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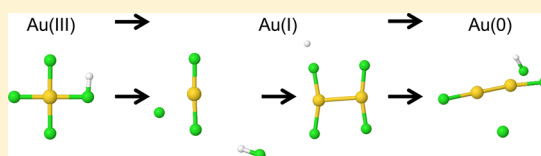
Prediction of Nonradical Au(0)-Containing Precursors in Nanoparticle Growth Processes

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S Supporting Information

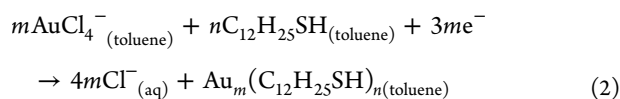
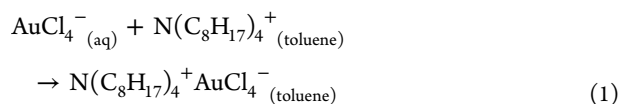
ABSTRACT: This density functional theory (DFT) investigation examines the formation of nonradical Au(0) species from the reduction of Au(I) species. The Au(I) complexes of interest are AuCl_2^- , AuBr_2^- , AuI_2^- , $\text{AuCl}(\text{H})\text{SCH}_3^{(-)}$, which are precursors for gold nanoparticle and cluster formation. Reaction of two of the Au(I) species with a hydride results in ejection of two of the ligands and formation of Au_2 with two ligands still attached. AuX_2^- (where X = Cl, Br, or I) reactions eject two halides and form $\text{Au}_2\text{X}_2^{2-}$. $\text{AuClL}^{(-)}$ (where L = PH_3 , HSCH_3 , or SCH_3^-) reactions can eject either chloride, HCl , PH_3 , HSCH_3 , or SCH_3^- and form $\text{Au}(0)\text{L}_2^{q-}$ or $\text{Au}(0)\text{CIL}^{q-}$ ($q = 0, 1, 2$). The $\text{Au}_2\text{Cl}_2^{2-}$ complex can further react with AuCl_2^- , which forms $\text{Au}_3\text{Cl}_3^{2-}$ and a chloride anion. The new $\text{Au}_3\text{Cl}_3^{2-}$ species can then react with AuCl_2^- or $\text{Au}_2\text{Cl}_2^{2-}$ or with another $\text{Au}_3\text{Cl}_3^{2-}$. Larger clusters can be formed from these precursors. In this work, reactions in both methanol and benzene solvents are considered as models for one-phase and two-phase gold nanoparticle growth processes. Overall, this investigation shows how Au(0)-containing species can be formed without assuming the formation of Au(0) atoms (radical species).



INTRODUCTION

Applications for gold nanoparticles include drug delivery and therapy,^{1,2} catalysts,³ sensors,⁴ electronics,⁵ and optics.⁶ Different nanoparticle morphologies such as spheres, cubes, wires, and rods have been synthesized and have diverse properties for these unique applications.⁷ Yet, how are these different morphologies created? Although some general principles are known, many syntheses rely on trial and error. A better understanding is needed of the growth mechanisms of nanoparticles, and in this work we examine the initial steps of nanoparticle growth in order to gain a better picture of how gold nanoparticles form.

Brust, Schiffrin, and co-workers⁸ first published a synthesis of stable gold–thiolate nanoparticles in 1994. The Brust–Schiffrin (B–S) synthesis starts with tetrachloroauric acid (HAuCl_4) or tetrachloroaurate (AuCl_4^-), which is phase-transferred into toluene by use of tetraoctylammonium bromide (eq 1). Once in the organic phase, the ligand, such as dodecanethiol ($\text{C}_{12}\text{H}_{25}\text{SH}$), and reducing agent, which is typically sodium borohydride (NaBH_4), are added to the solution (eq 2). In eq 2, Brust and Schiffrin use the expression 3me^- for the addition of electrons instead of explicitly considering NaBH_4 .



Brust, Schiffrin, and co-workers⁹ later described a related one-phase synthesis using methanol. Since the introduction of

the Brust–Schiffrin synthesis, several implicit assumptions about the growth mechanism have appeared in the literature, but scientific investigations into the precise growth mechanism have appeared only in the past few years. Two of these assumptions are that the formation of Au(I)–thiolate polymers precedes the final reduction to gold–thiolate nanoparticles and that Au(0) atoms can form and aggregate during the growth process.

The role of the formation of gold–thiolate polymers was first questioned in 2010, when Goulet and Lennox¹⁰ demonstrated that changing the thiol ligand to Au(III) salt ratio from 4:1 to 2:1 caused reduction to $\text{Au}(\text{I})\text{X}_2^-$ (X = halide) but did not lead to the formation of Au(I)–thiolate oligomers. Barngrover and Aikens¹¹ supported the hypothesis regarding the initial formation of $\text{Au}(\text{I})\text{X}_2^-$ species using density functional theory (DFT) calculations. However, they also demonstrated with DFT that reaction of $\text{Au}(\text{I})\text{X}_2^-$ with the thiol ligand can potentially lead to $\text{AuCl}(\text{H})\text{SR}^{(-)}$ species, at least in a polar solvent such as methanol.¹¹ Furthermore, they showed that deprotonated Au(I) units (AuClSR^-) can react with each other and grow longer $\text{ClAuSR}-(\text{AuSR})_n-$ oligomers. They also demonstrated that these oligomers can be reduced with hydrides to form possible nanoparticle precursors, although they did not discount growth mechanisms based on the reduction of AuX_2^- or $\text{Au}(\text{SR})_2^-$ species.¹² Nonetheless, Goulet and Lennox¹⁰ suggested that a 3:1 ratio of ligand to Au(III) salt does not form polymeric Au(I) species; instead the $\text{Au}(\text{I})\text{X}_2^-$ species remain in solution. Tong and co-workers¹³

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also agreed with Goulet and Lennox that the Au(I)X_2^- species remained in solution in the presence of the phase-transfer agent. However, Zhu et al.¹⁴ later showed that AuSRX^- and Au(SR)_2^- can be formed experimentally, depending on the concentration of reactants, and they suggested that polymeric Au(I) can form under certain conditions. Even so, the debate still exists regarding under what conditions Au(I) polymers can be formed during reduction and the importance of these species in the growth mechanism. Nevertheless, all groups agree that reduction occurs from Au(III) and that Au(I) is the primary species formed after reduction by thiol ligands, making it an important precursor in the growth of nanoparticles.

The starting ligands can be changed or introduced after the reduction has occurred. The typical ligand is a long-chain alkanethiol; however, other ligands can be used. Fluorinated thiolates can be employed as ligands as shown by Gentilini et al.¹⁵ In addition, phosphines can be used as demonstrated by Hudgens et al.¹⁶ Fink et al.¹⁷ and Petroski et al.¹⁸ showed that “bare” gold nanoparticles could form without the addition of a ligand; in this case, the nanoparticles are thought to be stabilized by the phase-transfer agent. As shown in our current work, these nanoparticles are likely stabilized at the surface by halide ligands remaining from the gold salt and/or the counterion of the phase transfer agent. Recently, Tong and co-workers^{13,19} suggested that, even in the B–S two-phase synthesis in which thiol ligands are present, the growth mechanism first proceeds via reduction of Au(I)X_2^- ($X = \text{halide}$) units to form metal clusters/nanoparticles prior to ligand exchange to form the metal–chalcogen bonds. Thus, understanding the reduction of Au(I)X_2^- units will provide necessary insights into gold nanoparticle growth processes. Tong and co-workers^{13,19} proposed that the phase-transfer agent could act as a reverse micelle and transport the gold precursor salt into the toluene phase, where it would then be reduced inside the reverse micelle. The phase-transfer agent acting as a transport vehicle has been recently studied by Joshi and Bigioni²⁰ for larger nanoparticles. By utilizing optical microscopy, they observed that a single ionic surfactant, dihexadecyldimethylammonium bromide (DHAB), could transport an aggregate of gold nanoparticles from water and inject it into toluene through capillary force created by the hydrophobicity of the aggregate in the aqueous phase.²⁰

A reducing agent such as sodium borohydride, lithium triethylborohydride, or triethylsilane^{17,18,21,22} is needed to cause complete reduction to Au(0). A common interpretation in the literature is that Au(0) is initially formed as an isolated gold atom without any ligands attached, which then cluster to form larger particles.^{16,23} This interpretation may possibly arise from addition of electrons leading to removal of the anionic ligands such as chlorides; however, isolated atoms of gold are radicals and would be expected to be highly reactive if formed. In addition, this assumption implicitly treats NaBH_4 as a one-electron donor instead of a two-electron (hydride) donor, yet it has been known to be a two-electron donor since its discovery in 1942.²⁴

As demonstrated by the above discussion, the underlying growth mechanism of nanoparticles is still under some debate. Currently, researchers agree that the first step is the formation of Au(I) species from the reduction of the Au(III) salt no matter what synthetic method is employed. However, formation of the Au(0)-containing species is still not understood. In this work, we examine how Au(I) species are reduced to form Au(0)-containing nanoparticles. We inves-

tigate possible precursors in the one-phase method (using a methanol solvent) as well as in the organic phase of a two-phase B–S approach (represented by benzene). We consider the hydride reduction of Au(I) species protected by various ligands including chloride, phosphine, and thiol(ate) to show that this leads to a dimeric Au(0)-containing species without formation of gold radicals. We also examine the growth of gold–chloride nanoparticles, which are applicable to understanding the growth mechanisms of “bare” gold nanoparticles and to the B–S synthesis in the “reverse micelle” hypothesis of Tong and co-workers. Although not discussed in this present work, thiolate-for-chloride ligand exchange is known to occur with low barrier heights (~ 0.35 eV in methanol),¹¹ so the gold–chloride nanoparticle precursors could easily undergo ligand exchange to form gold–thiolate nanoparticles. In addition, the physical insights gained here can be extended to the growth of gold–thiolate nanoparticles originating from reduction of Au(SR)_2^- .

■ COMPUTATIONAL DETAILS

All calculations are performed with the Amsterdam Density Functional (ADF)²⁵ package, via density functional theory with the Becke–Perdew (BP86)^{26,27} functional and a frozen-core polarized triple- ζ (TZP) basis set. BP86-D calculations including the Grimme dispersion correction²⁸ are considered where noted in the text. We include scalar relativistic effects by employing the zeroth order regular approximation (ZORA).²⁹ We incorporate methanol and benzene solvents using the conductor-like screening model (COSMO), which represents the solvent by its dielectric constant.^{30–32}

All intermediates and transition states are fully optimized; Hessian calculations have been performed to verify the existence of one imaginary frequency for the transition states. Absorption spectra, vibrational frequencies, and Raman tensor strengths have been calculated at the BP86/TZP level of theory.

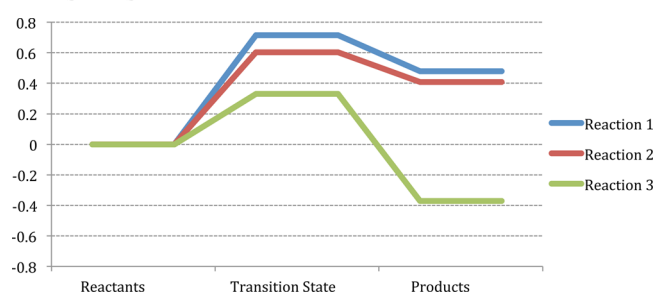
■ RESULTS AND DISCUSSION

Reduction of AuX_4^- to AuX_2^- ($X = \text{Cl, Br, or I}$). AuCl_4^- is the most common starting gold(III) salt for nanoparticle growth. However, other halides can be substituted into AuCl_4^- . The reaction energy to substitute a bromide ion into AuCl_4^- is -0.22 eV in methanol at the BP86/TZP level of theory. Thus, it is possible that bromide from the phase-transfer agent may substitute into AuCl_4^- prior to reduction. Iodide can also replace chloride in AuCl_4^- with a reaction energy of -0.96 eV in methanol.

AuCl_4^- can be reduced by two thiol ligands to form AuCl_2^- and a disulfide.^{10,11} This reaction in methanol with methylthiol ligands has an energy of -0.58 eV.¹¹ The analogous AuBr_4^- and AuI_4^- reactions have reaction energies of 0.07 and 0.48 eV, respectively. AuCl_4^- can also be reduced by a reducing agent such as sodium borohydride (NaBH_4) to form AuCl_2^- . The reaction energy with a hydride ion as the reducing agent in methanol is -3.43 eV. The reaction energies to reduce AuBr_4^- and AuI_4^- with hydride in methanol are -3.08 and -2.63 eV, respectively. The reduction of AuX_4^- is a key step in nanoparticle growth due to the fact that AuX_4^- does not react with itself. Instead, an aurophilic interaction, or a noncovalent attractive interaction, is present between AuX_4^- complexes. Further discussion on aurophilic interactions and dispersion corrections can be found in Supporting Information.

Reduction of AuX_2^- (X = Cl, Br, or I). AuCl_2^- is an important species because it is the primary precursor available after the reduction of AuCl_4^- . Properties of these precursors, including their calculated vibrational frequencies and absorption spectra, are provided in Supporting Information. AuCl_2^- also has an aurophilic interaction with a second AuCl_2^- molecule as previously mentioned for AuCl_4^- . Again, a more in-depth investigation of this interaction can be found in Supporting Information. A chemical reaction can occur between two AuCl_2^- species to form a Au_2Cl_3^- chain and a chloride ion (Chart 1). In methanol, the reaction energy is

Chart 1. Formation of Au_2Cl_3^- Chain in Methanol (Reaction 1) and in Water (Reaction 2) Compared to Formation of $\text{ClAu}_2(\text{SR})_2^-$ in Methanol (Reaction 3)



calculated to be 0.48 eV and the barrier height is 0.72 eV. In water, these values are slightly lower; however, this reaction is predicted to be endothermic and is less favorable to occur compared to the formation of the $\text{ClAuSCH}_3\text{AuSCH}_3$ chain from ref 11 (Chart 1).

Like AuX_4^- , bromide or iodide analogues of AuX_2^- can be made. AuX_2^- typically does not react with itself or with AuX_4^- to form covalent bonds. However, if one or more electrons are introduced either from a reducing agent or electric current,³³ AuX_2^- can react. In this work, we find that two AuX_2^- in close proximity will react with hydride to produce $\text{Au}_2\text{X}_2^{2-}$ and eject HX and X^- (Figure 1a). In methanol with hydride as the reducing agent, the reaction of two AuCl_2^- has an energy of -1.32 eV and a barrier height of 1.03 eV. This barrier height is notably low considering a total of three negative charges are present in the system. The reaction energies for AuBr_2^- and AuI_2^- reduction are -1.04 eV and -0.71 eV, respectively. $\text{Au}_2\text{X}_2^{2-}$ is an important species because it contains fully reduced gold and is a closed shell (nonradical) species. This molecule represents the first likely Au(0)-containing precursor under B–S synthesis conditions. Its characterization (UV–vis, IR, and Raman) is presented in Supporting Information for future experimental identification.

Reduction of $\text{AuClL}^{(-)}$ (L = PH_3 , HSCH_3 , or SCH_3). Other ligands have been investigated to grow nanoparticles, such as phosphines, thiols, and thiolates.^{8,10,11,12,15,16,21,34} We have examined the reduction of these species and find that they react similarly to AuX_2^- . Hydride reduction reactions with AuClPH_3 as a precursor can lead to the formation of Au–Au bonds and the detachment of Cl^- , HCl , or PH_3 . The reaction energy to form $\text{Au}_2(\text{PH}_3)_2$ from AuClPH_3 in methanol is -1.06 eV with a barrier height of 0.88 eV (Figure 1b), and the energy to form $\text{Au}_2\text{ClPH}_3^-$ is -0.73 eV. AuClHSCH_3 reactions are similar to phosphine reactions, where a chloride, HCl , or thiol ligand can be expelled. It is more favorable to form $\text{Au}_2(\text{HSCH}_3)_2$ than $\text{Au}_2\text{ClHSCH}_3$ with reaction energies of -1.36 and -1.21 eV, respectively (Figure 1c). The barrier height for formation of

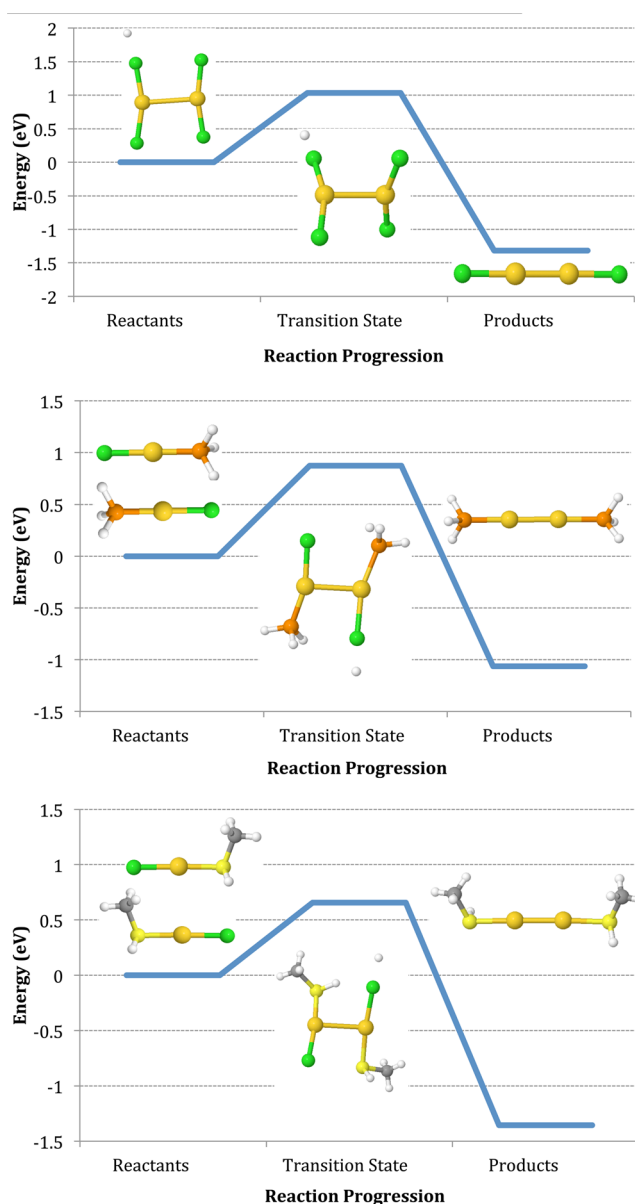


Figure 1. Hydride addition to (a, top) 2AuCl_2^- , (b, middle) 2AuClPH_3 , and (c, bottom) 2AuClHSCH_3 . Gold = gold, chloride = green, phosphorus = orange, sulfur = yellow, carbon = gray, and hydrogen = white.

$\text{Au}_2(\text{HSCH}_3)_2$ is 0.66 eV. AuClSCH_3^- can also be used as a precursor and it has the option to lose chloride, HCl , thiol, or thiolate. The most favored reaction is the formation of $\text{Au}_2\text{ClSCH}_3^{2-}$ plus a thiol and a chloride with a reaction energy of -1.21 eV. The next favored reaction is the formation of $\text{Au}_2(\text{SCH}_3)_2^{2-}$ plus a chloride and HCl with a reaction energy of -0.52 eV. The least favored reaction is the creation of $\text{Au}_2\text{ClSCH}_3^{2-}$ and a thiolate and HCl with a reaction energy of 0.009 eV. We have been unable at this time to find a transition state with a single imaginary frequency for hydride reduction of any of the thiolate species.

Reactions of $\text{Au}_2\text{Cl}_2^{2-}$. For the remainder of the paper, we discuss only gold–chloride complexes; however, we expect similar reactions with other ligands. Once the Au(0)-containing $\text{Au}_2\text{Cl}_2^{2-}$ precursor has been formed, it can react with species present in the reaction mixture. The reaction of two $\text{Au}_2\text{Cl}_2^{2-}$ -containing precursors is unfavorable, which is likely due to

Coulomb repulsion of the two dianionic species; reaction energies can be found in Supporting Information. However, $\text{Au}_2\text{Cl}_2^{2-}$ is unique in that it will react with AuCl_2^- . This reaction forms $\text{Au}_3\text{Cl}_3^{2-}$ and spontaneous ejection of a chloride occurs, with a reaction energy in methanol of -0.57 eV and a barrier height of 0.31 eV (Figure 2). $\text{Au}_3\text{Cl}_3^{2-}$ is not a true

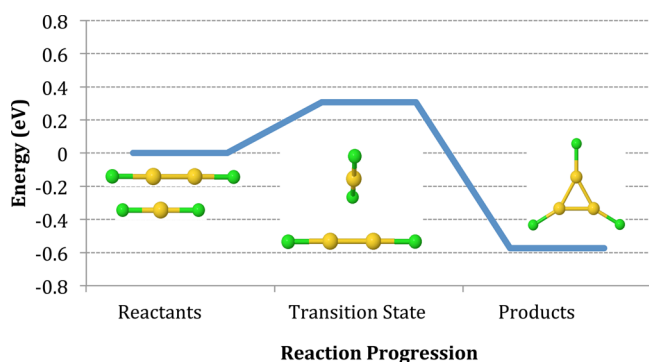


Figure 2. AuCl_2^- addition to $\text{Au}_2\text{Cl}_2^{2-}$. Gold = gold and chloride = green.

$\text{Au}(0)$ species: it is more accurate to describe it as two electrons delocalized over three gold atoms. For the purposes of this paper, we will refer to this cluster as a $\text{Au}(0)$ species although the formal charges on Au are $(+1/3)$. The characterization of $\text{Au}_3\text{Cl}_3^{2-}$ is also presented in Supporting Information.

Growing Larger Clusters. Larger clusters can be grown incrementally by adding AuCl_2^- to the previously mentioned $\text{Au}(0)$ species. For example, $\text{Au}_3\text{Cl}_3^{2-}$ and AuCl_2^- react to form $\text{Au}_4\text{Cl}_4^{2-}$ in methanol with a reaction energy of 0.09 eV. It is favorable to lose a chloride from $\text{Au}_4\text{Cl}_5^{3-}$ to yield $\text{Au}_4\text{Cl}_4^{2-}$ and Cl^- with an energy of -0.23 eV and a transition-state energy of 0.09 eV (Figure 3). $\text{Au}_4\text{Cl}_4^{2-}$ has a tetrahedral gold core with

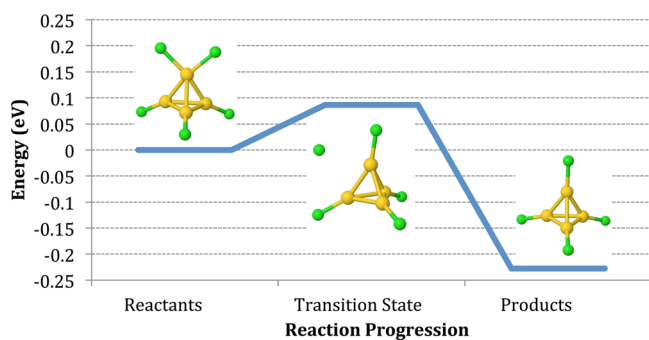


Figure 3. AuCl_2^- addition to $\text{Au}_3\text{Cl}_3^{2-}$ and subsequent chloride removal. Gold = gold and chloride = green.

two delocalized electrons, similar to known gold–phosphine clusters.^{16,34–37} This cluster could be a building block for the core of nanoparticles.^{38–41} Characterization of this cluster is also presented in Supporting Information. The reaction of $\text{Au}_4\text{Cl}_4^{2-}$ with AuCl_2^- results in a $\text{Au}_5\text{Cl}_5^{3-}$ structure with a reaction energy of 0.06 eV. In this case the removal of a chloride does not make the reaction exothermic but even more endothermic, with a chloride dissociation energy of 0.26 eV.

Addition of AuCl_2^- units does not lead to an increase in the electron count of the core, so in order to increase the number of electrons in the core, larger clusters can be grown by combining some of the $\text{Au}(0)$ species. As noted above,

$\text{Au}_2\text{Cl}_2^{2-}$ does not react with itself. However, $\text{Au}_2\text{Cl}_2^{2-}$ and $\text{Au}_3\text{Cl}_3^{2-}$ can react with each other. If the interaction occurs on the edge of $\text{Au}_3\text{Cl}_3^{2-}$, it forms $\text{Au}_5\text{Cl}_5^{4-}$ with a reaction energy of -0.06 eV in methanol (Figure 4a). If the interaction occurs

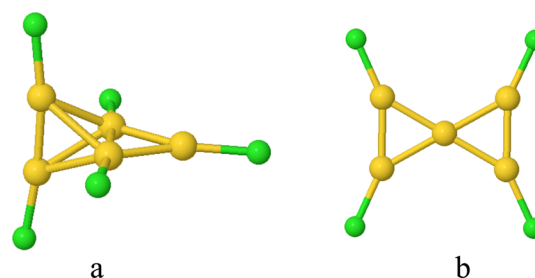


Figure 4. $\text{Au}_2\text{Cl}_2^{2-}$ addition to $\text{Au}_3\text{Cl}_3^{2-}$, (a) at the edge and (b) at the vertex. Gold = gold and chloride = green.

at the vertex of $\text{Au}_3\text{Cl}_3^{2-}$, the reaction can form $\text{Au}_5\text{Cl}_4^{3-}$ plus chloride in methanol with a reaction energy of -0.50 eV (Figure 4b). The reaction of $\text{Au}_4\text{Cl}_4^{2-}$ and $\text{Au}_2\text{Cl}_2^{2-}$ results in $\text{Au}_6\text{Cl}_6^{4-}$ with a reaction energy of -0.45 eV (Figure 5a).

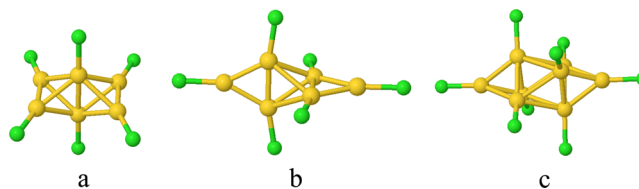


Figure 5. (a) $\text{Au}_2\text{Cl}_2^{2-}$ addition to $\text{Au}_4\text{Cl}_4^{2-}$. (b) $\text{Au}_3\text{Cl}_3^{2-}$ addition to $\text{Au}_3\text{Cl}_3^{2-}$. (c) $\text{Au}_4\text{Cl}_4^{2-}$ addition to $\text{Au}_4\text{Cl}_4^{2-}$. Gold = gold and chloride = green.

Dimers of $\text{Au}_3\text{Cl}_3^{2-}$ and $\text{Au}_4\text{Cl}_4^{2-}$ can combine to form $\text{Au}_6\text{Cl}_6^{4-}$ and $\text{Au}_8\text{Cl}_8^{4-}$, respectively (Figure 5b,c). In methanol, $\text{Au}_6\text{Cl}_6^{4-}$ forms with a reaction energy of -0.08 eV and $\text{Au}_8\text{Cl}_8^{4-}$ forms with a reaction energy of -0.18 eV.

Benzene. To understand the original B–S synthesis, we also examined the reaction in a representative organic solvent (benzene) since nanoparticles are often grown in the organic phase. Reduction of the starting gold salt, AuCl_4^- , with hydride in benzene has a reaction energy of -3.46 eV and forms AuCl_2^- . Two AuCl_2^- in the presence of a hydride can react as in methanol; however, this forms Au_2Cl^- , HCl , and two chloride ions with a reaction energy of -0.43 eV. The reaction of two Au_2Cl^- together yields $\text{Au}_4\text{Cl}_2^{2-}$; several isomers exist for this system. The formations of trans, Y, and linear isomers of $\text{Au}_4\text{Cl}_2^{2-}$ have reaction energies of 0.68 , 0.18 , and 0.07 eV, respectively, suggesting that these isomers are unlikely to form. The reaction of two AuCl_2^- to yield $\text{Au}_2\text{Cl}_2^{2-}$ is calculated to have a reaction energy of only -0.07 eV in benzene compared to -1.32 eV in methanol. The less favorable reaction energy is likely due to the buildup of two negative charges, which is unfavorable in nonpolar solvents such as benzene. In addition, it is important to note that the two AuCl_2^- have to be in close proximity to react. In methanol, the auophilic interaction of the $\text{Au}(I)$ species is predicted to be 0.073 eV at the BP86/TZP level of theory but is -0.148 eV at the BP86-D/TZP level of theory. The dispersion correction is required in order to predict an auophilic interaction for this system. The auophilic interaction in benzene is much weaker than the corresponding auophilic interaction in methanol. If the dispersion correction

is included in benzene, the aurophilic interaction has an energy of 0.966 eV, so the dimer is unlikely to form; if dispersion is not included, repulsive Coulombic interactions dominate and no local minimum with close intermolecular distances exists. If the two Au(I) species do not come close enough, the hydride will react with only one of the AuCl_2^- molecules and can either exchange the hydride for a chloride to form HAuCl^- or reduce AuCl_2^- to Au^- , HCl , and Cl^- . In this case, Au(0)-containing species are not formed.

For the benzene reaction to yield reasonable Au(0)-containing precursors similar to the methanol reaction, we find that the introduction of tetramethylammonium (TMA) is required. We believe that the TMA helps balance the buildup of charge on the small gold cluster and enables the Au(I) precursors to approach each other. This was also observed in a recent study examining thiol substitution into AuCl_2^- in benzene.⁴² Without dispersion, the interaction between the two TMA– AuCl_2^- complexes has an energy of -0.31 eV; with the dispersion correction, this interaction has an energy of -0.96 eV. With BP86-D, the two TMA and AuCl_2^- units construct a system with an inner layer of AuCl_2^- and an outer layer of TMA (Figure 6a). Hydride added to this system forms $\text{Au}_2\text{Cl}_2^{2-}$ (Figure 6b), unlike the addition of hydride to two isolated AuCl_2^- in benzene that yields Au_2Cl^- . With dispersion, the calculated gold–gold distance between AuCl_2^- units is 3.73 Å. The reaction energy is -2.02 eV. If dispersion effects are not included in the calculations, the AuCl_2^- units are computed to

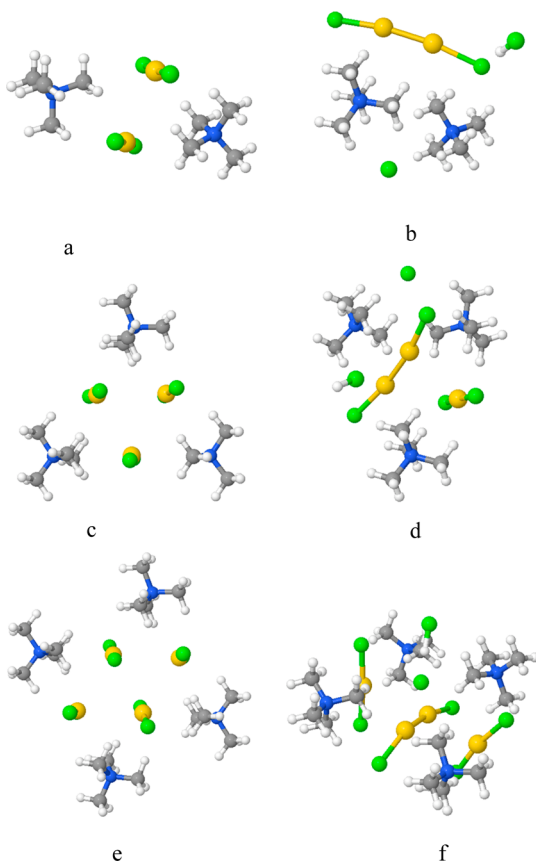


Figure 6. (a) Two tetramethylammonium (TMA^+) and 2 AuCl_2^- ; (b) hydride added to structure a. (c) Three TMA– AuCl_2^- ; (d) hydride added to structure c. (e) Four TMA– AuCl_2^- ; (f) hydride added to structure e. Gold = gold, chloride = green, nitrogen = blue, carbon = gray, and hydrogen = white.

have a gold–gold distance of 6.21 Å, and no reaction occurs when hydride is added. The addition of a third TMA and AuCl_2^- leads to a geometry with the three gold species in the inner layer and the three TMAs in the outer layer (Figure 6c). We do not believe this constitutes a reverse or inverse micelle but more of a counterion interaction, although much larger TMA– AuCl_2^- systems would need to be studied to investigate this. The introduction of a fourth TMA and AuCl_2^- expands the sphere of the layers, so all four Au(I) species are in the center and the four TMAs are on the outside (Figure 6e). The insertion of hydride into the systems containing three and four AuCl_2^- units leads to the reduction of two Au(I) species to Au(0) and the formation of $\text{Au}_2\text{Cl}_2^{2-}$ as reported earlier in methanol (Figure 6d,f) with reaction energies of -2.33 and -1.48 eV, respectively. This suggests that the phase-transfer agent plays a crucial role in the formation of small gold clusters in benzene. Once $\text{Au}_2\text{Cl}_2^{2-}$ is formed, growth can occur by addition of AuCl_2^- . The formation of $\text{Au}_3\text{Cl}_3^{2-}$ from the reaction of $\text{Au}_2\text{Cl}_2^{2-}$ and AuCl_2^- has a favorable reaction energy of -0.56 eV in benzene without considering the effect of TMA. $\text{Au}_3\text{Cl}_3^{2-}$ can further react with AuCl_2^- to form $\text{Au}_4\text{Cl}_4^{2-}$ with a reaction energy of -0.06 eV, again without TMA.

CONCLUSIONS

In this work we have demonstrated that closed-shell Au(0) species can be formed from hydride reduction of two Au(I) L_2 for a wide variety of ligands including halides, thiols, thiolates, and phosphines. AuX_2^- (where X = Cl, Br, or I) hydride reduction reactions eject two halides and form $\text{Au}_2\text{X}_2^{2-}$. AuClPH_3 reactions can eject chloride, HCl, or PH_3 , resulting in either $\text{Au}_2(\text{PH}_3)_2$ or $\text{Au}_2\text{ClPH}_3^-$. AuClHSCH_3 reactions are similar to phosphine reactions, where a chloride, HCl, or thiol can be ejected. The possible gold-containing products from the reaction are $\text{Au}_2(\text{HSCH}_3)_2$ or $\text{Au}_2\text{ClHSCH}_3^-$. AuClSCH_3^- reactions behave similarly to both of the previous reactions; these molecules have the option to eject chloride, HCl, thiol, or thiolate. The reactions result in the formation of $\text{Au}_2\text{ClSCH}_3^{2-}$, $\text{Au}_2(\text{SCH}_3)_2^{2-}$, or $\text{Au}_2\text{ClSCH}_3^{3-}$. The Au(0) species can react to form larger clusters through either incremental addition of AuCl_2^- or reactions with other Au(0) species. Some of the growth reactions become more favorable after the removal of a chloride, such as $\text{Au}_4\text{Cl}_5^{3-}$ to form $\text{Au}_4\text{Cl}_4^{2-}$.

Reactions in benzene initially do not behave like the corresponding ones in methanol; hydride reduction of two AuCl_2^- units favors the formation of Au_2Cl^- . However, Au_2Cl^- does not react favorably to form products. The introduction of TMA makes the benzene reactions perform similarly to the methanol reactions. Dispersion-corrected calculations are needed to account for the aurophilic interaction of gold(I) molecules so that they are in close proximity to react when hydride is added. The TMA– AuCl_2^- systems were found to form layered structures with AuCl_2^- on the inside.

ASSOCIATED CONTENT

Supporting Information

Additional text and three tables with dispersion-corrected calculations at the BP86/TZP and BP86-D levels of theory, and three figures showing absorption, Raman, and IR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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