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PAPER

# Reaction network governing diphosphine-protected gold nanocluster formation from nascent cationic platforms†

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We identify the reaction network governing gold monolayer protected cluster (MPC) formation during the reduction of Au(PPh<sub>3</sub>)Cl and L<sup>5</sup> (L<sup>5</sup> = 1,5-bis(diphenylphosphino)pentane) in solutions. UV-vis spectroscopy and electrospray ionization mass spectrometry (ESI-MS) monitored the formation of ligated Au<sub>x</sub>; 6 ≤ x ≤ 12 clusters, which comprise the reaction intermediates and final products. Initially, predominantly [Au<sub>2</sub>L<sub>2</sub>]<sup>2+</sup> complexes form through dissolution of Au(PPh<sub>3</sub>)Cl. These complexes control the reduction and nucleation reactions that form nascent phosphine-ligated Au<sub>8</sub> and Au<sub>10</sub> ionic clusters. [Au<sub>10</sub>L<sub>4</sub>]<sup>2+</sup> is an observed growth platform for ligated Au<sub>11</sub> and Au<sub>12</sub> clusters. The data for syntheses of Au:L<sup>5</sup> systems evidence that the nascent reaction products (*t* < 3 days) are less dependent on the chosen reducing agent (borane *tert*-butylamine complex or NaBH<sub>4</sub>); instead, after reduction ceases, subsequent solution phase processing provides greater control for tuning cluster nuclearity.

## Introduction

Significant work has been devoted to the development of phosphine protected gold nanoclusters of different nuclearity.<sup>1–9</sup> The structures of these gold-PPh<sub>3</sub> and other gold-phosphine ligand complexes, derived from X-ray crystallographic, (<sup>31</sup>P <sup>1</sup>H) NMR and Mössbauer data, helped validate polyhedral skeletal electron pair (PSEP) theory.<sup>10–12</sup> However, the gold reduction reaction typically yields a broad product distribution,<sup>13–15</sup> such that subsequent purification is necessary to isolate desired products.<sup>6,16,17</sup> The reduction of AuClPPh<sub>3</sub> is reported to be strongly controlled by kinetic parameters, similar to metal salt reduction.<sup>14,18</sup> Reduction of salts and AuClPPh<sub>3</sub> can result in single product syntheses through application of post-reduction solution phase processing, *e.g.*, oxidation or subsequent reactant addition. These post-reduction solution phase processes have been successful at producing different gold nuclearity clusters, unique geometries, and distinct properties of usually the most stable clusters.<sup>11,19–23</sup> Although these techniques have been successful, the controlling factors that narrow product distributions have not been elucidated. It is likely necessary to

identify the mechanism governing product formation in order to develop aimed approaches that lead to specific products. Detailed knowledge of the mechanism would promote significant advancement in rational synthesis design.

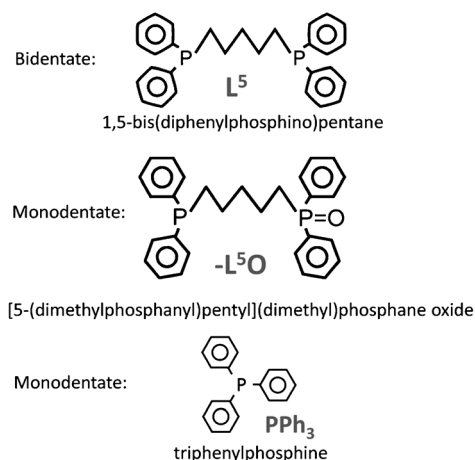
We have recently shown that phosphine ligands have the ability to both protect and proactively etch gold nanoclusters.<sup>14</sup> The ability of phosphines to etch metal cores allows “size-selective processing” to occur around stable nanoclusters. Size-selective processing requires that competing reactions of growth and etching around stable clusters result in a progressively narrower product distribution. It is a post-reduction, solution phase processing phenomenon. However, the prerequisite for applying size-selective processing is knowledge of the relative reaction rates around specific clusters, resulting in desired product formation. Therefore, an outline of the reaction network that controls product formation for ligated metal nanoclusters of distinct stoichiometry would provide a roadmap for construction of aimed syntheses.

The gold-phosphine system (L' = 1,*n*-bis(diphenylphosphino)alkane; Fig. 1), because it has shown the propensity to yield narrow product distributions.<sup>13,24</sup> Thus, it is an ideal system for (partially) elucidating the reaction network controlling product formation. Recently, research on the gold-diphosphine systems has intensified. A computational study by Hong *et al.*<sup>25</sup> has examined overall nanocluster stability and selectivity with diphosphines containing spacers of different lengths. They reported that diphosphines, such as L<sup>3</sup>, can selectively stabilize clusters of specific gold nuclearity; however, they also concluded that the conditions that make selectivity possible are more complex than stabilization alone. Experimental results support their conclusion. For example,

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**Fig. 1** Illustrations of the ligands, which are observed to form complexes with gold during this study.

ESI-MS data observed, as a 1 : 1  $L^6$  :  $Au(PPh_3)Cl$  solution is reduced by  $NaBH_4$  initially ( $t < 10$  min), exhibits ligated  $Au_8$  and  $Au_{10}$  clusters. Although reduction soon ceases, the solution continues to evolve. By  $t = 6$  days the  $Au_{10}$  signal is nil, and the solution exhibits only  $[Au_8L^6_4]^{2+}$ , but by  $t = 6$  days the solution exhibits mainly signal from  $[Au_9L^6_4Cl]^{2+}$  and trace abundances of  $Au_8$  and  $Au_{10}$  cations. As a second example, Shichibu and Konishi have reported that reduction of  $Au_2L^2_2Cl_2$  in air initially forms a disperse distribution of cationic ligated clusters ranging from  $Au_9$  to  $Au_{15}$ ; but, after addition of HCl, the solution yields monodisperse  $[Au_{13}L^2_5Cl_2]^{3+}$ .<sup>15</sup> Interestingly, diphosphine ligands with different alkane chain links did not result in  $Au_{13}$  clusters. Previously, van der Velden *et al.*<sup>26</sup> reported the synthesis of  $L^1$ -protected  $Au_{13}$  clusters *via* reduction of  $[Au_2L^1_2](NO_2)_2$ . Furthermore, etching of gold nanoclusters has also been promoted by halides and pseudohalides.<sup>27</sup> These different approaches result in narrow product distributions, but whether formation is through growth or degradation (etching) pathways is not established. Therefore, the major controlling factors for single product formation will continue to remain unidentified without an examination of the specific reactions governing formation.

For this study we have used electrospray mass spectrometry (ESI-MS) and UV-vis data to formulate a chemically-detailed reaction network governing the syntheses of  $Au : L^5$  clusters. The reaction network forms a basis for developing “size-selective” syntheses of  $Au_x : L^5$  nanoclusters. We find that the reaction pathways for  $Au : L^5$  clusters are built through stable  $Au_{10}$  platforms with further cluster processing controlled by solution equilibria. We report syntheses of new phosphine-protected gold-centered  $Au_{12}$  clusters. An important new insight into size-selective nanocluster syntheses is that nascent reaction products formed by the condensation of gold-phosphine complexes are relatively insensitive to the chosen reducing agent (*e.g.*, BTBC or  $NaBH_4$ ); instead, after reduction processes cease, subsequent solution phase processing provides greater control for tuning cluster nuclearity.

The reaction network comprises the chemical reactions and associated rate coefficients that lead to products. Measurements of

initial reactants, chemical intermediates, and products reveal those reactions with finite rate coefficients as well as those with effectively null reaction rates. For this task we have adjusted synthesis conditions in the  $Au : L^5$  system to maximize the number of active formation pathways observable with ESI-MS and UV-vis methods. These results identify possible monodisperse products that may be achieved through optimization of synthesis conditions. System optimization to create monodisperse products is the successive step performed after a reaction network is defined; hence, it is not the scope of the current study.

The reaction environment of the synthesis solutions was varied by conducting reactions in two solvent systems, under air and inert atmospheres, and by using two boron reducing agents that have different reduction rates. The observations provide evidence for several important reaction processes that control initial  $Au^I$  : phosphine complexes, grow metal cores, and modify core nuclearity. We use PSEP theoretical analyses<sup>10–12</sup> and apply the isolobal analogy<sup>28–32</sup> to help account for the reaction intermediates and products. Comparisons among the results of this and previous studies provide evidence that the gold-diphosphine systems are governed by disparate reaction pathways from different growth platforms (defined as the stable lower nuclearity cluster that resists etching and allows promotion of growth).<sup>24</sup> For the current  $Au : L^5$  system, the growth platforms are cationic clusters that form immediately after the addition of the reducing agent. In the absence of  $L^5$ , reduction of the  $[Au^I(PPh_3)_2]^+$  precursor complex results in the almost total extinguishment of all ionic signals, indicating the initial  $Au$  : ligand complex distribution affects which reduction and nucleation pathways predominate. These results identify a need for more research to better understand the role of different ligands during cluster formation.

## Experimental methods

The current study uses UV-vis and ESI-MS to monitor the distribution of  $[Au_xL^5_y(PPh_3)_w]^{z+}$  clusters. To the eye, nearly all phosphine ligated  $Au_x$ :  $2 \leq x \leq 13$  clusters display color, and their spectra exhibit distinct, broad absorption bands between 250 nm and 650 nm.<sup>3,11,24,33–36</sup> Conductivity and ESI-MS studies have established that stable, phosphine-ligated  $Au_x$ :  $2 \leq x \leq 13$  clusters carry positive charge; a finding that is also predicted by PSEP theory.<sup>5,22,26,33–35,37–42</sup>

Synthesis, storage, and analysis operations were conducted at ambient temperature ( $T = 21$  °C to 24 °C). All chemicals and solvents were purchased from Sigma-Aldrich and used as delivered.<sup>43</sup> The MPC synthesis solutions used during these experiments are similar to those reported previously.<sup>14,24</sup> Briefly,  $Au(PPh_3)Cl$  (99.9 + %),  $L^5$ , and a reducing reagent, borane *tert*-butylamine complex (BTBC, 97%) or  $NaBH_4$  ( $\geq 99\%$ ), were weighed out in a 1 : 1 : 5 molar ratio, and dissolved in either 1 : 1 methanol : chloroform or neat (100%) chloroform to give  $[Au(PPh_3)Cl] = 5.0 \times 10^{-3}$  mol  $L^{-1}$ . Cluster stability can change as function of solvent system.<sup>44</sup> These reaction conditions produced the greatest number of observed ionic species. We determined the optimum reducing agent to  $Au(PPh_3)Cl$  ratio by observing the threshold, where additional  $NaBH_4$  induced the appearance of  $(NaB(OCH_3)_4)_n^{z+}$

polymers, observed for  $>1200\ m/z$ , and  $[\text{Na}^+ \text{CH}_3\text{O}]_x$  clusters, observed for  $<800\ m/z$ .<sup>45</sup>

Deaerated synthesis solutions were prepared in a 20 mL borosilicate glass, crimp-sealed vial into which solvent,  $\text{Au}(\text{PPh}_3)\text{Cl}$ , and  $\text{L}^5$  were added. While the solution was being mixed with a magnetic stirbar, argon was bubbled through it to minimize the presence of dissolved gases. (Vial components and stirbars were never reused.) After the mixture of ligand complexes equilibrated ( $\approx 15\ \text{min}$ ),<sup>46</sup> dry reducing agent (BTBC or  $\text{NaBH}_4$ ) was quickly added (defining  $t = 0\ \text{min}$ ), the solution was again purged with argon, and the vial was crimp sealed. During these last operations the solution was temporarily stagnant. To minimize the introduction of oxygen, a syringe was used to remove samples through the septum.

To observe the effects of oxygen, a set of aerated syntheses were also conducted. The aerated syntheses were prepared in open containers and covered to prevent evaporation losses, but stirred in the presence of air; therefore, we will refer to solutions prepared with this procedure as aerated syntheses.

As the reactions progressed, small samples were collected and diluted in methanol for analysis either by UV-vis or ESI-MS (in  $10\times$  to  $10\,000\times$  dilution). Samples were analyzed within  $\approx 5\ \text{min}$  of their dilution. UV-vis spectra of aerated solutions were collected on a Varian Cary II dual beam spectrometer.

ESI-MS data were obtained in negative and positive ion modes. The mass spectrometer comprised an electrospray ion source (Analytica of Branford), coupled to a custom-built (by Ardra Technologies) Extrel CMS quadrupole mass spectrometer (mass range  $\approx 10\ m/z$  to  $\approx 3000\ m/z$ ). Samples were introduced to the ESI source *via* direct infusion ( $10\ \mu\text{L}\ \text{min}^{-1}$ ) through a glass capillary. The source was purged with  $\geq 1.0\ \text{mL}$  of methanol between samples. The source electrical potentials, temperature, curtain gas flow, and effusion rate were optimized to maximize ion intensities while minimizing fragmentation. Stable ion currents and the spectra presented here were obtained with the potential difference between the capillary exit and the skimmer set to 80 V; however, to assure data quality and consistency, additional spectra were systematically collected for voltages between 60 V and 140 V.

Dynamic light scattering (DLS) measurements were conducted using a Malvern Zetasizer Nano ZS equipped with a 4 mW 633 nm laser. Since domain-induced scattering within 1:1 methanol:chloroform solution corrupts measurements, DLS measurements were conducted on synthesis solutions prepared in 1:1 methanol:diethyl ether (Sigma Aldrich, CHROMASOLV, 99.9%, inhibitor free).<sup>47</sup> Prior to the addition of the precursor reagents, the methanol was passed through a  $0.2\ \mu\text{m}$  filter to remove dust. The competing product from the methanol: $\text{NaBH}_4$  reaction produced precipitate that was removed by centrifugation at  $\approx 1 \times 10^5\ \text{m}\ \text{s}^{-2}$  ( $10\ \text{kg}_n$ ) for 30 min. In addition, DLS measurements were conducted on solutions containing dissolved ligands,  $\text{Au}(\text{PPh}_3)\text{Cl}$  alone,  $\text{NaBH}_4$  alone, and dissolved  $\text{NaBH}_4$  and ligands together; these measurements exhibited null results, increasing the acceptance that the DLS distributions derived for reaction solutions correlate to  $[\text{Au}_x\text{L}^5]^{2+}$  containing colloid formation only.

## Results

### A. $\text{Au}_x$ cluster growth with BTBC

Fig. 2a shows the distribution of solution complexes that form with equimolar concentrations of  $\text{Au}(\text{PPh}_3)\text{Cl}$  and  $\text{L}^5$  in deaerated 1:1 methanol:chloroform. The ESI-MS ion signal is dominated by  $[\text{Au}_2\text{L}^5]^{2+}$ . The spectrum shows much weaker signals from  $[\text{Au}(\text{PPh}_3)_2]^+$ ,  $[\text{Au}(\text{PPh}_3)\text{L}^5]^+$ ,  $[\text{AuL}^5]^{2+}$ , and trace signal from  $[\text{Au}_2\text{L}^5_2\text{Cl}]^+$ .

The reduction reaction is initiated by the addition of 5 X molar excess BTBC to the equimolar  $\text{Au}(\text{PPh}_3)\text{Cl}:\text{L}^5$  1:1 methanol:chloroform solutions (Fig. 2). At  $t = 5\ \text{min}$ , the ESI-MS spectrum exhibits trace signals from  $[\text{Au}_8(\text{PPh}_3)\text{L}^5_3]^{2+}$  and  $[\text{Au}_8\text{L}^5_4]^{2+}$  (inset of Fig. 2a). In negative ion mode ESI-MS data exhibited only  $\text{Cl}^-$  in unreduced and reduced solutions.

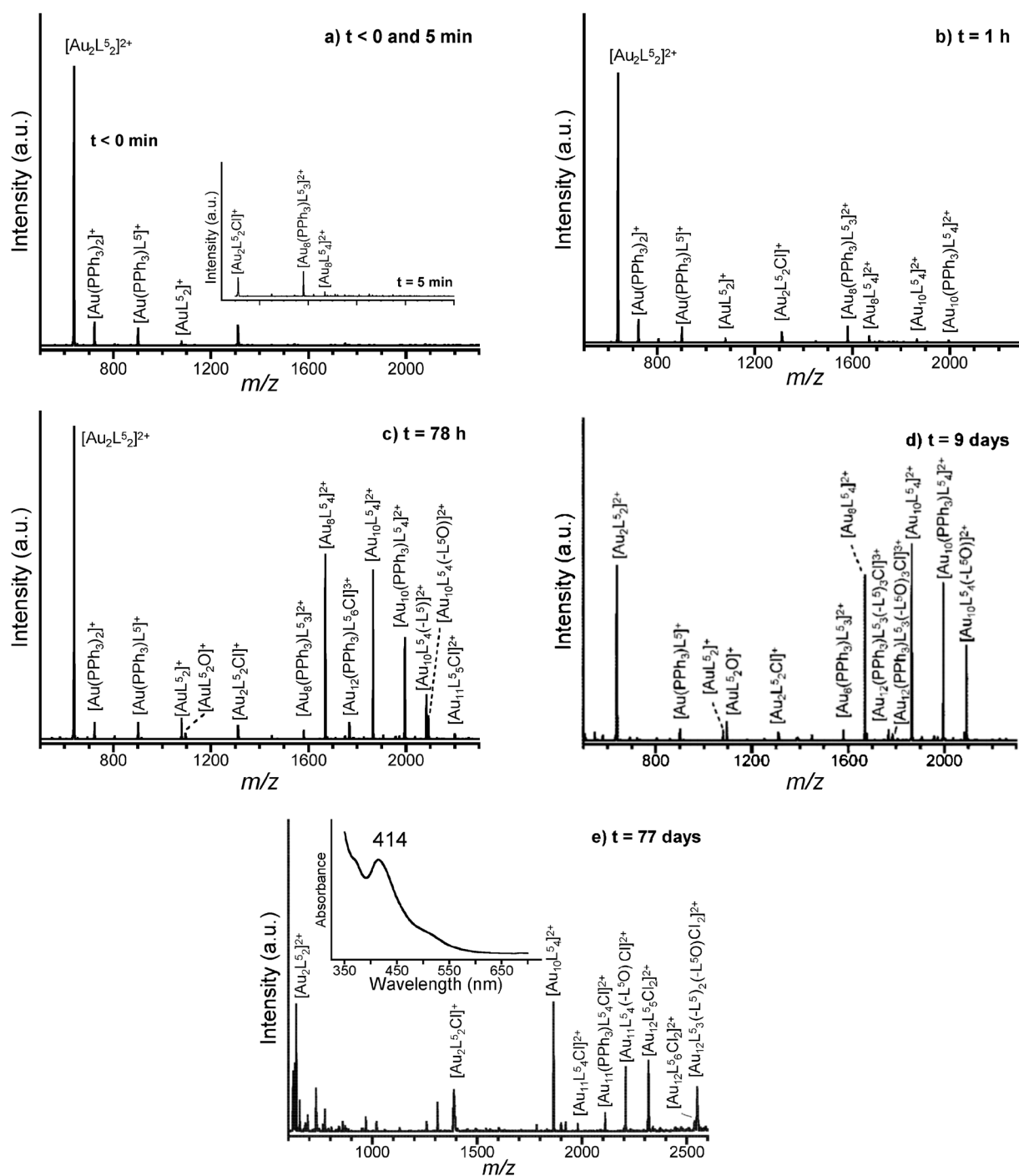
After BTBC is added, the solution gradually changes color from clear to light brown to orange to dark red, and it finally develops a dark colloid by  $t = 1.5\ \text{h}$ . For comparison, in solutions containing only  $\text{Au}(\text{PPh}_3)\text{Cl}$  that are reduced by 5 X molar excess BTBC the black colloidal suspension develops by  $t = 30\ \text{min}$ . This result indicates that the presence of  $\text{L}^5$  changes the rate of reduction.

With increasing time the ESI-MS data exhibit an emergence of new ionic products. At  $t = 1\ \text{h}$ , (Fig. 2b) the data exhibit new products:  $[\text{Au}_{10}(\text{PPh}_3)\text{L}^5_4]^{2+}$  and  $[\text{Au}_{10}\text{L}^5_4]^{2+}$ . The relative signal intensities of the ionic clusters appear to be similar to or greater than the initial complexes with the  $[\text{Au}_8\text{L}^5_4]^{2+}$  and  $[\text{Au}_{10}\text{L}^5_4]^{2+}$  products exhibiting the strongest signal intensities.

By  $t = 78\ \text{h}$  (Fig. 2c), the ESI-MS data show signal from  $[\text{Au}_{11}\text{L}^5_5\text{Cl}]^{2+}$ ,  $[\text{Au}_{10}\text{L}^5_4(-\text{L}^5)]^{2+}$ , and  $[\text{Au}_{12}(\text{PPh}_3)\text{L}^5_3(-\text{L}^5)_3\text{Cl}]^{3+}$ , where  $-\text{L}^5$  denotes monodentate complexation. In some cases presence of a monodentate  $-\text{L}^5$  ligand can be confirmed by covalent labeling of the free phosphine terminus with oxygen. A trace of free oxygen is admitted into the sample vial, which oxidizes the free phosphine terminus, forming the monodentate  $-\text{L}^5\text{O}$  ligand, where  $-\text{L}^5\text{O} = 1$ -diphenyl-5-diphenylphosphine oxide pentane, *cf.* Fig. 1. At 78 h ESI-MS signals observed from  $[\text{Au}_{10}\text{L}^5_4(-\text{L}^5\text{O})]^{2+}$  and  $[\text{AuL}^5(-\text{L}^5\text{O})]^+$  (Fig. 2c) identify the monodentate  $-\text{L}^5$  structures in the parent species.

At  $t = 9\ \text{days}$  (Fig. 2d), ESI-MS signals representing larger nuclearity clusters emerge. Signal from  $[\text{Au}_{12}(\text{PPh}_3)\text{L}^5_3(-\text{L}^5\text{O})_3\text{Cl}]^{3+}$ , confirms the structure of the  $[\text{Au}_{12}(\text{PPh}_3)\text{L}^5_3(-\text{L}^5)_3\text{Cl}]^{3+}$  cation. Interestingly, the signal from  $[\text{Au}_{11}\text{L}^5_5\text{Cl}]^{2+}$  is fully depleted, and the signal intensity of  $[\text{Au}_8\text{L}^5_4]^{2+}$  is diminished relative to the ligated  $\text{Au}_{10}$  clusters. The solution complex,  $\text{Au}(\text{PPh}_3)_2^+$ , is also depleted, and the relative intensity of  $[\text{Au}_2\text{L}^5_2]^{2+}$  is decreased.

At  $t = 77\ \text{days}$  ESI-MS data show increased ion intensities from larger nuclearity clusters (Fig. 2e). The ESI-MS data evince signal from  $[\text{Au}_{11}\text{L}^5_4\text{Cl}]^{2+}$ ,  $[\text{Au}_{11}(\text{PPh}_3)\text{L}^5_4\text{Cl}]^{2+}$ ,  $[\text{Au}_{11}\text{L}^5_5\text{Cl}]^{2+}$ ,  $[\text{Au}_{12}\text{L}^5_5\text{Cl}_2]^{2+}$ , and  $[\text{Au}_{12}\text{L}^5_6\text{Cl}_2]^{2+}$ . We determined that  $[\text{Au}_{12}\text{L}^5_6\text{Cl}_2]^{2+}$  has the structure,  $[\text{Au}_{12}\text{L}^5_3(-\text{L}^5)_3\text{Cl}_2]^{2+}$ , by observing trace ESI-MS signal from the covalently labeled  $[\text{Au}_{12}\text{L}^5_3(-\text{L}^5\text{O})_3\text{Cl}_2]^{2+}$  (not annotated in Fig. 2e), which confirms the  $-\text{L}^5$  count. ESI-MS signal from  $[\text{Au}_{11}\text{L}^5_5\text{Cl}]^{2+}$  has reappeared, mostly in its oxidized form,  $[\text{Au}_{11}\text{L}^5_4(-\text{L}^5\text{O})\text{Cl}]^{2+}$ , which also reveals one  $-\text{L}^5$ . The  $[\text{Au}_8\text{L}^5_4]^{2+}$  signal is depleted, as are signals from  $[\text{Au}_{12}(\text{PPh}_3)\text{L}^5_3(-\text{L}^5)_3\text{Cl}]^{3+}$  and  $[\text{AuL}^5]^+$ . The depletion of signal from  $\text{Au}_8$  clusters is



**Fig. 2** ESI-MS spectra of deaerated, 1 : 1 methanol : chloroform solutions, prepared with 1 : 1 molar ratio of  $\text{L}^5$  and  $\text{Au}(\text{PPh}_3)\text{Cl}$ , observed at (a)  $t < 0 \text{ min}$ , solution complexes prior to initiation of reduction (inset shows  $t = 5 \text{ min}$  after BTBC addition); (b)  $t = 1 \text{ h}$ ; (c)  $t = 78 \text{ h}$ ; (d)  $t = 9 \text{ days}$  and (e)  $t = 77 \text{ days}$  after the addition of 5 X molar ratio BTBC (Inset: UV-vis spectrum of the synthesis solution at  $t = 77 \text{ days}$ . Absorptions at  $\lambda_{\text{max}} = 414 \text{ nm}$  and the shoulder near  $367 \text{ nm}$  are features characteristic of  $\{\text{Au}_{11}, \text{Au}_{12}\}$  and  $\text{Au}_4$ , respectively. The weak absorption between  $\lambda = 480 \text{ nm}$  to  $540 \text{ nm}$  ( $\lambda_{\text{max}} \approx 510 \text{ nm}$  or  $520 \text{ nm}$ ) originates from agglomerations of primary clusters. See text.).

indicative of their reactive nature in the synthesis solution. The corresponding UV-vis spectrum (inset of 2e) displays a blue shifted absorption band centered at  $414 \text{ nm}$ , indicating a shift of the product distribution to larger gold nuclearity.<sup>48</sup>

The UV-vis spectrum also exhibits a weak absorption band centered between  $510 \text{ nm}$  and  $520 \text{ nm}$  that is consistent with the signature of agglomerated primary clusters.<sup>14,49</sup> In accord

with this assignment, addition of excess  $\text{L}^5$  (relative to initial  $\text{Au}(\text{PPh}_3)\text{Cl}$ ) extinguishes this absorption band, indicating that the agglomerated primary clusters are resorbed into solution, as they are transformed into more stable species.<sup>14</sup> Since the resulting UV-vis spectrum is little changed, the data suggest that the size distribution of the resorbed primary clusters is similar to that of the nascent solution species.



These species may include neutral clusters due to the distribution of complexes being reduced.

The evolution of the transient and final product distributions observed with ESI-MS is similar for the methanol:chloroform and pure chloroform solvent systems; however, product formation in the pure chloroform is faster. Fig. S1 shows the product formation from  $t = 5$  min to  $t = 9$  days.<sup>†</sup> Similar to the methanol:chloroform syntheses at  $t \approx 5$  min, ESI-MS data exhibit  $[\text{Au}_8(\text{PPh}_3)\text{L}_3]^{2+}$  and  $[\text{Au}_8\text{L}_4]^{2+}$  signals (Fig. S1a<sup>†</sup>). Signals from  $[\text{Au}_{10}(\text{PPh}_3)\text{L}_4]^{2+}$ ,  $[\text{Au}_{10}\text{L}_4]^{2+}$ ,  $[\text{Au}_{10}\text{L}_4(-\text{L}^5)]^{2+}$ ,  $[\text{Au}_{11}\text{L}_5\text{Cl}]^{2+}$  and  $[\text{Au}_{12}(\text{PPh}_3)\text{L}_3(-\text{L}^5)_3\text{Cl}]^{3+}$  are observed at  $t = 1$  h (Fig. S1b<sup>†</sup>). The relative ion current intensities of products to initial complexes are much greater in pure chloroform, as compared to the methanol:chloroform syntheses at similar time points. During product formation up to  $t = 9$  days, the relative signal intensities of  $[\text{Au}_8\text{L}_4]^{2+}$  and  $[\text{Au}_2\text{L}_2]^{2+}$  diminish as corresponding growth is observed among the ligated  $\text{Au}_{10}$ ,  $\text{Au}_{11}$  and  $\text{Au}_{12}$  clusters. Clusters containing  $(-\text{L}^5\text{O})$  also accompany these species (Fig. S1d<sup>†</sup>). In both pure chloroform and methanol:chloroform syntheses, signals from  $\text{Au}_6$ ,  $\text{Au}_7$  or  $\text{Au}_9$  species are not observed in the ESI-MS and UV-vis data. Overall, similar product formation and distributions are observed in both solvent systems.

When compared with deaerated methanol:chloroform syntheses initiated with BTBC, ESI-MS data observed at early time points in aerated solutions generally show a similar sequential emergence of increasing cationic cluster nuclearity. At  $t \approx 5$  min  $[\text{Au}_8(\text{PPh}_3)\text{L}_3]^{2+}$  is clearly observed (Fig. S2a<sup>†</sup>), followed by the emergence of  $[\text{Au}_8\text{L}_4]^{2+}$  and  $[\text{Au}_6\text{L}_3]^{2+}$  species at  $t = 30$  min (Fig. S2b<sup>†</sup>). The  $[\text{Au}_6\text{L}_3]^{2+}$  peak persists in aerated solutions for the duration of the experiment. By  $t = 8$  h (Fig. S2c<sup>†</sup>), ESI-MS signal from  $[\text{Au}_9\text{L}_4]^{3+}$  appears and grows in intensity over the subsequent seven days (Fig. S2d and e<sup>†</sup>). As the reaction progresses,  $[\text{Au}(\text{PPh}_3)_2]^+$  and  $[\text{Au}(\text{PPh}_3)\text{L}]^+$  are depleted, but  $[\text{AuL}_2]^+$  is only slightly diminished; this result indicates that the reduction rate of  $[\text{AuL}_2]^+$  is slower than for  $\text{PPh}_3$  containing complexes. ESI-MS data for these aerated solutions do not exhibit signal from higher nuclearity clusters nor from any cluster containing a  $\text{Cl}^-$  ligand.

The aerated and deaerated ESI-MS data show the full depletion of ligated  $\text{Au}_8$  clusters with increasing time, providing corroborating evidence for their reactive nature. However, the fate of the ligated  $\text{Au}_8$  clusters is difficult to determine through comparisons of the fractional ion intensities. Ligated  $\text{Au}_{10}$  cluster signals do not increase with the depletion of the ligated  $\text{Au}_8$  clusters (Fig. S2<sup>†</sup>), as was observed for the deaerated systems (Fig. 2), which limits the ability to follow transient products in aerated systems beyond  $t = 24$  h. Overall, the aerated systems produce distinct clusters, *e.g.*,  $[\text{Au}_9\text{L}_4]^{3+}$  and  $[\text{Au}_6\text{L}_3]^{2+}$ , that appear before  $t = 8$  h, and these species remain present for the entire time period monitored. After synthesis initiation with BTBC,  $[\text{Au}_8(\text{PPh}_3)\text{L}_3]^{2+}$  and  $[\text{Au}_8\text{L}_4]^{2+}$  are the earliest ionic clusters observed in both deaerated and aerated systems, indicating a limiting role for the oxidative environment during nucleation and core growth.

The synchronous UV-vis spectra provide temporal sampling of the cationic and neutral cluster distributions for almost all  $\text{Au}_x$ :  $x \leq 13$  clusters, allowing comparison of the total

distribution to the cationic species present in the ESI-MS data at early time points. Fig. S3 shows the accumulated, temporally resolved UV-vis spectra of a stirred, aerated synthesis solution that is reduced with BTBC in 1:1 methanol:chloroform.<sup>†</sup> The spectra show that the 420 nm band is present almost immediately ( $t \leq 5$  min), and by  $t \approx 1$  h, the synthesis solutions exhibit a broad molecular absorbance band centered at  $\lambda_{\text{max}} \approx 420$  nm. After  $t = 24$  h, the UV-vis spectra of the reaction solution remain relatively unchanged for the remaining duration of the experiment. The decreasing rate in reduction promotes an environment containing similar reaction rates for growth and degradation through oxidation.

Timed, UV-vis spectra of aerated solutions that are reduced by BTBC (Fig. S3<sup>†</sup>) exhibit neither the dark appearance of agglomerates nor the weak UV-vis absorption band that evidences agglomerates. ESI-MS data for the aerated solutions are absent of  $\text{Cl}^-$  containing clusters. The absence of both agglomeration peaks in UV-vis and  $\text{Cl}^-$ -containing clusters in the ESI-MS suggests that oxidative degradation can serve as a deagglomeration agent.

In summary, deaerated methanol:chloroform reaction solutions reduced with BTBC initially produce ligated  $\text{Au}_8$  and  $\text{Au}_{10}$  clusters. The ESI-MS signal from ligated  $\text{Au}_8$  clusters is depleted by  $t = 77$  days, and the fractional ion intensity of the ligated  $\text{Au}_{10}$  clusters is proportionately increased. During this same time period ligated  $\text{Au}_{11}$  and  $\text{Au}_{12}$  clusters emerge (Fig. 2e). Similar formation and degradation products are observed in both solvent systems with the rate of processing occurring faster in pure chloroform. By  $t = 77$  days both the ESI-MS and UV-vis data report a shift of the cluster distribution to higher gold nuclearity. The UV-vis spectra show that clusters form almost immediately and that the growth of cluster absorption bands is significant within a few hours after BTBC addition.

The ESI-MS total ion signal in deaerated systems shows a proportionate transfer of total ion signal from low nuclearity complexes, *e.g.*,  $[\text{Au}_2\text{L}_2]^{2+}$ , to higher nuclearity clusters, *e.g.*, ligated  $\text{Au}_8$  and  $\text{Au}_{10}$ . Evolution of the ESI-MS data indicate that  $[\text{Au}_8(\text{PPh}_3)\text{L}_3]^{2+}$  forms before or simultaneously with  $[\text{Au}_8\text{L}_4]^{2+}$ , that  $[\text{Au}_8\text{L}_4]^{2+}$  forms before the  $\text{Au}_{10}$  cations (*e.g.*,  $[\text{Au}_{10}\text{L}_4]^{2+}$ ,  $[\text{Au}_{10}(\text{PPh}_3)\text{L}_4]^{2+}$ , and  $[\text{Au}_{10}\text{L}_4(-\text{L}^5)]^{2+}$ ), and that the ligated, cationic  $\text{Au}_8$  species are consumed to depletion in deaerated MPC syntheses. Finally, in aerated solutions, the formation of ligated  $[\text{Au}_6\text{L}_3]^{2+}$  and  $[\text{Au}_9\text{L}_4]^{3+}$  is observed promptly at  $t \approx 0.5$  h and  $t = 8$  h, respectively.

## B. $\text{Au}_x$ cluster growth with $\text{NaBH}_4$

We conducted deaerated experiments with  $\text{NaBH}_4$  to observe the effects of a faster reducing agent upon  $\text{Au}:\text{L}^5$  syntheses in methanol:chloroform solutions. Prior to reaction initiation, a similar complex distribution observed in the BTBC syntheses is measured (Fig. 2a). Again, reduction was initiated by adding 5 X molar excess  $\text{NaBH}_4$ . Immediately, the solution turned dark brown in color, forming colloids of agglomerated primary clusters.<sup>14</sup> During the next 30 min, the solution developed a distinct reddish tint and decreased turbidity. The corresponding absorption band is observed in the UV-vis spectrum at  $\lambda_{\text{max}} = 420$  nm. The absorption band at 420 nm is

characteristic of ligated  $\text{Au}_8$  and  $\text{Au}_{10}$  clusters,<sup>24</sup> and its intensity correlates with signal intensities observed by ESI-MS among the ionic products.

Fig. 3a shows the ESI-MS spectrum twenty minutes after  $\text{NaBH}_4$  addition. ESI-MS signal from the initial complexes:  $[\text{Au}_2\text{L}_2]^{2+}$ ,  $[\text{Au}(\text{PPh}_3)\text{L}^5]^+$ ,  $[\text{Au}(\text{PPh}_3)_2]^+$ , and  $[\text{AuL}^5_2]^+$  are depleted or greatly diminished. These signals are replaced by abundant ESI-MS signal from  $[\text{Au}_8\text{L}^5_4]^{2+}$ ,  $[\text{Au}_{10}\text{L}^5_4]^{2+}$ ,  $[\text{Au}_{10}(\text{PPh}_3)\text{L}^5_4]^{2+}$ , and  $[\text{Au}_{10}\text{L}^5_4(-\text{L}^5)]^{2+}$ . Notably, signal from  $[\text{Au}_8(\text{PPh}_3)\text{L}^5_3]^{2+}$  is absent. The rapid depletion of the  $[\text{Au}_2\text{L}_2]^{2+}$  species likely allows cluster formation to be dominated by condensation reactions among fully or partially reduced digold complexes.

At  $t = 67$  days, ESI-MS signals from  $[\text{Au}_8\text{L}^5_4]^{2+}$ ,  $[\text{Au}_{10}\text{L}^5_4]^{2+}$ , and  $[\text{Au}_{10}(\text{PPh}_3)\text{L}^5_4]^{2+}$  persist along with oxidized  $[\text{Au}_{12}(\text{PPh}_3)\text{L}^5_3(-\text{L}^5\text{O})_3\text{Cl}]^{3+}$  and  $[\text{Au}_{10}\text{L}^5_4(-\text{L}^5\text{O})]^{2+}$  (Fig. 3b). It is at this time that  $[\text{Au}_8(\text{PPh}_3)\text{L}^5_3]^{2+}$  is first observed. Reappearance of  $[\text{Au}_2\text{L}_2]^{2+}$  and  $[\text{Au}(\text{PPh}_3)_2]^+$  in the ESI-MS spectra is observed, which suggests that less stable

clusters have been etched back into solution,<sup>14</sup> and the resulting gold complexes become partitioned between  $[\text{Au}_2\text{L}_2]^{2+}$  and  $[\text{Au}(\text{PPh}_3)_2]^+$ , in accord with solution equilibrium. Signals from  $[\text{Au}_6\text{L}^5_3]^{2+}$  and  $[\text{Au}_9\text{L}^5_4]^{2+}$  are absent, which is consistent among all deaerated syntheses. In contrast to the BTBC initiated syntheses, solutions reduced by  $\text{NaBH}_4$ , do not exhibit ligated  $\text{Au}_{11}$  and  $\text{Au}_{12}$  clusters.

The UV-vis spectrum at  $t = 67$  days (Fig. 3b inset) exhibits an absorption maximum,  $\lambda_{\text{max}} \approx 417$  nm, that is red-shifted relative to the corresponding  $\lambda_{\text{max}}$  observed in synthesis solutions reduced with BTBC. The ESI-MS data show the absence of larger nuclearity clusters built from the ligated  $\text{Au}_{10}$  platform, thus, accounting for the red-shift. The weak absorption, centered at  $\lambda_{\text{max}} \approx 500$  nm, fits the UV-vis absorption signature observed for solutions containing agglomerated primary clusters.<sup>3</sup>

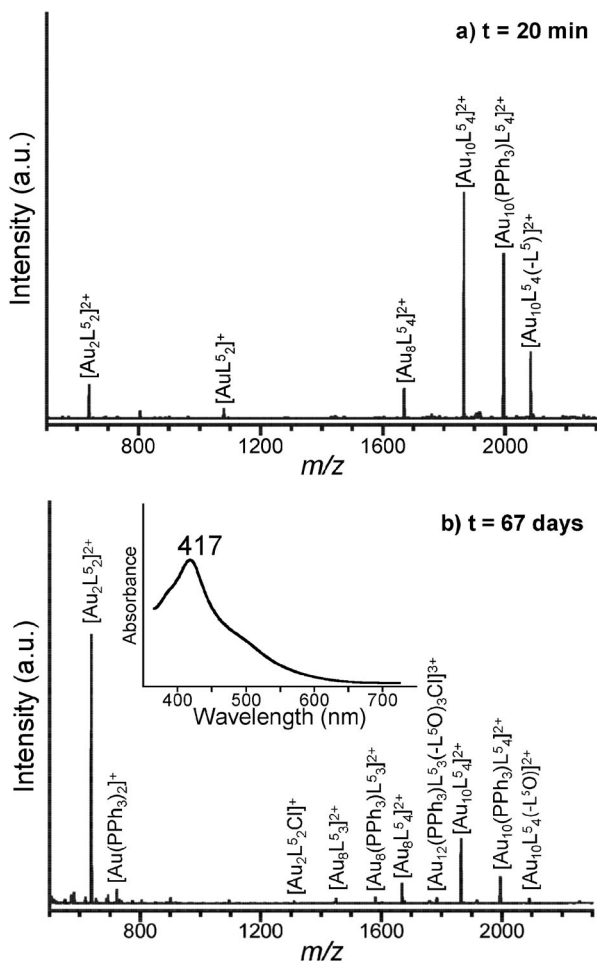
Dynamic light scattering experiments demonstrate that the  $\text{L}^5$  ligand exercises strong control on colloidal size distribution. As previously reported, the reduction of a 1 : 1 methanol : diethyl ether solution of  $\text{Au}(\text{PPh}_3)\text{Cl}$  by  $\text{NaBH}_4$  (in the absence of  $\text{L}^3$  or  $\text{L}^5$ ) produces colloids of agglomerated primary clusters within 5 min.<sup>14</sup> The DLS data find that the colloids have a wide distribution of mean diameters (Fig. S4†). However, subsequent addition of 3 X molar excess  $\text{L}^5$  to the  $\text{Au}(\text{PPh}_3)\text{Cl}$  product rapidly narrows the size distribution to  $D_h \approx 100$  nm in < 10 min, indicating the ability of  $\text{L}^5$  to exert strong control on the product distribution *via* solution processing. We note that the identification of chemical species present during nucleation with a gold-phosphine precursor is currently an active area of research.<sup>50</sup>

## Discussion

### A. Active reaction classes during syntheses

During these studies, the synchronously measured UV-vis and ESI-MS data support the development of the (partial) reaction network that governs  $\text{L}^5$ -protected cluster formation in methanol and methanol : chloroform mixtures. We accomplish this goal by identifying transient and final clusters present in the reaction network and then associate these species with reaction pathways. Identifying the reaction network with relative rate information (—most importantly identifying whether specific channels are active or not—) allows a roadmap to be developed for the possible products that can be selectively produced.

The data reveal important features about the reaction network. First, the rapid growth of the absorption band centered near 420 nm indicates that most of the ligated  $\text{Au}_8$  and  $\text{Au}_{10}$  cores form quickly. Second, the growth of ESI-MS signal, corresponding to ligated  $\text{Au}_8$  and  $\text{Au}_{10}$  cores, appears to track the growth of the 420 nm UV-VIS signal; consequently, we conclude that the majority of nascent, ligated  $\text{Au}_8$  and  $\text{Au}_{10}$  clusters form as cations. This result differs greatly from the reduction of monogold complexes, where efficient reduction of the gold complex distribution yields mostly neutral, ligated  $\text{Au}_x$  clusters.<sup>14,45</sup> Third, the end products of BTBC and  $\text{NaBH}_4$  syntheses differ. In syntheses reduced by  $\text{NaBH}_4$ , the relative signal intensities of the nascent ligated  $\text{Au}_8$  and  $\text{Au}_{10}$  clusters are preserved for long periods of time ( $t > 67$  days).

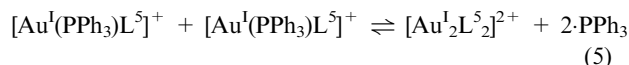
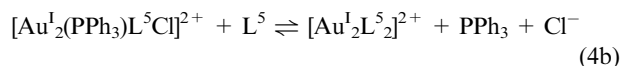
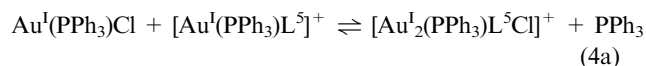
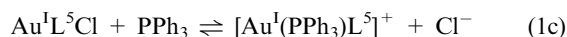
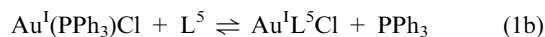
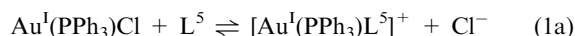


**Fig. 3** ESI-MS spectra of a stirred, deaerated solution, prepared with 1 : 1 molar ratio of  $\text{L}^5$  and  $\text{Au}(\text{PPh}_3)\text{Cl}$  in 1 : 1 methanol : chloroform, observed at a)  $t = 20$  min and b)  $t = 67$  days after the addition of 5 X molar ratio  $\text{NaBH}_4$  (Inset: Associated UV-vis absorption spectrum exhibiting  $\lambda_{\text{max}} = 417$  nm and a shoulder centered near 365 nm. The weak absorption, centered at  $\lambda_{\text{max}} = 500$  nm, originates from agglomerations of primary clusters. See text.)

In contrast, the cluster evolution during BTBC syntheses shows continued growth from ligated  $\text{Au}_8$  to  $\text{Au}_{10}$  species, followed by the appearance of larger ligated  $\text{Au}_{11}$  and  $\text{Au}_{12}$  clusters. Finally, syntheses conducted in aerated systems yield unique gold nuclearity clusters.

Discussion of the reaction classes and corresponding reaction pathways are presented. Since the present study is insensitive to clusters of  $m/z > 3000$  in the ESI-MS and to neutral clusters of  $\text{Au}_x$ :  $13 < x < 25$  in the UV-vis data, this survey of the reacting species is likely incomplete; however, the presently observed species serve as sign-posts along the synthetic path from initial reactants to larger product clusters.

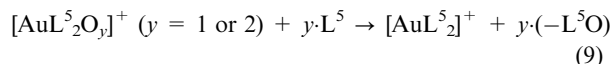
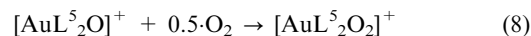
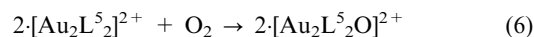
**(1) Ligand-exchange induced dissolution of  $\text{Au}^{\text{I}}(\text{PPh}_3)\text{Cl}$ .** Dissolution of  $\text{Au}^{\text{I}}(\text{PPh}_3)\text{Cl}$  to ionic species determines the distribution of Au:ligand complexes present prior to reduction. Bergeron *et al.* have previously proposed a set reactions that produce monogold, two-coordinate complexes;<sup>51</sup> however, the current data are dominated by reactions involving the digold complex,  $[\text{Au}_2\text{L}_2]^{2+}$ , so dissolution to form an equilibrated solution likely proceeds *via* the following reactions:



Reactions (1) through (5) account for the majority of complexes observed by ESI-MS in equilibrated solutions. This reaction scheme is incomplete, as the equilibria include chlorinated-complexes and likely other ternary and quaternary phosphine containing complexes. Other dimeric  $\text{Au}(\text{PPh}_3)\text{Cl}$  species have been predicted to be stable species by maximizing dipole interactions;<sup>52</sup> therefore, ligand exchange with these dimeric species is predicted to occur at higher concentrations of  $\text{L}^5$ . Above, we treat  $[\text{Au}_2\text{L}_2]^{2+}$  and  $[\text{Au}_2\text{L}_2\text{Cl}]^+$  as species stabilized by bridging  $\text{L}^5$  ligands, which is in accord with the structure of  $[\text{Au}_2\text{L}_2]^{2+}$  ( $\text{L}^1 = \text{bis}(\text{diphenylphosphino})\text{methane}$ ).<sup>38</sup> We only treat  $\text{Au}^{\text{I}}\text{L}^5\text{Cl}$  as a transient intermediate that is not present (and not reduced) in equilibrated solutions.

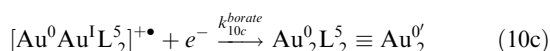
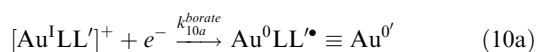
The complexes present in solution are susceptible to oxidation when stirred in ambient conditions. Bergeron *et al.*<sup>51</sup> previously demonstrated *via* ESI-MS that  $[\text{AuL}^5_2]^+$  was the salient feature observed at  $[\text{L}^5]/[\text{Au}(\text{PPh}_3)\text{Cl}] = 12$  in aerated, pure chloroform solvent systems. Experiments conducted under argon in deaerated solutions of neat  $\text{CHCl}_3$  without reducing agents show that the formation and persistence of

$[\text{Au}_2\text{L}^5_2]^{2+}$  species is consistent with the initial solution complex distributions in methanol:chloroform mixtures (Fig. 2a). When the vial is open to air, oxidation of the complexes is readily observable, indicating an oxidation degradation pathway for the  $[\text{Au}_2\text{L}^5_2]^{2+}$  complex to  $[\text{AuL}^5_2]^+$  that occurs quickly. These data are consistent with the reaction sequence:



Additional data are needed to confirm this reaction sequence; however, the reaction scheme predicts the formation of  $[\text{AuL}^5_2]^+$ , which putatively promotes the production of the observed ligated  $\text{Au}_9$  cores in stirred, aerated synthesis solutions under ambient conditions (Fig. S2†). In contrast, stirred, deaerated synthesis solutions do not form cationic  $[\text{Au}_9\text{L}_x\text{O}_y]^{z+}$  clusters at any time in synthesis solutions, and they do not promote the increasing formation of  $[\text{AuL}^5_2]^+$  (Fig. 2 and 3, S1 and S2†). See supporting information for more complete details on the stability of complexes and clusters in aerated solutions.

**(2) Reduction of  $[\text{Au}^{\text{I}}\text{LL}]^+$  and  $[\text{Au}^{\text{I}}_2\text{L}^5_2]^{2+}$  to form reduced gold species.** In the current study, we provide evidence for disparate reduction rates and reduction efficiencies of complexes containing  $\text{PPh}_3$  and fully exchanged  $\text{L}^5$ -containing complexes. Solution-phase reduction of complexes is symbolized as:



where  $\text{Au}^{\text{I}}$  is a gold complex cation (e.g.,  $[\text{Au}(\text{PPh}_3)_2]^+$ ,  $[\text{Au}(\text{PPh}_3)\text{L}^5]^+$  and  $[\text{AuL}^5_2]^+$ ),  $\text{Au}^{0'}_2$  is a reduced, ligated Au species (e.g.,  $\text{Au}^0_2\text{L}^5_2$ ),  $\text{Au}^{0'}\text{Au}^{\text{I}}$  is a free radical gold species with 0.5 reduction efficiency (e.g.,  $[\text{Au}^0\text{Au}^{\text{I}}\text{L}^5_2]^+\bullet$ ). The electron is donated by the borane reducing agent, BTBC or  $\text{NaBH}_4$ ;<sup>53–55</sup>  $\text{L}$ ,  $\text{L}' = (\text{PPh}_3, \text{L}^5)$ ; and  $k_{10}^{\text{borate}}$  is the global reduction rate of the specified gold species for the reducing reagent solution. Prior work on the reduction of  $\text{Au}^{\text{I}}$  species in solution has reported that the alcohol radical manifests insufficient potential to promote formation of  $\text{Au}^0$ ;<sup>56</sup> therefore, the reduction is dependent on the availability of the boron reducing agent (BTBC or  $\text{NaBH}_4$ ). For simplicity, we define  $\text{Au}^{0'}$  to denote a generalized  $\text{Au}^0\text{LL}'\bullet$  free radical and  $\text{Au}^{0'}\text{Au}^{\text{I}}$  to denote the  $[\text{Au}^0\text{Au}^{\text{I}}\text{L}^5_2]^+\bullet$  free radical cation, so that we may present subsequent reactions without explicitly accounting for the ligands on the gold reactants and products.

Important factors controlling product formation related to the reduction process with boron include: (i) the relative rate

of reduction for NaBH<sub>4</sub> and BTBC in solvent systems and (ii) the efficiency of the reduction process, *i.e.*, the percentage of Au<sup>I</sup> conversion in a complex to Au<sup>0</sup>. The reaction with NaBH<sub>4</sub> and methanol has a reported half-life  $t_{1/2} < 0.5$  h;<sup>53</sup> therefore, because Au<sup>I</sup> reduction occurs rapidly and the characteristic signal from the methanol-NaBH<sub>4</sub> is absent in ESI-MS spectra, the reduction rate of the gold complexes is equal to or greater than the NaBH<sub>4</sub> reaction with methanol. By comparison, the relative reduction rates of Au<sup>I</sup> solution complexes by BTBC are slower than by NaBH<sub>4</sub>, indicating a longer lifetime of the BTBC reducing environment. The change in the reducing rate observed for Au(PPh<sub>3</sub>)Cl *vs.* Au(PPh<sub>3</sub>)Cl:L<sup>5</sup> solutions, reduced by BTBC provides evidence for disparate rates of reduction for each solution complex.

For the current system, the complex distribution is dominated by [Au<sub>2</sub>L<sup>5</sup>]<sup>2+</sup> (Fig. 2a). As captured by reactions (10b) and (10c), the immediate transfer of ionic character from complexes to cluster products in solutions reduced by NaBH<sub>4</sub> suggests that reduction efficiency drives the nascent cluster distribution. Recombination reactions among fully (reaction (10c)) and partially reduced (reaction (10b)) complexes result in cationic cluster formation. These reactions account for the predominance of L<sup>5</sup>-ligated Au<sub>10</sub> clusters at early time for solutions reduced by NaBH<sub>4</sub> (Fig. 3).

The present and a prior study<sup>51</sup> show the persistence of [AuL<sup>5</sup>]<sup>+</sup> in the ESI-MS data, indicating that this complex is much less reactive. The diminished reactivity could arise if solution phase [AuL<sup>5</sup>]<sup>+</sup> is a complex and the reduction intermediates comprise ternary and quaternary gold-phosphine borohydride complexes (formed by attachment of a borohydride ligand). Fully chelated [AuL<sup>5</sup>]<sup>+</sup> would be expected to react more slowly than unchelated complexes, [Au(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> and [Au(PPh<sub>3</sub>)L<sup>5</sup>]<sup>+</sup>. Regardless of the mechanism, the greater reduction rates observed for [Au(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> and [Au(PPh<sub>3</sub>)L<sup>5</sup>]<sup>+</sup> suggest that nascent MPCs should contain both PPh<sub>3</sub> and L<sup>5</sup> ligands, especially in syntheses initiated by BTBC.

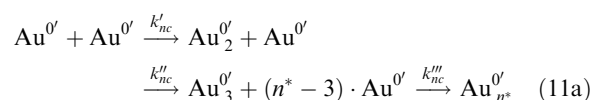
**(3) Nucleation and core growth of ligated Au<sub>x</sub> clusters.** Cluster formation occurs through two distinct stages. Stage 1 comprises reduction and nucleation, and stage 2 comprises the subsequent solution phase processing. The rate and duration of reduction will control the amount of overlap between the stages. For this work the initial formation (stage 1) of gold nanoclusters is illustrated with a classical nucleation model because no current experimental setup can track individual species during reduction and nucleation events.

Theoretical results indicate that the classical model can serve as a mathematical approximation of the actual chemical reaction network leading to ligated Au<sub>7</sub> clusters. Evans and Mingos<sup>57</sup> have shown that the binding for ligated gold clusters of the form, [Au–PPh<sub>3</sub>]<sub>n</sub>; 2 ≤ n ≤ 6, can be described by the hy(s – z) orbitals of the Au–PPh<sub>3</sub> fragments. X-ray crystallography and <sup>197</sup>Au Mössbauer and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy of [Au<sub>7</sub>(PPh<sub>3</sub>)<sub>7</sub>]<sup>+</sup> find that the [Au–PPh<sub>3</sub>]<sub>n</sub> structural form extends to n = 7.<sup>1</sup> Since the Au–PPh<sub>3</sub> fragment is isolobal to [Au<sup>0</sup>(PPh<sub>3</sub>)<sub>2</sub>]<sup>•</sup>,<sup>30,48,57</sup> we hypothesize that [Au<sup>0</sup>(PPh<sub>3</sub>)<sub>2</sub>]<sup>•</sup> self-reaction and reactions of [Au<sup>0</sup>(PPh<sub>3</sub>)<sub>2</sub>]<sup>•</sup> with other (Au–PPh<sub>3</sub>)<sub>n</sub> (n < 8) clusters will have low barriers to condensation.<sup>30</sup> Alternately, Guidez *et al.*<sup>50</sup> have also proposed a set of stable

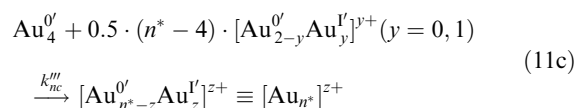
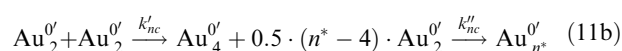
phosphine-protected gold clusters, Au<sub>x</sub>; x ≤ 4, built from the Au(PPh<sub>3</sub>)Cl precursor. Although these kinetically driven condensation reactions allow the formation of higher energy, metastable species, the more active fraction of the reaction network will comprise low energy pathways that can be predicted by consideration of the isolobal principle. Thus, the chemical reaction network that generates low nuclearity clusters can be approximated by fitting data with a classical nucleation model. The model itself provides insight into the growth process.

The distribution of complexes resulting from equimolar concentration of Au(PPh<sub>3</sub>)Cl and L<sup>5</sup> is dominated by bridging, digold clusters, *e.g.*, [Au<sub>2</sub>L<sup>5</sup>]<sup>2+</sup>. Two nucleation models are incorporated to account for the immediate formation of stable, neutral and cationic clusters above the critical nucleus, n\*, where dΔG<sup>o</sup>/dn = 0. ΔG<sup>o</sup> is the Gibb's reaction energy for the addition of an atom to the ligated Au<sub>n</sub> cluster.<sup>18</sup> Importantly, the nucleation models are dependent upon the recombination reactions of free radical complexes; hence, the nucleation rates are driven by the reduction rates of Au<sup>I</sup> species (reactions (10)).

Nucleation Model 1 (reduced [Au<sup>I</sup>LL']<sup>+</sup> complexes):



Nucleation Model 2 (reduced [Au<sup>I</sup><sub>2</sub>L<sup>5</sup>]<sup>2+</sup> complexes):



where z specifies the number of [Au<sup>0</sup>Au<sup>I</sup>L<sup>5</sup>]<sup>+</sup> added during the reaction sequence indicated in reaction (11c). For Nucleation Model 1 and Model 2 particle growth data can be characterized with the global nucleation reaction rate coefficient, k<sub>nc</sub>. Note, the nascent nucleation products reflect both the metal atom count and the nature of the phosphine ligand complexation. The presence of both mono- and digold complexes likely portends that both nucleation models will be active and weighted by the distribution of complexes present.

For the present synthesis experiments involving slower reduction by BTBC, it is possible that a significant fraction of the Au<sub>x</sub> ensemble may never reach the critical nucleus size n\*; therefore, product yield may diminish. However, for synthesis experiments involving rapid reduction by NaBH<sub>4</sub>, which yields immediate formation of predominately cationic clusters, we presume Nucleation Model 2 should dominate. The immediate formation of ligated, cationic Au<sub>8</sub> and Au<sub>10</sub> clusters induced by reduction with NaBH<sub>4</sub> indicates reduction efficiencies of less than 1 for the digold complexes. This is also consistent with previously reported cationic cluster formation through the rapid reduction of [Au<sub>2</sub>L<sup>6</sup>]<sup>2+</sup>.<sup>24</sup>

ESI-MS spectra from BTBC syntheses show the initial formation of [Au<sub>8</sub>(PPh<sub>3</sub>)L<sup>5</sup>]<sup>3+</sup> (Fig. 2, S1, and S2†), which is



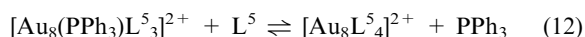
consistent with the  $\text{PPh}_3$ -containing complexes being preferentially reduced (or having an increased reduction rate compared to the  $[\text{Au}_2\text{L}^5_2]^{2+}$  complexes). Therefore, in BTBC syntheses the initial formation of  $\text{Au}_x$  clusters obtains contributions from both nucleation models.

Both nucleation models contain reaction paths leading to the formation of neutral clusters. For example, for a solution that is rapidly reduced by  $\text{NaBH}_4$  (or BTBC) at early times the abrupt elevated concentration of neutral complexes may rapidly react, for instance, through the sequence of reactions (11a) involving  $[\text{Au}^0\text{LL}']^\bullet$  ( $\text{L}, \text{L}' = \text{PPh}_3, \text{L}^5$ ) and reactions (11b) involving  $\text{Au}^0_2\text{L}^5_2$ , yielding a distribution of neutral  $\text{Au}_w\text{L}_x\text{L}'_y$ ;  $w \geq n^*$  clusters. In the present experiments with solutions reduced by BTBC the formation of neutral species is supported by the increased reduction rate of the  $\text{PPh}_3$ -containing complexes that follow Nucleation Model 1. Although neutrals have a certain probability of forming, the predominance of ionic complexes, e.g.,  $[\text{Au}^0\text{Au}^{\text{I}}\text{L}^5_2]^{+ \bullet}$ , increases the likelihood that reaction (11c) will interpose into the reaction sequence, thus, converting the neutrals into cationic clusters.

The ESI-MS spectra of the  $\text{NaBH}_4$  syntheses do not immediately exhibit  $[\text{Au}_8(\text{PPh}_3)\text{L}^5_3]^{2+}$ . This absence is expected when cluster formation is dominated by the reduction of  $[\text{Au}_2\text{L}^5_2]^{2+}$ . Although  $[\text{Au}^{\text{I}}(\text{PPh}_3)_n\text{L}^{5}_{2-n}]^+$  ( $n = 1$  or  $2$ ) complexes are reduced simultaneously with  $[\text{Au}_2\text{L}^5_2]^{2+}$ , the liberation of excess  $\text{L}^5$  initiates fast ligand exchange on the nascent clusters, producing  $[\text{Au}_8\text{L}^5_4]^{2+}$  from  $[\text{Au}_8(\text{PPh}_3)\text{L}^5_3]^{2+}$ . As previously stated, the relative rate of reduction for  $\text{NaBH}_4$  is very fast; thus, all available species are rapidly reduced, which effectively eliminates the observation of preferential reduction of specific complexes. The majority of the distribution of complexes (predominantly  $[\text{Au}_2\text{L}^5_2]^{2+}$ ) is reduced, and the nucleation process should be driven by Nucleation Model 2. Note, the sequential addition of  $\text{Au}^{0'}_2$  and  $\text{Au}^{0'}\text{Au}^{\text{I}}$  species can be changed, but the final nucleation products will comprise the same stable, cationic clusters.

The reduction efficiency of the complexes in solution cannot be well modelled in the current system, but the proportionate transfer of ion signal intensity from complexes to yield intense signals from ligated  $\text{Au}_8$  and  $\text{Au}_{10}$  clusters indicates that the majority of initial products should be cationic instead of neutral, as is predicted by Nucleation Model 2. Fast product formation is consistent with observation of the corresponding ligated  $\text{Au}_8$  and  $\text{Au}_{10}$  ion peaks in the ESI-MS and distinct red color in solution within  $t = 0.5$  h (inset of Fig. 3).

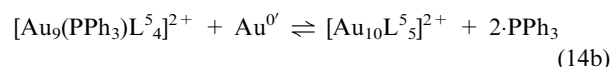
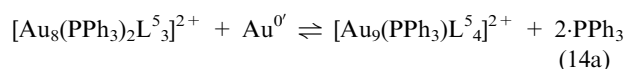
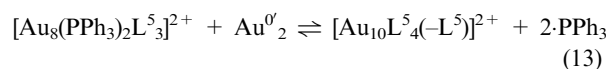
**(4) Ligand exchange reactions at the  $\text{Au}_x$  core.** ESI-MS data in aerated and deaerated systems show that  $[\text{Au}_8(\text{PPh}_3)\text{L}^5_3]^{2+}$  appears prior to  $[\text{Au}_8\text{L}^5_4]^{2+}$  during BTBC syntheses. This result evidences the activity of ligand exchange reactions among the  $\text{Au}_8$  species, e.g.,



Ligand exchange reactions that replace  $\text{PPh}_3$  with  $\text{L}^5$  are favored because  $\text{L}^5$  binds more strongly with gold.<sup>51,58</sup> Thus, ligand exchange reactions analogous to reaction (12) are available to all gold species containing  $\text{PPh}_3$ . Although  $\text{L}^5$  is

a bidentate ligand, the nascent addition complex may involve monodentate complexation, which is followed by an auto-ligand exchange that forms a fully complexed  $\text{L}^5$  while displacing a  $\text{PPh}_3$  or  $\text{Cl}^-$ . Over time, the ligand caps of almost all  $\text{Au}_x$  species in a mixture will exchange, and the ligand cap of the end-products will predominantly contain the stronger binding ligand.

**(5) Product Formation from cationic platforms.** During deaerated syntheses with BTBC, ligated  $\text{Au}_8$  cations appear first in the ESI-MS data. The subsequent appearance of ligated  $\text{Au}_{10}$  cluster cations is evidence for core growth from the ligated  $\text{Au}_8$  clusters. Ligated  $\text{Au}_{10}$  can form through the addition of ligated, reduced gold species, e.g.,



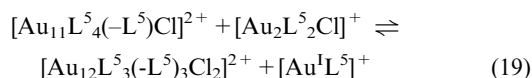
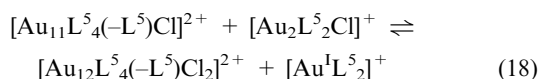
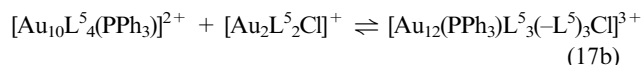
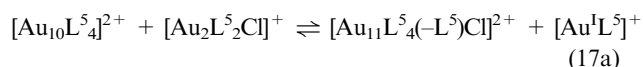
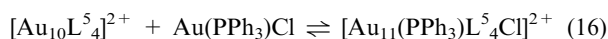
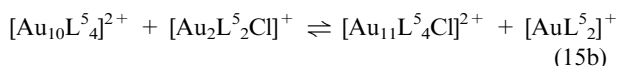
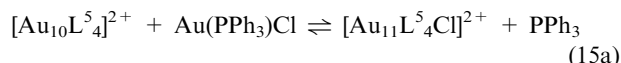
The ligands on the  $\text{Au}^{0'}$  and  $\text{Au}^{0'}_2$  species that are not incorporated in the cluster product are predicted to be liberated into solution. Similar addition reactions involving  $[\text{Au}_8\text{L}^5_4]^{2+}$  will also be active. Reaction (13) incorporates the addition of a fully reduced digold complex,  $\text{Au}^{0'}_2$ , which represents  $\text{R}_3\text{P}-\text{Au}^0-\text{Au}^0-\text{PR}_3$  ( $\text{PR}_3 = \text{PPh}_3$  or  $\text{L}^5$ ). We expect the substitution of  $\text{L}^5$  for the  $\text{PPh}_3$  protecting ligand on the  $\text{Au}^{0'}_2$  species will affect stability.<sup>50,59</sup> Using relativistic SCF calculations, Schwerdtfeger *et al.*<sup>29</sup> have described the orbital structure of the related stable species,  $\text{PH}_3-\text{Au}^0-\text{Au}^0-\text{PH}_3$ .

Reaction (14) is an alternative pathway to the formation of ligated  $\text{Au}_{10}$  clusters. The mechanism involves a sequence of reactions that add  $\text{Au}^{0'}$  to  $\text{Au}_8$  and  $\text{Au}_9$  species. However, the ESI-MS data show no evidence for  $\text{Au}_9$  clusters. The absence of ligated  $\text{Au}_9$  signals indicates that reaction (14) is essentially inactive. Therefore, based on the predicted stability of the  $\text{Au}^{0'}_2$  and on the absence of  $\text{Au}_9$  clusters, we conclude that reaction (13) depicts the dominant pathway to  $[\text{Au}_{10}\text{L}^5_5]^{2+}$ . The absence of ligated  $\text{Au}_9$  clusters due to digold addition (reaction (13)) is consistent with previously observed formation pathways with  $\text{L}^6$ -protected  $\text{Au}_8$  clusters that form  $[\text{Au}_{10}\text{L}^6_5]^{2+}$ .<sup>24</sup>

When considering the total number of valence electrons in a cluster ( $n_{\text{ve}}$ ), PSEP theory predicts that stable, phosphine-protected, gold centered clusters have their peripheral gold atoms in toroidal ( $n_{\text{ve}} = (12n_s + 16)e^-$ ) or spherical ( $n_{\text{ve}} = (12n_s + 18)e^-$ ) arrangements, where  $n_s$  is the number of skeletal electrons donated by the peripheral gold atoms.<sup>3,10,57</sup> PSEP analyses of  $[\text{Au}_8(\text{PPh}_3)\text{L}^5_3]^{2+}$  and  $[\text{Au}_8(\text{PPh}_3)_2\text{L}^5_3]^{2+}$  find total valence electron counts (each Au, P, and  $\text{Cl}^-$  correspondingly contributes 11, 2 and 1 valence electrons) of 100  $e^-$  and 102  $e^-$ , which cause their peripheral gold atoms to lie in toroidal and spherical arrangements, respectively.  $[\text{Au}_{10}\text{L}^5_4(-\text{L}^5)]^{2+}$ ,  $[\text{Au}_{10}(\text{PPh}_3)\text{L}^5_4]^{2+}$ , and  $[\text{Au}_{10}\text{L}^5_4(-\text{L}^5\text{O})]^{2+}$  each contains 126  $e^-$  and nine peripheral gold atoms ( $n_s = 9$ ); thus, each is a stable species that has its peripheral gold atoms in spherical arrangements (i.e.,  $n_{\text{ve}} = (12n_s + 18) = 12(9) + 18 = 126 e^-$ ). Likewise, PSEP theory finds that

$[\text{Au}_{10}\text{L}^5_4]^{2+}$  (124  $e^-$ ), which has an uncovered gold atom, is stable with its peripheral gold atoms in a toroidal arrangement. Although  $[\text{Au}_{10}\text{L}^5_4\text{L}']^{2+}$  ( $\text{L}' = \text{PPh}_3, -\text{L}^5, -\text{L}^5\text{O}$ ) and  $[\text{Au}_{10}\text{L}^5_4]^{2+}$  are observed during experiments, the predominance of  $[\text{Au}_{10}\text{L}^5_4]^{2+}$  among the final products (Fig. 2e and 3b) may reflect the effects of steric hindrance within the ligand cap. The product formations can be described with the total valence  $e^-$  and topographical structures:  $[\text{Au}_{11}\text{L}^5_4\text{Cl}]^{2+}$  (136  $e^-$ , toroidal),  $[\text{Au}_{11}(\text{PPh}_3)\text{L}^5_4\text{Cl}]^{2+}$  (138  $e^-$ , spherical),  $[\text{Au}_{11}\text{L}^5_4(-\text{L}^5)\text{Cl}]^{2+}$  (138  $e^-$ , spherical),  $[\text{Au}_{12}\text{L}^5_4(-\text{L}^5)\text{Cl}_2]^{2+}$  (150  $e^-$ , spherical),  $[\text{Au}_{12}\text{L}^5_3(-\text{L}^5)_3\text{Cl}_2]^{2+}$  (150  $e^-$ , spherical), and  $[\text{Au}_{12}(\text{PPh}_3)\text{L}^5_3(-\text{L}^5)_3\text{Cl}]^{3+}$  (150  $e^-$ , spherical), indicating that these species can be expected to be stable and to contain a central gold atom. The accord enhances confidence in the assignment of the ESI-MS peaks.

At longer time periods during the BTBC syntheses, the formation of larger clusters is observed through the addition of  $\text{Au}:\text{L}^5$  complexes to  $[\text{Au}_{10}\text{L}^5_4]^{2+}$ . The growth pathways can all be described through ligated gold additions, which are isolobal to the fragments in the gold-centered clusters, to the  $\text{Au}_{10}$  platform:



These ligated  $\text{Au}_{11}$  and  $\text{Au}_{12}$  clusters appear in pure chloroform solution but on much faster time scales than observed in methanol:chloroform solvent. This difference indicates that the BTBC reduction environment is more important for product formation than the solvent mixture itself. Formation pathways involving the addition of free  $\text{Cl}^-$  in solution can also be developed, but these pathways are not predicted to significantly contribute to product formation.<sup>24</sup>

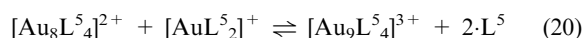
The phosphine-ligated  $\text{Au}_{12}$  clusters produced during syntheses are novel, as the ligand configurations determined by ESI-MS are those that PSEP theory predicts for gold cores containing a central gold atom. The other confirmed  $\text{Au}_{12}$ :phosphine cluster contains no central atom.<sup>60</sup> The preponderance of  $\text{Au}_{12}$  clusters ligated by  $\text{L}^5$  engaged in monodentate complexation, may indicate that steric hindrance among ligands determines much of the structure.

Considerations of stabilization energy and steric hindrance can account for the reactivities observed among ligated  $\text{Au}_8$ ,  $\text{Au}_{10}$ ,  $\text{Au}_{11}$  and  $\text{Au}_{12}$  clusters. PSEP theory finds that the ligated clusters appearing in the ESI-MS data are all minimum

electronic energy structures; however, steric hindrance from ligands can increase with nuclearity. Although persistent solutions of  $[\text{Au}_8(\text{PPh}_3)\text{L}^5_3]^{2+}$  and  $[\text{Au}_8\text{L}^5_4]^{2+}$  can be prepared, structure determinations of analogous  $[\text{Au}_8(\text{PPh}_3)_n]^{2+}$  ( $n = 7, 8$ ) clusters<sup>22,41</sup> reveal metal frameworks that are wide open to  $[\text{Au}_2\text{L}^5_2\text{Cl}_n]^{2+}$  ( $n = 0, 1$ ) addition; hence, ligated  $\text{Au}_{10}$  clusters are readily prepared from  $\text{Au}_8$  complexes. In solution, ligated  $\text{Au}_{10}$  clusters existent with an uncovered peripheral gold atom are open to addition of a gold complex (reactions (15)–(17)), forming stable, fully-ligated  $\text{Au}_{11}$  species. Although  $\text{L}^5$ ,  $-\text{L}^5$ ,  $\text{PPh}_3$ , and  $\text{Cl}^-$  ligands cover most of the  $\text{Au}_{10}$  or  $\text{Au}_{11}$  cores, these clusters remain available for reaction, forming ligated  $\text{Au}_{12}$  clusters (reactions (17b)–(20)).

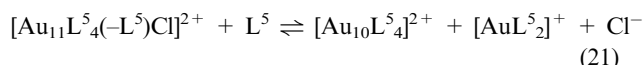
Interestingly, the syntheses do not form  $\text{Au}_{13}:\text{L}^5$  clusters, which theoretically are very stable, due to a closed skeletal shell.<sup>10–12,37</sup> The absence of this product may arise from steric hindrance at the crowded  $\text{Au}_{12}$  surface that blocks  $\text{AuLL}'$  and  $[\text{Au}_2\text{L}^5_2\text{Cl}_n]^{2+}$  ( $n = 0, 1$ ) addition.

**(6) Etching processes.** The products,  $[\text{Au}_6\text{L}^5_3]^{2+}$  and  $[\text{Au}_9\text{L}^5_4]^{3+}$ , are unique to the aerated synthetic solutions. These products form under conditions where the oxidation of the  $[\text{Au}_2\text{L}^5_2]^{2+}$  to  $[\text{AuL}^5_2]^+$  is expected (reactions (6)–(9)). The formation of  $[\text{Au}_9\text{L}^5_4]^{3+}$  is expected to occur through the addition of  $[\text{AuL}^5_2]^+$ :



With increasing time  $[\text{Au}_9\text{L}^5_4]^{3+}$  grows concurrently with increasing  $[\text{AuL}^5_2]^+$  concentration (Fig. S2†). More evidence is provided by the concurrent formation of  $[\text{Au}_9\text{L}^5_4]^{3+}$  with the decreasing peak intensity of the  $[\text{Au}_8\text{L}^5_4]^{2+}$ . In aerated syntheses the formation of  $[\text{Au}_6\text{L}^5_3]^{2+}$  occurs within  $t = 0.5$  h after BTBC addition. Its formation may be promoted through an increased concentration of available oxygen that supports an etching process. Additional studies are ongoing to better characterize the reaction.

Evidence for etching of  $\text{Au}_{11}$  clusters is observed in deaerated solutions. Fig. 2 shows that signal from  $[\text{Au}_{11}\text{L}^5_4(-\text{L}^5)\text{Cl}]^{2+}$  is depleted by  $t = 9$  days. The net etching reaction likely occurs through:



The product distribution in the BTBC syntheses is likely to include some cationic clusters outside the  $m/z$  range of our instrument, indicating that other etching reactions from higher nuclearity clusters may account for the formation of some observed products.

In conclusion, ligated, cationic  $\text{Au}_8$  and  $\text{Au}_{10}$  clusters form quickly in both solvent systems and with both reducing agents.  $[\text{Au}_8\text{L}^5_4]^{2+}$  is more reactive than  $[\text{Au}_{10}\text{L}^5_4]^{2+}$ , as evidenced by the diminished signal of ligated  $\text{Au}_8$  clusters in both solvents. The  $[\text{Au}_{10}\text{L}^5_4]^{2+}$  cluster is a growth platform for larger nuclearity clusters forming through further addition reactions and is resistant to degradation. Solutions reduced by  $\text{NaBH}_4$  do not form  $\text{Au}_{11}$  and only a trace of  $\text{Au}_{12}$  species, possibly indicating that the product yield for ligated  $\text{Au}_8$  and  $\text{Au}_{10}$  clusters is higher than observed with BTBC. Finally, in aerated

syntheses unique product formation is observed that is attributed to the oxidation of the initial complexes.

## B. Comparison of $\text{Au}_x:\text{L}^3$ and $\text{Au}_x:\text{L}^5$ cluster formation

We recently examined the reaction network governing cluster formation in the  $\text{Au}(\text{PPh}_3)\text{Cl}:\text{L}^3$  system with similar experimental protocol.<sup>45</sup> Although the protecting diphosphine ligands are electronically similar, the reduction of complexes containing either  $\text{L}^3$  or  $\text{L}^5$  reacts *via* different formation and degradation pathways.

The initial complex distributions formed by equal molar additions of  $\text{Au}(\text{PPh}_3)\text{Cl}$  and  $\text{L}^n$  ( $n = 3$  or  $5$ ) are different, and these differences strongly influence the reduction efficiencies of the complex ensemble. For unreduced solutions that contain  $\text{L}^5$ , mass spectra indicate that  $\sim 85 \pm 10\%$  of the TIC can be attributed to complexes containing no  $\text{PPh}_3$ . In contrast, for unreduced solutions that contain  $\text{L}^3$ , only  $\sim 55 \pm 10\%$  of the TIC is due to complexes containing no  $\text{PPh}_3$ . This fact indicates that  $\text{L}^5$  replaces  $\text{PPh}_3$  more efficiently than  $\text{L}^3$ . Furthermore, the complex distribution arising in an equimolar solution of  $\text{L}^5$  and  $\text{Au}(\text{PPh}_3)\text{Cl}$  is dominated by digold complexes, whereas the distribution in the  $\text{Au}(\text{PPh}_3)\text{Cl}:\text{L}^3$  solution is dominated by monogold complexes. Critically, these complexes are the starting materials for the reduction and nucleation reactions that lead to cluster formation. Thus, the tendency of the digold complexes to degrade to monogold complexes *via* oxidation under ambient conditions is of special interest.

The initial complex distribution determines which nucleation model is applicable to cluster formation after reduction.<sup>61</sup> ESI-MS data indicate differences in the reduction rate of the ligated  $\text{Au}^{\text{I}}$  species as a function of protecting ligands and coordination number. In systems reduced with BTBC, complexes containing  $\text{PPh}_3$  are always diminished prior to the complexes that contain exclusively  $\text{L}^n$  ( $n = 3$  or  $5$ ) (Fig. 2, S1 and S2†). Although the reduction of complexes containing  $\text{L}^n$  is expected, the relative reduction rates are slower. For BTBC syntheses the slower reduction rates of the  $[\text{Au}_2\text{L}^n_2\text{Cl}_y]^{(2-y)+}$  ( $y = 0$  or  $1$ ) species result in the nucleation process being initially dominated by the free radical recombination of  $\text{Au}^0\text{LL}'^\bullet$  (Nucleation Model 1). Because the equimolar  $\text{L}^5$  system has much less initial monogold complexes, its contribution of neutral nucleation products is expected to be limited, and nucleation products should be controlled by Nucleation Model 2, which forms cationic clusters. Similarly, the equimolar  $\text{L}^3$  systems consist of more  $\text{PPh}_3$ -containing complexes, and the subsequent nucleation products are predominantly neutral clusters formed *via* Nucleation Model 1. Another contributing factor in the  $\text{L}^3$  system governed by nucleation model 1 is that the reduction efficiency of  $[\text{Au}_x\text{L}^3_x]^{x+}$  is 1; whereas, a significant portion of  $[\text{Au}_2\text{L}^5_2]^{2+}$  has a reduction efficiency less than 1.

The contrasting formation of ionic and neutral nucleation products for  $\text{L}^5$  and  $\text{L}^3$ , respectively, is enhanced in syntheses reduced with  $\text{NaBH}_4$ , where preferential reduction is minimized by the fast reduction rate. For  $\text{L}^5$  syntheses, cationic  $\text{Au}_8$  and  $\text{Au}_{10}$  clusters form immediately and persist for the duration of the experiment. The persistence of the ligated  $\text{Au}_8$  and  $\text{Au}_{10}$

clusters likely arises from the dynamic processing of growth and etching reactions, defined as size-selective processing.<sup>14</sup> In contrast, the almost complete reduction of the  $\text{L}^3$  complex ensemble by  $\text{NaBH}_4$  does not significantly increase ESI-MS cluster signal intensities; instead, the dark colloidal suspension mainly comprises neutral species, which are observed with UV-vis spectroscopy and DLS.

The nucleation product distribution and inherent properties of each diphosphine ligand contribute to the disparate final products observed in the two studies. For  $\text{L}^5$ , few reaction pathways are observed after cessation of nucleation, but growth to the larger nuclearity clusters builds from the  $[\text{Au}_{10}\text{L}^5_4]^{2+}$  cluster platform. Precedence for growth platforms is reported from Pettibone and Hudgens,<sup>24</sup> where  $\text{L}^6$ -protected Au clusters grow from the  $[\text{Au}_8\text{L}^6_4]^{2+}$  platform. The growth from  $[\text{Au}_{10}\text{L}^5_4]^{2+}$  is observed and subsequent product formation is described in reactions (15)–(19).

When comparing the number and type of active reactions that form ligated clusters, the reaction network involving  $\text{L}^3$  is more complicated. The initial neutral clusters, which are the principal nucleation products in the  $\text{L}^3$  system, are converted to ionic species through cationic addition reactions. Simultaneously, ligand exchange reactions are prevalent because phosphine ligands are liberated into solution after nucleation. Ligand exchange of  $\text{PPh}_3$  with  $\text{L}^3$  on the surface of ligated  $\text{Au}_8$  and  $\text{Au}_9$  clusters can promote etching reactions to form  $[\text{Au}_6\text{L}^3_4]^{2+}$ .<sup>2,14</sup> In summary, the initial formation of cationic reduction products controls the nucleation process much more tightly in  $\text{L}^5$  syntheses than in  $\text{L}^3$  syntheses, thus limiting the number of subsequent reactions that can occur to form the most thermodynamically stable products.

Although the  $\text{L}^3$  and  $\text{L}^5$  syntheses produce dissimilar final gold nuclearity clusters in deaerated systems, syntheses conducted under aerated conditions produce a distribution of overlapping cluster nuclearity. The oxidation of  $[\text{Au}_2\text{L}^5_2]^{2+}$  produces increased concentration of  $[\text{AuL}^5_2]^+$  (reactions (6)–(9)), which promotes the formation of  $[\text{Au}_9\text{L}^5_4]^{3+}$  (reaction (20)). The presence of oxidative species also promotes the formation of  $[\text{Au}_6\text{L}^5_3]^{2+}$ . Both  $[\text{Au}_9\text{L}^5_4]^{3+}$  and  $[\text{Au}_6\text{L}^5_3]^{2+}$  are analogous to observed products in the  $\text{Au}:\text{L}^3$  systems.

## Conclusions

We have used UV-vis spectroscopy and ESI-MS to elucidate the active reaction network during syntheses of gold nano-clusters. The data provide evidence for the activity of different chemical reaction classes that form the solution complexes, that grow the metal cores, and that remodel core nuclearity, culminating in the formation of stable MPCs. Unlike  $\text{L}^3$  syntheses,  $\text{L}^5$  protected cluster formation proceeds predominantly through the initial formation of cationic species with only small contributions from neutral clusters. Thus, these properties limit the size of the active reaction network. The immediate formation of cationic MPCs is preserved in deaerated solutions with the faster reducing agent,  $\text{NaBH}_4$ . The role of the reduction and subsequent nucleation processes is controlled by the solution complex distribution. The data for syntheses of  $\text{Au}:\text{L}^5$  systems evidence that the nascent reaction products ( $t < 3$  days) are less dependent on the chosen reducing agent

(BTBC or NaBH<sub>4</sub>); instead, after reduction ceases, subsequent solution phase processing provides greater control for tuning cluster nuclearity.

The production of persistent [Au<sub>10</sub>L<sub>4</sub>]<sup>2+</sup> by the slower reduction rate of BTBC leads to higher nuclearity gold clusters that are built from a reaction network centered around the [Au<sub>10</sub>L<sub>4</sub>]<sup>2+</sup> platform. Although [Au<sub>10</sub>L<sub>4</sub>]<sup>2+</sup> production is not affected by reducing rate, the fast reduction of (nearly) the entire complex distribution with NaBH<sub>4</sub> restrains subsequent growth of ligated Au<sub>11</sub> and Au<sub>12</sub> clusters. The absence of further growth is due to the absence of excess gold species, which is minimized by the faster reduction rate with NaBH<sub>4</sub>.

By using simple electron counting rules based on PSEP analysis and isolobal relationships, we have accounted for the observed reaction intermediates and final MPC products. When constructing models of MPC syntheses, counting rules can help identify candidate solution-phase reactions. Importantly, the incorporation of covalent labelling with O-containing complexes along with PSEP analyses have allowed the confident assignment of numerous peaks in the ESI-MS that would have been otherwise difficult to identify.

The role of oxidation on the product formation was more pronounced for the L<sup>5</sup> syntheses, as compared to the L<sup>3</sup> syntheses, due to the greater susceptibility of the digold complexes to oxidation. Under ambient conditions, overlapping channels are observed in the L<sup>3</sup> and L<sup>5</sup> systems, which are not active in the deaerated systems. These experiments support the previously reported relationship between initial Au:ligand complex distribution and product formation described by Pettibone and Hudgens.<sup>24</sup> Specifically, ambient conditions manipulate the complex distribution, and subsequent product formation of ligated Au<sub>6</sub> and Au<sub>9</sub> clusters is not observed in the deaerated systems. Overall, the development of the reaction network for L<sup>5</sup> containing MPCs is controlled through the ligated Au<sub>8</sub> and Au<sub>10</sub> platforms.

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