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## Metal-Ligand Interface in the Chemical Reactions of Ligand-**Protected Noble Metal Clusters**

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ABSTRACT: We discuss the role of the metal-ligand (M-L) interfaces in the chemistry of ligand-protected, atomically precise noble metal clusters, a new and expanding family of nanosystems, in solution as well as in the gas phase. A few possible mechanisms by which the structure and dynamics of M-L interfaces could trigger intercluster exchange reactions are presented first. How interparticle chemistry can be a potential mechanism of Ostwald ripening, a well-known particle coarsening process, is also discussed. The reaction of  $Ag_{s0}(2,5-DCBT)_{32}$  (DCBT = dichlorobenzenethiol) with 2,4-DCBT leading to the formation of  $Ag_{44}(2,4-DCBT)_{30}$  is presented, demonstrating the influence of the ligand structure in ligand-induced chemical transformations of clusters. We also discuss the structural isomerism of clusters such as  $Ag_{44}(SR)_{30}$  (-SR = alkyl/aryl thiolate) in the gas phase wherein the occurrence of isomerism is attributed to the structural rearrangements in the M-L bonding network. Interfacial bonding between  $Au_{25}(SR)_{18}$  clusters leading to the formation of cluster dimers and trimers is also discussed. Finally, we show that the desorption of phosphine and hydride ligands on a silver cluster,  $[Ag_{18}(TPP)_{10}H_{16}]^{2+}$  (TPP = triphenylphosphine) in the gas phase, leads to the formation of a naked silver cluster of precise nuclearity, such as  $Ag_{17}^+$ . We demonstrate that the nature of the M-L interfaces, i.e., the oxidation state of metal atoms, structure of the ligand, M-L bonding network, and so forth, plays a key role in the chemical reactivity of clusters. The structure, dynamics, and chemical reactivity of nanosystems in general are to be explored together to obtain new insights into their emerging science.

### INTRODUCTION

Metal-ligand (M-L) interfaces play key roles in dictating the physical properties, chemical reactivity, and interparticle interactions of ligand-protected metal nanosystems. Atomically precise noble metal clusters,<sup>1,2</sup> such as  $Au_{102}(SR)_{44}$ ,  $M_{25}(SR)_{18}$  (M = Ag/Au),<sup>4,5</sup> and Ag<sub>44</sub>(SR)<sub>30</sub>,<sup>6,7,2,7</sup>(-SR = alkyl/aryl thiolate), serve as convenient models for investigating the properties of M-L interfaces owing to their welldefined compositions, structures, and molecule-like properties.<sup>8–10</sup> Such clusters have a well-defined metal core protected by a ligand shell. The feasibility of incorporating a variety of ligands such as phosphines,  $^{11-13}$  thiols,  $^{7,14-19}$  selenols,  $^{20-22}$ and alkynes,<sup>23</sup> also makes them suitable systems for studying the M-L interfaces. Early in the literature, these clusters were referred to as "monolayer protected clusters",<sup>24</sup> assuming that the ligands form an extended ordered layer on particle surfaces,<sup>25</sup> which in turn resemble crystallographic planes of the corresponding metals. Single-crystal X-ray crystallography

revealed that the M-L interfaces in many of these clusters assume well-defined, short M<sub>x</sub>L<sub>y</sub> oligomeric units. For example,  $Au_{25}(SR)_{18}$  is composed of a  $Au_{13}$  core and six  $Au_2(SR)_3$  units, often referred to as staple motifs. Similarly, Ag<sub>44</sub>(SR)<sub>30</sub> consists of an Ag<sub>32</sub> core protected by six Ag<sub>2</sub>(SR)<sub>5</sub> mounts. This structural model has been referred to as the "divide and protect" model<sup>26</sup> wherein these clusters are viewed as a core containing a precise number of metal atoms protected by a specific number of M<sub>x</sub>L<sub>y</sub> oligomeric units. Structural correlations between these clusters and that of M-L complexes and self-assembled monolayers have also been identified.<sup>27</sup> Recently, a few other structural models<sup>28-30</sup> in which these clusters have been considered as interlocked rings,

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**Figure 1.** Crystal structure of  $Au_{25}(C_6H_5CH_2CH_2S)_{18}$  (A), schematic showing the icosahedral core and the six  $Au_2(SR)_3$  staples (B), negative ion ESI MS spectrum (C), and UV/vis absorption spectrum of  $Au_{25}(C_6H_5CH_2CH_2S)_{18}$  (D). The  $C_6H_5CH_2CH_2$  groups of the ligands are omitted in panel B for clarity. The structures are intended to highlight the ligand–core interface. Color codes of atoms: Au atoms at the surface of the  $Au_{13}$  icosahedral core (black), in the center of the  $Au_{13}$  icosahedron (green), in the staples (orange), sulfur (yellow), carbon (gray), and hydrogen (white). Distinct features in the mass and the UV/vis spectra are also marked in panels C and D. The isotopic resolution of the molecular ion features of  $Au_{25}(C_6H_5CH_2CH_2S)_{18}$  at m/z 7391 is shown in the inset of panel C along with a comparison of the theoretical (black) and experimental (red) spectra. The abbreviation PET (phenylethanethiolate) in Figure 1C correspond to the ligand tail group  $C_6H_5CH_2CH_2S$ .

instead of distinct staples or mounts, have been proposed to understand the properties of these clusters. Irrespective of the structural model, the actual structure of the ligands, their spatial distribution on the cluster surface, binding modes of the ligands with the metal atoms, and oxidation states of metal atoms need to be considered in order to understand the M-Linterfaces in these clusters.

The nature of ligands such as the types of tail groups (alkyl and aryl) and the positions<sup>31</sup> (ortho, meta, and para) of functional groups ( $-CH_3$ , -COOH, etc.) in them drastically influence the nuclearity, geometry, solubility, and other properties of clusters.<sup>32,33</sup> Weak van der Waals and/or  $\pi-\pi$  interactions between the ligands is shown to be responsible for their chiroptical properties,<sup>34,35</sup> supramolecular interactions,<sup>36</sup> and cluster assemblies.<sup>37–39</sup> The electronic interaction between the ligands and the metal core influences the optical absorption<sup>40</sup> and luminescence<sup>41,42</sup> features. Metal atoms in the staples serve as the true catalytic sites in such clusters. A variety of chemical transformations of these clusters such as ligand exchange,<sup>43–47</sup> metal atom substitution,<sup>48–53</sup> ligand-induced core etching<sup>54,55</sup> and core transformation, <sup>56–58</sup> were reported in the past few years. Recently, reactions between clusters in the solution phase were also reported.<sup>59–64</sup> These reactions invariably involve the metal atoms and ligands in the staple or mount motifs of these clusters.<sup>65–68</sup> The dynamic nature of the staple motifs or mounts<sup>69–74</sup> and the reactions of these clusters have been studied, mostly in the solution phase.

The stability and the dynamics of these M-L interfaces in gaseous phase, and the resulting chemical reactivity of ligandprotected clusters remain poorly understood. In order to understand the chemical reactivity of these clusters, a better understanding of their M-L interfaces is essential.

In this invited feature article, we discuss the role of M-L interfaces in dictating the solution as well as gas-phase reactions of ligand-protected, atomically precise noble metal clusters. We discuss the role of the staples or mount motifs in such clusters in triggering the intercluster exchange reactions. We propose that interparticle chemistry, as demonstrated between atomically precise clusters, can be helpful in understanding the chemical events behind Ostwald ripening, a well-known particle-coarsening process. Next, we show that the ligand-induced transformation of  $Ag_{59}(2,5-DCBT)_{32}$  to  $Ag_{44}(2,4-DCBT)_{30}$  (DCBT = dichlorobenzenethiol) occurs in the solution phase through the dissociation of metal ligand fragments.<sup>75</sup> Then we discuss three examples wherein the gasphase dynamics and reactivity of M-L interfaces are demonstrated. We present ion mobility mass spectrometric studies showing that ligand-protected clusters such as Ag44(SR)30 exhibit structural isomerism in the gas phase wherein the isomerism is attributed to the structural rearrangements in the metal-ligand bonding network.<sup>76</sup> Interfacial bonding between Au<sub>25</sub>(SR)<sub>18</sub> clusters leading to the formation of cluster dimers and trimers is also presented.<sup>77</sup> Finally, we show that the desorption of phosphine and hydride



**Figure 2.** (A) Visualization of  $Au_{25}S_{18}$  as the ring structure consisting of three interlocked  $Au_8S_6$  rings. (B) Topological configuration of the Borromean rings, with the three  $Au_8S_6$  rings being colored red, blue, and green. (C) Two-dimensional schematic diagram of the Borromean rings formed by a planar projection of the  $Au_{25}S_{18}$  ring structure shown in panel A, wherein the  $Au_8S_6$  rings formed by pairs of coplanar staples are shown as ellipses. In panel C, the gold atoms in the  $Au_{13}$  icosahedral core are shown by gray circles, and yellow stars represent the positions of S atoms of the thiolate ligand. The orange circles in panel C represent the position of Au atoms in the Au8S6 rings. The core Au atoms are numbered from 1 to 12, and the staple atoms are numbered clockwise from the end of the staple, from 1 to 5. The lines that join core Au atoms on opposite ends of the same staple are shown by the dotted lines. The three perpendicular  $C_2$  axes are marked with the associated Cartesian axes directions in parentheses. The staple directions are labeled by the six staple locants D1–D6, marked in blue. The  $Au_8S_6$  rings in panel C are formed by joining three sets of coplanar staples, i.e., D1–D2, D3–D4, and D5–D6. Color codes of atoms in panel A: Au atoms in the icosahedral core (gray), center of the  $Au_{13}$  icosahedron (green), staples (orange), and sulfur (yellow). (Adapted with permission from ref 28.)

ligands on a silver cluster,  $[Ag_{18}(TPP)_{10}H_{16}]^{2+}$  in the gas phase, leads to the formation of naked silver clusters of specific nuclearity, such as  $Ag_{17}^{+,78}$  We conclude the article with a summary and brief discussion of future perspectives.

Intercluster Reactions: What Is the Role of the Metal-Ligand Interface? As mentioned above, thiolateprotected noble metal clusters have traditionally been viewed as composed of a core consisting of a definite number of metal atoms, protected with a well-defined shell of metal-ligand oligomeric complexes. The single crystal X-ray crystallographic structure of  $Au_{25}(C_6H_5CH_2CH_2S)_{18}$ , for example, is shown in Figure 1A,B. This cluster consists of an inner Au<sub>12</sub> icosahedral core (black spheres in Figure 1A,B) encapsulating a central Au atom (green spheres in Figure 1A,B), and the ligands are distributed in six distinct Au<sub>2</sub>(SR)<sub>3</sub> staple motifs (orange and yellow spheres in Figure 1B). The composition and charge state of these clusters are further confirmed through electrospray ionization mass spectrometry (ESI MS) as well, as shown in Figure 1C. The high-resolution mass spectrum (inset of Figure 1C) shows the isotopic features. Although Au has only one isotope, the isotopes of S ( $^{32}$ S,  $^{33}$ S,  $^{34}$ S, and  $^{36}$ S), C ( $^{12}$ C and <sup>13</sup>C), and H (<sup>1</sup>H and <sup>2</sup>H) produce a rich spectrum. Such richness can be used to confirm the composition of the cluster by comparing with the theoretical spectrum. Electronic structure calculations show that the distinct electronic absorption features of these clusters (Figure 1D) originate from various transitions in their discrete electronic energy levels. Thus, crystallography and electronic structure calculations support this structural model of these ligand-protected noble metal clusters. However, in order to understand the chemical reactivity of these clusters, it is necessary to consider other structural models. We discuss some of these aspects in the following sections.

Recently, intercluster reactions, resulting in the exchange of metal atoms, ligands, and metal-ligand fragments between them, have been demonstrated.<sup>59,60,62,63</sup> However, the mechanisms of such reactions, especially how such reactions are triggered, remain unknown. In this section, we discuss a

few possible ways by which the structure and the dynamics of M-L interfaces trigger intercluster reactivity. For this, we consider the reaction between two structurally and compositionally analogous noble metal clusters, Ag<sub>25</sub>(SR)<sub>18</sub> and Au<sub>25</sub>(SR)<sub>18</sub>.<sup>59</sup> As mentioned above, these clusters have traditionally been viewed as composed of a distinct M<sub>13</sub> core protected by  $M_2(SR)_3$  (M = Ag/Au) staples. According to the superatom theory,<sup>27</sup> valence electrons of metal atoms in their staples are localized by polar covalent bonds with the sulfur atoms of the ligands. Furthermore, each of the  $M_2(SR)_3$  staples localizes the valence electron of one of the metal atoms in the  $M_{13}$  core. Therefore, all of the metal atoms in the six  $M_2(SR)_3$ staples and six of the metal atoms in the M113 core are considered to be in the +1 oxidation state. The remaining seven valence electrons of the Au<sub>13</sub> core and an acquired negative charge make the eight-electron superatom,  $[Au_{25}(SR)_{18}]^{-}$ . In the crystal structure, charge neutrality is provided by the metal ions or ammonium ions. The studies presented in this article are performed with this  $Au_{25}(SR)_{18}$ anion in solution, although this may not be mentioned explicitly.

We think that the difference in the oxidation states of metal atoms in the core and the staples, as explained above, plays a crucial role in triggering the intercluster reactions. Because of this difference in oxidation states, redox-like reactions could occur between two clusters. Let us consider two such possibilities, taking the reaction between  $Ag_{25}(SR)_{18}$  and  $Au_{25}(SR)_{18}$  as an example. In the first case, an  $Ag_{25}(SR)_{18}$ molecule reacts with the  $Au_2(SR)_3$  staples of  $Au_{25}(SR)_{18}$ , wherein Au of  $Au_2(SR)_3$  staples is in the +1 oxidation state. Note that redox reactions between silver clusters and Au(I) thiolates are known.<sup>49</sup> Alternatively, an  $Au_{25}(SR)_{18}$  molecule reacts with the  $Ag_2(SR)_3$  staples of  $Ag_{25}(SR)_{18}$ , wherein Ag of the  $Ag_2(SR)_3$  staple is in the +1 oxidation state. Such reactions between  $Au_{25}(SR)_{18}$  and Ag(I) thiolates are also known.<sup>48</sup> It remains unclear as to how the difference in oxidation states of metal atoms in the core and the staples contributes to the chemical reactivity of these clusters. Apart from these

possibilities, it has also been intuitively suggested in the reaction between  $Au_{25}(SR)_{18}$  and  $Ag_{44}(SR)_{30}$  that the interaction between these two intact clusters could result in the formation of small reactive fragments such as  $Ag(SR)_2^{-}$ , which react with the  $Au_2(SR)_3$  staples of  $Au_{25}(SR)_{18}$ , resulting in an exchange of metal atoms, ligands, and M–L fragments.<sup>62</sup> In this context, it is important to understand how much the chemistry of these clusters differ from that of the M–L complexes. In other words, do these clusters behave as unique entities in their reactions wherein the overall electronic structures of both of the reacting clusters need to be considered in order to explain their reactivity (rather than attributing their chemistry to the reaction between one of the clusters and the staples or the mounts of the other, as explained earlier)?

A new structural model, namely, the Borromean rings model,<sup>28</sup> has been proposed for the Au<sub>25</sub>(SR)<sub>18</sub> noble metal cluster by Natarajan et al., wherein Au<sub>25</sub>(SR)<sub>18</sub> has been considered to be part of three interlocked  $Au_8(SR)_6$  rings surrounding the central Au atom (Figure 2). In this, all of the metal and sulfur atoms, except the central metal atom, belong to a unique structural component, the  $Au_8(SR)_6$  ring. This model suggests that disconnecting any ring leads to two unlinked rings, which is a defining characteristic of the Borromean rings bonding topology (Figure 2B). The Borromean rings model also applies to a silver cluster,  $Ag_{25}(SR)_{18}$ , which is a structural analogue of  $Au_{25}(SR)_{18}$ . Natarajan et al. also noted that interlocked metal-thiolate ring structures have been found in the core and staple structures of a few gold-thiolate clusters which have crystal structures available, both smaller and larger than  $Au_{25}(SR)_{18}$ , namely,  $Au_{10}(SR)_{10}$ ,<sup>79</sup>  $Au_{20}(SR)_{16}$ ,<sup>80</sup> and  $Au_{144}(SR)_{60}$ .<sup>30,81</sup> They suggested that the interlocked ring structures form a strong framework for the clusters and may possibly represent a unified viewpoint for the structure of monolayer-protected clusters. According to this interlocked-ring structural model, these clusters being formed out of and stabilized by ring structures are more dynamic in nature than one would expect from the core/staple model because in the latter the M<sub>13</sub> core has been viewed as a distinct, compact structural unit which undergoes structural distortion with difficulty. Furthermore, if the cluster existed in solution as a distinct, structurally rigid Au<sub>13</sub> core and  $Au_2(SR)_3$  staples, then the exchange of metal atoms into the core would not have been feasible. However, the exchange of metal atoms in the core also occurs during the reaction between  $Ag_{25}(SR)_{18}$  and  $Au_{25}(SR)_{18}$ , suggesting that the icosahedral Au13 core is flexible and dynamic in nature, as experimentally proven by Tsukuda et al.<sup>29</sup> Ghosh et al. have shown that the dynamics of M-L interfaces can be controlled by using dithiolates which bind to the metal core in a bidentate fashion and thereby reduce the flexibility of the metal-ligand bonding network.<sup>82</sup> Hence, we think that an interlocked-ring model of the structure can better explain the enhanced dynamics of M-L interfaces and the reactivity of clusters.

Even though the mechanistic details are not known, it has been suggested that interactions between the M–L interfaces might occur in the initial stages of these reactions. In the reaction between  $Au_{25}(SR)_{18}$  and  $Ag_{25}(SR)_{18}$ , we detected a dimeric species,  $[Ag_{25}Au_{25}(DMBT)_{18}(PET)_{18}]^{2-}$  (DMBT and PET are 2,4-dimethylbenzenethiolate and 2-phenylethanethiolate, respectively), which could be one of the intermediates of the reaction.<sup>59</sup> Density functional theory (DFT) calculations revealed that this adduct could be formed through weak covalent bonding between them via interstaple metal–sulfur bonds.<sup>59</sup> Recently, Zhang et al. attempted to detect such intermediates during the reaction between  $Au_{38-x}Ag_x(SR)_{24}$  and  $Au_{38}(SR)_{24}$  using in situ X-ray absorption fine structure (XAFS) measurements.<sup>66</sup> However, the detection of exchanged Ag atoms in the staples was not successful, possibly due to a shorter residence time of the exchanged Ag atoms in the staples.

Ostwald Ripening and Interparticle Reactions. Ostwald ripening is one of the important mechanisms of nanocrystal growth<sup>83</sup> wherein larger particles grow larger at the expense of smaller ones in solution. The thermodynamic driving force behind this process is the difference in surface energies of (smaller and larger) particles in a polydisperse solution/dispersion. Smaller particles possess a higher surface energy, and hence they disappear more easily compared to the larger particles in the same solution/dispersion. Ostwald ripening occurs by the diffusion of the smaller particles toward the larger particles and subsequent reactions between them resulting in the growth of the particle.<sup>83</sup> This makes the larger particles grow larger, consuming or reducing the size of the smaller ones. However, it remains unclear as to how the constituents (atoms, ions, or molecules) of smaller particles are transported to the larger ones, i.e., by a direct interparticle exchange or an exchange of their fragments, in such processes. Details of chemical events in such processes are not known clearly. It was shown that in the case of noble metal clusters, exchanges of metal atoms, ligands, and metal ligand fragments occur through direct interaction or collision between the reacting clusters. How do these two processes i.e., intercluster exchange and Ostwald ripening, differ from each other? Can Ostwald ripening be interpreted or understood as interparticle exchange reactions between larger particles and smaller ones?

Let us discuss this briefly in the context of ligand-protected metal nanosystems. For example, consider a dispersion of thiolate-protected metal nanoparticles, which are typically polydisperse in size. In such a mixture, smaller particles could be more reactive compared to the larger ones for reasons other than the surface energy differences, such as changes in the oxidation states, differences in the redox potentials of (smaller and larger) particles, and differences in metal—ligand binding modes, as mentioned previously in the context of atomically precise clusters. Do such factors contribute to the interparticle reactions (between larger and smaller particles) resulting in Ostwald ripening?

In the intercluster exchange reactions reported so far, the size, structure, composition (i.e., number of metal atoms and ligands), and charge state remain unaltered. This could be due to the tendency of these clusters to retain their compact, highly symmetric, geometrically and electronically stable structures. Furthermore, these clusters are molecule-like and are of comparable sizes, wherein electronic factors, such as shell closing effects rather than geometrical factors, determine the stability. However, in Ostwald ripening, the particle size changes, as mentioned above. In this context, it is interesting to determine whether there is a clear particle size limit at which an intercluster/interparticle exchange reaction and Ostwald ripening can be discriminated by the change or constancy of the particle size? Maran et al. have recently reported the formation of Au<sub>38</sub>(SR)<sub>24</sub> from a smaller cluster, Au<sub>25</sub>(SR)<sub>18</sub>, which they referred to as "gold fusion". However, it remains unclear whether this reaction can be understood as an example of Ostwald ripening of atomically precise clusters.<sup>84</sup> The above



Figure 3. Schematic of the ligand-induced conversion pathway of  $Ag_{59}(2,5-DCBT)_{32}$  to  $Ag_{44}(2,4-DCBT)_{30}$ . L and L\* denote 2,5-DCBT and 2,4-DCBT, respectively. (Reproduced with permission from ref 75.)

discussion implies that it is important to investigate the (surface/interfacial) chemical events *between* particles in an Ostwald ripening process, at least in the context of ligand-protected nanosystems.

**Influence of Ligand on Cluster Transformations.** Atomically precise clusters with a wide variety of nuclearity, geometry, and protecting ligands have been reported in the past decade. However, it remains unknown as to how the actual structure of the ligands influences the nuclearity and geometry of the clusters. One of the ways to investigate this aspect is to study the reactions of ligand-protected clusters with free ligands. Often, ligand exchange occurs in these reactions without altering the overall structure and charge states of the clusters.<sup>45–47,85</sup> However, in some cases, reactions of a cluster with a new type of ligand transform the cluster to completely new entities.<sup>86</sup>

Khatun et al. demonstrated that such a reaction wherein a monothiolate-protected cluster,  $Ag_{59}(2,5-DCBT)_{32}$ , upon reaction with the 2,4-DCBT ligand slowly converts it to  $Ag_{44}(2,4-DCBT)_{30}$ .<sup>75</sup> Note that ligands 2,4-DCBT and 2,5-DCBT differ only in the positions of the substituent Cl groups (isomeric thiols). This reaction demonstrates that such minute changes in the structure of the ligands drastically change the nuclearity of the cluster. This could be due to the position-dependent (ortho, para, or meta) changes in the electron-

donating or electron-withdrawing inductive (+I or - I) effects of the methyl groups of the ligands. The  $\pi$ - $\pi$  interactions and steric hindrance between the substituent groups might also play roles in these transformations. Mass spectrometric measurements reveal that the reaction involves the formation of small metal-ligand fragments of clusters (Figure 3). Ligand exchange was proposed to be one of the initial stages of such transformations;<sup>87</sup> however, in this case, no ligand exchanges were observed because the molecular masses of both thiols were the same. The use of different thiols such as FTP (4fluorothiophenol) and CTP (4-chlorothiophenol) shows ligand-exchanged peaks. Another reason could be the sensitivity of certain structural motifs such as staples and mounts to the structure of the incoming ligands; i.e., a given M-L motif may not be able to accommodate a new type of incoming ligand retaining their geometry and bonding network. Simulations and experimental techniques with better temporal resolution are essential to probing such dynamics of the M-L interfaces.

**Gas-Phase Dynamics and Reactivity of M–L Interfaces.** The dynamics of M–L interfaces have been studied mostly in the solution phase; however, such studies on the structure, dynamics, and reactivity of isolated, ligand-protected metal clusters in the gas phase remain largely unexplored. One of the techniques for probing the gas-phase dynamics of



**Figure 4.** Schematic structures of the isomers of  $[Ag_{44}(SH)_{30}]^{4-}$ . Geometries of  $[Ag_{44}(SH)_{30}]^{4-}$  with (A) and without (B) the core atoms and its three structural isomers (C–E) with one staple opened structure (C), two cis staple opened structures (D), and two trans staple opened structures (E). Closed  $Ag_2(SH)_5$  mounts in A–E are shown with blue (silver), yellow (sulfur), and white (hydrogen) colors. Open  $Ag_2(SH)_5$  mounts in C–E are shown in cyan (silver), green (sulfur), and red (hydrogen). Because the structures of the  $Ag_{12}$  icosahedron (gray in A) and the  $Ag_{20}$  dodecahedron (pink in A) are retained in their isomers, these core atoms are not shown in C–E to clearly distinguish the changes in the staple arrangements in its isomers. Because the actual ligands are not shown here, additional structural isomers due to the difference in the ligand conformations are not presented here. (Adapted with permission from ref 76.)



**Figure 5.** Interfacial bonding between two  $[Au_{25}(SR)_{18}]^-$  clusters resulting in the formation of dimers. (A and B) DFT-optimized structures of possible structural isomers of  $[Au_{50}(SR)_{36}]^{2-}$  considering intercluster bonding via common  $Au_2S_3$  staples. In panel A, there is bonding between the two clusters by two parallel  $Au_2S_3$  chains. The view shown is along the negative *z* direction (top view). In panel B, a twisted linkage between the  $Au_2S_3$  staples of two clusters is shown with the cluster on the right being rotated by 90° anticlockwise about the *x* axis and coming out of the paper. Cartesian axes are shown. The ligand R groups have been removed for clarity. Color codes of atoms: gold (yellow) and sulfur (orange). (Adapted with permission from ref 77.)

molecular systems is ion mobility mass spectrometry (IM MS).<sup>88</sup> This technique has been traditionally used for the gasphase analysis of small molecules<sup>88</sup> and conformational studies of proteins;<sup>76</sup> however, it has recently been utilized to probe the thiolate-protected metal clusters as well.<sup>89</sup> In this technique, molecules are ionized and taken into the gaseous phase using standard mass spectrometric techniques, and then they are separated according to their mobility in the presence of a buffer gas. The mobility of the molecules depends on their mass to charge ratio, size, and shape. Here we present the results of IM MS measurements of  $Ag_{44}(SR)_{30}$ . The crystal structure of  $Ag_{44}(SR)_{30}$  shows that it consists of a  $Ag_{32}$  core protected by six  $Ag_2(SR)_5$  mounts.  $Ag_{44}(SR)_{30}$  is an interesting system in this regard because of its multishell structures and unusual geometry of  $Ag_2(SR)_5$  mounts (Figure 4B). Furthermore, this cluster occurs in different charge states in



**Figure 6.** Schematic of the desorption of triphenylphosphine (TPP) ligands from  $[Ag_{18}(TPP)_{10}H_{16}]^{2+}$ , leading to the formation of naked,  $Ag_{17}^{+}$  (A). ESI mass spectra of  $[Ag_{18}(TPP)_{10}H_{16}]^{2+}$  (B) and  $Ag_{17}^{+}$  (C). The insets of panels B and C show the matching of the theoretical (red) and experimental (blue in C, green in B) isotopic patterns of the corresponding ions. Color codes of atoms in panel A: silver (yellow) and hydrogen (red). (Adapted with permission from ref 78.)

the gas phase. For these experiments,  $Ag_{44}(SR)_{30}$  clusters were brought into the gas phase using a conventional electrospray ionization (ESI) technique. Ion mobility measurements on these clusters reveal the presence of structural isomers, as depicted in Figure 4.<sup>76</sup> Here we have used a model system,  $Ag_{44}(SH)_{30}$ , to represent the structure.

DFT calculations suggest that the isomerism arises from the difference in the bonding network of the metal-ligand interface in these clusters. Note that the  $Ag_2(SR)_5$  mounts have complicated bonding compared to those in the  $Au_2(SR)_3$ staples; therefore, it is likely that some of the bonds in the  $Ag_2(SR)_5$  mounts could break, leading to more stable, open structures. However, these isomers possess the same Ag<sub>32</sub> core structure as in the crystal structure. Note that these structures possess exactly the same molecular formulas,  $Ag_{44}(SR)_{30}$ , and differ from each other only in terms of the structures of a few of their mount motifs and hence are structurally isomeric. Hence, this study reveals that rearrangements in the metalligand interface can generate structural isomerism in these clusters. However, if the real ligands are involved, then their conformations also have to be taken into account when their structural isomerism is discussed. However, such an analysis is beyond the scope of this article.

In another example of IM MS experiments, we show that  $Au_{25}(SR)_{18}$  clusters form dimers,  $[Au_{50}(SR)_{36}]^{2-}$ , for example, and trimers in gas-phase experiments. DFT calculations show that these dimers were formed by the bonding between  $Au_2(SR)_3$  staple motifs, as shown in Figure 5.<sup>77</sup> Spectroscopic evidence of such bonding in the gas phase is not available; however, interstaple bonding has been detected in crystals.<sup>38</sup> Note that this type of interstaple bonding has not altered the total number of metal atoms, ligands, and the charge states of

individual clusters in these dimers. Furthermore, the existence of such isomers further supports the dynamic nature of the metal–ligand interface in such clusters. Also, we think that the Borromean rings model is better suited to explaining the formation of such dimers because the longer  $Au_8(SR)_6$  rings are expected to be more dynamic in nature, compared to the shorter  $Au_2(SR)_3$  staples, which could facilitate their breaking and reforming, leading to intercluster bonding.

**Desorption of Ligands: A New Route for Naked Metal Clusters.** The strength of the chemical bond between the metal atoms and the anchoring atom of the ligands (Au–S bond in  $Au_{25}(SR)_{18}$ , for example) largely determines the stability of the clusters. The fragmentation behavior of these clusters was also studied using mass spectrometry<sup>89,90</sup> and computations.<sup>91</sup> For example, phosphines are known to bind to metal atoms less strongly, compared to thiolates, through weak covalent bonds. In this context, it is interesting to test whether it is possible to detach the ligands from phosphine-protected noble metal clusters, in the gaseous or liquid phase, so that naked clusters, with precise nuclearity, are generated. Conventionally, naked metal clusters are generated by techniques such as laser ablation or electrospray ionization which require sophisticated instrumentation for mass selection.

Ghosh et al. demonstrated that it is indeed possible to generate atomically precise naked metal clusters from a silver cluster,  $[Ag_{18}(TPP)_{10}H_{16}]^{2+}$ , protected by phosphine and hydride ligands. The ligands on the  $[Ag_{18}(TPP)_{10}H_{16}]^{2+}$  can be sequentially desorbed to generate naked silver clusters of specific nuclearity, such as  $Ag_{17}^{+}$ .<sup>78</sup> For this,  $[Ag_{18}(TPP)_{10}H_{16}]^{2+}$  was introduced into the gas phase using an ESI source. Sequential fragmentation of the ligands was carried out by successively increasing the ionization voltages in

the ESI setup. Figure 6 shows that  $[Ag_{18}(TPP)_{10}H_{16}]^{2+}$  initially transforms to  $Ag_{17}H_{14}^{+}$ , which finally loses all of the hydride ions, generating  $Ag_{17}^{+}$ . Note that the desorption of ligands in this case occurred through the breaking of the bond between the metal and the anchoring atom of the ligand, i.e., the Ag-P bond. This is in contrast to the case of thiolate-protected clusters wherein the S-C bond breaks and the metal-sulfur bond is retained. The formation of naked clusters from thiolate-protected clusters has never been observed. This could be attributed to the fact that the Ag/Au-S bond is much stronger than the Ag-P bond. Similarly, ligands such as pyridine and its analogues might also act as weaker ligands for these types of clusters, and such systems also could lead to the formation of naked clusters. However, the example presented above indicates that the desorption of ligands depends on the nature of the ligands as well as the strength of the bond between the metal atom and the anchoring atom of the ligands. Such ligand desorption can occur also in ambient air, leading to naked clusters.

#### SUMMARY AND FUTURE PERSPECTIVES

We presented a few examples demonstrating the role of the structure and dynamics of the metal-ligand interface in dictating the chemical reactivity of monolayer-protected noble metal clusters in solution as well as in the gas phase. We suggested that the difference in the oxidation states of metal atoms at the M-L interface could be a key factor triggering intercluster reactions. The structure of the M-L ligand bonding network (staples vs mounts and monodentate vs bidentate) and the dynamics (interlocked (Borromean) rings model vs core-staple model) dictate the type as well as the extent of the exchange processes. Furthermore, these studies imply that a single structural model is inadequate for explaining spontaneous reactions between these clusters; a consideration of multiple structural models is essential to a better understanding of their properties.

We proposed that interparticle chemistry may not be limited to metal clusters, but such reactions might also occur in other nanosystems, which could be a potential mechanism in particle coarsening processes such as Ostwald ripening. We also showed that the nature of the ligands, i.e., their structure and electron-donating and electron-withdrawing properties, is crucial to controlling the geometry and nuclearity of these clusters. The dynamics of the M-L interfaces is not limited to the solution phase; structural rearrangements and interfacial bonding occur in the gas phase as well, leading to the formation of geometrical isomers and cluster assemblies. Finally, we showed that the ligands can be desorbed completely in the gas phase, leading to the formation of atomically precise naked metal clusters. This study indicates that phosphines can be promising ligands for generating naked clusters of other metals as well.

Even though we demonstrated that a number of factors concerning the M-L interfaces, such as oxidation states of metal atoms and the actual structure of the ligands, are important when considering the chemistry of these clusters, the contribution of each of these factors has not been understood in isolation. Among the reasons is the limitation in making many of the clusters by varying only one aspect alone at one time, such as specific ligands.

Probing the interfacial properties of these clusters is essential to creating cluster assembled materials and new types of hybrid materials comprising distinctly different types of nanosystems. Probing the kinetics and thermodynamics and the real-time monitoring of interfacial phenomena in these clusters have rarely been addressed. The gas-phase dynamics of these clusters remain largely unexplored. Probing the chiroptical properties of these clusters in the gaseous phase could be a potential new direction in this regard. Further efforts are needed to clearly understand the contribution of metal—ligand interfaces in dictating the geometrical structures, dynamics, and chemical reactivity of ligand-protected metal clusters. We think that the dynamic interfacial chemistry is not limited to metal clusters, and hence the structure, dynamics, and chemical reactivity of nanosystems in general are to be explored in greater detail, which might unveil new directions in materials chemistry.

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#### REFERENCES

(1) Jin, R.; Zeng, C.; Zhou, M.; Chen, Y. Atomically Precise Colloidal Metal Nanoclusters and Nanoparticles: Fundamentals and Opportunities. *Chem. Rev.* **2016**, *116*, 10346–10413.

(2) Chakraborty, I.; Pradeep, T. Atomically precise clusters of noble metals: Emerging link between atoms and nanoparticles. *Chem. Rev.* **2017**, *117*, 8208–8271.

(3) Jadzinsky, P. D.; Calero, G.; Ackerson, C. J.; Bushnell, D. A.; Kornberg, R. D. Structure of a thiol monolayer-protected gold nanoparticle at 1.1 Å resolution. *Science* **2007**, *318*, 430–433.

(4) Heaven, M. W.; Dass, A.; White, P. S.; Holt, K. M.; Murray, R. W. Crystal structure of the gold nanoparticle  $[N(C_8H_{17})_4]$ - $[Au_{25}(SCH_2CH_2Ph)_{18}]$ . J. Am. Chem. Soc. **2008**, 130, 3754–3755.

(5) Joshi, C. P.; Bootharaju, M. S.; Alhilaly, M. J.; Bakr, O. M.  $[Ag_{25}(SR)_{18}]^-$ : The "Golden" silver nanoparticle. *J. Am. Chem. Soc.* **2015**, 137, 11578–11581.

(6) Desireddy, A.; Conn, B. E.; Guo, J.; Yoon, B.; Barnett, R. N.; Monahan, B. M.; Kirschbaum, K.; Griffith, W. P.; Whetten, R. L.; Landman, U.; Bigioni, T. P. Ultrastable silver nanoparticles. *Nature* **2013**, *501*, 399–402.

(7) Harkness, K. M.; Tang, Y.; Dass, A.; Pan, J.; Kothalawala, N.; Reddy, V. J.; Cliffel, D. E.; Demeler, B.; Stellacci, F.; Bakr, O. M.; McLean, J. A.  $Ag_{44}(SR)_{30}^{-4}$ : a silver-thiolate superatom complex. *Nanoscale* **2012**, *4*, 4269–4274.

(8) Zhu, M.; Aikens, C. M.; Hollander, F. J.; Schatz, G. C.; Jin, R. Correlating the crystal structure of a thiol-protected Au<sub>25</sub> cluster and optical properties. *J. Am. Chem. Soc.* **2008**, *130*, 5883–5885.

(9) Zhu, M.; Aikens, C. M.; Hendrich, M. P.; Gupta, R.; Qian, H.; Schatz, G. C.; Jin, R. Reversible switching of magnetism in thiolate-protected Au<sub>25</sub> superatoms. *J. Am. Chem. Soc.* **2009**, *131*, 2490–2492.

(10) Antonello, S.; Perera, N. V.; Ruzzi, M.; Gascón, J. A.; Maran, F. Interplay of charge state, lability, and magnetism in the molecule-like Au<sub>25</sub>(SR)<sub>18</sub> cluster. *J. Am. Chem. Soc.* **2013**, *135*, 15585–15594.

(11) Bellon, P.; Manassero, M.; Sansoni, M. An octahedral gold cluster: crystal and molecular structure of hexakis[tris-(p-tolyl)-phosphine]-octahedro-hexagold bis(tetraphenylborate). J. Chem. Soc., Dalton Trans. 1973, 22, 2423–2427.

(12) Bellon, P. L.; Cariati, F.; Manassero, M.; Naldini, L.; Sansoni, M. Novel gold clusters. Preparation, properties, and X-ray structure determination of salts of octakis(triarylphosphine)enneagold, [Au<sub>9</sub>L<sub>8</sub>]X<sub>3</sub>. J. Chem. Soc. D **1971**, 22, 1423–1424.

(13) Yao, H.; Iwatsu, M. Water-Soluble Phosphine-Protected Au11 Clusters: Synthesis, Electronic Structure, and Chiral Phase Transfer in a Synergistic Fashion. *Langmuir* **2016**, *32*, 3284–3293.

(14) Akola, J.; Kacprzak, K. A.; Lopez-Acevedo, O.; Walter, M.; Grönbeck, H.; Häkkinen, H. Thiolate-protected Au<sub>25</sub> superatoms as building blocks: dimers and crystals. *J. Phys. Chem. C* **2010**, *114*, 15986–15994.

(15) Akola, J.; Walter, M.; Whetten, R. L.; Hakkinen, H.; Gronbeck, H. On the structure of thiolate-protected Au<sub>25</sub>. *J. Am. Chem. Soc.* **2008**, *130*, 3756–3757.

(16) Walter, M.; Akola, J.; Lopez-Acevedo, O.; Jadzinsky, P. D.; Calero, G.; Ackerson, C. J.; Whetten, R. L.; Grönbeck, H.; Häkkinen, H. A unified view of ligand-protected gold clusters as superatom complexes. *Proc. Natl. Acad. Sci. U. S. A.* **2008**, *105*, 9157–9162.

(17) Abdul Halim, L. G.; Ashraf, S.; Katsiev, K.; Kirmani, A. R.; Kothalawala, N.; Anjum, D. H.; Abbas, S.; Amassian, A.; Stellacci, F.; Dass, A.; Hussain, I.; Bakr, O. M. A scalable synthesis of highly stable and water dispersible  $Ag_{44}(SR)_{30}$  nanoclusters. *J. Mater. Chem. A* **2013**, *1*, 10148–10154.

(18) AbdulHalim, L. G.; Kothalawala, N.; Sinatra, L.; Dass, A.; Bakr, O. M. Neat and complete: thiolate-ligand exchange on a silver molecular nanoparticle. *J. Am. Chem. Soc.* **2014**, *136*, 15865–15868.

(19) Yang, H.; Wang, Y.; Huang, H.; Gell, L.; Lehtovaara, L.; Malola, S.; Häkkinen, H.; Zheng, N. All-thiol-stabilized  $Ag_{44}$  and  $Au_{12}Ag_{32}$  nanoparticles with single-crystal structures. *Nat. Commun.* **2013**, *4*, 2422.

(20) Chakraborty, I.; Kurashige, W.; Kanehira, K.; Gell, L.; Häkkinen, H.; Negishi, Y.; Pradeep, T.  $Ag_{44}(SeR)_{30}$ : A Hollow Cage Silver Cluster with Selenolate Protection. *J. Phys. Chem. Lett.* **2013**, *4*, 3351–3355.

(21) Kurashige, W.; Yamaguchi, M.; Nobusada, K.; Negishi, Y. Ligand-Induced Stability of Gold Nanoclusters: Thiolate versus Selenolate. *J. Phys. Chem. Lett.* **2012**, *3*, 2649–2652.

(22) Ossowski, J.; Wächter, T.; Silies, L.; Kind, M.; Noworolska, A.; Blobner, F.; Gnatek, D.; Rysz, J.; Bolte, M.; Feulner, P.; Terfort, A.; Cyganik, P.; Zharnikov, M. Thiolate versus Selenolate: Structure, Stability, and Charge Transfer Properties. *ACS Nano* **2015**, *9*, 4508– 4526.

(23) Maity, P.; Takano, S.; Yamazoe, S.; Wakabayashi, T.; Tsukuda, T. Binding motif of terminal alkynes on gold clusters. *J. Am. Chem. Soc.* **2013**, *135*, 9450–9457.

(24) Templeton, A. C.; Wuelfing, W. P.; Murray, R. W. Monolayerprotected cluster molecules. *Acc. Chem. Res.* **2000**, *33*, 27–36.

(25) Hakkinen, H. The gold-sulfur interface at the nanoscale. *Nat. Chem.* **2012**, *4*, 443-455.

(26) Häkkinen, H.; Walter, M.; Grönbeck, H. Divide and Protect: Capping Gold Nanoclusters with Molecular Gold–Thiolate Rings. J. Phys. Chem. B 2006, 110, 9927–9931.

(27) Walter, M.; Akola, J.; Lopez-Acevedo, O.; Jadzinsky, P. D.; Calero, G.; Ackerson, C. J.; Whetten, R. L.; Grönbeck, H.; Häkkinen, H. A unified view of ligand-protected gold clusters as superatom complexes. *Proc. Natl. Acad. Sci. U. S. A.* **2008**, *105*, 9157–9162.

(28) Natarajan, G.; Mathew, A.; Negishi, Y.; Whetten, R. L.; Pradeep, T. A unified framework for understanding the structure and modifications of atomically precise monolayer protected gold clusters. *J. Phys. Chem. C* **2015**, *119*, 27768–27785.

(29) Yamazoe, S.; Takano, S.; Kurashige, W.; Yokoyama, T.; Nitta, K.; Negishi, Y.; Tsukuda, T. Hierarchy of bond stiffnesses within icosahedral-based gold clusters protected by thiolates. *Nat. Commun.* **2016**, *7*, 10414.

(30) Tlahuice-Flores, A.; Black, D. M.; Bach, S. B. H.; Jose-Yacaman, M.; Whetten, R. L. Structure & bonding of the gold-subhalide cluster I-Au<sub>144</sub>Cl<sub>60</sub><sup>[z]</sup>. *Phys. Chem. Chem. Phys.* **2013**, *15*, 19191–19195.

(31) Chen, Y.; Zeng, C.; Kauffman, D. R.; Jin, R. Tuning the Magic Size of Atomically Precise Gold Nanoclusters via Isomeric Methylbenzenethiols. *Nano Lett.* **2015**, *15*, 3603–3609.

(32) Rambukwella, M.; Sakthivel, N. A.; Delcamp, J. H.; Sementa, L.; Fortunelli, A.; Dass, A. Ligand Structure Determines Nanoparticles' Atomic Structure, Metal-Ligand Interface and Properties. *Front. Chem.* **2018**, *6*, 330.

(33) Zeng, C.; Qian, H.; Li, T.; Li, G.; Rosi, N. L.; Yoon, B.; Barnett, R. N.; Whetten, R. L.; Landman, U.; Jin, R. Total Structure and Electronic Properties of the Gold Nanocrystal  $Au_{36}(SR)_{24}$ . Angew. Chem., Int. Ed. **2012**, 51, 13114–13118.

(34) Dolamic, I.; Knoppe, S.; Dass, A.; Bürgi, T. First enantioseparation and circular dichroism spectra of Au<sub>38</sub> clusters protected by achiral ligands. *Nat. Commun.* **2012**, *3*, 798.

(35) Dolamic, I.; Varnholt, B.; Burgi, T. Chirality transfer from gold nanocluster to adsorbate evidenced by vibrational circular dichroism. *Nat. Commun.* **2015**, *6*, 7117.

(36) Mathew, A.; Natarajan, G.; Lehtovaara, L.; Häkkinen, H.; Kumar, R. M.; Subramanian, V.; Jaleel, A.; Pradeep, T. Supramolecular functionalization and concomitant enhancement in properties of Au<sub>25</sub> clusters. *ACS Nano* **2014**, *8*, 139–152.

(37) Yoon, B.; Luedtke, W. D.; Barnett, R. N.; Gao, J.; Desireddy, A.; Conn, B. E.; Bigioni, T.; Landman, U. Hydrogen-bonded structure and mechanical chiral response of a silver nanoparticle superlattice. *Nat. Mater.* **2014**, *13*, 807–811.

(38) De Nardi, M.; Antonello, S.; Jiang, D.-e.; Pan, F.; Rissanen, K.; Ruzzi, M.; Venzo, A.; Zoleo, A.; Maran, F. Gold nanowired: a linear  $(Au_{25})_n$  polymer from  $Au_{25}$  molecular clusters. *ACS Nano* **2014**, *8*, 8505–8512.

(39) Som, A.; Chakraborty, I.; Maark, T. A.; Bhat, S.; Pradeep, T. Cluster-mediated crossed bilayer precision assemblies of 1D nanowires. *Adv. Mater.* **2016**, *28*, 2827–2833.

(40) Gell, L.; Häkkinen, H. Theoretical analysis of the  $M_{12}Ag_{32}(SR)_{40}^{4-}$  and  $X@M_{12}Ag_{32}(SR)_{30}^{4-}$  nanoclusters (M = Au, Ag; X = H, Mn). J. Phys. Chem. C 2015, 119, 10943-10948.

(41) Wu, Z.; Jin, R. On the ligand's role in the fluorescence of gold nanoclusters. *Nano Lett.* **2010**, *10*, 2568–2573.

(42) Mathew, A.; Varghese, E.; Choudhury, S.; Pal, S. K.; Pradeep, T. Efficient red luminescence from organic-soluble Au<sub>25</sub> clusters by ligand structure modification. *Nanoscale* **2015**, *7*, 14305–14315.

(43) Niihori, Y.; Kikuchi, Y.; Kato, A.; Matsuzaki, M.; Negishi, Y. Understanding ligand-exchange reactions on thiolate-protected gold clusters by probing isomer distributions using reversed-phase highperformance liquid chromatography. *ACS Nano* **2015**, *9*, 9347–9356.

(44) Ni, T. W.; Tofanelli, M. A.; Phillips, B. D.; Ackerson, C. J. Structural basis for ligand exchange on  $Au_{25}(SR)_{18}$ . *Inorg. Chem.* **2014**, *53*, 6500–6502.

(45) Dass, A.; Holt, K.; Parker, J. F.; Feldberg, S. W.; Murray, R. W. Mass spectrometrically detected statistical aspects of ligand populations in mixed monolayer  $Au_{25}L_{18}$  nanoparticles. *J. Phys. Chem. C* 2008, 112, 20276–20283.

(46) Song, Y.; Huang, T.; Murray, R. W. Heterophase ligand exchange and metal transfer between monolayer protected clusters. *J. Am. Chem. Soc.* **2003**, *125*, 11694–11701.

(47) Song, Y.; Murray, R. W. Dynamics and extent of ligand exchange depend on electronic charge of metal nanoparticles. *J. Am. Chem. Soc.* **2002**, *124*, 7096–7102.

(48) Wang, S.; Song, Y.; Jin, S.; Liu, X.; Zhang, J.; Pei, Y.; Meng, X.; Chen, M.; Li, P.; Zhu, M. Metal exchange method using Au<sub>25</sub> nanoclusters as templates for alloy nanoclusters with atomic precision. *J. Am. Chem. Soc.* **2015**, *137*, 4018–4021.

(49) Krishnadas, K. R.; Udayabhaskararao, T.; Choudhury, S.; Goswami, N.; Pal, S. K.; Pradeep, T. Luminescent AgAu alloy clusters derived from Ag nanoparticles - Manifestations of tunable Au(I)-Cu(I) metallophilic interactions. *Eur. J. Inorg. Chem.* 2014, 2014, 908–916.

(50) Walter, M.; Moseler, M. Ligand-protected gold alloy clusters: doping the superatom. J. Phys. Chem. C 2009, 113, 15834–15837.

(51) Tian, S.; Yao, C.; Liao, L.; Xia, N.; Wu, Z. Ion-precursor and ion-dose dependent anti-galvanic reduction. *Chem. Commun.* **2015**, *51*, 11773–11776.

(52) Wu, Z. Anti-Galvanic reduction of thiolate-protected gold and silver nanoparticles. *Angew. Chem., Int. Ed.* **2012**, *51*, 2934–2938.

(53) Udayabhaskararao, T.; Sun, Y.; Goswami, N.; Pal, S. K.; Balasubramanian, K.; Pradeep, T. Ag<sub>7</sub>Au<sub>6</sub>: A 13-atom alloy quantum cluster. *Angew. Chem., Int. Ed.* **2012**, *51*, 2155–2159.

(54) Dreier, T. A.; Ackerson, C. J. Radicals are required for thiol etching of gold particles. *Angew. Chem., Int. Ed.* **2015**, *54*, 9249–9252.

(55) Udaya Bhaskara Rao, T.; Pradeep, T. Luminescent  $Ag_7$  and  $Ag_8$ clusters by interfacial synthesis. *Angew. Chem., Int. Ed.* **2010**, *49*, 3925–3929.

(56) Shichibu, Y.; Negishi, Y.; Tsukuda, T.; Teranishi, T. Large-scale synthesis of thiolated  $Au_{25}$  clusters via ligand exchange reactions of phosphine-stabilized  $Au_{11}$  clusters. *J. Am. Chem. Soc.* **2005**, *127*, 13464–13465.

(57) Shichibu, Y.; Negishi, Y.; Watanabe, T.; Chaki, N. K.; Kawaguchi, H.; Tsukuda, T. Biicosahedral gold clusters  $[Au_{25}(PPh_3)_{10}(SC_nH2_{n+1})SCl_2]^{2+}$  (n = 2–18): A stepping stone to cluster-assembled materials. J. Phys. Chem. C 2007, 111, 7845–7847.

(58) Li, M.-B.; Tian, S.-K.; Wu, Z.; Jin, R. Peeling the core-shell Au<sub>25</sub> nanocluster by reverse ligand-exchange. *Chem. Mater.* **2016**, *28*, 1022–1025.

(59) Krishnadas, K. R.; Baksi, A.; Ghosh, A.; Natarajan, G.; Pradeep, T. Structure-conserving spontaneous transformations between nanoparticles. *Nat. Commun.* **2016**, *7*, 13447.

(60) Krishnadas, K. R.; Baksi, A.; Ghosh, A.; Natarajan, G.; Pradeep, T. Manifestation of Geometric and Electronic Shell Structures of Metal Clusters in Intercluster Reactions. *ACS Nano* **2017**, *11*, 6015–6023.

(61) Krishnadas, K. R.; Baksi, A.; Ghosh, A.; Natarajan, G.; Som, A.; Pradeep, T. Interparticle Reactions: An Emerging Direction in Nanomaterials Chemistry. *Acc. Chem. Res.* **2017**, *50*, 1988–1996.

(62) Krishnadas, K. R.; Ghosh, A.; Baksi, A.; Chakraborty, I.; Natarajan, G.; Pradeep, T. Intercluster reactions between  $Au_{25}(SR)_{18}$  and  $Ag_{44}(SR)_{30}$ . J. Am. Chem. Soc. **2016**, 138, 140–148.

(63) Zhang, B.; Salassa, G.; Burgi, T. Silver migration between  $Au_{38}(SC_2H_4Ph)_{24}$  and doped  $AgxAu_{38-x}(SC_2H_4Ph)_{24}$  nanoclusters. *Chem. Commun.* **2016**, *52*, 9205–9207.

(64) Xia, N.; Wu, Z. Doping Au<sub>25</sub> nanoparticles using ultrasmall silver or copper nanoparticles as the metal source. *J. Mater. Chem. C* **2016**, *4*, 4125–4128.

(65) Bootharaju, M. S.; Sinatra, L.; Bakr, O. M. Distinct metalexchange pathways of doped Ag25 nanoclusters. *Nanoscale* **2016**, *8*, 17333–17339.

(66) Zhang, B.; Safonova, O. V.; Pollitt, S.; Salassa, G.; Sels, A.; Kazan, R.; Wang, Y.; Rupprechter, G.; Barrabes, N.; Burgi, T. On the mechanism of rapid metal exchange between thiolate-protected gold and gold/silver clusters: a time-resolved in situ XAFS study. *Phys. Chem. Chem. Phys.* **2018**, *20*, 5312–5318.

(67) Yao, Q.; Feng, Y.; Fung, V.; Yu, Y.; Jiang, D.-e.; Yang, J.; Xie, J. Precise control of alloying sites of bimetallic nanoclusters via surface motif exchange reaction. *Nat. Commun.* **2017**, *8*, 1555.

(68) Wang, S.; Abroshan, H.; Liu, C.; Luo, T.-Y.; Zhu, M.; Kim, H. J.; Rosi, N. L.; Jin, R. Shuttling single metal atom into and out of a metal nanoparticle. *Nat. Commun.* **2017**, *8*, 848.

(69) Varnholt, B.; Oulevey, P.; Luber, S.; Kumara, C.; Dass, A.; Bürgi, T. Structural Information on the Au–S Interface of Thiolate-Protected Gold Clusters: A Raman Spectroscopy Study. *J. Phys. Chem. C* **2014**, *118*, 9604–9611.

(70) Burgi, T. Properties of the gold-sulphur interface: from self-assembled monolayers to clusters. *Nanoscale* 2015, 7, 15553–15567.

(71) Salassa, G.; Sels, A.; Mancin, F.; Bürgi, T. Dynamic Nature of Thiolate Monolayer in Au25(SR)18 Nanoclusters. *ACS Nano* 2017, *11*, 12609–12614.

(72) Salorinne, K.; Malola, S.; Wong, O. A.; Rithner, C. D.; Chen, X.; Ackerson, C. J.; Häkkinen, H. Conformation and dynamics of the

ligand shell of a water-soluble Au<sub>102</sub> nanoparticle. *Nat. Commun.* **2016**, *7*, 10401.

(73) Ouyang, R.; Jiang, D.-e. Ligand-Conformation Energy Landscape of Thiolate-Protected Gold Nanoclusters. J. Phys. Chem. C 2015, 119, 21555–21560.

(74) Pradeep, T.; Mitra, S.; Nair, A. S.; Mukhopadhyay, R. Dynamics of alkyl chains in monolayer-protected Au and Ag clusters and silver thiolates: a comprehensive quasielastic neutron scattering investigation. *J. Phys. Chem. B* **2004**, *108*, 7012–7020.

(75) Khatun, E.; Ghosh, A.; Ghosh, D.; Chakraborty, P.; Nag, A.; Mondal, B.; Chennu, S.; Pradeep, T.  $[Ag_{59}(2,5\text{-}DCBT)_{32}]^{3}$ : a new cluster and a precursor for three well-known clusters. *Nanoscale* **2017**, *9*, 8240–8248.

(76) Baksi, A.; Ghosh, A.; Mudedla, S. K.; Chakraborty, P.; Bhat, S.; Mondal, B.; Krishnadas, K. R.; Subramanian, V.; Pradeep, T. Isomerism in Monolayer Protected Silver Cluster Ions: An Ion Mobility-Mass Spectrometry Approach. *J. Phys. Chem. C* **2017**, *121*, 13421–13427.

(77) Baksi, A.; Chakraborty, P.; Bhat, S.; Natarajan, G.; Pradeep, T.  $[Au_{25}(SR)_{18}]_2^{2-2}$ : a noble metal cluster dimer in the gas phase. *Chem. Commun.* **2016**, *52*, 8397–8400.

(78) Ghosh, A.; Bodiuzzaman, M.; Nag, A.; Jash, M.; Baksi, A.; Pradeep, T. Sequential Dihydrogen Desorption from Hydride-Protected Atomically Precise Silver Clusters and the Formation of Naked Clusters in the Gas Phase. *ACS Nano* **2017**, *11*, 11145–11151.

(79) Wiseman, M. R.; Marsh, P. A.; Bishop, P. T.; Brisdon, B. J.; Mahon, M. F. Homoleptic Gold Thiolate Catenanes. J. Am. Chem. Soc. 2000, 122, 12598–12599.

(80) Zeng, C.; Liu, C.; Chen, Y.; Rosi, N. L.; Jin, R. Gold-Thiolate Ring as a Protecting Motif in the Au20(SR)16 Nanocluster and Implications. J. Am. Chem. Soc. 2014, 136, 11922–11925.

(81) Yan, N.; Xia, N.; Liao, L.; Zhu, M.; Jin, F.; Jin, R.; Wu, Z. Unraveling the long-pursued Au<sub>144</sub> structure by x-ray crystallography. *Science Advances* **2018**, *4*, eaat7259.

(82) Ghosh, A.; Ghosh, D.; Khatun, E.; Chakraborty, P.; Pradeep, T. Unusual reactivity of dithiol protected clusters in comparison to monothiol protected clusters: studies using  $Ag_{51}(BDT)_{19}(TPP)_3$  and  $Ag_{29}(BDT)_{12}(TPP)_4$ . *Nanoscale* **2017**, *9*, 1068–1077.

(83) Viswanatha, R.; Sarma, D. D. Growth of Nanocrystals in Solution. In *Nanomaterials Chemistry*; Rao, C. N. R.; Müller, A., Cheetham, A. K., Eds.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, 2007.

(84) Dainese, T.; Antonello, S.; Bogialli, S.; Fei, W.; Venzo, A.; Maran, F. Gold Fusion: From  $Au_{25}(SR)_{18}$  to  $Au_{38}(SR)_{24}$ , the Most Unexpected Transformation of a Very Stable Nanocluster. *ACS Nano* **2018**, *12*, 7057–7066.

(85) Guo, R.; Song, Y.; Wang, G.; Murray, R. W. Does core size matter in the kinetics of ligand exchanges of monolayer-protected Au clusters? *J. Am. Chem. Soc.* **2005**, *127*, 2752–2757.

(86) Bootharaju, M. S.; Burlakov, V. M.; Besong, T. B. D.; Joshi, C. P.; AbdulHalim, L. G.; Black, D. M.; Whetten, R. L.; Goriely, A.; Bakr, O. M. Reversible Size Control of Silver Nanoclusters via Ligand-Exchange. *Chem. Mater.* **2015**, *27*, 4289–4297.

(87) Bootharaju, M. S.; Joshi, C. P.; Alhilaly, M. J.; Bakr, O. M. Switching a nanocluster core from hollow to nonhollow. *Chem. Mater.* **2016**, *28*, 3292–3297.

(88) Lapthorn, C.; Pullen, F.; Chowdhry, B. Z. Ion mobility spectrometry-mass spectrometry (IMS-MS) of small molecules: separating and assigning structures to ions. *Mass Spectrom. Rev.* **2013**, *32*, 43–71.

(89) Angel, L. A.; Majors, L. T.; Dharmaratne, A. C.; Dass, A. Ion mobility mass spectrometry of  $Au_{25}(SCH_2CH_2Ph)_{18}$  nanoclusters. *ACS Nano* **2010**, *4*, 4691–4700.

(90) Chakraborty, P.; Baksi, A.; Khatun, E.; Nag, A.; Ghosh, A.; Pradeep, T. Dissociation of Gas Phase Ions of Atomically Precise Silver Clusters Reflects Their Solution Phase Stability. *J. Phys. Chem.* C 2017, *121*, 10971–10981.

(91) Liu, C.; Lin, S.; Pei, Y.; Zeng, X. C. Semiring chemistry of  $Au_{25}(SR)_{18}$ : Fragmentation pathway and aatalytic active site. J. Am. Chem. Soc. **2013**, 135, 18067–18079.

(92) Jash, M.; Reber, A. C.; Ghosh, A.; Sarkar, D.; Bodiuzzaman, M.; Basuri, P.; Baksi, A.; Khanna, S. N.; Pradeep, T. Preparation of gas phase naked silver cluster cations outside the mass spectrometer from ligand protected clusters in solution. *Nanoscale* **2018**, *10*, 15714– 15722.