



# Bis(diphenylphosphino)methane ligated gold cluster cations: Synthesis and gas-phase unimolecular reactivity



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Dedicated to the memory of Prof. Detlef Schroeder an inspiration chemist. We will sorely miss our lively discussions.

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## ABSTRACT

Electrospray ionization mass spectrometry (ESI-MS) and UV–vis spectroscopy were used to monitor the condensed phase synthesis of gold cluster cations via  $\text{NaBH}_4$  reduction of  $\text{Ph}_3\text{PAuCl}$  in the presence of  $\text{Ph}_2\text{P}-(\text{CH}_2)_n-\text{PPh}_2$  (dppm,  $L^1$ ) a capping ligand. ESI-MS highlights that upon mixing of  $\text{Ph}_3\text{PAuCl}$  and dppm a range of ligated Au(I) cations are present, including  $[\text{Au}_2L^1_2]^{2+}$ ,  $[\text{Au}(\text{PPh}_3)_2]^+$ ,  $[\text{Au}_2L^1_3]^{2+}$ ,  $[\text{Au}L^1_2]^+$  and  $[\text{Au}_2\text{CIL}^1_2]^+$ . These cationic precursors to reduction can be controlled by the ratios of the two reactants. For a ratio of 1:2 of  $\text{Ph}_3\text{PAuCl}$  and dppm,  $[\text{Au}L^1_2]^+$  is a major ion, while  $[\text{Au}(\text{PPh}_3)_2]^+$ , which has previously been postulated to be a key precursor to gold colloid formation (J.M. Pettibone, J.W. Hudgens, *Small* 8 (2012) 715) is essentially absent. Upon  $\text{NaBH}_4$  reduction of a solution of this stoichiometry ( $\text{Ph}_3\text{PAuCl}:\text{dppm}$ , 1:2), the following types of gold nanocluster ions are observed via ESI-MS:  $[\text{Au}_5L^1_3(\text{CH}(\text{PPh}_2)_2)]^{2+}$ ,  $[\text{Au}_9L^1_4]^{3+}$ ,  $[\text{Au}_9L^1_5]^{3+}$ ,  $[\text{Au}_{10}L^1_4]^{2+}$ ,  $[\text{Au}_{11}L^1_5]^{3+}$ ,  $[\text{Au}_{11}L^1_6]^{3+}$ ,  $[\text{Au}_{13}L^1_6]^{3+}$  and  $[\text{Au}_{14}L^1_6(\text{CH}(\text{PPh}_2)_2)]^{3+}$ . The gas phase unimolecular chemistry of these clusters and their fragment ions were examined in a LTQ FT Hybrid Linear Ion Trap (LIT) Mass Spectrometer. Low-energy collision induced dissociation (CID) produced a range of novel gas-phase clusters of the type,  $[\text{Au}_xL^1_y]^{z+}$  ( $x=2, 3, 6-13$ ;  $y=1-6$  and  $z=1-3$ ) and  $[\text{Au}_xL^1_y(\text{CH}(\text{PPh}_2)_2)]^{z+}$  ( $x=5, 14$ ;  $y=2, 5$ ;  $z=2, 3$ ), via ligand loss and core fission fragmentation pathways. In addition fragmentation channels due to C–P bond activation were also observed. Electron capture dissociation (ECD) on the Au cluster cations resulted in either one or a combination of three fragmentation channels: (i) charge reduction, (ii) charge reduction accompanied by ligand loss and/or (iii) charge reduction accompanied by C–P bond activation.

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## 1. Introduction

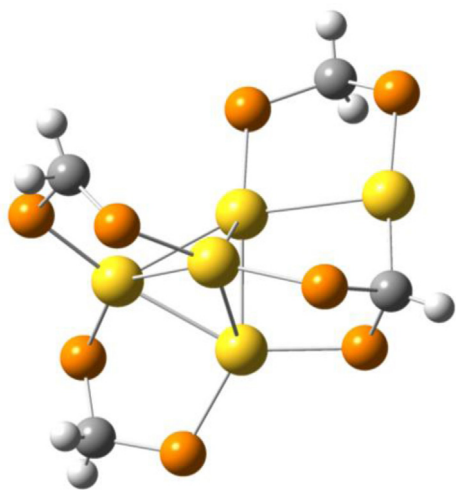
Electrospray ionization mass spectrometry (ESI-MS) has emerged as a valuable tool to monitor the solution phase growth [1,2] and reactivity [3] of coinage metal nanoclusters and to direct their bulk synthesis [4,5]. These studies are driven by an interest in the synthesis of monodisperse, ligand-capped nanoclusters [6] and their applications in materials science and catalysis [7]. Stoichiometrically and structurally well-defined gold nanoclusters predate ESI-MS by around 2 decades and form a cornerstone of Mingos' theory on the structures of metal clusters [8]. An early review of the field [9] has highlighted three methods for the

synthesis of gold nanoclusters with 4–13 core atoms capped by chelating bis(diphenylphosphino)alkane ligands  $\text{Ph}_2\text{P}-(\text{CH}_2)_n-\text{PPh}_2$  ( $=L^n$ , where  $n=1-6$ ) to retard growth into colloids: (i) reduction of Au(I) compounds in the presence of bis(diphenylphosphino)alkane ligands; (ii) reaction of atomic Au prepared by the evaporation of metallic gold in the presence of bis(diphenylphosphino)alkane ligands; (iii) transformation of gold cluster compounds by reaction with bis(diphenylphosphino)alkane ligands or other reagents. Methods (i) and (ii) can give rise to different clusters, even for the same capping ligand [10a]. For example X-ray crystallography has been used to characterize the clusters formed with the use of bis(diphenylphosphino)methane (dppm): reduction of an ethanolic solution of  $\text{Au}_2(\text{dppm})(\text{NO}_3)_2$  with  $\text{NaBH}_4$  resulted in the formation of the icosahedral  $\text{Au}_{13}(\text{dppm})_6$  cluster cation (method (i)) [10b]; evaporation of metallic gold into an ethanolic solution of dppm and  $\text{NH}_4\text{NO}_3$  results in the formation of  $[\text{Au}_5(\text{dppm})_3(\text{dppm-H})(\text{NO}_3)_2]$  (method (ii)) [10]. The cluster formed via metal evaporation has an interesting structure (Fig. 1), that consists of an Au tetrahedral core with an exopolyhedral organometallic  $\text{Au}(\text{CH}(\text{PPh}_2)_2)$  resulting from coordination of the deprotonated dppm ligand to an Au. It represents one of

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**Fig. 1.** Structure of the bis-diphenylphosphine methane protected gold cluster  $[\text{Au}_5\text{L}^{13}(\text{CH}(\text{PPh}_2)_2)]^{2+}$  determined via X-ray crystallography [10a]. Counterions and phenyl groups are omitted for clarity.

the first examples of a rare class of organometallic gold clusters that are capped by a combination of phosphine ligands and formal “carbanionic” ligands [11].

Recent studies utilizing ESI-MS and UV-vis spectroscopy have revealed that the growth of bis-phosphine capped gold nanoclusters upon reduction of Au(I) salts is complex and depends on a range of factors including [1e]: the solvent(s) used, the type of reductant used, the gold salt used, the type of bis-phosphine used and the molar ratio of the gold salt to the bis-phosphine. Furthermore, the temporal evolution of gold nanoclusters can be classified into several processes: formation of ligated gold(I) precursors prior to reduction, reduction and growth, cluster etching, post synthetic reactions and cluster transformation reactions. In recent work Pettibone and Hudgens have shown that the molar ratio of the gold salt to the bis-phosphine controls the types of Au(I) species present in solution prior to reduction [1k] and have postulated that the presence of  $[\text{Au}(\text{PPh}_3)_2]^+$  is undesirable as it leads to colloid formation. Here we use: ESI-MS to examine the formation of precursors to cluster growth upon mixing of different ratios of  $\text{Ph}_3\text{PAuCl}$  and dppm; and a combination of ESI-MS and UV-vis spectroscopy to examine the growth of gold nanoclusters upon sodium borohydride reduction of  $\text{Ph}_3\text{PAuCl}$  and dppm. We also take advantage of the multistage mass spectrometry capabilities of a hybrid ion trap – FT-ICR mass spectrometry to explore the gas phase unimolecular chemistry of a range of dppm ligated gold cluster cations,  $[\text{Au}_x\text{L}_y]^{z+}$  under conditions of low energy collision induced dissociation (CID) and electron capture dissociation (ECD).

## 2. Experimental

### 2.1. Materials

The following suppliers were used to purchase chemicals, which we used without further purification: (i) Aldrich: bis(diphenylphosphino)propane ( $\text{L}^1$ ) (97%), (ii) STREM: chloro(triphenylphosphine)gold(I) (99%), AJAX: sodium borohydride (97%), and (iv) Merck: chloroform and methanol (AR grade for synthesis and HPLC grade for ESI-MS<sup>n</sup> experiments).

### 2.2. Gold cluster synthesis

Condensed phase synthesis of the bis-phosphine protected gold clusters  $[\text{Au}_5\text{L}^{13}(\text{CH}(\text{PPh}_2)_2)]^{2+}$ ,  $[\text{Au}_9\text{L}^{14}]^{3+}$ ,

$[\text{Au}_9\text{L}^{15}]^{3+}$ ,  $[\text{Au}_{10}\text{L}^{14}]^{2+}$ ,  $[\text{Au}_{11}\text{L}^{15}]^{3+}$ ,  $[\text{Au}_{11}\text{L}^{16}]^{3+}$ ,  $[\text{Au}_{13}\text{L}^{16}]^{3+}$  and  $[\text{Au}_{14}\text{L}^{16}(\text{CH}(\text{PPh}_2)_2)]^{3+}$  was performed using the method of Hudgens and co-workers [1b–e]. Briefly, 50  $\mu\text{mol}$  of  $\text{NaBH}_4$  in 1 mL of methanol:chloroform (50:50) solution was added to a solution of 10  $\mu\text{mol}$   $\text{Ph}_3\text{PAuCl}$  and 20  $\mu\text{mol}$  bis(diphenylphosphino)methane in 14 mL of methanol:chloroform (50:50) to give a total of 15 mL. The mixture was allowed to stir at room temperature in an 18 mL polyethylene glass vial (50 mm H  $\times$  25 mm D) for at least 24 h. A 15 mm  $\times$  4.5 mm Teflon magnetic stirrer bar was used, centred and set to spin at 500 rpm. Solutions were stored in capped vials and used when needed. They were analyzed without further purification.

### 2.3. UV-vis spectroscopy

The synthesis of the bis-phosphine protected gold clusters was monitored by UV-vis spectroscopy using a Cary 5 UV-Vis-NIR Spectrophotometer operating in the dual beam reference mode. Sample concentrations were 0.5 mM.

### 2.4. Mass spectrometry

Mass spectrometry experiments were conducted by diluting solutions from the gold cluster synthesis above, with methanol to typical gold concentrations of 10–50  $\mu\text{M}$  and injecting at a sample flow rate of 5  $\mu\text{L min}^{-1}$  into the Finnigan ESI source of a LTQ FT Hybrid Linear Ion Trap (LIT) Mass Spectrometer (Thermo, Bremen, Germany) described in detail elsewhere [12]. Typical electrospray source conditions involved needle potentials of 3.8–5.2 kV with the capillary temperature set at ca. 250 °C. The tube lens voltage was set to 35.0 V, and the capillary voltage was set to 30.0 V. For the unimolecular reactions, the gold cluster cation of interest was mass selected with a window of 15  $m/z$  units and then subjected to either CID or ECD. In CID experiments, the normalized collision energy was selected to deplete the parent ion to a relative abundance of ca. 20% for an activation  $Q$  of 0.25 and activation time of 30 ms with the scan mass range set between the low  $m/z$  cut-off for an ion trap and  $m/z$  3500. For high-resolution mass analysis and the ECD experiments, the gold cluster cations were transferred to the FT-ICR cell ( $<1.5 \times 10^{-9}$  Torr) via the ion optics transfer region ( $\sim 2 \times 10^{-7}$  Torr). The ECD experiments were carried out as previously described [12]. Briefly, an indirectly heated emitter cathode located downstream of the FT-ICR cell was used to supply the cell with low-energy electrons whose energy is determined by the potential difference between the emitter cathode with an ECD offset of  $-3.2$  V and the grid positioned in front of the cathode, which is variable. The gold cluster cations were bombarded with electrons of energy 5 eV for 70 ms.

## 3. Results

### 3.1. Types of clusters formed for dppm

As noted in Section 1, the growth of bis-phosphine capped gold nanoclusters upon reduction of Au(I) salts is complex. In the next sections we examine: (i) the types of Au(I) species that are formed prior to reduction; (ii) the growth of gold nanoclusters upon sodium borohydride reduction of  $\text{Ph}_3\text{PAuCl}$  in the presence of dppm; (iii) compare the types of gold nanoclusters for dppm with those previously described for other bis-phosphine ligands.

#### 3.1.1. Cationic precursors formed upon mixing of $\text{Ph}_3\text{PAuCl}$ and dppm

A range of metal to ligand ratios were used to determine the most suitable pre reduction environment to facilitate the

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