Reactive Intermediates

Gas-Phase Synthesis of $[Ag_4H]^+$ and Its Mediation of the C–C Coupling of Allyl Bromide**

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The formation of carbon–carbon bonds mediated by metal surfaces and nanoparticles continues to attract considerable attention.[1,2] Recent work on the interaction of allyl halides (C_3H_5X) with a range of metal surfaces revealed different reactivity that depends on both the metal as well as the halide.[3,4] Of all the metal surfaces examined, silver surfaces appear to be the most effective at mediating carbon–carbon bond coupling of allyl halides to give 1,5-hexadiene. Two distinct pathways have been observed:[4a] 1) dissociative adsorption of C_3H_5X to give surface-bound allyl groups, which then undergo coupling, and 2) a coupling reaction between C_3H_5X and a surface-bound allyl group. Surface defects play a significant role in the selectivity of 1,5-hexadiene formation which increases from 20% to greater than 60% when chlorine atoms are preadsorbed on silver surfaces.[4b] Also of interest are the largely forgotten results of Tamura and Kochi,[5] who synthesized silver nanoparticles over 30 years ago and showed that they reacted with allyl bromide to give 1,5-hexadiene and silver bromide [Eq. (1)]. Here we describe the gas-phase assembly of the subvalent silver hydride cluster $[Ag_4H]^{+}$[6] and its subsequent ion–molecule reactions with allyl bromide.

$$\mathrm{Ag}_x + x\,\mathrm{CH_2{=}CHCH_2Br} \rightarrow (\mathrm{AgBr})_x + x/2\,\mathrm{CH_2{=}CH(CH_2)_2CH{=}CH_2} \tag{1}$$

$[Ag_4H]^+$ was "synthesized" in the gas phase by collision-induced dissociation (CID) of a silver–amino acid precursor in a quadrupole ion trap (QIT) mass spectrometer.[7] The precursor was the silver ion cluster $[(M+Ag\text{-}H)_3+Ag]^+$ (M = *N,N*-dimethylglycine), which was formed through electrospray ionization (ESI) of a mixture of silver nitrate ($AgNO_3$) and the amino acid.[8] A total of three stages of CID (MS^4) with consecutive neutral losses of 101 Th ($-C_4H_7NO_2$; Th = Thomson) and 103 Th ($-C_4H_9NO_2$) yielded $[Ag_4H]^+$ in high abundance. Other silver clusters such as $[Ag_n]^+$ ($n = 3, 5, 7$) and $[Ag_nH]^+$ ($n = 2, 6$) have been formed in related CID reactions of $[(M+Ag\text{-}H)_m+Ag]^+$ clusters (M = glycine or *N,N*-dimethylglycine). These reactions represent the first gas-phase assembly of silver clusters mediated by simple biomolecules.[9,10] Interestingly, the anionic amino acid ligands act as the reductants; this is in contrast to the condensed-phase assembly of silver clusters and nanoparticles on biomolecular templates which requires the addition of reductants.[11]

The ion–molecule reactions of these silver clusters with the allyl halides, $CH_2{=}CHCH_2X$ (X = Cl, Br, and I) were examined.[12,13] $[Ag_4H]^+$ ($m/z = 433$)[14] exhibits the highest selectivity for C–C bond coupling with allyl bromide, $CH_2{=}CHCH_2Br$ (Figure 1). The first molecule of allyl bromide reacts with $[Ag_4H]^+$ by a metathesis reaction to yield $[Ag_4Br]^+$ ($m/z = 511$)[14] as the major ionic product (Figure 1a and Equation (2)). $[Ag_4Br]^+$ subsequently reacts with a second molecule of allyl bromide to form the ion $[Ag_4Br_2(C_3H_5)]^+$ ($m/z = 633$)[14] (Figure 1b, Equation (3)). Reaction of $[Ag_4Br_2(C_3H_5)]^+$ with a third molecule of allyl bromide results in the formation of the silver organometallic ion $[Ag(C_3H_5)_2]^+$ ($m/z = 189$)[14] in combination with the neutral cluster $[Ag_3Br_3]$[15] (Figure 1c, Equation (4)). Overall, these equations combine to give a rare example of a metal-mediated C–C bond-coupling reaction [Eq. (5)] in the gas phase.[16]

$$[\mathrm{Ag_4H}]^+ + \mathrm{CH_2{=}CHCH_2Br} \rightarrow [\mathrm{Ag_4Br}]^+ + \mathrm{CH_2{=}CHCH_3} \tag{2}$$

$$[\mathrm{Ag_4Br}]^+ + \mathrm{CH_2{=}CHCH_2Br} \rightarrow [\mathrm{Ag_4Br_2(C_3H_5)}]^+ \tag{3}$$

$$[\mathrm{Ag_4Br_2(C_3H_5)}]^+ + \mathrm{CH_2{=}CHCH_2Br} \rightarrow [\mathrm{Ag(C_3H_5)_2}]^+ + [\mathrm{Ag_3Br_3}] \tag{4}$$

$$[\mathrm{Ag_4H}]^+ + 3\,\mathrm{CH_2{=}CHCH_2Br} \rightarrow [\mathrm{Ag(C_3H_5)_2}]^+ + [\mathrm{Ag_3Br_3}] + \mathrm{CH_2{=}CHCH_3} \tag{5}$$

Additional CID studies and DFT (density functional theory) calculations[17] were carried out to gain further support that C–C bond coupling had occurred. CID of $[Ag(C_3H_5)_2]^+$ results in only the formation of Ag^+ [Eq. (6)]. No formation of $[Ag(C_3H_5)]^+$ through the loss of an allyl radical is observed. These results suggest that C–C bond coupling has occurred, however no information about the

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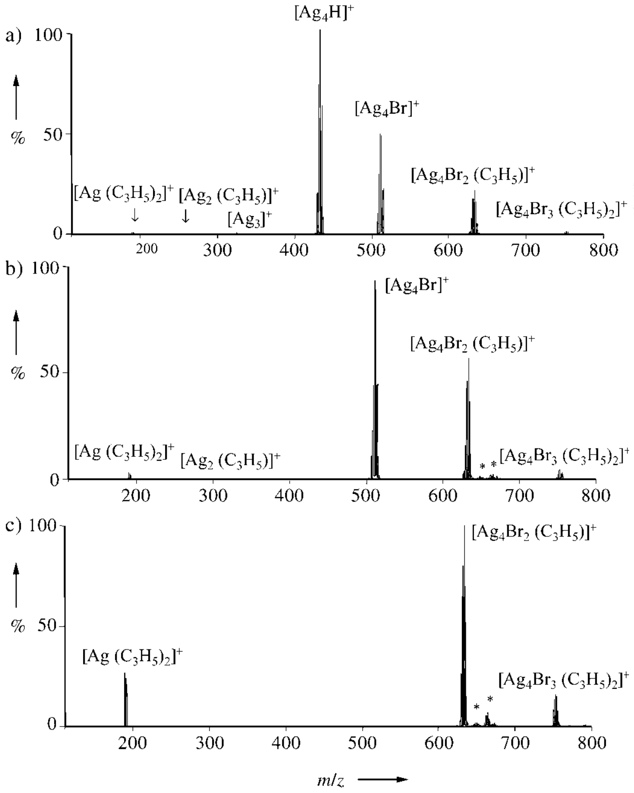

Figure 1. Ion–molecule reactions of allyl bromide with the following mass-selected ions: a) $[Ag_4H]^+$ ($m/z = 433$) to produce $[Ag_4Br]^+$ ($m/z = 511$), b) $[Ag_4Br]^+$ ($m/z = 511$) to produce $[Ag_4Br_2(C_3H_5)]^+$, and c) $[Ag_4Br_2(C_3H_5)]^+$ ($m/z = 633$) to produce $[Ag(C_3H_5)_2]^+$ ($m/z = 189$). The presence of H_2O and MeOH adducts is marked with asterisks. All spectra shown were acquired after a reaction time of 30 ms and a constant pressure of approximately 1×10^{-7} Torr of the neutral reagent C_3H_5Br.

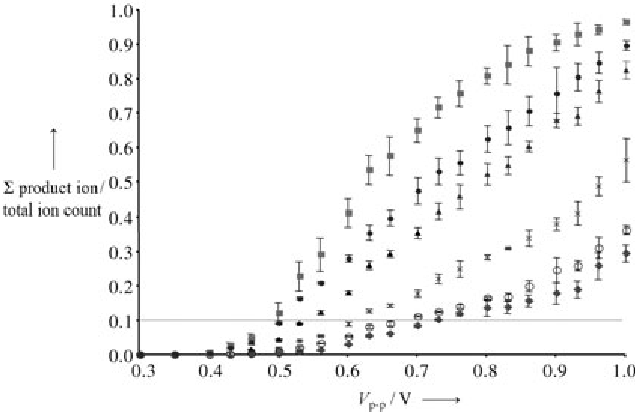

Figure 2. Energy-resolved CID spectra of various isomeric $[Ag(C_6H_{10})]^+$ ions. Plot of reaction extent (Σ product ions/total ion count) versus activation voltage ($V_{p\text{-}p}$) for the elimination of C_6H_{10} ligands from the complexes $[Ag(L)]^+$ (L = 1,3-hexadiene (■), 1,4-hexadiene (▲), 2,4-hexadiene (×), 1,5-hexadiene (○), cyclohexane (●), and the $[Ag(C_3H_5)_2]^+$ ion formed (◆; see Figure 1 c and Equation (4)). The horizontal line corresponds to the 10% arbitrary threshold at which the reactivity of each of the isomeric $[Ag(C_6H_{10})]^+$ ions can be compared. The error bars represent the standard deviation of the three independent measurements for each $[Ag(C_6H_{10})]^+$ ion.

structure of the $(C_3H_5)_2$ ligand is provided. Although there are many ligands with a molecular formula of C_6H_{10} that could fragment by the loss of a ligand [Eq. (6)], previous condensed-phase studies suggest that the most likely coupled product is 1,5-hexadiene.[4,5] Thus, energy-resolved CID[18] was used to gain insight into the nature of the coupled product by comparing the energy-resolved CID spectrum of the product of [Eq. (5)] to those of authentic ion structures formed independently by ESI-MS.[19] Figure 2 shows the energy-resolved CID spectra of six $[Ag(C_3H_5)_2]^+$ systems: 1) the ion of "unknown" structure formed through the reaction depicted in [Eq. (5)], 2) the $[Ag(1,5\text{-hexadiene})]^+$ ion with an authentic structure, 3) the isomeric $[Ag(1,3\text{-hexadiene})]^+$ ion, 4) the isomeric $[Ag(1,4\text{-hexadiene})]^+$ ion, 5) the isomeric $[Ag(2,4\text{-hexadiene})]^+$ ion, and 6) the isomeric $[Ag(\text{cyclohexene})]^+$ ion. It is clear that the energy-resolved CID spectrum of $[Ag(C_3H_5)_2]^+$ formed by [Eq. (5)] closely matches that of the authentic $[Ag(1,5\text{-hexadiene})]^+$ ion. Moreover, the $[Ag(L)]^+$ ions (L = 1,3-hexadiene, 1,4-hexadiene, 2,4-hexadiene, cyclohexene) all require less energy to dissociate, suggesting that these ligands have lower Ag^+ binding energies.[19–22] Assuming that the 10% threshold in Figure 2 is an indicator of the relative binding energies, this suggests a relative Ag^+ binding order 1,3-hexadiene ≈ cyclohexene < 1,4-hexadiene < 2,4-hexadiene < 1,5-hexadiene. Although we have not quantified the experimental binding energies, these gas-phase results are consistent with equilibrium constants of silver–diene complexes determined by GC which show that the most stable complexes are those in which the two double bonds are separated by two methylene units.[23,24]

$$[Ag(C_3H_5)_2]^+ \rightarrow Ag^+ + (C_3H_5)_2 \qquad (6)$$

To gain further insight into these isomeric $[Ag(L)]^+$ complexes (L = 1,3-hexadiene, 1,4-hexadiene, 2,4-hexadiene, 1,5-hexadiene, cyclohexene), we carried out further DFT calculations.[17,22] Although the ranking of the relative binding energies of the ligands (1,3-hexadiene (33.6 $kcal\,mol^{-1}$) < 2,4-hexadiene (35.2 $kcal\,mol^{-1}$) < 1,4-hexadiene (45.1 $kcal\,mol^{-1}$) < cyclohexene (47.0 $kcal\,mol^{-1}$) < 1,5-hexadiene (52.1 $kcal\,mol^{-1}$)) is different to that of Figure 2, both experiment and theory suggest that Ag^+ binds strongest to 1,5-hexadiene and that the product of the reactions described in [Eqs. (2)–(4)] is $[Ag(1,5\text{-hexadiene})]^+$.[21] Further calculations allow us to evaluate the overall energetics associated with the reactions described in [Eqs. (2)–(4)] by estimating the overall energy of the reaction in Equation (5) for the case where the product is $[Ag(1,5\text{-hexadiene})]^+$. The overall reaction sequence is determined to be exothermic by −166.3 $kcal\,mol^{-1}$ from the DFT data, consistent with the formation of the $[Ag(1,5\text{-hexadiene})]^+$ product ion through ion–molecule reactions at the near room temperature conditions of the QIT.[7b]

The gas-phase reactivity of the silver $[Ag_4H]^+$ cluster appears to represent a simple molecular model for the C–C bond coupling of allyl bromide mediated by silver surfaces[4] and nanoparticles.[5] Remarkably, the hydrogen defect plays a significant role in initiating the reaction sequence by [Eq. (2)] as the "pure" $[Ag_3]^+$ and $[Ag_5]^+$ silver clusters do not react with allyl bromide to promote C–C bond coupling. This appears to be consistent with the observation that chlorine surface defects play a role in the selectivity for 1,5-hexadiene formation on silver surfaces.[4b] Further work is underway to examine other aspects of metal-mediated C–C bond coupling reactions in the gas phase.

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[20] The isomeric $[Ag(L)]^+$ complexes (L = 1,3-hexadiene, 1,4-hexadiene, 2,4-hexadiene, 1,5-hexadiene, cyclohexene) also exhibit different bimolecular reactivity towards neutral reagents such as water and methanol (data not shown).

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