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Silver Hydrides

Synthesis, Structure and Gas-Phase Reactivity of a Silver Hydride Complex $[Ag_3\{(PPh_2)_2CH_2\}_3(\mu_3\text{-}H)(\mu_3\text{-}Cl)]BF_4$**

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In memory of Detlef Schröder

Coinage metal hydrides continue to attract attention because of their interesting structural and physical properties, as well as for their role as reagents or intermediates in the transformation of organic substrates. For example, several copper hydride compounds have been structurally characterized and developed as catalysts for 1,4 reduction reactions of enones and for hydrocupration of alkynes.[1] In contrast, whereas their heavier congeners have been implicated as reactive intermediates in oxidation and other reactions,[2] and have been characterized in the gas phase,[3] as well as by matrix isolation experiments,[4] few silver and gold hydride compounds have been synthesized and structurally characterized by X-ray crystallography.[5]

We have been examining the role of coinage-metal cluster compounds in C−C bond coupling reactions,[6] click chemistry,[7] and C−X bond activation[3,8] of organic substrates. In our work, methods based on mass spectrometry (MS) are employed to explore cluster formation and reactivity, and to direct condensed phase synthesis and characterization of novel clusters.[9] As part of this cluster chemistry program, we became interested in extending the method of generating bis(phosphino)-protected gold nanoclusters by sodium borohydride reduction of gold salts[10] to generate related silver nanoclusters.[11] Herein, we report on the serendipitous MS-based discovery of a novel silver hydride cluster, $[Ag_3HClL_3]^+$ (L = bis(phosphino) ligand), which has prompted its mass-spectrometry-directed synthesis[12] and X-ray and neutron crystallographic structural characterization, which reveal a $\{Ag_3(\mu_3\text{-}H)(\mu_3\text{-}Cl)\}^+$ core structure.[13,14] The gas-phase reactivity of this cluster is also explored.

Electrospray ionization mass spectrometry (ESI-MS) analysis of methanol/chloroform solutions of silver(I) trifluoroacetate $[Ag^I(tfa)]$ that had been treated with sodium borohydride in the presence of 1,1-bis(diphenylphosphino)-methane (designated hereafter as L) showed evidence of the formation of silver hydride cluster cations (Figure 1; see also the Supporting Information, Figure S1), which, based on isotope patterns (Figures S2 and S3) and high resolution accurate mass measurements (Table S1), are formulated as: $[Ag_3HL_3]^{2+}$, $[Ag_3HClL_3]^+$, $[Ag_3Cl_2L_3]^+$ and $[Ag_{10}H_8L_6]^{2+}$. The species $[Ag_3H_2L_3]^+$ was not observed in any of the spectra recorded. Replacing $NaBH_4$ with sodium borodeuteride confirmed that $NaBH_4$ is the source of the hydride in the clusters (for example, formation of $[Ag_3DL_3]^{2+}$ and not $[Ag_3HL_3]^{2+}$; Figures S4 and S5).

The observation of abundant silver hydride cluster cations by ESI-MS encouraged us to refine the condensed-phase synthetic route (Supporting Information, Method A) to allow the isolation of a crystalline salt suitable for characterization by IR and ^1H NMR spectroscopy (Figures S6 and S7, as well as supporting text), as well as structural determination by single-crystal X-ray diffraction and neutron diffraction. The presence of the abundant trinuclear silver hydride cluster ligated by the trifluoroacetate (tfa) anion, $[Ag_3H(tfa)L_3]^+$ (Figure 1), in the MS studies led us to use a silver salt with a non-coordinating anion. Indeed, treatment of silver(I) tetrafluoroborate with sodium borohydride followed by crystallization (Supporting Information, Method B) gave rise to three distinct crystalline morphologies that were revealed by X-ray crystallographic analysis to be: 1) $[Ag_3\{(Ph_2P)_2CH_2\}_3(\mu_3\text{-}Cl)(\mu_3\text{-}H)]BF_4$, (**1**; Figure 2),[15] 2) $[Ag_3\{(Ph_2P)_2CH_2\}_3(\mu_3\text{-}Cl)_2]BF_4$ (**2**; Figure S9), and 3) $NaB(OCH_3)_4$.[16]

The structure of **1** (Figure 2) features a triangular Ag_3 core surrounded by three bidentate bisphosphine ligands to give three Ag_2P_2C five-membered rings. The Ag_3 array is capped by a μ_3-chloride on one side and one μ_3-H on the other side. The Ag···Ag distances within the triangular Ag_3 array of 2.8988(2) Å are suggestive of significant argentophilic interactions. This structure is comparable to previously synthesized and structurally characterized clusters of the halides $[Ag_3X_2L_3]^+$, X = Cl, Br, I.[17] However, a marked difference is the close proximity of the silver atoms of the trinuclear silver core to the hydride (Figure 2; Ag–H distance of 1.91(2) Å) in comparison to the chloride (Ag–Cl distance of 2.859(1) Å).

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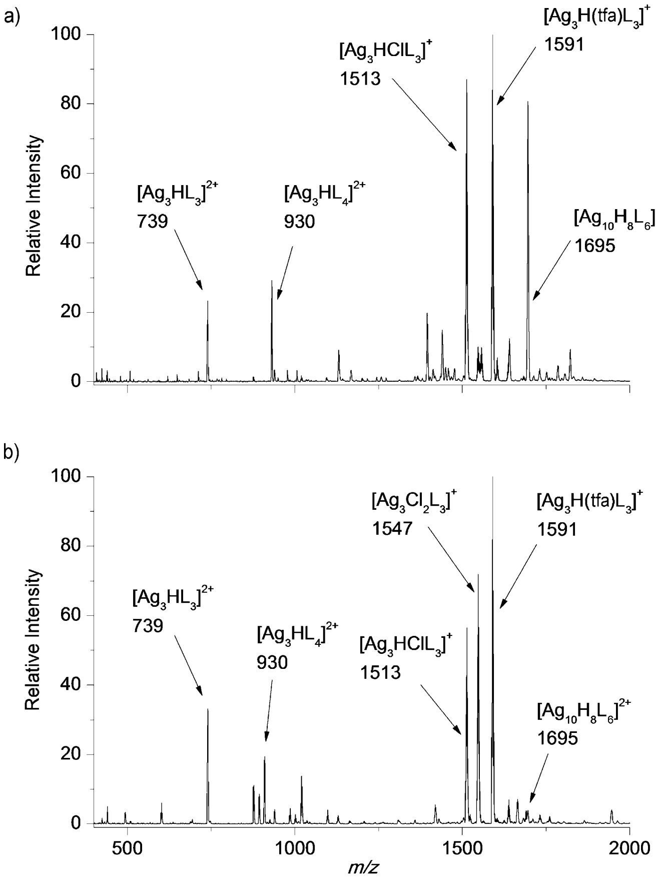

Figure 1. Full LTQ ESI-MS of silver clusters synthesized by solution phase Method A (see the Supporting Information). a) Immediately after addition of borohydride. b) After 24 h reaction time. The *m/z* values shown are of the most intense peak in the cluster. Solutions containing condensed phase silver clusters were diluted to 50 mM in methanol.

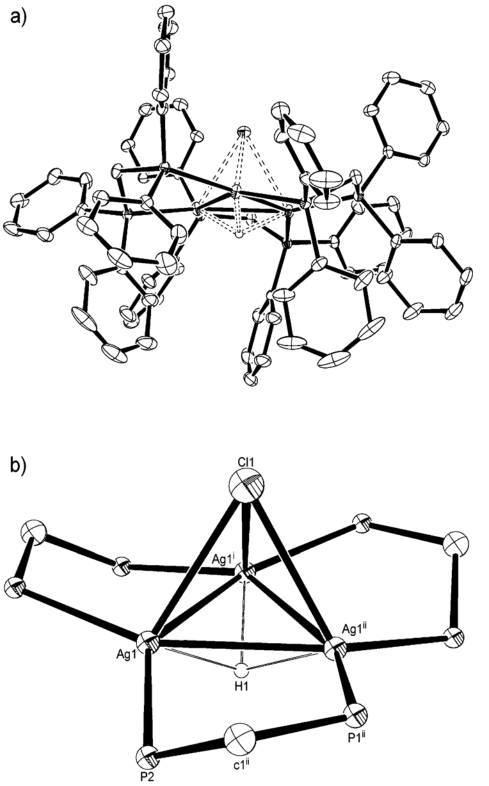

Figure 2. ORTEP-3 representations of a) the cation present in [Ag$_3${(Ph$_2$P)$_2$CH$_2$}$_3$(μ_3-Cl)(μ_3-H)]BF$_4$ and b) the distorted trigonal bipyramidal Ag(μ_3-Cl)(μ_3-H) core, where the phenyl groups are omitted for clarity. Displacement ellipsoids set at the 20% probability level. Ag(1)–Ag(1) 2.8998(4) Å, Ag(1)–Cl 2.859(1) Å; Ag(1)–P(2) 2.4421(9) Å, Ag(1)–H 1.91(2) Å. The hydrogen atom is clearly established by a neutron Laue diffraction study and is freely refinable.

This Ag–H distance is comparable to that asserted in the diselenophosphate-protected cuboctahedral silver hydride described by Liu and co-workers, which has a Ag$_4$(μ_4-H)(μ_3-Ag)$_4$ core and claims Ag–H distances from 1.8723(13) to 2.0306(17).[5b] The Laue neutron diffraction[18] study reported here (Figure 2; see also the Supporting Information) definitively locates the nuclear position of the hydride atom, despite the considerable electron density associated with the three silver atoms.

We next turned our attention to exploring the gas phase chemistry of the silver cluster cation [Ag$_3$HClL$_3$]$^+$ (*m/z* 1513). Its unimolecular chemistry was studied by collision-induced desorption (CID; Figure S10a).[19] Loss of one or two ligands to generate [Ag$_3$HClL$_2$]$^+$ [Eq. (1)] and [Ag$_3$HClL]$^+$ [Eq. (2)] were the main fragmentation pathways (Figure S8a). [Ag$_2$ClL]$^+$, [Ag$_2$ClL$_2$]$^+$, and [AgL]$^+$ were observed as very minor product ions (relative intensities of < 1%). To establish whether these are formed through secondary fragmentation of [Ag$_3$HClL$_2$]$^+$ and [Ag$_3$HClL]$^+$, each of these ions were mass selected and subjected to a further stage of CID in MS^3 experiments. The CID of [Ag$_3$HClL$_2$]$^+$ (Figure S10b) generates [Ag$_3$HClL]$^+$ as the dominant species [Eq. (3)] with [Ag$_2$ClL]$^+$ and [Ag$_2$ClL$_2$]$^+$ as the next most abundant products [Eqs. (4) and (5)]. A relatively small peak is observed at 983 *m/z*, which corresponds to the loss of neutral AgCl from the parent to yield [Ag$_2$HL$_2$]$^+$ [Eq. (6)], which is less intense than the fragmentation that arises from the loss of AgH [Eq. (5)]. The reductive elimination of HCl [Eq. (7)] is also observed; the CID of [Ag$_3$HClL]$^+$ (Figure S10c) generated [Ag$_2$ClL]$^+$ and [AgL]$^+$ as the sole ionic products [Eqs. (8) and (9)].

$$[Ag_3HClL_3]^+ \rightarrow [Ag_3HClL_2]^+ + L \tag{1}$$

$$\rightarrow [Ag_3HClL]^+ + 2L \tag{2}$$

$$[Ag_3HClL_2]^+ \rightarrow [Ag_3HClL]^+ + L \tag{3}$$

$$\rightarrow [Ag_2ClL]^+ + AgHL \tag{4}$$

$$\rightarrow [Ag_2ClL_2]^+ + AgH \tag{5}$$

$$\rightarrow [Ag_2HL_2]^+ + AgCl \tag{6}$$

$$\rightarrow [Ag_3L_2]^+ + HCl \tag{7}$$

$$[Ag_3HClL]^+ \rightarrow [Ag_2ClL]^+ + AgH \tag{8}$$

$$\rightarrow [AgL]^+ + Ag_2HCl \tag{9}$$

Finally, the bimolecular chemistry of [Ag$_3$HClL$_3$]$^+$ was examined by subjecting it to ion–molecule reactions.[20] It is unreactive towards a range of neutral molecules, such as

2-cyclohexen-1-one, 2,3-butanedione, 3-hexyne, allyl iodide, methanol, and water, several of which have been shown to react with the bare silver hydride cluster cations, $Ag_{n-1}H^+$ ($n = 3$ and 5).[3a,6a] It is likely that the bulky electron-rich phosphine ligands provide some degree of steric protection towards the approach of the substrates to the silver hydride $\{Ag_3H\}$ cluster core (Figure S11). Indeed, this is consistent with the fact that the crystalline material (Figure S12) collected from the synthesis of **1** following Method B can be stored under ambient conditions for at least 18 days, and when redissolved in methanol, the dominant species observed in the ESI mass spectrum of this solution corresponds to $[Ag_3\{(Ph_2P)_2CH_2\}_3(\mu_3\text{-Cl})(\mu_3\text{-H})]^+$ (Figure S13).

In conclusion, mass spectrometry continues to be a powerful tool to explore cluster formation and reactivity, and to direct the synthesis of novel materials.[9,12,21] Nanoclusters comprised of only a few metal atoms are particularly suitable for MS-based studies. Herein, we have shown that treatment of silver salts with sodium borohydride in the presence of a bis(phosphino) bidentate ligand yields silver hydride clusters rather than leading to the all-metallic clusters observed for related reductions of gold salts.[10] Further work is underway to study the formation, structures, physical properties, and reactions of other silver hydride nanocluster cations. The $[Ag_{10}H_8L_6]^{2+}$ cluster is particularly intriguing as a potential model for hydrogen storage.[22]

Experimental Section

Synthesis of bisdiphenylphosphino bridged silver hydride clusters (Figure 1): Silver hydride clusters were synthesized in the condensed phase. Silver(I) trifluoroacetate (2.2 mg, 0.010 mmol) and bisdiphenylphosphinomethane (3.8 mg, 0.010 mmol) in 20 mL MeOH/$CHCl_3$ (1:1) were added to a 25 mL quickfit Erlenmeyer flask equipped with a magnetic stirbar and stopper. All reagents were kept in the dark, and the flasks covered in foil. A freshly prepared solution of sodium borohydride (2.0 mg, 0.050 mmol) was then added, resulting in a color change from colorless to light yellow, thus indicating the formation of silver clusters.

Synthesis of crystalline (**1**) and (**2**): Silver (I) tetrafluoroborate (12.64 mg, 0.650 mmol) and bisdiphenylphosphinomethane (25 mg, 0.650 mmol) were added to a degassed solution of chloroform/methanol (1:1; ca. 3 mL) in a Schlenk tube covered in foil. The addition of sodium borohydride (12.3 mg, 0.325 mmol) resulted in a yellow solution, which was left at room temperature for 1 h with intermittent shaking of the contents. The solution was then frozen, layered with dry diethyl ether (ca. 10 mL), and allowed to stand undisturbed for 3 days to yield crystals (Figure S12) of $[Ag_3\{(Ph_2P)_2CH_2\}_3(\mu_3\text{-Cl})(\mu_3\text{-H})]BF_4{\cdot}0.5\,CHCl_3$ (**1**) and crystals of $[Ag_3\{(Ph_2P)_2CH_2\}_3(\mu_3\text{-Cl})_2]BF_4$ (**2**), both suitable for X-ray crystallography. A larger crystal, suitable for neutron diffraction, was manually isolated from this crystal mixture.

Mass spectrometry: Mass spectra were recorded using a Finnigan hybrid linear triple-quadrupole (LTQ) Fourier transform ion cyclotron resonance (FTICR) mass spectrometer. The silver clusters prepared in the condensed phase were introduced into the mass spectrometer via a syringe pump set at a flow rate of 5 $\mu L\,min^{-1}$ to the ESI capillary. The typical ESI conditions used, for optimum intensity of the target ions, were: spray voltage, 4.2–5.0 kV, capillary temperature, 250 °C, nitrogen sheath gas pressure, 5 (arbitrary units), capillary voltage 15 V. Selected ions were transferred to the FTICR cell for accurate mass measurement with the use of selected ion monitoring (SIM) and selected reaction monitoring (SRM) to obtain the most reliable results.

Crystal data for **1**: $C_{75-5}H_{67.5}BCl_{2.5}F_4P_6Ag_3$ $M = 1599.98$, $T = 130.0(2)$ K, $\lambda = 0.7107$ Å, cubic, space group $Pa\bar{3}$ $a = 24.1128(3)$ Å, $V = 14019.8(3)$ Å^3, $Z = 8$, $\rho_{cald} = 1.516\ mg\,M^{-3}$ μ(Mo-Kα) 1.116 mm^{-1}, X-ray: $F(000)$; 6676, crystal size 0.39 × 0.35 × 0.32 mm. 52469 reflections measured, 5359 independent reflections ($R_{int} = 0.0595$), the final R was 0.041 $[I > 3\sigma(I)]$ and $wR(F)$ (all data) was 0.075. Laue Neutron $F(000) = 2900$, crystal size 0.6 × 0.8 × 1.0 mm. 46000 reflections measured, 1147 independent reflections (Merging $R = 15(7)\,\%$, 832 $I > 3\sigma(I)$ used in refinement, the final R was 0.096 weighted = 0.090 for 217 parameters.

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