Throughout the transformations, the structure of the alloy moiety is preserved, and the system energy is decreased by 7.5 kcal mol$^{-1}$.

From Dimer-6, the target Au$_7$ block of Au$_5$P$_8$ could be formed via the binding of Au$^+$ to the Au$^+$ faceted of the Au$_6$ block, and the dissociation of the Au$^+$-P$_3$ bond (Fig. 8). According to the calculation results, the binding of Au$^+$ is exothermic by 3.2 kcal mol$^{-1}$ and occurs with a very low barrier of <5 kcal mol$^{-1}$ (Fig. S9†). From Dimer-7, the Au$^+$-P$_3$ cleavage occurs to generate Au$_5$P$_8$ and a by-product Au$_5$Ag$_3$P$_8$. In contrast, the progress of moving an Ag$^+$ from Au$_5$Ag$_3$P$_8$-3 to Au$_5$P$_8$ to generate Au$_5$Ag$_3$P$_8$ is thermodynamically less feasible (−18.7 kcal mol$^{-1}$), see exothermic by only 2.3 kcal mol$^{-1}$. The total reaction energy of Au$_5$P$_8$ + Au$_5$Ag$_3$P$_8$-3 $\rightarrow$ Au$_5$P$_8$ + Au$_5$Ag$_3$P$_8$ is −31.4 kcal mol$^{-1}$. See Scheme S3† for more details, demonstrating that the alloy cluster after Ag$^+$ doping is a good [Au$^+$] donor, but not a good [Ag$^+$] donor.

Due to the lack of experimental evidence and the complexity of the reaction system, we are not able to confirm the final state of Ag at this stage. However, in view of the bare Au$^+$ atom and the dangling P$^+$ atom, we assumed that Au$_5$Ag$_3$P$_8$ could possibly undergo the P$^3$-Ag$^+$ coordination to generate a more stable intermediate. The calculation results (Au$_5$Ag$_3$P$_8$ $\rightarrow$ Au$_5$Ag$_3$P$_8$-2, Scheme S4†) indicate this step to be highly feasible (exothermic by 26.8 kcal mol$^{-1}$). In particular, after the Au-P coordination, the Au$_6$ atom was further extruded from the metallic core and could possibly act as the second [Au$^+$] source to regulate the second Au$_5$P$_8$ $\rightarrow$ Au$_5$P$_8$ conversion. The formed Au$_5$Ag$_3$P$_8$ could undergo further Ag-P coordination (Scheme S4†) or comprehensive nucleation/decomposition processes. Due to the complexity of the target reaction system, the details for the conversion of Au$_5$Ag$_3$P$_8$ are still ambiguous and deserve more studies.

Experimentally, AgBF$_4$ was not largely excessive, and thus, the transformation from Au$_5$P$_8$ to Au$_5$P$_8$ might deviate from a pseudo-first-order reaction. Hence, the reaction pathways using Au$_5$Ag$_3$P$_8$-2 and Au$_5$Ag$_3$P$_8$-4 as [Au$^+$] sources were also examined. As shown in Scheme S5, the Au$^+$ migration from Au$_5$Ag$_3$P$_8$-2 or Au$_5$Ag$_3$P$_8$-3 to the Au$_6$ skeleton was as feasible as that from Au$_5$Ag$_3$P$_8$. Energy demands are all lower than 15 kcal mol$^{-1}$. According to the aforementioned results and discussion, the Ag$^+$ induced size conversion from Au$_5$P$_8$ to Au$_5$P$_8$ could occur via a series of competitive pathways. For clarity, the most feasible pathway deduced in this study is shown in Scheme 3 (the relative energies are given with the reference states of Au$_5$P$_8$ and AgBF$_4$).

In this mechanism, the continuous doping of Au$_5$P$_8$ clusters with Ag$^+$ (dominant doping product: Au$_5$Ag$_3$P$_8$-2) activates the terminal Au atoms and generates the [Au$^+$] source for...
subsequent size conversion. After that, Au–P coordination between the dangling phosphine ligand of the Au₆ precursor and the formal [Au⁺] occurs, followed by the intramolecular migration of [Au⁺] through a series of isomerization steps (on the diphosphine ligand). Finally, the Au₇P₈ product is formed via the Au–P dissociation and the release of the alloy cluster block. Albeit the comprehensive calculations, the experimental evidence for the proposed mechanism is still lacking, predominantly due to the rapid reaction rate and the lability of the formed [Au₇(dppp)₄](BF₄)₃ to convert to [Au₈(dppp)₄Cl₂]. Moreover, some other mechanistic possibilities, such as the formation of the target Au₇ products via the reaction of one alloy intermediate with another one, could not be excluded.

**Conclusions**

Herein, a plausible mechanism for the Ag⁺ induced conversion from [Au₆(dppp)₄]²⁺ to [Au₇(dppp)₄]³⁺ was proposed with DFT calculations. The size growth starts with the successive doping of Ag⁺ (preferentially adopts high nucleation), associated with the gradual formation of formal Au(I) terminal sites and the weakened metal–metal bonding interactions. In this context, the release of the terminal Au atom (i.e. the activated Au(i) atom) to the Au₆ precursor occurs easily to generate the Au₇ cluster product, while the alloy cluster could further function as a “Au(I)” donor to regulate another group of the Au₆P₈/Au₇P₈ conversion. Due to the complexity of the target reaction system, the full details on the overall size growth remain to be established. Nevertheless, the mechanism insights, such as the preferential doping site of Ag⁺ on the cluster precursor (on the most nucleophilic site, and favorably forms structures with a higher degree of nucleation), the activation of exterior Au atom(s) via the gradual incorporation of Ag⁺ (i.e. formation of formal Au(i) and its subsequent dissociation, re-assembly, etc.), and the easy structure tautomerization in the metallic core and the diphosphine ligands, will be helpful for understanding the inherent correlation between different nanoclusters and their alloying reactivity in future studies.

**Author contributions**

H. Y. conceived and supervised the project. Y. L. carried out the experimental planning, simulations, and data analysis. X. W. and S. H. provided constructive suggestions.

**Conflicts of interest**

There are no conflicts to declare.
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