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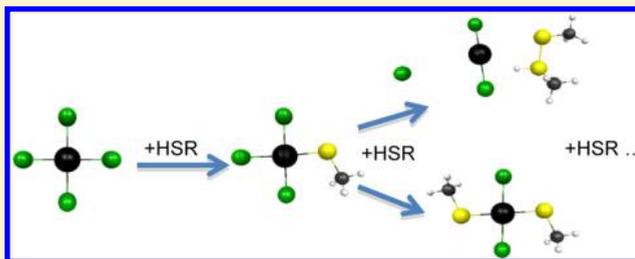
The Golden Pathway to Thiolate-Stabilized Nanoparticles: Following the Formation of Gold(I) Thiolate from Gold(III) Chloride

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S Supporting Information

ABSTRACT: Pathways for the formation of gold thiolate complexes from gold(III) chloride precursors AuCl_4^- and AuCl_3 are examined. This work demonstrates that two distinct reaction pathways are possible; which pathway is accessible in a given reaction may depend on factors such as the residue group R on the incoming thiol. Density functional theory calculations using the BP86 functional and a polarized triple- ζ basis set show that the pathway resulting in gold(III) reduction is favored for R = methyl. A two-to-one ratio of thiol or thiolate to gold can reduce Au(III) to Au(I), and a three-to-one ratio can lead to polymeric Au(SR) species, which was first suggested by Schaaff et al. *J. Phys. Chem. B*, **1997**, *101*, 7885 and later confirmed by Goulet and Lennox *J. Am. Chem. Soc.*, **2010**, *132*, 9582. Most transition states in the pathways examined here have reasonable barrier heights around 0.3 eV; we find two barrier heights that differ substantially from this which suggest the potential for kinetic control in the first step of thiolate-protected gold nanoparticle growth.



INTRODUCTION

Gold thiolate nanoparticles have been synthesized for many years without a good understanding of the reaction pathway between the gold(III) chloride species and the thiols. Gold nanoparticles are often synthesized using the Brust–Schiffrin method¹ or a modified version.^{2–5} Until now, a limited number of studies have examined the synthesis mechanism. The Brust–Schiffrin synthesis is a two-phase synthesis that starts with tetrachloroaurate in water, which is phase-transferred into toluene where the thiol ligands are then introduced in a three-to-one ratio. The reducing agent, in this case sodium borohydride, is then added resulting in 1–3 nm diameter gold particles. This synthesis method is often chosen for the reliability of the resulting monodisperse gold thiolate nanoparticles. Modified versions of the Brust–Schiffrin synthesis include changes in the ratio of thiol ligands to gold halide salt⁶ and in the number of phases that the reaction takes place in, usually a change from two phases to a single phase.^{6,7} The use of the original Brust–Schiffrin or a modified version depends on the desired size and morphology of the synthesized gold thiolated nanoparticles, because these characteristics affect the physical and chemical properties of the nanoparticles.^{8,9}

A three-to-one thiol to gold ratio was first suggested by Schaaff et al. to cause the formation of gold–thiolate oligomers.¹⁰ Later Goulet et al. verified that a three-to-one ratio does form oligomers of gold thiolate.² They also concluded in their work that a two-to-one ratio of thiol ligands to gold salt causes reduction of the gold salt from Au(III) to Au(I) and forms a disulfide.²

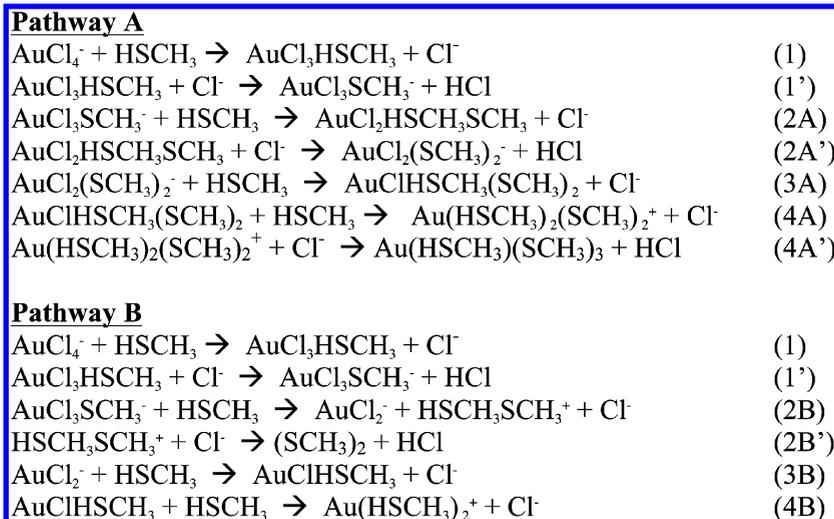
Anionic chain oligomers of $\text{Au}(\text{SR})_2^-$ and $\text{Au}_2(\text{SR})_3^-$ are of significant interest since they are attached to the outside of

many gold nanoparticles including $\text{Au}_{25}(\text{SR})_{18}^-$, $\text{Au}_{38}(\text{SR})_{24}$, and $\text{Au}_{102}(\text{SR})_{44}$.^{3,11–15} They have also been predicted to passivate $\text{Au}_{144}(\text{SR})_{60}$ ¹⁶ and are observed on self-assembled monolayers (SAMs).^{17–20} Longer chains of $\text{Au}_3(\text{SR})_4^-$ are suggested by Zeng et al. and Jiang et al. to passivate $\text{Au}_{20}(\text{SR})_{16}$ and by Garzon et al. to passivate $\text{Au}_{18}(\text{SR})_{14}$.^{21–23} In addition, some anti-arthritis drugs are helical or ring-like gold–thiolate oligomers that have been characterized with X-ray crystallography.^{24,25} These chains or rings could be involved in the growth of nanoparticles. Barngrover and Aikens recently demonstrated that hydride addition in the second step of the Brust–Schiffrin synthesis reduces the chains and rings and forms gold–gold bonds, which could represent the start of gold nanoparticle growth.²⁶ Zeng et al. determined that reduced rings could be interlocked to form catenane ring structures and could be brought together to form $\text{Au}_{20}(\text{SR})_{16}$.²⁷

Other modified Brust–Schiffrin syntheses use different Au(III) precursor molecules, for example, AuCl_3 can be substituted in place of AuCl_4^- .²⁸ Furthermore, thiolates can be employed instead of thiols in the pursuit of synthesizing gold thiolate nanoparticles. Thiolates allow the synthesis to occur in fewer steps, since removal of the thiol proton is not necessary during the chloride ligand replacements. However, due to their unstable nature in aqueous solutions, thiolates must be stabilized with long halogenated alkyl chains⁵ or with electron-withdrawing groups.²⁹

Received: March 29, 2012

Published: July 24, 2012

Scheme 1. Overall Reaction of Four Thiol Additions to AuCl_4^- ^a

^aPathway A leads to Au(III) product, while pathway B leads to Au(I) product.

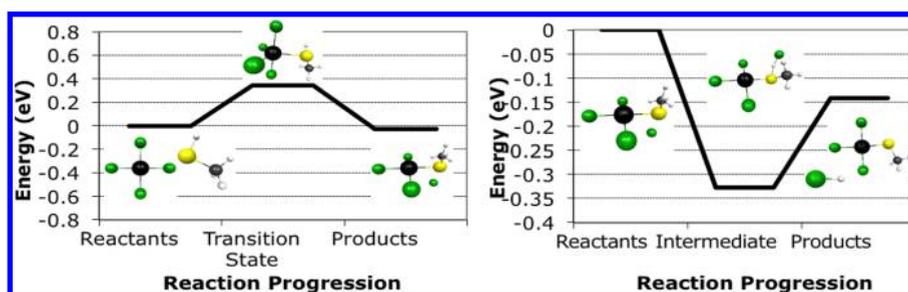


Figure 1. Reaction pathway for the first thiol addition to AuCl_4^- and subsequent proton dissociation.

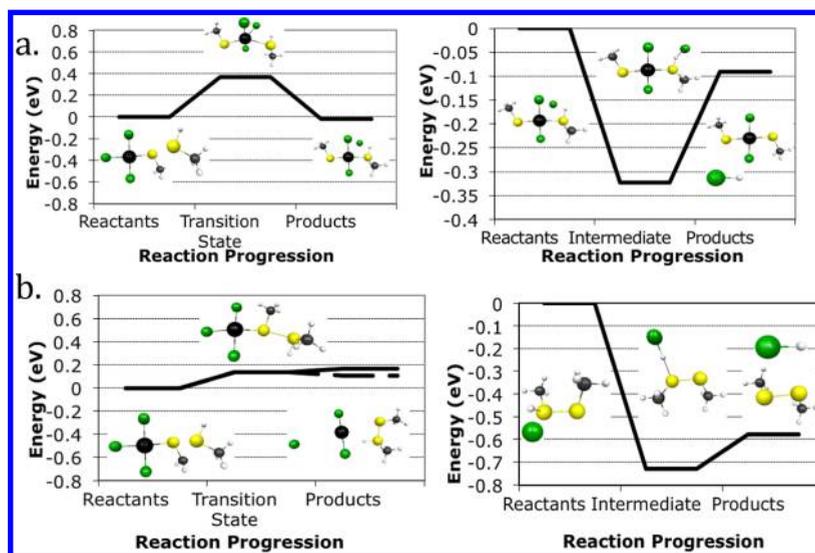


Figure 2. (a) Reaction pathway A for second thiol addition leading to Au(III) product followed by proton dissociation. (b) Reaction pathway B leading to Au(I) product followed by proton dissociation from the disulfide. The dotted line in (b) is the single point energy of the dissociated products, whereas the solid line represents the energy of the infinitely separated products; the discrepancy may be due to interactions between the species or basis set superposition error.

COMPUTATIONAL DETAILS

All calculations are performed with the Amsterdam Density Functional (ADF)³⁰ package, using density functional theory with the Becke Perdew (BP86)^{31,32} functional and a frozen-core polarized triple- ζ (TZP) basis set. We include scalar relativistic effects by employing the

Zero Order Regular Approximation (ZORA).³³ We incorporate the methanol solvent using the Conductor-like Screening Model (COSMO), which represents the solvent by its dielectric constant.^{34–37}

Calculations described in this work employ the methyl group on the thiol or thiolate ligand unless otherwise stated. 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. Energies reported in this work include zero-point energy corrections, which are typically on the order of hundredths of an eV.

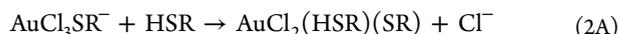
RESULTS AND DISCUSSIONS

First Thiol Reaction. In this work, we investigate the stepwise addition of methylthiol to gold(III) chloride in a methanol solvent. The entire pathway involving four thiol additions is shown in Scheme 1. The first addition proceeds through a bipyramidal transition state with a calculated barrier height of 0.34 eV and results in the dissociation of a chloride ion with a reaction energy of -0.03 eV (Figure 1). The chloride ion can subsequently react with the thiol proton to cause the proton to dissociate and bind to the chloride. The proton dissociation has an energy of -0.14 eV. These two steps may be summarized as



where the prime (eq 1') denotes the proton dissociation step. In neutral solution, the Cl^- species is more likely to perform this acid–base reaction than the solvent or free thiol (Table S1, Supporting Information). The two steps that occur during the first thiol addition have not yet been observed experimentally.

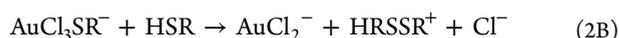
Second Thiol Reaction. The second addition of thiol to the now monosubstituted gold complex has two different potential reaction pathways. The first pathway (eq 2A) is the less kinetically favored pathway for the methyl ligand, where the thiol reacts through another bipyramidal transition state with a barrier height of 0.37 eV and ejects a chloride ion off the monosubstituted gold to form a disubstituted Au(III) complex (Figure 2a) according to



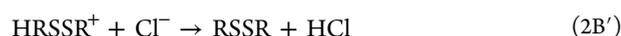
In this pathway the trans configuration is preferred over the cis configuration with reaction energies of 0.03 and 0.04 eV, respectively. In step 2A' (eq 2A'), the recently ejected chloride ion is able to react with the proton attached to the newly added thiol, which causes the proton to dissociate analogously to step 1' (eq 1'). This proton dissociation has a reaction energy of -0.09 eV.



In the second, more kinetically favored pathway 2B (eq 2B), the thiol reacts with the thiolate and forms a protonated disulfide (Figure 2b). When the protonated disulfide forms, the remaining gold chloride complex is reduced to a gold(I) species and a chloride ion is released.



This reaction has a barrier height of 0.14 eV. The overall reaction energy is computed to be 0.16 eV for infinitely separated products; since this does not account for various molecular interactions and basis set superposition error, a single point energy calculation for all three products is performed, and the overall reaction energy is computed to be 0.11 eV. Although this reaction (which forms the protonated disulfide) has a positive reaction energy, the overall reaction energy can be lowered by -0.58 eV if a chloride ion deprotonates the protonated disulfide (Figure 2b) according to



Goulet and Lennox found that one equivalent of thiol led to a half of an equivalent of the Au(I) complex;² this suggests that the second thiol addition step occurs faster than the first step, which is in agreement with the barrier heights found in our current work.

Although we have focused the above discussion on the two most preferred pathways, other products could potentially be formed from the addition of two thiols to AuCl_4^- ; the overall energies for these additional reactions are shown in Table 1. In

Table 1. Overall Reaction Energies of Two Thiol Additions

products	reaction energies (eV)
$2\text{HCl} + \text{RSSR} + \text{AuCl}_2^-$	-0.58^b
$2\text{HCl} + \text{AuCl}_2(\text{SR})_2^-$	-0.01^a
$2\text{HCl} + \text{Cl}_2 + \text{Au}(\text{SR})_2^-$	1.70
$\text{HCl} + \text{Cl}^- + \text{RSSRH}^+ + \text{AuCl}_2^-$	-0.01
$\text{HCl} + \text{Cl}^- + \text{AuCl}_2(\text{HSR})(\text{SR})$	0.33
$\text{HCl} + \text{Cl}^- + \text{Cl}_2 + \text{Au}(\text{HSR})(\text{SR})$	1.25
$2\text{Cl}^- + \text{HRSSRH}^{2+} + \text{AuCl}_2^-$	1.53
$2\text{Cl}^- + \text{AuCl}_2(\text{HSR})_2^+$	0.11
$2\text{Cl}^- + \text{Cl}_2 + \text{Au}(\text{HSR})_2^+$	1.15
$\text{H}_2 + \text{Cl}_2 + \text{RSSR} + \text{AuCl}_2^-$	1.56
$\text{H}_2 + \text{Cl}_2 + \text{AuCl}_2(\text{SR})_2^-$	2.14
$\text{H}_2 + 2\text{Cl}_2 + \text{Au}(\text{SR})_2^-$	3.85

^aPathway A. ^bPathway B.

general, reduction of Au(III)- to Au(I)-containing species is thermodynamically favored. The formation of free anions is also thermodynamically favored over the formation of the related diatomic gas. The proton from the incoming thiol can transfer to the disulfide making it a singly or doubly protonated species, bind with chloride to form HCl, or remain on the thiol. The most thermodynamically favored option is for the proton to bind with chloride resulting in HCl and an unprotonated disulfide and gold complex. The option of protonating the disulfide is the least favored.

Third Thiol Reaction. Now we turn to the addition of the third thiol in pathways A and B. In the third addition step 3A, we see the continuing trend of chloride ion removal and the formation of a trisubstituted gold(III) complex; however, this chloride does not dissociate the thiol proton. This reaction energy is less than -0.01 eV and the barrier height is 0.62 eV (Figure 3a).



In pathway 3B (eq 3B) the thiol also reacts and ejects a chloride ion to form a monosubstituted gold(I) complex with a reaction energy of -0.10 eV and a barrier height of 0.26 eV (Figure 3b).



For the methyl ligand examined in this work, pathway 3B (eq 3B) is both kinetically and thermodynamically favored over pathway 3A (eq 3A). The proton does not dissociate upon subsequent interaction with the chloride ion. Since the barrier height of pathway 3B is higher than for pathway 2B, the second thiol addition is likely to complete before pathway 3B becomes operative, which again agrees with the results of Goulet and Lennox that AuCl_2^- is formed after addition of two equivalents of thiol.²

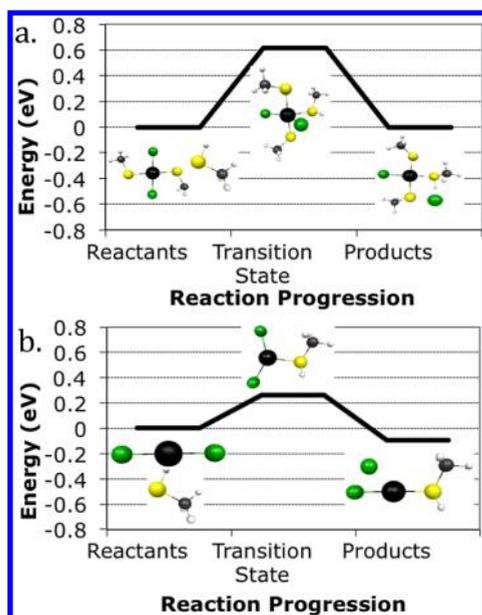


Figure 3. Third thiol addition in (a) pathway A with Au(III) species and (b) pathway B with Au(I) species.

Fourth Thiol Reaction. The fourth addition to pathways A and B (eqs 4A and 4B) causes the removal of the remaining chloride ligand, resulting in a fully substituted gold complex. The barrier height for the gold(III) pathway 4A is 0.34 eV with

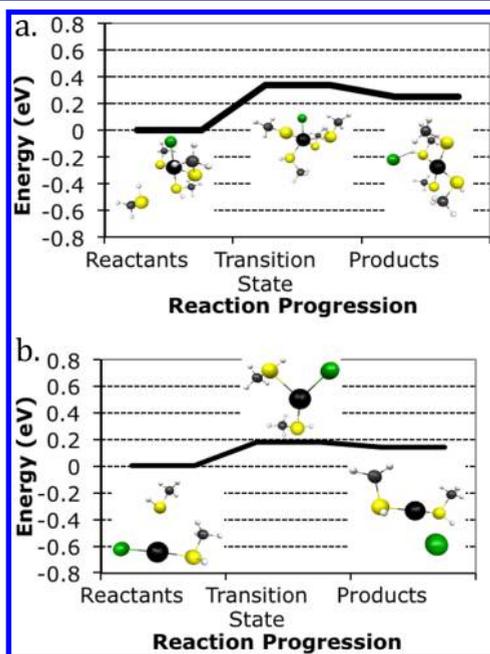
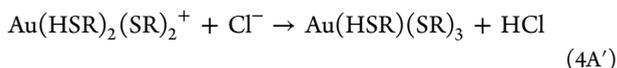
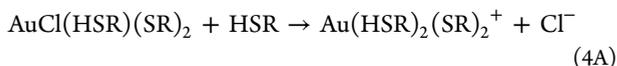


Figure 4. Fourth thiol addition in (a) pathway A (Au(III) species) and (b) pathway B (Au(I)).

a reaction energy of +0.25 eV (Figure 4a). Proton dissociation lowers the overall reaction by -0.33 eV (eq 4A').



The gold(I) pathway 4B has a barrier height of 0.18 eV and a corresponding reaction energy of 0.14 eV (Figure 4b). The proton dissociation is not favored thermodynamically.



The overall energy for pathway A (eq 4A) is -0.08 eV, and the overall energy for pathway B (eq 4B) is -0.54 eV. These pathways are summarized in Scheme 1. Table 2 displays the

Table 2. Overall Reaction Energies of Four Thiol Additions

products	reaction energies (eV)
$4\text{Cl}^- + \text{HRSSRH}^{2+} + \text{Au(HSR)}_2^+$	1.58
$4\text{Cl}^- + \text{Au(HSR)}_4^{3+}$	1.66
$3\text{Cl}^- + \text{HCl} + \text{RSSRH}^+ + \text{Au(HSR)}_2^+$	0.04
$3\text{Cl}^- + \text{HCl} + \text{Au(HSR)}_3(\text{SR})^{2+}$	0.62
$2\text{Cl}^- + 2\text{HCl} + \text{RSSR} + \text{Au(HSR)}_2^+$	-0.54^b
$2\text{Cl}^- + 2\text{HCl} + \text{RSSRH}^+ + \text{Au(HSR)(SR)}$	0.14
$2\text{Cl}^- + 2\text{HCl} + \text{HRSSRH}^{2+} + \text{Au(SR)}_2^-$	2.13
$2\text{Cl}^- + 2\text{HCl} + \text{Au(HSR)}_2(\text{SR})_2^+$	0.25
$1\text{Cl}^- + 3\text{HCl} + \text{RSSR} + \text{Au(HSR)(SR)}$	-0.44
$1\text{Cl}^- + 3\text{HCl} + \text{RSSRH}^+ + \text{Au(SR)}_2^-$	0.59
$1\text{Cl}^- + 3\text{HCl} + \text{Au(HSR)(SR)}_3$	-0.08^a
$4\text{HCl} + \text{RSSR} + \text{Au(SR)}_2^-$	0.01
$4\text{HCl} + \text{Au(SR)}_4^-$	0.08

^aPathway A. ^bPathway B.

overall reactions possible for the addition of four thiols. Many products can form from the addition of four thiols to AuCl_4^- . However, only the two most likely pathways are discussed in detail in this paper. The most thermodynamically favored products are disulfide and the doubly protonated Au(I) complex. The singly protonated Au(I) species is the second most favored product. The related doubly and singly protonated Au(III) species are also thermodynamically favored compared to the other Au(III) complexes but not as much as the Au(I) complexes for the $\text{R} = \text{CH}_3$ ligand. Although the chloride ion often accepts a proton in the first two steps of the reaction, the thiol proton can remain attached to the gold complex in the last two steps.

R Group Dependence. Methyl as the residue group does not lead to proton dissociation from AuClHSCH_3 . A more electron-withdrawing group could cause the thiol proton to become quite acidic and dissociate. We see a significant change in reaction energy of chloride ion-induced proton dissociation from AuClHSR , depending on the R group. When the residue group is phenyl, this reaction has an overall reaction energy of less than 0.01 eV compared to methyl as a residue group, which has an overall reaction energy of 0.32 eV. Another option is for the reaction to take place in a basic solution, which will help dissociate the proton. Energies for other bases used to remove the thiol proton can be found in the Table S1, Supporting Information. This is important because the removal of the proton allows for the formation of chains and rings as described below, which may be the precursor to gold thiolate nanoparticles.

It should also be noted that Bachman et al. demonstrated that if electron-withdrawing ligands are used, the Au(III) complex can be obtained instead of the Au(I) species.²⁹ This suggests that variation of the R group may be used to provide kinetic and/or thermodynamic control of pathways A and B.

Thiolate vs Thiol Addition. One-step additions can occur if thiolates are used instead of thiols. Thiolate additions proceed

in either one of the two pathways through the gold(III) or the gold(I) species. The gold(I) pathway with the reduction to $\text{Au}(\text{SCH}_3)_2^-$ and the formation of the disulfide is slightly more favored with a reaction energy of -4.63 eV compared to that of the gold(III) analog, which has a reaction energy of -4.56 eV (Table 3). The thiolate additions are much more thermody-

Table 3. Overall Reaction Energies of Four Thiolate Additions

products	reaction energy (eV)
$4\text{Cl}^- + \text{RSSR} + \text{Au}(\text{SR})_2^-$	-4.63
$4\text{Cl}^- + \text{Au}(\text{SR})_4^-$	-4.56

namically favored than their thiol analogs. This could be advantageous or could be a hindrance due to the spontaneity of the reaction, leaving little control of the reaction.

Effect of Thiol Ratio. Varying the ratio of thiol to tetrachloroaurate allows for different degrees of ligand substitution. A one-to-one ratio usually results in a single substitution of ligands, the removal of chloride ion, and the addition of thiol. Increasing the ratio to two-to-one can result in either a second ligand exchange or in the formation of a disulfide and a reduction of the gold(III) to gold(I), which is in agreement with Goulet et al.² Note that control over the barrier heights of steps 1 and 2 is needed to lead to monosubstituted products since current procedures instead lead to a half of an equivalent of disubstituted products.² This could potentially be achieved with the use of various residue groups, such as electron-withdrawing groups. Further increasing the ratio to three-to-one results in either the trisubstituted gold(III) complex or the first substitution on the gold(I) complex. A final increase of the ratio to four-to-one produces the gold(III) thiol(ate) complex or the gold(I) thiol complex; the gold(III) thiol(ate) species is possible with electron-withdrawing ligands.²⁹

Reactions Starting from AuCl_3 . Tetrachloroaurate is the most common starting material, although AuCl_3 is occasionally used as well.²⁸ The only difference occurs in the first thiol addition; addition of thiol to AuCl_4^- causes the ejection of a chloride ion, whereas reactions with AuCl_3 do not eject this ion. Addition to AuCl_3 results in a greater overall reaction energy (Table 4). The product, AuCl_3HSR , can then react in the same manner as described above.

Table 4. Reaction Energies of AuCl_4^- and AuCl_3 with Thiol and Thiolate

	AuCl_4^-	AuCl_3
thiol	-0.17 eV ^a / -0.03 eV ^b	-2.54 eV
thiolate	-1.33 eV	-3.84 eV

^aThiol proton dissociated to chloride. ^bNo thiol proton dissociation.

Formation of Gold–Thiolate Chains and Rings.

Removal of the thiol proton after the third addition of thiol is important because sulfur will then have two lone pairs, which allows it to react with another gold atom. This leads to the dimerization of two AuClSCH_3^- (Figure 5). When the two monomers react, the internal chlorine is ejected to form a chloride ion, allowing the sulfur and gold to form a bond; this dimerization has a reaction energy of -0.37 eV and a barrier height of 0.33 eV. The new subunit has a terminal chlorine, which can be used to initiate further monomer additions to

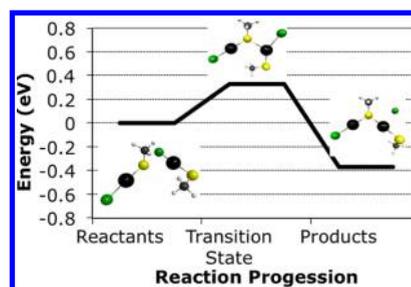


Figure 5. Dimerization of AuClSCH_3^- .

form a long chain. We investigated trimers, tetramers, and octomers. The trimer can be formed from the dimer and a monomer with an overall reaction energy of -0.35 eV. The tetramer can be formed from the previous trimer and a monomer with an overall energy of -0.36 eV. The octomer investigated in this work is formed from two tetramers to demonstrate that longer chains could be made in this manner instead of adding monomers to the progressively growing chains; this reaction has an energy of approximately -0.3 eV (not including zero-point energy). Once a chain is formed, it can also cyclize. An example of cyclization is illustrated in Figure 6; this process has an overall reaction energy of -0.22

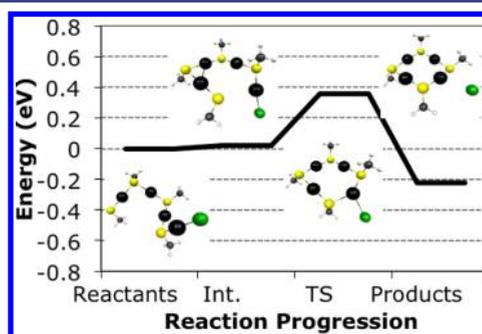


Figure 6. Cyclization of $\text{Au}_4(\text{SCH}_3)_4\text{Cl}^-$. Int. = intermediate and TS = transition state.

eV and a barrier height of 0.36 eV. A ΔS correction value has been calculated for the cyclization process with an energy of 0.026 eV, which suggests that the entropy change is not significant for this process. Cyclized products, such as $(\text{AuSR})_4$, have been observed experimentally by various mass spectrometry methods by multiple groups, including Gies et al., Dass and co-workers, and Negishi et al.^{38–43} In addition, these oligomers may be involved in the second step of gold nanoparticle growth.²⁶

CONCLUSIONS

Gold(I) thiolate nanoclusters and nanoparticles have been synthesized for many years with little understanding of the mechanism that is responsible for their formation. This work suggests a mechanism for the first step of the Brust–Schiffrin synthesis method. Our calculations with a two-to-one ratio of methylthiol to gold salt show that reduction of gold(III) to gold(I) and the formation of a disulfide are thermodynamically favored, which agree with previous experimental work. The fate of the thiol proton is determined, and it does not have to remain on the thiol; it is actually thermodynamically favored to dissociate to bind with the chloride ion. We have also demonstrated that a three-to-one ratio of thiol to gold salt

can lead to polymeric chains of AuSR, an idea first proposed by Schaaff et al. in 1997 and later confirmed by Goulet et al. These polymeric chains can grow to various sizes or cyclize into rings, such as (AuSR)₄, which have been seen experimentally in mass spectrometry work. Those chains and rings could then be reduced in the second step of the Brust–Schiffirin synthesis, as discussed previously in ref 26. Our investigation also examined the transition states for the thiol additions to the gold species and revealed that the gold(III) structures go through a trigonal bipyramidal transition state with reasonable barrier heights of about 0.3 eV. Two distinct pathways were examined: one that leads to the reduction of gold(III) to gold(I) and the other that exchanges all of the halide ligands on Au(III) for sulfur-containing ligands. Either pathway can be potentially relevant depending on the type of residue groups attached to the sulfur, such as long halogenated alkyl chains or electron-withdrawing groups. In addition, reactions with thiolates and with a AuCl₃ precursor have been studied in this work.

■ ASSOCIATED CONTENT

● Supporting Information

Acid–base reaction energies for removal of the first thiol proton and optimized BP86/TZP coordinates of all gold-containing species. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors would like to thank the Alfred P. Sloan Foundation for a Sloan Research Fellowship (2011–2013) and the Camille and Henry Dreyfus Foundation for a Camille Dreyfus Teacher-Scholar Award (2011–2016). The authors would also like to thank Kansas State University for additional funding that supported this research.

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