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Synthesis of gold clusters with flexible and rigid diphosphine ligands and the effect of spacer and solvent on the size selectivity

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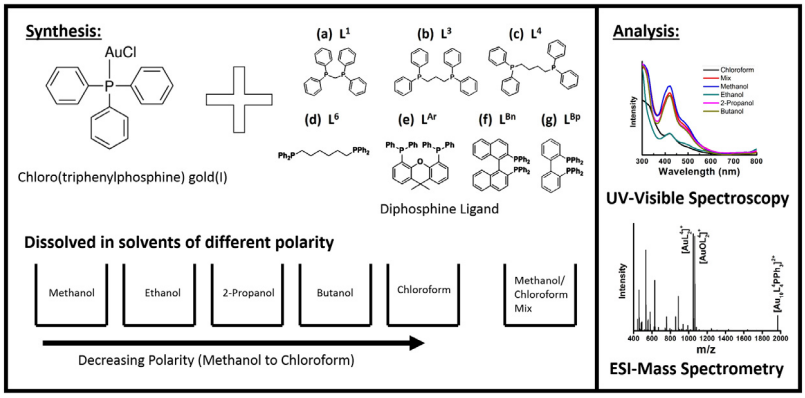
HIGHLIGHTS

- Small gold cluster formation and stability is examined by varying length and flexibility/rigidity of diphosphine ligands and the polarity of the solvent.
- Stability and size selectivity of diphosphine ligated gold clusters is dependent on size and flexibility of the spacer and is not strongly dependent on solvent.
- The small/flexible ligands (L3, L4, and L6) exhibited the greatest size selectivity toward small cluster formation and stability.

GRAPHICAL ABSTRACT



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ABSTRACT

The relationship between ligand rigidity and solvent polarity and the size and dispersity of Au cluster suspensions was investigated. Solutions were prepared which contained 10^{-3}mol/L of Chloro(triphenylphosphine) gold(I) [$Au(PPh_3)Cl$], the same concentration of diphosphine ligand, and 5×10^{-3}mol/L of borane-*tert*-butylamine (BTBC) as the reducing agent. Diphosphine ligands were used which consisted of phosphorus atoms connected by chains with increasing length and rigidity. Specifically we employed a short flexible chain $PPh_2(CH_2)_3PPh_2$, i.e., 1,3-bis(diphenylphosphino)propane, denoted by L^3, a long, flexible chain, $PPh_2(CH_2)_6PPh_2$ i.e., 1,6-bis(diphenylphosphino)hexane denoted by L^6, two rigid ligands, 4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene (xantphos) denoted by L^{Ar}, and 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP) denoted by L^{Bn}, and a moderately flexible spacer 2,2'-Bis(diphenylphosphino)biphenyl (Biphenyl) denoted by L^{Bp}. Materials were dissolved in solvents of increasing polarity; from highest to lowest, methanol, ethanol, propanol, butanol and chloroform were used. Samples were characterized using UV–Visible spectroscopy and electrospray ionization mass spectrometry. We observed the formation of stable monodisperse clusters with the shortest ligand, (L^3), independent of solvent. With a longer flexible ligand, (L^6), we observed primarily Au_{8-10} cores depending on the

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ratio of L^6/PPh_3. All other ligands yielded polydisperse distributions. These dispersions contained clusters with a nuclearity between 8 and 11, for example $[Au_{10}(PPh_3)_9]^{3+}$ in L^{Bn} and $[Au_8(PPh_3)_7]^{2+}$ in L^{Bp}, were observed in the initial stages, but they were not stable and precipitated out or plated the glass vial. We also observed that the polarity of the solvent did not play a significant role in the formation of MPC's, however a correlation between the size of the solvent and MPC formation was observed. Selectivity was observed in the smallest solvents, methanol and chloroform, which are the most and least polar solvents, respectively.

1. Introduction

Synthetic developments of monodisperse monolayer protected clusters (MPC's) are rapidly becoming an exciting area of research [1–3]. Gold nanoclusters exhibit optical properties that make them candidates for applications such as data storage, ultrafast switching and gas sensors [4]. Additionally, gold nanoclusters have the potential to be utilized in drug delivery systems, cancer therapy and treatment for Alzheimer's disease, and for their use in catalysis [2,5–8]. Most current synthetic techniques however typically produce polydisperse suspensions. Monodispersity can be obtained only with difficulty and it often requires additional processing steps, such as crystallization or separation (e.g. chromatography) [9,10]. Phosphine based ligands are commonly used to form metal complexes and have shown to be an efficient, size selective capping agent, including a significant body of literature utilizing triphenylphosphine (PPh_3). However, diphosphines have recently gained considerable attention as capping agents, due to their size selectivity, and simplified processing [4,11–13].

A synthetic pathway to attain size selective, ultra-small Au MPC's with diphosphine ligands $PPh_2(CH_2)_MPPh_2$ in a single phase one pot scheme was achieved previously by our group [11]. This method involves the dissolving of Chloro(triphenylphoshine) gold(I) ($Au(PPh_3)Cl$) and a diphosphine ligand in an organic solvent with the addition of borane-*tert*-butylamine (BTBC) as the reducing agent. The effect of varying the aliphatic bridge length M on size selectivity of the MPCs has been studied for the $M = 3, 5, 6$ and 10 ligands [4,14,15]. The flexibility of spacer and the strength of the ligand–gold interaction are responsible for this selectivity. For example, the largest selectivity was achieved with the shortest spacer, $M = 3$, and as the length or flexibility of spacer group was increased, the selectivity decreased. This indicates that the more flexible ligands can adopt new geometries that can increase bond strength between the Au and ligand, resulting in the size-selecting control of L^3 toward small gold clusters. The reaction network for L^3 and L^5 ligands was proposed by Hudgens et al. [12,16]. This work showed that alkyldiphosphines are ideal ligands for studying the effect of chain length and flexibility on size selectivity, but the conditions that are responsible for the selectivity are much more complex than just using different chain lengths of the alkyl spacer [17].

Another ligand relevant to this work is PPh_3. This ligand is commonly used in the formation of closed shell metal clusters and has been shown to be an effective etching agent [18]. However, PPh_3 is not a size selective ligand and it yields polydisperse suspensions [11,17,19,20]. This lack of selectivity is due to the kinetics of the reaction, which can be manipulated based on reduction rates and trends are expected according to nucleation theory. For example, in benzene, the $Au(PPh_3)Cl$ precursor can form nanoparticles, demonstrating the lack of kinetic control on the reduction process for PPh_3, that is observed with the diphosphines. This is especially true in the presence of a strong reducing agent such as sodium borohydride [17,19,20]. In these environments the formation of nascent, stable metal clusters and their growth is favored, hence the size selectivity is lost [21–23]. However, a recent attempt was made to develop accurate models of the relative rates of formation and growth for PPh_3-protected clusters by following the temporal change in the populations of different cluster nuclearities using a colorimetric assay [18]. Pettibone and Reardon compared Au-PPh_3 and Au-L^3 dissolved in a $MeOH/CHCl_3$ mixture reduced with BTBC and $NaBH_4$ at 0 °C and 20 °C. The change in the reduction rate by change in temperature or reducing agent demonstrated the dependence on size distribution present in the Au-PPh_3 system, which is consistent with rate dependences outlined in nucleation theory. In contrast, the evolution of the product distributions in the Au-L^3 system were nearly identical irrespective of reducing agent and temperature, which demonstrates the control wielded by the diphosphine ligands in cluster formation [24].

Size selectivity in Au MPCs has been reported to depend on several factors, including temperature (controlling reduction rates and secondary processing rates), time, solvent, and ligand length and flexibility. Theoretical calculations have shown that length and flexibility of spacer are critical for size selectivity as well as ligand–metal bond strength and verified by experiment [4]. However, these calculations do not include solvent effects. Besides changing the rates of metal reduction or solubility of the precursors and products, solvents can affect the solubility of the reaction products and, consequently, cluster size and monodispersity. For example, the bond between gold and diphosphines is stronger in polar solvents such as methanol and is weaker in solvents of moderate polarities for such as chloroform [14,21,25]. Because the polar protic solvents have the ability to affect the metal–ligand interaction in ligand exchange reactions, they can alter the selectivity of different core sizes [25].

In this paper we examine the roles of length and flexibility of the aliphatic/alkyl chain of the diphosphine ligand and of solvent polarity on the distribution of ultrasmall Au MPC's.

To study the effect of the spacer on size selectivity, we selected diphosphine ligands with different lengths and rigidity, but with nearly identical electronic structure; the shortest chain $PPh_2(CH_2)PPh_2$, i.e., 1,1-bis(diphenylphosphino)methane, denoted by L^1, two short chains $PPh_2(CH_2)_3PPh_2$, i.e., 1,3-bis(diphenylphosphino)propane, denoted by L^3, and $PPh_2(CH_2)_4PPh_2$, i.e., 1,4-bis(diphenylphosphino)butane, denoted by L^3, a long, flexible chain, $PPh_2(CH_2)_6PPh_2$ i.e., 1,6-bis(diphenylphosphino)hexane denoted by L^6, two rigid ligands, 4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene (xantphos) denoted by L^{Ar}, and 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP) denoted by L^{Bn}, and a moderately flexible spacer 2,2′-Bis(diphenylphosphino)biphenyl (Biphenyl) denoted by L^{Bp} (Fig. 1). Furthermore we examined the effect of solvent on the core sizes of gold nanoclusters and on the stability of molecular ion complexes by altering the solution from polar to non-polar solvents:

Methanol (highest polarity) → Ethanol → Propanol
→ Butanol → $CHCl_3$ (lowest polarity).

We observed that size selectivity was achieved with our most flexible ligands, L^3 and L^6. The more rigid ligands displayed short term