International Journal of Mass Spectrometry 413 (2017) 97–105

Contents lists available at ScienceDirect

International Journal of Mass Spectrometry

journal homepage: www.elsevier.com/locate/ijms

# ESI/MS investigation of routes to the formation of silver hydride nanocluster dications $[Ag_xH_{x-2}L_y]^{2+}$ and gas-phase unimolecular chemistry of $[Ag_{10}H_8L_6]^{2+}$☆

Marjan Krstić[a,1], Athanasios Zavras[b,1], George N. Khairallah[b], Philippe Dugourd[c], Vlasta Bonačić-Koutecký[a,d], Richard A.J. O'Hair[b,*]

[a] Center of Excellence for Science and Technology—Integration of Mediterranean region (STIM) at Interdisciplinary Center for Advanced Science and Technology (ICAST), University of Split, Meštrovićevo šetalište 45, Split 21000, Croatia
[b] School of Chemistry and Bio21 Molecular Science and Biotechnology Institute, The University of Melbourne, 30 Flemington Rd, Parkville, Victoria 3010, Australia
[c] Institut Lumière Matière, Université Lyon 1-CNRS, Université de Lyon, 69622 Villeurbanne cedex, France
[d] Humboldt-Universität Berlin, Institut für Chemie, Berlin 12489, Germany

## ARTICLE INFO

*Article history:*
Received 30 April 2016
Accepted 27 May 2016
Available online 28 June 2016

*Keywords:*
Electrospray
Mass spectrometry
Gas-phase
Ligated silver hydride nanoclusters

## ABSTRACT

When the bis(diphenylphosphino)methane (dppm) ligated silver hydride nanocluster salt $[Ag_3(L)_3(\mu_3\text{-}H)](BF_4)_2$ is allowed to react with $NaBH_4$ in a methanol/chloroform solution for 5 mins., and then diluted with acetonitrile and subjected to electrospray ionization mass spectrometry (ESI/MS), a range of silver hydride nanocluster dications are observed including: $[Ag_8H_6L_5]^{2+}$ and $[Ag_xH_{x-2}L_6]^{2+}$, where x = 9–15 and L = dppm. All of these clusters are no longer present in the ESI mass spectrum at 40 mins after mixing. Multistage mass spectrometry ($MS^n$) experiments were carried out to determine the fragmentation chemistry of $[Ag_{10}H_8L_6]^{2+}$ under conditions of collision-induced dissociation (CID). The initial CID reactions involve sequential loss of two ligands (L) to produce $[Ag_{10}H_8L_4]^{2+}$. Further isolation and CID of $[Ag_{10}H_8L_4]^{2+}$ resulted in a rich series of product ions which arise from three classes of fragmentation reactions: (i) cluster fission to yield complementary ion pairs $[Ag_{10-x}H_{8-(x-1)}L_{4-y}]^+$ and $[Ag_xH_{x-1}L_y]^+$ (x = 1, 2 and 4); (ii) ligand loss associated with cluster fission to yield pairs of singly charged clusters $[Ag_{10-x}H_{8-(x-1)}L_{4-y}]^+$ and $[Ag_xH_{x-1}L_{y-1}]^+$ (x = 1–4); (iii) ligand loss with concomitant loss of all the hydrides, presumably as four molecules of hydrogen to give the ligated silver cluster, $[Ag_{10}L_3]^{2+}$. The subsequent fragmentation reactions of the product ions were also examined. Most of the singly charged ligated silver hydride clusters fragment to form $[Ag_xH_{x-1}L_y]^+$. The exceptions are $[Ag_9H_8L_2]^+$ and $[Ag_7H_6L_2]^+$ which, upon ligand loss also release all of the hydrides to form the ligated silver clusters, $[Ag_9L]^+$ and $[Ag_7L]^+$ respectively. DFT calculations were carried out to examine how the cluster geometry changes for the following processes: $[Ag_{10}H_8L_6]^{2+} \rightarrow [Ag_{10}H_8L_4]^{2+} + 2L \rightarrow [Ag_{10}H_8L_3]^{2+} + L \rightarrow [Ag_{10}L_3]^{2+} + 4H_2$. Losses of 2 L from $[Ag_{10}H_8L_6]^{2+}$ and L from $[Ag_{10}H_8L_4]^{2+}$ were calculated to be endothermic by 2.9 and 1.9 eV respectively, but the subsequent loss of $4H_2$ from $[Ag_{10}H_8L_3]^{2+}$ is exothermic by 0.2 eV.

## 1. Introduction

The chemistry of alkali metal borohydrides reacting with coinage metal salts in the presence of ligands or other additives has been studied for over 6 decades [1]. A rich series of products are formed including metal borohydrides [2–4], metal hydrides [5–7], mixed metal hydride-borohydrides [8] and reduced metal species [9–14]. These products can span multiple length scales ranging from discrete mononuclear compounds [2–4] through to ligand capped nanoclusters [5–11], nanoparticles, and colloids capped with various species [12–14]. There is growing evidence that ligand capped nanoclusters can act as precursors to nanoparticles and colloids [5,15]. In many instances electrospray ionization (ESI) and matrix assisted laser desorption ionization (MALDI) have been used to establish the molecular formulas and polydispersity of these

---

☆ Dedicated to the memory of Prof. Nico Nibbering, a true friend of International Mass Spectrometry, whose seminal contributions to the physical organic chemistry of gas phase ions inspired a generation of scientists.

[*] Corresponding author.
*E-mail address:* rohair@unimelb.edu.au (R.A.J. O'Hair).

[1] These authors contributed equally to the work.

http://dx.doi.org/10.1016/j.ijms.2016.05.022

products [16,17]. In the case of bisphosphine capped gold nanoclusters, mechanisms for the condensed-phase growth of these clusters have been proposed by Hudgens et al. using a combination of ESI/MS and UV/vis spectroscopy [18]. Tandem mass spectrometry approaches have been used to examine the fundamental gas-phase chemistry of these coinage metal nanoclusters [19,20].

The nature of the product(s) formed and their polydispersity are influenced by a range of factors including the nature of coinage metal salt, borohydride and ligand(s) used, the solvent, the temperature and the reaction time. For example, ESI/MS monitoring of the reaction of $NaBH_4$ of gold salts in the presence of the bis(diphenylphosphino)methane (dppm) ligand, L, gave rise to gold nanoclusters with the stoichiometry: $[Au_5L_3(L-H)]^{2+}$, $[Au_9L_4]^{3+}$, $[Au_9L_5]^{3+}$, $[Au_{10}L_4]^{2+}$, $[Au_{11}L_5]^{3+}$, $[Au_{11}L_6]^{3+}$, $[Au_{13}L_6]^{3+}$ and $[Au_{14}L_6(L-H)]^{3+}$ [20c]. In contrast, ESI/MS of solutions of $NaBH_4$ of silver salts in the presence of the dppm ligand reveals the formation of silver hydride nanoclusters with the stoichiometry: $[Ag_3(H)(Cl)L_3]^+$ [6e]; $[Ag_3(H)(BH_4)L_3]^+$ [8]; $[Ag_3(H)L_3]^{2+}$ [6f] and $[Ag_{10}H_8L_6]^{2+}$ [6e]. Clusters with the same stoichiometries were formed when the bis(dimethylphosphino)methane (dmpm) ligand was used instead, except for $[Ag_{10}H_8L_6]^{2+}$ which was not observed [19b]. In the case of the dppm ligand, variations in the solution phase conditions allowed the isolation and structural characterization via X-ray crystallography of the following salts: $[Ag_3(L)_3(\mu_3\text{-H})(\mu_3\text{-Cl})]BF_4$ [6e]; $[Ag_3(L)_3(\mu_3\text{-H})](BF_4)_2$ [6f] and $[Ag_3(L)_3(\mu_3\text{-H})(\mu_3\text{-BH}_4)]BF_4$ [8]. Although we have not successfully isolated salts of $[Ag_{10}H_8L_6]^{2+}$ for structure determination using X-ray crystallography, we recently reported on experiments and DFT calculations of its gas-phase ionization energy, which allowed us to suggest a likely structure [19c].

Here we use: (i) ESI experiments to examine the types of cluster ions formed from when $NaBH_4$ is added to the $[Ag_3(L)_3(\mu_3\text{-BH}_4)](BF_4)_2$ salt; (ii) $MS^n$ experiments to probe the gas phase fragmentation chemistry of ligated silver hydride cluster cations, particularly $[Ag_{10}H_8L_6]^{2+}$ (where L = dppm) and its subsequent fragment ions to establish whether the coordinated hydride ligands remain bound to the silver clusters or whether they are lost as molecular hydrogen. DFT calculations were used to examine the energetics and structural changes associated with the formation of $[Ag_{10}L_3]^{2+}$ from $[Ag_{10}H_8L_6]^{2+}$.

## 2. Methods

### 2.1. Experimental

The following suppliers were used to purchase chemicals, which were used without further purification: (i) Aldrich: bis(diphenylphosphino)methane (dppm, L) (97%), sodium borodeuteride (98%), silver tetrafluoroborate (98%), (ii) Chemsupply: silver nitrate (99%), (iii) Ajax Finechem: sodium borohydride (97%), (iv) Merck: chloroform and methanol (AR grade for synthesis and HPLC grade for $ESI/MS^n$ experiments), (v) Burdick & Jackson: acetonitrile (HPLC grade).

#### 2.1.1. Cluster synthesis

Silver hydride nanoclusters were synthesized by dissolving 16.5 mg (10 μmol) of the silver hydride nanocluster $[Ag_3(\mu_3\text{-H})(dppm)_3]$ $(BF_4)_2$ in 20 mL of solvent (acetonitrile or a 1:1 methanol:chloroform mixture), followed by addition of $NaBH_4$ (3.6 mg, 100 μmol). The solution was then stirred for ca. 5 min and the sample was diluted in acetonitrile or a 1:1 methanol:chloroform mixture to 50 μM prior to analysis by ESI/MS. Upon addition of sodium borohydride the solution changed from colourless to light orange over 40 min. In order to determine the source of hydride in the clusters, the same procedure was followed, but by replacing sodium borohydride with sodium borodeuteride (4.2 mg, 100 μmol).

#### 2.1.2. Mass spectrometry

Solutions containing silver hydride nanoclusters were injected at a sample flow rate of 5 μL $min^{-1}$ into the Finnigan ESI source of a LTQ FT Hybrid Linear Ion Trap (LIT) Mass Spectrometer (Thermo, Bremen, Germany) described in detail elsewhere [21]. Typical electrospray source conditions involved needle potentials of 3.6–4.8 kV with the capillary temperature set at ca. 250 °C. The tube lens voltage was set to 20.0 V, and the capillary voltage was set to 10.0 V. For the unimolecular reactions, the silver cluster cation of interest were mass selected with a window of 15 *m/z* units and then subjected to CID under multi collision conditions using the helium bath gas as the collision gas, and where a normalized collision energy was selected to deplete the parent ion to a relative abundance generally less than 20% for an activation *Q* of 0.25 and activation time of 30 ms. The scan mass range set between the low *m/z* cut-off for an ion trap and *m/z* 2000. For high-resolution mass analysis, the silver 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). Since all isotopologues are isolated during the mass selection process, confirmation of the assignment of the products ions formed during the CID steps was carried out by an analysis of both their isotope envelopes and exact masses, as carried using the Thermo Scientific™ Xcalibur™ software.

### 2.2. Computational

The Turbomole [22] program was used with the Perdew-Burke-Ernzerhof (PBE) RI functional [23,24] and 19-electron relativistic effective core potential (19e-RECP) basis set for silver atoms [25] in combination with the split-valence-plus-polarization (SVP) atomic basis set for all other atoms [26] to fully optimize structures of silver hydride nanocluster dications $[Ag_{10}H_8L_y]^{2+}$ (y = 3, 4 and 6) and the silver nanocluster dication $[Ag_{10}L_3]^{2+}$ to determine relative energies for removal of ligands and hydrogen atoms. All structures presented were fully optimized using gradient minimization techniques and stationary points were characterized as minima by calculating the vibrational frequencies. The structural search has been carried out taking advantage of structural properties obtained for fully ligand protected complex $[Ag_{10}H_8L_6]^{2+}$ [19c] by removing subsequently ligands which induced changes in the structures of the silver cores. Consequently, an extensive search for structural changes within the cores of ligated complexes has been carried out. Similar procedures have been employed for the search of the structures after removal of hydrogen atoms.

## 3. Results & discussion

### 3.1. The crucial role of the silver precursor in forming silver hydride nanocluster dications $[Ag_xH_{x-2}L_y]^{2+}$

As noted in the introduction, we have previously observed that ESI/MS of solutions of $NaBH_4$ of silver salts in the presence of the dppm ligand results in the formation of silver hydride nanoclusters with the stoichiometry: $[Ag_3(H)(Cl)L_3]^+$ [6e]; $[Ag_3(H)(BH_4)L_3]^+$ [8]; $[Ag_3(H)L_3]^{2+}$ [6f] and $[Ag_{10}H_8L_6]^{2+}$ [6e]. The relative abundances of these ions depend on a number of factors including the solvent system, and the relative stoichiometries of the silver salt, ligand and $NaBH_4$. Fig. 1a shows optimal solution phase conditions to maximize the signal of $[Ag_{10}H_8L_6]^{2+}$. In order to find the optimal solution phase conditions to isolate the $[Ag_3(L)_3(\mu_3\text{-BH}_4)](BF_4)_2$ salt, we previously tried several other solvents systems and discovered that by switching from methanol:chloroform (1:1 v/v) to pure acetonitrile, we were able to generate bulk $[Ag_3(L)_3(\mu_3\text{-BH}_4)](BF_4)_2$