Molecular “surgery” on a 23-gold-atom nanoparticle

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Compared to molecular chemistry, nanotechnology is still far from being capable of tailoring particle structure and functionality at an atomic level. Numerous effective methodologies that can precisely tailor specific groups in organic molecules without altering the major carbon bones have been developed, but for nanoparticles, it is still extremely difficult to realize the atomic-level tailoring of specific sites in a particle without changing the structure of other parts (for example, replacing specific surface motifs and deleting one or two metal atoms). This issue severely limits nanotechnologists from knowing how different motifs in a nanoparticle contribute to its overall properties. We demonstrate a site-specific “surgery” on the surface motif of an atomically precise 23-gold-atom [Au23(SR)16]− nanoparticle by a two-step metal-exchange method, which leads to the “resection” of two surface gold atoms and the formation of a new 21-gold-atom nanoparticle, [Au21(SR)12(Ph2PCH2PPh2)2]+, without changing the other parts of the starting nanoparticle structure. This precise surgery of the nanoparticle reveals the different reactivity of the surface motifs and the inner core: the least effect of surface motifs on optical absorption but a distinct effect on photoluminescence (that is, a 10-fold enhancement of luminescence after the tailoring). First-principles calculations further reveal the thermodynamically preferred reaction pathway for the formation of [Au21(SR)12(Ph2PCH2PPh2)2]+. This work constitutes a major step toward the development of atomically precise, versatile nanotechnology for the precise tailoring of the nanoparticle structure to control its properties.

INTRODUCTION

Recent years have witnessed significant research efforts on atomically precise ultrasmall metal nanoparticles (often called nanoclusters) (1–4). Major advances have been achieved in the synthesis of gold, silver, and Au/Ag alloy nanoclusters and the identification of aesthetic structural patterns (5–22). Exploring effective methods to exquisitely tailoring the size, structure, and composition of atomically precise nanoclusters constitutes an ultimate goal in this field, which will offer opportunities to pursue fundamental understanding of the properties of nanoclusters (23–26) and establish definitive structure-property relationships (1, 5, 27). With precise formulas, molecular purity, and total structures solved by single-crystal x-ray analysis, it has become possible to investigate the transformation chemistry of nanoclusters at the atomic level (28–31), akin to organic transformation chemistry. This atomic-level nanotechnology may provide new opportunities to discover some unexpected chemical reactions, which so far remain a mystery.

Although different precise synthesis methods have been developed in the past decade, realizing the atomic-level tailoring of specific sites in a nanoparticle without changing the structure of other parts (for example, replacing specific surface motifs and deleting one or two metal atoms) remains extremely difficult. This “molecular surgery,” which is highly desirable but is so far the least feasible in nanotechnology, hinders the fundamental understanding of how different motifs in a nanoparticle contribute to its overall properties.

Here, we report the first case of molecular surgery on the nanocluster surface via site-specific tailoring of the protecting motif (Fig. 1A), which leads to the “resection” of two gold atoms from the [Au23(SR)16]− (R: cyclo-C6H11) nanocluster and thus the formation of a new [Au21(SR)12(Ph2PCH2PPh2)2]+ (abbreviated as P−C−P hereafter) nanocluster. Direct transformation did not occur; thus, our method consists of a two-step metal exchange via the formation of a critical [Au23−xAgx(SR)16]− (x ~ 1) intermediate. We determined the structures of [Au21(SR)12(P−C−P)x]2+ and [Au23−xAgx(SR)16]− (x ~ 1) by single-crystal x-ray analysis. First-principles calculations further reveal the critical role of the first-step silver doping (step 1) in opening up the thermodynamically favorable pathway of surface motif exchange from RS−Au−SR to P−C−P motifs in the second step. Meanwhile, a new metal-exchange scenario in which an Ag dopant goes to a counterion is also presented.

RESULTS

The starting material, [Au23(SR)16]− (counterion: tetraoctylammonium (TOA+)), was synthesized by a previously reported method (32). Single-crystal x-ray analysis revealed the details of the two-step molecular surgery process for the transformation of [Au23(SR)16]− to the [Au21(SR)12(P−C−P)x]2+ nanocluster (Fig. 1B). In the first step, a small amount of Ag(SR) at a molar ratio of Au/Ag = 1:0.07 was added to target-dope the [Au23(SR)16]−, and a silver-doped Au cluster, [Au23−xAgx(SR)16]− (x ~ 1), was obtained. The dopant Ag was found to be at two specific positions (centrosymmetric) in [Au23−xAgx(SR)16]− (Fig. 1B, middle). In the next step, [Au23−xAgx(SR)16]− was transformed to [Au21(SR)12(P−C−P)x]2+ by reacting with a gold(I)-diphosphine complex, Au2Cl2(P−C−P)2. It was found that the dopant Ag was reversely replaced by Au, and meanwhile, the two monomeric RS−Au−SR motifs, which protect the dopant Ag sites, are also exchanged by the P−C−P motif from the Au2Cl2(P−C−P)3 reactant. This simultaneous exchange of metal and surface motif produced the new [Au21(SR)12(P−C−P)x]2+ cluster and a silver-containing counterion, AgCl2−, which was formed after the dopant Ag was pulled out from the cluster.

Details of the x-ray structures of [Au23(SR)16]−, [Au23−xAgx(SR)16]−, and [Au21(SR)12(P−C−P)x]2+ are shown in Fig. 2. A previous study (32)
reported on the structure of [Au23(SR)16]−, which has a 15-atom bipyramidal Au core, that is, a 13-atom cuboctahedron plus two extra “hub” gold atoms (Fig. 2A, in blue) that links the surface-protecting staple motifs together. The core is protected by two belt-like trimeric Au6(SR)4 and two monomeric Au(SR)2 staple motifs, as well as four simple bridging SR ligands. The structure of [Au23–Ag6(SR)16]− is shown in Fig. 2B. The 15-atom bipyramidal Au–Ag core is shown on the left. There are only two specific sites (centrosymmetric) where Ag can be found. This is different from previously reported Au/Ag alloy nanoclusters in which the Ag atoms are distributed in many sites (31, 34, 35). The occupancy of Ag is determined to be 31.5 and 30.0% at position 1 in the two crystallographically independent clusters, whereas position 2 has a lower occupancy, determined to be 12.7 and 6.4%. The x-ray crystallography–averaged composition is [Au22.13Ag0.87(SR)16]−, and the fractional occupancy is caused by the compositional variation of the Au or Ag atom. One TOA+ counterion was found, although it shows heavy disorder, indicating that the −1 charge is retained in [Au23–Ag6(SR)16]− during the silver doping process of [Au23(SR)16]−.

The structure of [Au23–Ag6(SR)16]− is shown in Fig. 2C. Although the 15-atom bipyramidal core is retained in [Au23(SR)12(P–C–P)3]3+, the positions of the two hub gold atoms shift. In [Au23(SR)16]−, the two hub gold atoms (labeled Au-2) are closer to Au-3, with distances of 3.234 and 3.245 Å (Fig. 2A), whereas the distance between Au-1 and Au-2 is so large (3.462 Å) that no bond is formed. However, in [Au23(SR)12(P–C–P)3]3+, the Au-2 atom is closer to Au-1, with a much shorter distance of 2.934 Å; therefore, a bond forms. The distance between Au-2 and Au-3 is 3.425 Å in [Au23(SR)12(P–C–P)3]3+, with no Au2–Au1 bond formed. The average lengths of core Au–Au bonds in [Au23(SR)12(P–C–P)3]3+ and [Au23(SR)16]− are 2.95 and 2.98 Å, respectively. For the surface Au–Au bonds, the average lengths in [Au23(SR)12(P–C–P)3]3+ and [Au23(SR)16]− are 3.08 and 3.16 Å, respectively. The shorter bond distances in Au21 might enhance the radiative decay of the photoexcited particles. More significant changes occur on the surface. Surprisingly, the two monomeric S–Au–S motifs, which originally protect the two dopants Ag-1 and Ag-2 (partial occupancy), are exchanged by the P–C–P motifs from the Au23Cl3(P–C–P) complexes; in addition, the two doping sites become homogold. The two P atoms are bonded with the Au-1 and Au-2 with distances of 2.288 and 2.293 Å, respectively. The motif exchange leads to the loss of two staple gold atoms and thus gives rise to [Au23(SR)12(P–C–P)3]3+.

As shown in Fig. 3A, two phenyl rings are arranged in parallel through π-π stacking in each P–C–P motif. A silver-containing counterion, AgCl2−, is also identified. The AgCl2− anion has been previously reported in the Cs complex (36), but in metal nanoclusters, before this current work the Ag-containing counterion has never been identified. The Ag–Cl bond length is 2.348 Å, and the AgCl2− shows a nearly linear configuration (the angle of Cl–Ag–Cl is about 175°), which is similar to the previously reported metal complex (36). The packing of [Au23(SR)12(P–C–P)3]3+[AgCl2]− in the single crystal is shown in Fig. 3B, and each unit comprises two [Au23(SR)12(P–C–P)3]3+ and [AgCl2]−. The presence of the AgCl2− counterion in a one-to-one ratio with the cluster indicates a +1 charge of [Au23(SR)12(P–C–P)3]3+.

In view of the monovalent thiolate ligand and the neutral phosphine ligand, the nominal count of gold core free valence electrons (6s1) is...
Fig. 2. Comparison of the [Au21(SR)12(P−C−P)]3+ structures. (A) Crystal structure of [Au23(SR)16]−: Left: 15-atom Au bipyramidal core. Right: Au25S16 framework. (B) Crystal structure of [Au23−Ag(SR)16]−: Left: 15-atom Au−Ag bipyramidal core. Right: Au25−AgS16 framework. (C) Crystal structure of [Au21(SR)16(C−P−P)]3+: Left: 15-atom bipyramidal core. Right: Au21S12(P−C−P) framework. Magenta and blue, Au; gray, Ag; yellow, S; orange, P; green, C. Other C and all H atoms are omitted for clarity. The counterions TOA+ and AgCl2− are also omitted.

8e (that is, 21 − 12 − 1 = 8e), which is isoelectronic as [Au23(SR)16]− and [Au25−Ag(SR)16]−.

It can be concluded from the above single-crystal analysis that the new [Au23(SR)16(P−C−P)]3+ cluster holds a very similar atomic structure to the starting [Au23(SR)16]−, except for the site-specific replacement of the surface motif. It will be interesting to study how this targeted surgery influences the nanocluster’s overall property. The optical absorption spectrum of [Au23(SR)16(P−C−P)]3+ is shown in Fig. 3C, and is similar to that of [Au25(SR)16]− as well as [Au23−Ag(SR)16]− (Fig. S1), all with a distinct peak at ~570 nm and a less prominent one at 460 nm. Surprisingly, the photoluminescence (PL) efficiency of [Au23(SR)12(P−C−P)]3+ is found to be enhanced ~10 times compared to that of [Au23(SR)16]− (Fig. 3D). This 10-fold improvement may arise from the motif exchange–induced change of electronic interaction between the surface motifs and the Au core, leading to enhanced radiative recombination of the electron-hole pair, as reported in gold and other nanoparticles (37, 38). These results unambiguously reveal the surface motifs have little effect on optical absorption but a distinct effect on PL.

Matrix-assisted laser desorption ionization (MALDI) spectra of the three clusters are also shown in fig. S2, and confirm the composition of the three clusters. The positive-mode electrospray ionization (ESI) spectrum of [Au23(SR)12(P−C−P)]3+ is shown in fig. S3, and the 1-Da spacing of the isotropic peaks confirms the +1 charge of the cluster. The experimental isotope pattern is consistent with the simulated pattern. No signals of silver-doped [Ag2Au21−x(SR)12(P−C−P)]3+ can be observed in the ESI mass spectrum. Energy-dispersive x-ray spectroscopic (EDS) measurement under scanning electron microscopy (SEM) was also conducted on several [Au21(SR)12(P−C−P)]3+ [AgCl2]− crystals to further confirm the elemental ratio of Au/Ag. The average elemental ratio of Au/Ag from a number of crystals is calculated to be 21:1.04 (table S1), which is very close to 21:1 determined by single-crystal X-ray analysis. In addition, a 31P nuclear magnetic resonance (31P-NMR) experiment was also carried out, which showed a doublet peak at ~24/26 parts per million (fig. S4), corresponding to the Au2(P−C−P) environment in the Au21 cluster. To gain insight into the Au21 transformation to Au21 via the (Au−Ag)23 intermediate, we performed a control experiment in which the Au2Cl2(P−C−P) complex was directly reacted with [Au23(SR)16]− under the same conditions, but no [Au25(SR)12(P−C−P)]2− was obtained. This result suggests the importance of the intermediate product of [Au23−Ag(SR)16]− (x ~ 1), which is deemed to serve as a prerequisite for [Au23(SR)12(P−C−P)]2−. More Au complex/salt [for example, Au(SR) and AuCl] have been tested to investigate how the composition or structure of Au complex/salt influences structural transformation. The control experimental results show that [Au23−Ag(SR)16]− (~ x = 1) was retained when reacting with Au(SR), whereas the reaction with AuCl led to the conversion of [Au23−Ag(SR)16]− (~ x = 1) to other clusters. These results indicate that the Cl− may act as the driving force to extract the dopant Ag out of the cluster. Meanwhile, the structure of P−C−P in the Au complex, which perfectly matches the original S–Au–S motif, is also critical to stabilize the whole structure of the cluster.

On the other hand, structure/size transformation of [Au23(SR)16]− to [Au25−Ag(SR)18]− upon heavy silver doping (x ~ 19) was reported in our previous work (31). Compared to the present work, the different results (Au23−Ag with light doping versus Au25−Ag, with heavy doping) arise from the different amounts of Ag(SR) added in the reaction. The evolution of ultraviolet-visible (UV-Vis) absorption spectrum from [Au23(SR)16]− that reacted with increasing amounts of Ag(SR) is shown in fig. S5, which suggests the transformation from [Au23(SR)16]− through
[Au23−xAgx(SR)16]− to [Au25−xAgx(SR)18]−. The x-ray structure of Ag-doped [Au25−xAgx(SR)18]− (x ~ 4) is also solved (fig. S6), and the entire transformation pathway from [Au23(SR)16]− to the heavily doped [Au25−xAgx(SR)18]− is thus unveiled. As shown in fig. S7, the [Au23(SR)16]− is first transformed to [Au23−xAgx(SR)16]− (x = 1 to 2), and then it undergoes a size/structural change to [Au25−xAgx(SR)18]− (x ~ 4), with the dopant Ag located exclusively on the sites of the 12-atom icosahedral inner shell. Upon heavy doping, the dopant Ag will also go onto the surface motifs, and the heavily doped [Au25−xAgx(SR)18]− is accordingly obtained. These results suggest that the number of dopant Ag atoms is very important for the final structure of the alloy nanocluster product in this case. The doping-induced transformation from [Au23(SR)16]− to [Au21(SR)12(P–C–P)2]+ and [Au25−xAgx(SR)18]− is summarized in Fig. 4. Here, a small amount of Ag(SR) is critical to place the necessary dopant Ag atoms in specific positions (targeted doping) and retain the structure of the original [Au23(SR)16]−, which provides the way for the subsequent motif exchange to obtain [Au21(SR)12(P–C–P)2]+.

To further understand the driving forces in the synthesis of [Au23(SR)12(P–C–P)2]+ and [Au25−xAgx(SR)18]−, we performed a thermodynamic analysis of elementary growth steps using density functional theory (DFT) calculations as shown in Fig. 5 (see the Supplementary Materials for computational details). The growth and doping reaction steps involving the addition of M′(SR) species (M = Au or Ag) have been referenced to the energies of the thermodynamically very stable tetramer species [M4(SR)4] that have been both computationally (39) and

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**Fig. 3. Single-crystal structure and optical properties of [Au21(SR)12(P–C–P)2]+[AgCl2]−.** (A) The counteranion [AgCl2]− and coordination of PPh2CH2PPh2 motifs. Other carbon tails and all H atoms are removed for clarity. (B) Total structure and arrangement of [Au21(SR)12(P–C–P)2]+[AgCl2]− in a single-crystal unit cell. Magenta, Au; gray, Ag; yellow, S; orange, P; green, C; light green, Cl; white, H. (C) UV-Vis absorption spectrum of [Au21(SR)12(P–C–P)2]+. (D) PL spectrum of the Au21 (solid line); the PL efficiency is enhanced ~10 times compared to Au23 (dashed line). Inset shows a photograph of the Au21 sample under 365-nm UV light.

**Fig. 4. Metal-exchange transformation from [Au23(SR)16]− to [Au21(SR)12(P–C–P)2]+ and [Au25−xAgx(SR)18]−.**
experimentally (40) observed in thiolated group XI metal complexes (this reference selection does not affect the relative thermodynamic stability of the species and results in accurate reaction energy calculations; see table S4). First, we observe that for the [Au23(SR)16]− and [Au22Ag(SR)16]− clusters, Ag doping reactions are exothermic and slightly preferred over growth reactions to form [Au25−xAgx(SR)18−x]− nanoclusters. Additionally, we see that the growth of [Au23(SR)16]− to [Au25(SR)18]− is unfavorable. However, for the [Au21Ag(SR)16]− cluster, growth to [Au21Ag2(SR)16]− becomes energetically more preferred than the doping step to [Au20Ag5(SR)18]−, rationalizing the lack of observed [Au20Ag5(SR)16]−. This preference in the Ag growth step over Ag doping is further enhanced in the reaction of [Au20Ag6(SR)16]− to form [Au20Ag6(SR)18]− over [Au19Ag5(SR)16]−. This demonstrates an increasing energetic preference for growth to [Au25−xAgx(SR)18−x]− nanoclusters, in agreement with the observation that [Au23−xAgx(SR)16−x], with x more than 2, is not formed. Next, we observe a significantly uphill thermodynamic reaction between Au2Cl2(P−C−P) and [Au23(SR)16]− to form the [Au21(SR)12(P−C−P)2AuCl2]− cluster (representing motif exchange reactions). However, when Ag atoms are doped into [Au23(SR)16]− to form [Au21Ag(SR)16]−, the presence of the higher-energy (2,2) isomer of [Au21Ag(SR)16]− creates an almost thermoneutral path, enabling the formation of [Au21(SR)12(P−C−P)2AgCl2]−. Note that all these theoretical findings are in agreement with the experimental observations, demonstrating that a thermodynamic (free energy) analysis can capture the growth behavior of these nanoclusters (at least for the systems of interest).

DISCUSSION
Here, a two-step metal-exchange method has been developed for site-specific surface motif exchange on [Au23(SR)16]− to form a new [Au23(SR)12(P−C−P)2]− nanocluster. Both experimental and DFT calculations indicate that the formation of the [Au23−xAgx(SR)16]− (x = 1 to 2) intermediate is critical, and the dopant Ag atoms are target-doped at two specific positions (partial occupancy). Doping lowers the transformation barrier and thus enables transformation from Au23 to Au21 when [Au23−xAgx(SR)16]− reacts with Au2Cl2(P−C−P), whereas the reaction with more Ag1 (SR) leads to size/structure changes and the formation of Au25−xAgx. This work offers a promising strategy for molecular surgery on nanoclusters to tailor their structure and functionality.

MATERIALS AND METHODS

**Chemicals**
Tetrachloroauric(III) acid (HAuCl4·3H2O, 99.99%; Sigma-Aldrich), cyclohexanethiol (C6H11SH, 99%; Sigma-Aldrich), bis[chlorogold(I)] bis(diphenylphosphino)methane [Au23Cl2(P−C−P), 97%; Sigma-Aldrich], sodium borohydride (NaBH4, 99.9%; Sigma-Aldrich), tetracyclammonium bromide (TOAB, 98%; Fluka), pentane [high-performance liquid chromatography (HPLC) grade, 99.9%; Sigma-Aldrich], ethanol (HPLC grade; Sigma-Aldrich), methanol (HPLC grade, 99%; Sigma-Aldrich), and dichloromethane (DCM) (HPLC grade, 99.9%; Sigma-Aldrich) were used as received.

**Synthesis and crystallization**
To synthesize [Au23−xAgx(SR)16]− (x = 1 to 2), 20 mg of molecularly pure [Au23(SR)16]− made using a previously reported method (32) was first dissolved in 3 ml of DCM, and 1.2 mg of Ag1(SR) (powder) (29) was added, with a molar ratio of elemental Au/Ag in reactants of 1:0.07. The reaction was allowed to proceed for ~1 hour and was monitored by MALDI mass and UV-Vis spectroscopy. After [Au23(SR)16]− was converted to [Au23−xAgx(SR)16]− (judging from MALDI spectra), the DCM solution containing the [Au23−xAgx(SR)16]− product was directly transferred to a glass tube, and pentane was diffused into the solution at room temperature for crystallization of clusters. After ~2 days, crystals of [Au23−xAgx(SR)16]− were obtained on the inner wall and at the bottom of the glass tube. Notably, this crystallization step also serves as isolation/purification of the [Au23−xAgx(SR)16]− product, and to obtain high-quality single crystals, the crystals were redisolved and then recrystallized for several times. The product yield of [Au23−xAgx(SR)16]− was ~70% (crystals after the final step).

To synthesize [Au22(SR)12(P−C−P)2]−, 30 mg of accumulated [Au23−xAgx(SR)16]− crystals was first redissolved in 6 ml of DCM, and 8.0 mg of the Au2Cl2(P−C−P) complex was added (molar ratio of reactants = 1:2). The reaction was allowed to proceed at room temperature for ~3 hours, which was also monitored by MALDI mass and UV-Vis spectroscopy. After [Au23−xAgx(SR)16]− was converted to [Au22(SR)12(P−C−P)2]−, the DCM solution containing [Au22(SR)12(P−C−P)2]− clusters was transferred to a glass tube, to which pentane was diffused at room temperature for crystallization. After 3 to 5 days, black crystals of [Au22(SR)12(P−C−P)2]− were observed at the bottom and side wall of the glass tube and then collected. The redissolving and recrystallization processes were performed to obtain high-quality [Au22(SR)12(P−C−P)2]− single crystals. The product yield was ~80% at the final step. Notably, if [Au23(SR)16]− was used as the reference, then the product yield of [Au22(SR)12(P−C−P)2]− would be ~56%.

For the synthesis of [Au25−xAgx(SR)18]− (x ~ 4), 20 mg of molecularly pure [Au23(SR)16]− was first dissolved in 3 ml of DCM, and 4 mg of Ag1(SR) (powder) was then added (molar ratio of elemental Au/Ag in reactants = 1:0.23). The reaction was allowed to proceed overnight at 0°C, and was monitored by MALDI mass and UV-Vis spectroscopy until the [Au23(SR)16]− reactant was converted to [Au25−xAgx(SR)18]−. Next, the solution containing [Au25−xAgx(SR)18]− was mixed with acetoni-trile (DCM/acetonitrile ratio = 3:2) and was allowed to evaporate...
slowly for ~4 days at 4°C. Black crystals of [Au_{23−x}Ag_{x}(SR)_{16}]− were observed at the bottom and side wall of the glass tube and then collected. The product yield of [Au_{23−x}Ag_{x}(SR)_{16}]− was ~30%.

**Characterization**

UV-Vis spectra of the clusters (dissolved in CH2Cl2) were acquired on a Hewlett-Packard Agilent 8453 diode array spectrophotometer at room temperature. MALDI mass spectrometry was performed on a PerSeptive Biosystems Voyager DE super-STR time-of-flight (TOF) mass spectrometer. ESI mass spectra were recorded using a Waters Q-Tof mass spectrometer equipped with Z-Spray Source. 31P-NMR mass spectrometer. ESI mass spectra were recorded using a Waters PerSeptive Biosystems Voyager DE super-STR time-of-flight (TOF) mass spectrometry. MALDI mass spectrometry was performed on a TURBOMOLE 6.6 package (gray). Geometry optimizations were carried out using the quasi–Newton-Raphson method without any symmetry constraints. Gibbs free energies were calculated using the harmonic oscillator approach applied to the vibrational modes calculated for the entire nanoparticles at 298.15 K. See equations below for reference in the calculation of free energy

\[ E_{\text{tot}} = E_{\text{electronic}} + ZPE + RT - RT \times \ln(q_{\text{tot}} \times q_{\text{vib}} \times q_{\text{trans}}) \]

where \( E_{\text{tot}} \) represents the total molar free energy, \( E_{\text{electronic}} \) represents the electronic energy, ZPE represents the zero-point vibrational energy, \( R \) is the ideal gas constant, \( T \) is the temperature, \( q_{\text{tot}} \) is the rotational partition function, \( q_{\text{vib}} \) is the vibrational partition function, and \( q_{\text{trans}} \) is the translational vibrational motion (set to 1 atomic unit to neglect in this case).

\[ q_{\text{vib}} = \prod_{i} \frac{1}{1 - \exp(-w \cdot e(i)/k_{B}T)} \]

where \( e(i) \) represents the vibrational energy of the \( i \)th vibrational state and \( k_{B} \) is Boltzmann’s constant. The factor of \( w = 0.9914 \) was used as a correction to the vibrational energies (47).

\[ q_{\text{tot}} = \frac{(2 \times \pi \times k_{B} \times T)^{2} \times A \times B \times C^{0.5}}{\pi} \]

where \( A, B, \) and \( C \) represent the moments of inertia of the molecules and \( \sigma \) represents the symmetry number.

The [Au_{23}(SR)_{16}]− and [Au_{25}(SR)_{18}]− structures were taken from previously published crystallographic information, the R groups of the thiolates were substituted by methyl groups, and the positive counterions were removed (15, 32). The structure of [Au_{23}(SR)_{12}(P−C−P)(AgCl_{2})]− was taken from table S3, and the R groups (−C_{6}H_{17}) of the thiolates were substituted for (−CH_{3}). Note that the BP86 functional has been successfully used on thiolated metal nanocluster systems (48), and R = methyl group substitution has had little impact on RS−Au bond strength, as has been previously applied in computational nanoparticle structural determinations (48). From the optimized [Au_{23}(SCH_{3})_{16}]− particle, Au atoms were substituted for Ag atoms in each position, and the optimized isomers and relative energies are presented in fig. S8. From the [Au_{25}(SCH_{3})_{18}]− particle, Ag atoms were substituted into the icosahedral core, where Ag is determined to preferentially sit, to form [Au_{25−x}Ag_{x}(SCH_{3})_{18}]− (x = 1 to 5) and were then relaxed (35). Gibbs free energies for Ag doping and growth reactions are presented in table S4. Tetramers [M_{4}(SR)]− were used as a common reference for the growth and doping reactions for the M_{4}(SR) complexes (\( M = \text{Au or Ag} \)) because these tetramers have been previously shown to be highly thermodynamically stable (39) and similar in structure to the surface staple motifs of the clusters. Moreover, these tetramers have been experimentally observed as prenucleation species in thiolated group XI bimetallic solutions (40).

**X-ray analysis**

Details of the x-ray crystallographic analysis are provided in the Supplementary Materials.

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/3/5/e1603193/DC1

**X-ray Experiments**

fig. S1. UV-Vis absorption spectra of [Au_{23}(SR)_{16}]− and [Au_{25−x}Ag_{x}(SR)_{16}]−.

fig. S2. MALDI mass spectra of [Au_{23}(SR)_{16}]− (black), [Au_{25−x}Ag_{x}(SR)_{16}]− [green], and [Au_{25}(P−C−P)_{12}]− (gray) sample.

fig. S3. ESI mass spectrum of [Au_{25}(P−C−P)_{12}]−.

fig. S4. 31P-NMR spectrum of [Au_{25}(P−C−P)_{12}]−.

fig. S5. UV-Vis absorption spectra of samples with increasing mass ratio of Ag(SR) that reacted with [Au_{25}(SR)_{2}]−.

fig. S6. X-ray crystal structure of [Au_{25−x}Ag_{x}(SR)_{16}]− (x = 4).

fig. S7. AgI(SR) complex–induced transformation from [Au_{25−x}Ag_{x}(SR)_{16}]− to heavily Ag-doped [Au_{25−x}Ag_{x}(SR)_{16}]−.

fig. S8. DFT-relaxed [Au_{23}(SR)_{16}]− (x = 1 to 3) and [Au_{25−x}Ag_{x}(SR)_{16}]− (y = 2, 3) nanoclusters and associated relative electronic energies.

table S1. Atomic percentages of Au and Ag in the [Au_{21}(SR)_{12}(P−C−P)_{2}]−[AgCl_{2}]−


table S2. DFT free energies of reactions of intermediates and possible reaction pathways.


table S3. Crystal data and structure refinement for [Au_{23}(SR)_{16}]− [AgCl_{2}]−.


table S4. Crystal data and structure refinement for [Au_{25}(SR)_{18}]− [AgCl_{2}]−.


table S5. Crystal data and structure refinement for [Au_{25}(SR)_{18}]− [P−C−P]_{12}]−[AgCl_{2}]−.

**REFERENCES AND NOTES**


Acknowledgments: This work was financially supported by the Air Force Office of Scientific Research under award no. FA9550-15-1-0000. M.G.T. acknowledges support from the NSF Graduate Research Fellowship under grant no. 1247842. Author contributions: Q.L. and R.J. designed the research; Q.L. performed synthesis and crystallization; M.G.T. and G.M. obtained the materials; A. M. performed DFT calculations; and T.-Y.L. and N.L.R. conducted x-ray crystallographic analysis. All authors analyzed data and contributed to the writing of the manuscript. Competing interests: The authors declare that they have no competing interests. Data and materials availability: All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

Submitted 15 December 2016
Accepted 20 March 2017

Molecular "surgery" on a 23-gold-atom nanoparticle
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Sci Adv 3 (5), e1603193.
DOI: 10.1126/sciadv.1603193

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