Supplementary Information for:

Reaction Network Governing Diphosphine-Protected Gold Nanocluster Formation from Nascent Cationic Platforms

John M. Pettibone and Jeffrey W. Hudgens*

Materials Measurement Laboratory, National Institute of Standards and Technology, 100 Bureau Drive, MS-8362, Gaithersburg, MD 20899-8362

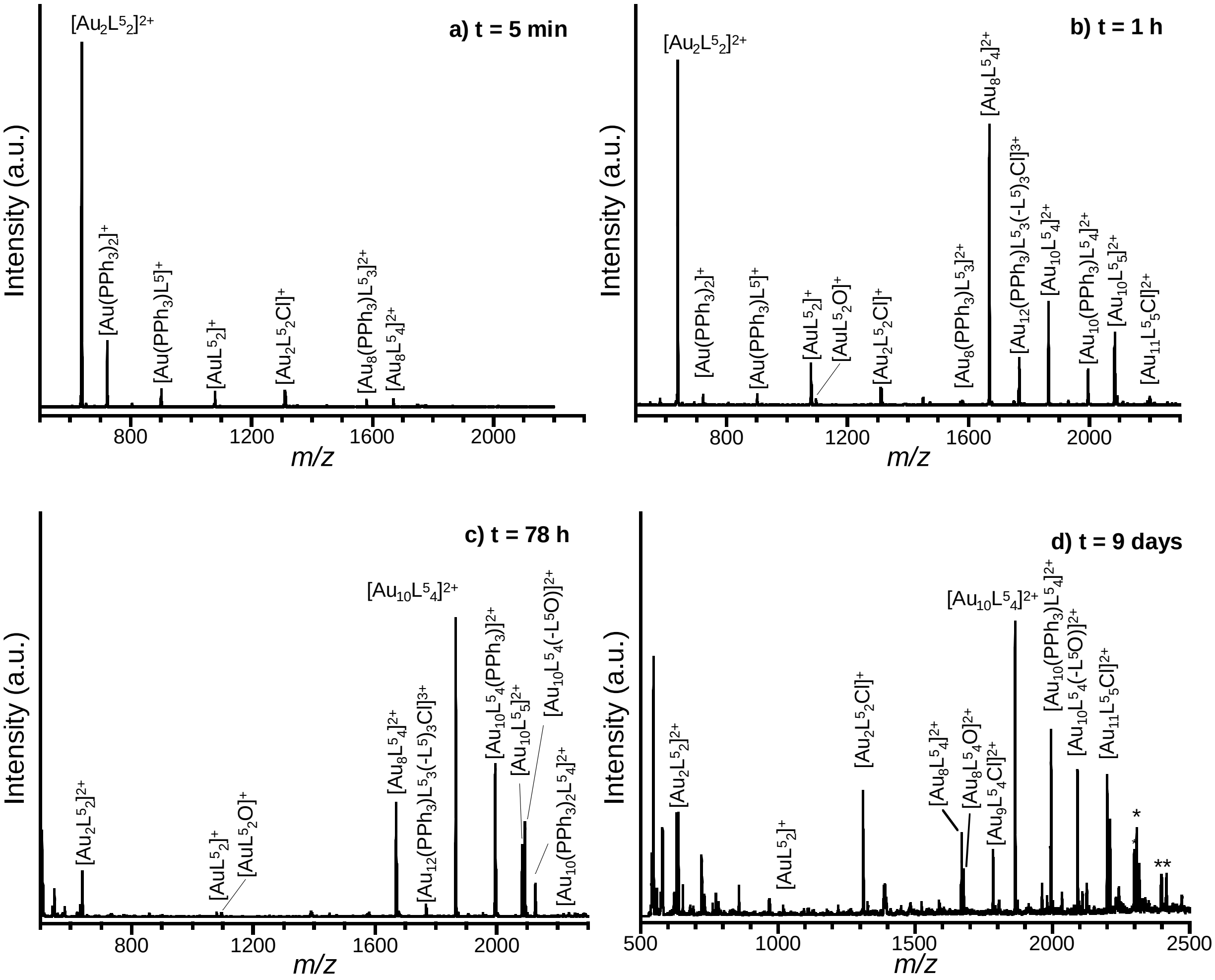

Fig. S1. ESI-MS data of deaerated in chloroform solutions, prepared with 1:1 molar ratio of L^5 and $Au(PPh_3)Cl$, observed at a) *t* = 5 minutes, b) *t* = 1 hour, c) *t* = 2 hours, d) *t* = 78 hours and e) *t* = 9 days after the addition of 5x molar ratio BTBC. The symbols, * and **, represent peaks without firm assignments, but the ratio of charge to O atoms is predicted to be 2:1 and 1:1, respectively, based on satellite peak spacing.

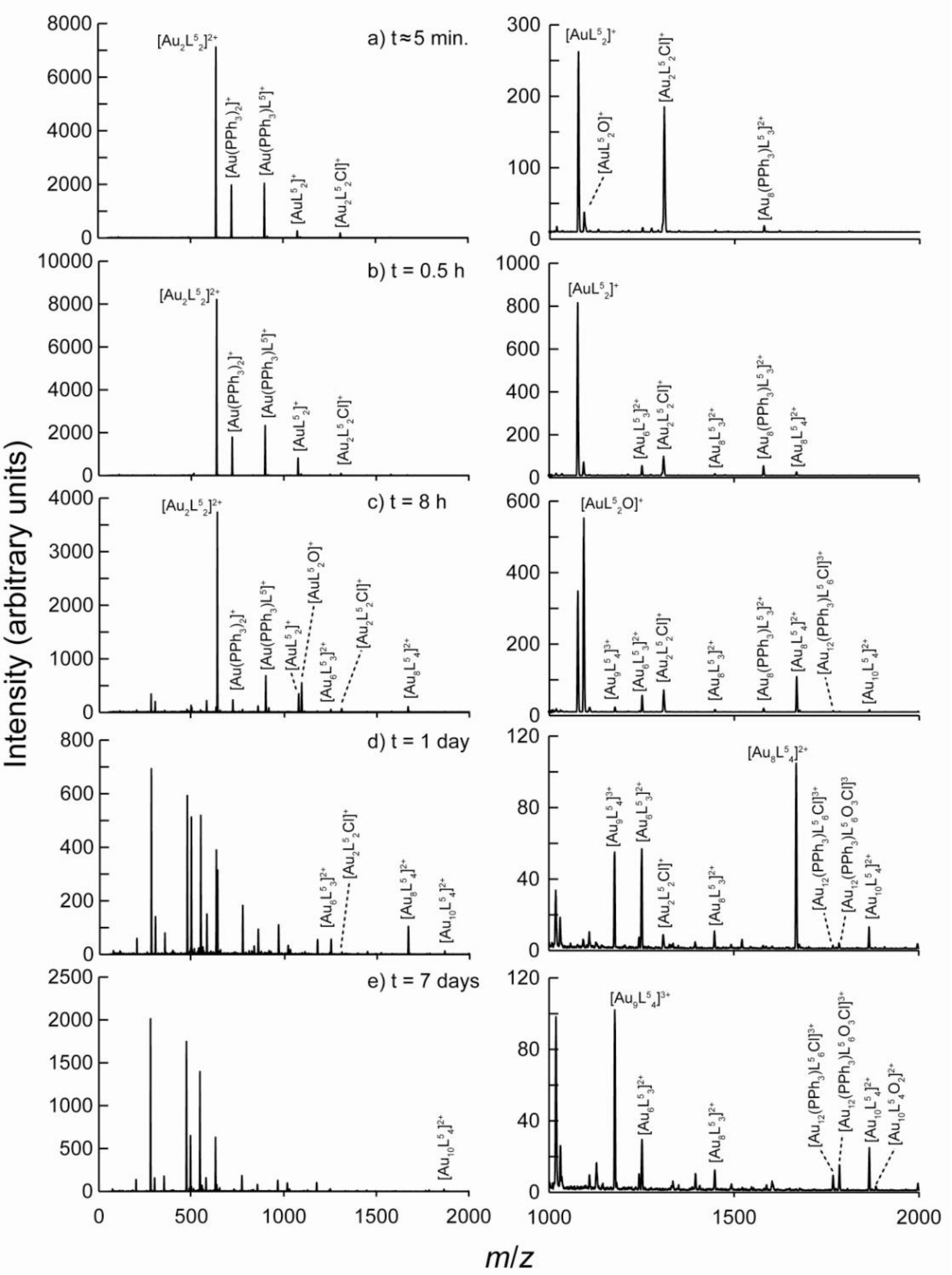

Fig. S2. ESI-MS data observed at reaction times following the preparation of a stirred, aerated 1:1 methanol:chloroform synthesis solution containing $Au(PPh_3)Cl$, L^5, and BTBC reducing agent. Panels depict data for the reaction times: a) $t \approx 5$ minutes, b) $t = 0.5$ hours, c) $t = 8$ hours, d) $t = 1$ day, and e) $t = 7$ days. The right column shows an expanded view of the 1000 *m/z* to 2000 *m/z* region.

Role of Oxidation on stability of complexes and cluster formation

The resistance of the most stable clusters and complexes to degradation caused by exposure to ambient conditions are examined by comparison of aerated and deaerated systems. ESI-MS studies indicate that a major degradation pathway for Au:L^5 MPCs involves oxidation via O atom incorporation. ESI-MS data collected from methanol:chloroform synthesis solutions exhibit peaks corresponding to minor amounts of oxygen atom uptake (Figs. 2, 3b, S1, and S2). For example, as early as t = 8 hours in aerated solutions, the ESI-MS data exhibit a m/z 1093 peak, corresponding to $[AuL^5{}_2O]^+$ (Fig. S2c).

The incorporation of oxygen atoms into the synthesis products in deaerated systems is also observed. Note, though solutions were purged and capped as quickly as possible, the reactions were not conducted in completely oxidation free environments. Although not all oxidative agents from ambient air are removed, distinct differences in the product formation and stability indicate sufficient removal is achieved. For clusters synthesized in chloroform (Fig. S1), the ESI-MS reveal that degradation pathways via O atom incorporation occur more quickly, *e.g.*, $[AuL^5{}_2O]^+$ becomes prominent by t = 2 h, and $[AuL^5{}_2O_2]^+$, $[Au_8(PPh_3)L^5{}_3O]^{2+}$, $[Au_8L^5{}_4O]^{2+}$, and $[Au_9L^5{}_4O]^{2+}$ become prominent by t = 8 hours. ESI-MS data collected at later times (especially in Fig. S1d) contain several unlabeled peaks, particularly in the higher m/z range.

Incorporation of O atoms in the deaerated solutions is generally observed on clusters where monodentate linkage ($-L^5$) of the diphosphine ligand is predicted. The observation of oxidized ligands is also exploited as an assignment tool (covalent labeling). Oxygen addition is observed on the $[Au_{10}L^5{}_4(-L^5)]^{2+}$ and $[Au_{12}(PPh_3)L^5{}_3(-L^5)_3Cl]^{3+}$, forming $[Au_{10}L^5{}_4(-L^5O)]^{2+}$ and $[Au_{12}(PPh_3)L^5{}_3(-L^5O)_3Cl]^{3+}$, respectively. At the longest time points measured in the $NaBH_4$ syntheses the metal-ligand complexes do not show significant oxidation.

Oxygen atom addition on the $[Au_{10}L^5{}_4]^{2+}$ cluster is not observed in the ESI-MS data, but evidence suggests the cluster has an uncapped gold on the surface that is catalytically active for oxidation to form ($-L^5O$) species. The slow, observed shift from the $[Au_{10}L^5{}_4(-L^5)]^{2+}$ to $[Au_{10}L^5{}_4(-L^5O)]^{2+}$ is clearly captured in the time resolved deaerated BTBC data in methanol:chloroform solutions. The seemingly observable selective oxidation by phosphine-protected Au clusters is the topic of ongoing research in our laboratory.

The initial Au:L^5 solution complexes are also susceptible to oxidation, which changes the complex distributions and thus strongly influences the product formation.[1] Bergeron et al.[2] previously demonstrated via ESI-MS that **[**$AuL^5{}_2]^+$ was the salient feature observed at $[L^5]/[Au(PPh_3)Cl] = 12$ in aerated, pure chloroform solvent systems. Experiments conducted under argon in deaerated solutions of neat $CHCl_3$ without reducing agents show that the formation and persistence of $[Au_2L^5{}_2]^{2+}$ 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 $[Au_2L^5{}_2]^{2+}$ complex to $[AuL^5{}_2]^+$ that occurs quickly. These data are consistent with the reaction sequence:

$$2\cdot[Au_2L^5{}_2]^{2+} + O_2 \longrightarrow 2\cdot[Au_2L^5{}_2O]^{2+} \qquad (1)$$

$$[Au_2L^5{}_2O]^{2+} + 2\cdot L^5 \longrightarrow [AuL^5{}_2]^+ + [AuL^5{}_2O]^+ \qquad (2)$$

$$[AuL^5{}_2O]^+ + 0.5\cdot O_2 \longrightarrow [AuL^5{}_2O_2]^+ \qquad (3)$$

$$[AuL^5{}_2O_y]^+\ (y = 1 \text{ or } 2) + y\cdot L^5 \longrightarrow [AuL^5{}_2]^+ + y\cdot(-L^5O)(4)$$

Additional data is needed to confirm this reaction sequence; however, the reaction scheme predicts the formation of $[AuL^5{}_2]^+$, which putatively promotes the production of the observed ligated Au_9 cores in stirred, aerated synthesis solutions under ambient conditions (Fig. S2). In contrast, stirred, deaerated synthesis solutions do not form cationic $[Au_9L_xO_y]^{z+}$ clusters at any time in synthesis solutions and do not promote the increasing formation of $[AuL^5{}_2]^+$.

References

1. J. M. Pettibone and J. W. Hudgens, *J. Phys. Chem. Lett.*, 2010, **1**, 2536-2540.
2. D. E. Bergeron, O. Coskuner, J. W. Hudgens and C. A. Gonzalez, *J. Phys. Chem. C*, 2008, **112**, 12808-12814.

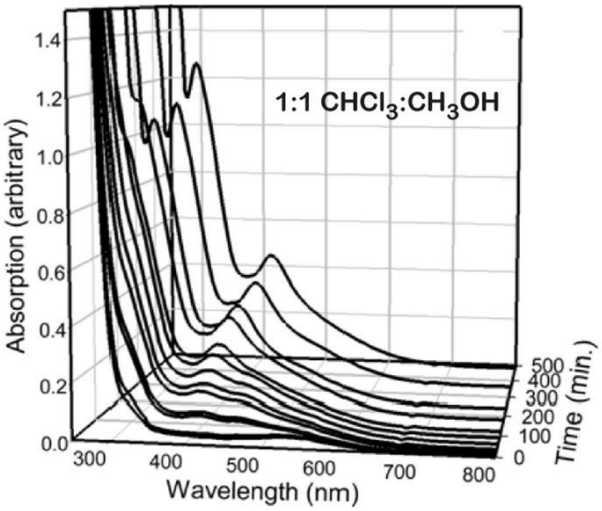

Fig. S3. UV-Vis absorption spectra as a function of time (*t* ≈ 5 minutes to *t* = 500 minutes) of synthesis solutions that produced Au:L^5 clusters by the action of BTBC reducing agent in aerated 1:1 methanol:chloroform solution (stirred).

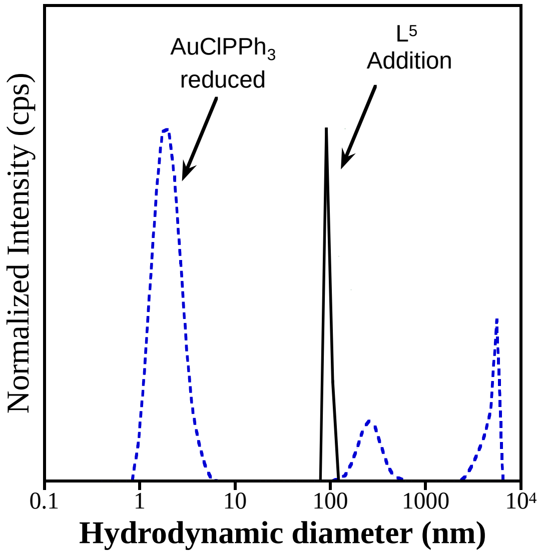

Fig. S4. Dotted lines: DLS data for the colloid distribution, comprised of agglomerated primary clusters, that formed *t* = 5 min after $NaBH_4$ was added to a methanol:diethyl ether solution of dissolved $Au(PPh_3)Cl$. The DLS data indicate the presence of a broad distribution of gold colloids. Solid line: DLS data observed for the above solution within 10 minutes after the addition of a large excess of L^5 (with respect to the initial $Au(PPh_3)Cl$ concentration). The rapid homogenization of D_h evidences strong control of the colloid and primary cluster sizes through ligand exchange of L^5 for PPh_3.