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Role of cluster size and substrate in the gas phase C–C bond coupling reactions of allyl halides mediated by Ag_n^+ and $Ag_{n-1}H^+$ cluster cations

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Dedicated to Prof. Mike Bowers, on the occasion of his 70th birthday and in recognition of his important contributions to organic, inorganic, organometallic and biological mass spectrometry and his service to the scientific community.

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ABSTRACT

Previous studies have demonstrated that the silver hydride cluster cation Ag_4H^+ promotes C—C bond coupling of allylbromide [G.N. Khairallah, R.A.J. O'Hair, Angewandte Chemie International Edition 44 (2005) 728]. Here the influence of both the nature and the size of the silver cluster cation and the substrate on C—C bond coupling are examined. Thus each of the cations Ag_2H^+, Ag_4H^+, $Ag_3{}^+$, and $Ag_5{}^+$ were allowed to react with three different halides: allyl chloride, allyl bromide and allyl iodide. No C—C bond coupling is observed in the reactions of the cluster cations with allyl chloride. There are four main reaction sequences that result in C—C bond coupling for allyl bromide and allyl iodide mediated by Ag_n^+ and $Ag_{n-1}H^+$ clusters:

(i) A sequence involving the reactions of silver cluster cations with two molecules of C_3H_5X: $Ag_n{}^+ \rightarrow Ag_n(C_3H_5X)^+ \rightarrow Ag_nX_2{}^+$. This only occurs in the cases of: $n = 3$ and X = I; $n = 5$ and X = Br.
(ii) A sequence involving the reactions of silver cluster cations with two molecules of C_3H_5X via an organometallic intermediate: $Ag_n{}^+ \rightarrow Ag_{n-1}(C_3H_5)^+ \rightarrow Ag_{n-1}X^+$. This only occurs in the cases of: $n = 5$ and X = Br and I.
(iii) A sequence involving the reactions of silver hydride cluster cations with three molecules of C_3H_5X: $Ag_{n-1}H^+ \rightarrow Ag_{n-1}X^+ \rightarrow Ag_{n-1}X(C_3H_5X)^+ \rightarrow Ag(C_3H_5)_2{}^+$ and $Ag_{n-1}X_3{}^+$. This only occurs in the cases of: $n = 5$ and X = Br and I.
(iv) A sequence involving the reactions of silver hydride cluster cations with three molecules of C_3H_5X via an organometallic intermediate: $Ag_{n-1}H^+ \rightarrow Ag_{n-1}X^+ \rightarrow Ag_{n-3}(C_3H_5)^+ \rightarrow Ag(C_3H_5)_2{}^+$ and $Ag_{n-3}X^+$. This only occurs in the cases of: $n = 5$ and X = I.

1. Introduction

Metal mediated C—C coupling reactions represent the cornerstone of many organic syntheses since they allow the assembly of complex carbon frameworks from readily available precursors in predictable ways [1–3]. Despite decades of use, there is still much interest in developing new approaches for C—C bond coupling, and recent attention has focussed on a range of areas including the development of new catalysts [4], design of water based organometallics [5] and the use of metallic nanoparticles [6]. One of the most widely studied classes of C—C bond coupling reactions are metal mediated reductive coupling of organohalides, the so called "Wurtz" reaction [7]. For example, reductive coupling of allylhalides has been examined with a range of metal species [8–23] including gas phase iron cations [24] and metal surfaces [25–27]. Both silver surfaces [28,29] and silver nano-particles [30] are effective at mediating carbon—carbon bond coupling of allyl halides to give 1,5-hexadiene. Two distinct pathways have been observed for silver surfaces [28]: (i) dissociative adsorption of C_3H_5X to give surface bound allyls, which then undergo coupling; (ii) a coupling reaction between C_3H_5X and a surface bound allyl group. This surface chemistry has analogies with the organometallic chemistry of allylhalides, where coupling can occur via: (i) reductive elimination from bis allyl organometallics [31,32]; (ii) the reaction between an allylorganometallic and an allylsubstrate [33]. Other mechanisms can operate in organometallic chemistry including dissociation via allyl radical formation [34].

One of the powerful aspects of gas phase metal cluster chemistry is that it is possible to examine reactivity as a function of cluster size using mass spectrometry based techniques [35]. The gas phase formation and ion-molecule reactions of silver cluster ions have been

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examined by a number of groups [36–42]. The Bowers group has made a number of important contributions to size selective effects in silver cluster cation reactions [43–47]. Most of these previous studies utilized laser based methods to generate silver cluster ions. In contrast, we have discovered that silver and silver hydride cluster cations can be synthesized in the gas phase via the combined use of electrospray ionisation and collision induced dissociation on silver amino acid clusters [48]. Using this method, we have been exploring analogies between the chemistry of these gas phase clusters [49–51] and silver surfaces [28,29] and silver nanoparticles [30]. Thus we have shown that the Ag_4H^+ cluster mediates C—C bond coupling with allylbromide, $CH_2{=}CHCH_2Br$ [51]. In the first step, allylbromide reacts with Ag_4H^+ via a metathesis reaction to yield Ag_4Br^+ (Eq. (1)), which subsequently reacts with a second molecule of allylbromide to form the ion $Ag_4Br_2(C_3H_5)^+$ (Eq. (2)). Reaction of $Ag_4Br_2(C_3H_5)^+$ with a third molecule of allylbromide results in the formation of the silver organometallic ion $Ag(C_3H_5)_2{}^+$ in combination with the neutral cluster Ag_3Br_3 (Eq. (3)). Overall these equations combine to give the C—C bond coupling reaction (Eq. (4)). CID of $Ag(C_3H_5)_2{}^+$ results in the sole formation of Ag^+ (Eq. (5)), providing support that C—C bond coupling had occurred. Furthermore, the identity of the C—C bond coupled C_6H_{10} product was shown to be 1,5-hexadiene via a comparison of the energy resolved collision induced dissociation (CID) spectrum of the $Ag(C_6H_{10})^+$ ion with a range of ions of "authentic" structures. Thus this small gas phase cluster appears to be a simple molecular model for C—C bond coupling on silver surfaces and nanoparticles. More recently, we have shown that allyiodide reacts with silver and silver hydride cluster cations via a range of pathways including iodine abstraction [49]. Here we used the multistage mass spectrometry capabilities of the quadrupole ion trap mass spectrometer [52] to examine the role of both the silver cluster as well as the substrate in C—C bond coupling by comparing the reactions of the silver, $Ag_n{}^+$, and silver hydride, $Ag_{n-1}H^+$, cluster cations ($n = 3$ and 5) with the allyl halides, $CH_2{=}CHCH_2X$ (where X = Cl, Br and I).

$$Ag_4H^+ + CH_2{=}CHCH_2Br \rightarrow Ag_4Br^+ + CH_2{=}CHCH_3 \quad (1)$$

$$Ag_4Br^+ + CH_2{=}CHCH_2Br \rightarrow Ag_4Br_2(C_3H_5)^+ \quad (2)$$

$$Ag_4Br_2(C_3H_5)^+ + CH_2{=}CHCH_2Br \rightarrow Ag(C_3H_5)_2{}^+ + Ag_3Br_3 \quad (3)$$

$$Ag_4H^+ + 3CH_2{=}CHCH_2Br \rightarrow Ag(C_3H_5)_2{}^+ + Ag_3Br_3 + CH_2{=}CHCH_3 \quad (4)$$

$$Ag(C_3H_5)_2{}^+ \rightarrow Ag^+ + (C_3H_5)_2 \quad (5)$$

2. Experimental

All reagents were used as supplied: $AgNO_3$ (Chem-Supply, Australia), Glycine [Gly, H_2NCH_2COOH] (Sigma), Dimethyl glycine [DMGly, $(CH_3)_2NCH_2COOH$] (Aldrich Chemical Co.), and allyl halides [C_3H_5X, X = Cl, Br, I] (Aldrich Chemical Co.).

All experiments were carried out using a modified commercial ion trap mass spectrometer (Finnigan Mat) as described in detail elsewhere [53,54]. The gas phase "synthesis" of the silver and silver hydride cluster cations has been described in detail previously [49]. Briefly, electrospray samples were prepared in 50:50:1 methanol:water:acetic acid solutions and the desired reactants mixed in a *ca.* 1:3 ratio ($AgNO_3$:Glycine (or DMGly)) and directly injected in the mass spectrometer via the ESI probe at a rate of 5 μL/min. The sheath air, capillary voltage and temperature were adjusted to *ca.* 30–60, 4.2–4.8 kV and 150–200 °C, respectively. The CID experiments were performed following standard procedures [53,54] by mass selecting the desired precursor ion, with a selection window of 1.5–15 Th (depending on the desired isotope distribution), and then subjecting it to a corresponding normalized collision energy of 12–40 and an activation (*Q*) of 0.25–0.45 for a period of *ca.* 30–100 ms. The acquisition mass range was between 100 and 1250 Th. When undertaking the ion-molecule reactions, the desired cluster was trapped and the neutral reagent was introduced via the custom made delivery line [53,54] at a known background pressure.

2.1. Rate measurements

For all the rate measurements, the neutral reagent concentration was kept constant while the ion-molecule reaction time was varied between 1 and 10,000 ms. A new helium inlet was recently installed. Since this inlet delivers both the helium and the neutral reagents into the trap, the entire system was recalibrated to the literature S_N2 rate between bromide and methyliodide, as discussed in a previous paper [53].

2.2. Branching ratios

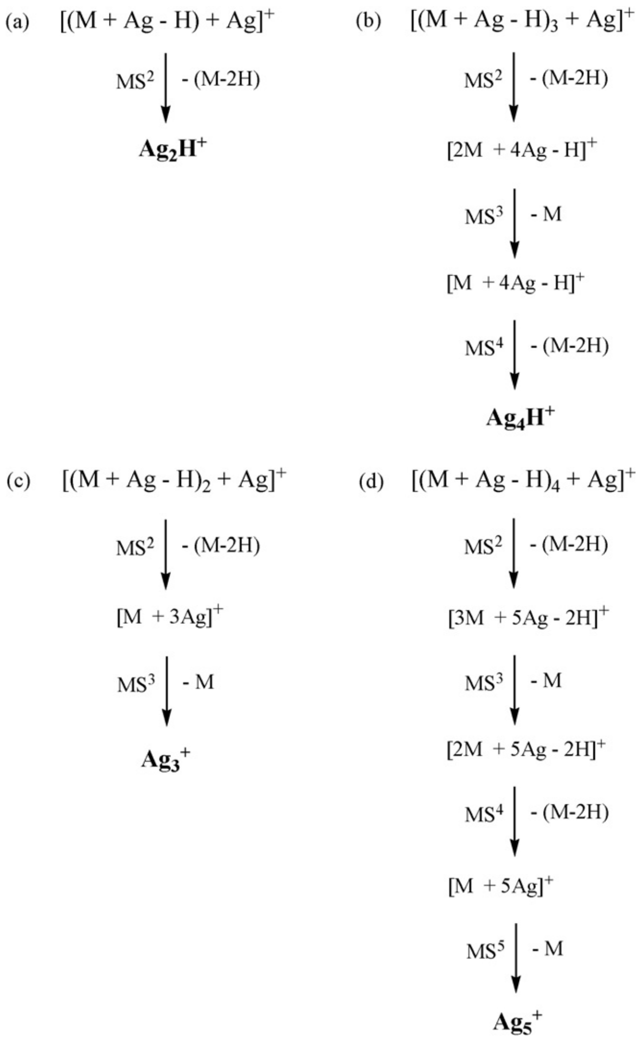
Spectra from the rate measurements were used to determine the branching ratios for different reaction channels. These spectra were chosen at short reactions times so as to minimize the secondary reactions products. The branching ratios were determined by integrating the ion signal across the isotope cluster for each of the different reaction channels. In cases of fast reactions, the signal from the secondary products were integrated and added to that of the appropriate primary reaction channel. The branching ratios are uncorrected for mass discrimination.

3. Results

The silver hydride and silver cluster cations can be formed via CID on a range of different precursors, as discussed in detail in a previous publication [49]. The specific routes to the formation of Ag_2H^+, Ag_4H^+, $Ag_3{}^+$ and $Ag_5{}^+$ are given in Scheme 1. Briefly:

(1) Ag_2H^+ was formed in a MS^2 sequence (Scheme 1a) in which $[(Gly + Ag\text{-}H) + Ag]^+$ was subjected to CID and the main fragmentation channel involved the loss of (Gly-2H) and formation of Ag_2H^+.
(2) Ag_4H^+ was formed in a MS^4 sequence (Scheme 1b) in which $[(DMGly + Ag\text{-}H)_3 + Ag]^+$ was subjected to three stages of CID and the final main fragment corresponded to the formation of Ag_4H^+ which involved the total loss of (3DMGly-4H).
(3) $Ag_3{}^+$ was formed in a MS^3 sequence (Scheme 1c) in which $[(DMGly + Ag\text{-}H)_2 + Ag]^+$ was subjected to two steps of CID and the final main fragment corresponded to formation of $Ag_3{}^+$ which involved the total loss of (2DMGly-2H).
(4) $Ag_5{}^+$ was formed in a MS^5 sequence (Scheme 1d) in which $[(DMGly + Ag\text{-}H)_4 + Ag]^+$ was subjected to four steps of CID and the final main fragment corresponded to formation of $Ag_5{}^+$ which involved the total loss of (4DMGly-4H).

The metal mediated C—C bond coupling reactions of the allyl halides depend on both the size of the silver or silver hydride cluster cations as well as the nature of the halide. Given that the C—C bond coupling reactions are multistep reactions (e.g., Eqs (1)–(3)), we first present the ion-molecule reaction product spectra at intermediate reaction times and describe the overall reaction kinetics associated with the decay of the Ag_2H^+, Ag_4H^+, $Ag_3{}^+$ and $Ag_5{}^+$ in the presence of each of the three different allylhalides (i.e., a total of twelve different systems). We next describe the: primary reaction channels observed; and the subsequent reactions associated with each of the twelve systems. The requirements for specific types of C—C bond coupling and potential types of mechanisms are described in Section 4.



Scheme 1. Fragmentation of amino acid clusters $[(M + Ag\text{-}H)_n + Ag]^+$ to form: (a) Ag_2H^+ (where M = glycine); (b) Ag_4H^+ (where M = N,N-dimethylglycine); (c) $Ag_3{}^+$ (where M = N,N-dimethylglycine); (d) $Ag_5{}^+$ (where M = N,N-dimethylglycine).

3.1. Reactions of Ag_2H^+, Ag_4H^+, $Ag_3{}^+$ and $Ag_5{}^+$ with allylchloride, allylbromide and allyliodide

3.1.1. Spectra and kinetics

A range of different types of primary products are formed as described further below, and many of these undergo subsequent ion-molecule reactions with the allylhalide to form a series of different types of product ions. Each of the 12 different combinations of cluster ion and allyliodide were studies over a wide range of reaction times. Table 1 lists the overall reaction trends for all systems studied, while Figs. 1–3 show the ion-molecule reactions of Ag_2H^+, Ag_4H^+, $Ag_3{}^+$ and $Ag_5{}^+$ with allylchloride (Fig. 1a–d), allylbromide (Fig. 2a–d) and allyliodide (Fig. 3a–d), respectively. Intermediate reaction times were chosen for these figures to show the reactant ion as well as primary and subsequent product ions. For the sake of simplicity, we label the $[Ag_aX_b(C_3H_5)_c]^+$ (with X = Cl, Br, I) product ions as (a,b,c) in these figures, to reflect the numbers of silver, halide and allyl components of the product ion clusters.

A general comparison of Figs. 1–3 and shows that the reactions of the cluster cations: with allyliodide (Fig. 3) give the richest series of product ions; follow a reactivity order of allylchloride (Fig. 1) < allylbromide (Fig. 2) < allyliodide (Fig. 3). This is bourne out by the kinetic studies summarized in Table 1. In this table, comparing the reaction efficiencies for the same allyl halide, one can observe that the efficiency increases from the smaller cluster to the larger one (i.e., from Ag_2H^+ to Ag_4H^+ and from $Ag_3{}^+$ to $Ag_5{}^+$) with $Ag_5{}^+$ being the most reactive of all the cluster cations. The presence of an “H defect” changes the reactivity in an unpredictable order. Thus while Ag_2H^+ is more reactive than $Ag_3{}^+$, the order is reversed for Ag_4H^+ and $Ag_5{}^+$. This table also clearly shows the increase in reaction efficiency, in the order: allylchloride < allylbromide < allyliodide.

3.1.2. Primary reaction channels

An examination of Figs. 1–3 shows that the silver hydride and silver cluster cations exhibit different types of primary product ions and that the relative yields of these primary product ions vary as a function of both the cluster size and allylhalide used.

3.1.2.1. Primary products arising from Ag_2H^+ and Ag_4H^+. Only two types of primary reactions are generally observed between $Ag_{n-1}H^+$ clusters and the allylhalides: adduct formation (Eq. (6a)); and the metathesis reaction, which results in the formation of the silver halide cluster cations, $Ag_{n-1}X^+$ (Eq. (6b)). Which of these reactions is observed, depends on both the size of the clusters as well as the substrate. Adduct formation (Eq. (6a)) occurs in the following three cases: $n = 3$, X = Cl (Fig. 1a) and Br (Fig. 2a); $n = 5$, X = Cl (Fig. 1b). The metathesis reaction (Eq. (6b)) is observed in the following cases: $n = 3$, X = Br (Fig. 2a) and I (Fig. 3a); $n = 5$, X = Cl (Fig. 1b), Br (Fig. 2b) and I (Fig. 3b). This metathesis reaction appears to be favoured for the more reactive halides (it follows the order allyliodide > allylbromide > allylchloride) and for the larger cluster, Ag_4H^+. Both types of primary products formed in Eqs. (6a) and (6b) undergo

Table 1
Kinetics associated with the ion-molecule reactions of Ag_2H^+, Ag_4H^+, $Ag_3{}^+$, and $Ag_5{}^+$ with allyl chloride, allyl bromide and allyl iodide.

Substrate	Rate data[a]	Ag_2H^+	Ag_4H^+	$Ag_3{}^+$	$Ag_5{}^+$
Allyl chloride	Absolute rate, $k_{\text{experimental}}$	1.81E−10	5.46E−10	5.72E−11	1.49E−9
	$k_{\text{theoretical}}$[b]	1.54E−9	1.43E−9	1.47E−9	1.43E−9
	Reaction efficiency[c]	3.7%	11.9%	1.2%	33.0%
Allyl bromide	Absolute rate, $k_{\text{experimental}}$	7.64E−10	2.35E−9	2.13E−10	3.95E−9
	$k_{\text{theoretical}}$[b]	1.28E−9	1.16E−9	1.16E−9	1.14E−9
	Reaction efficiency[c]	18.6%	63.3%	5.5%	108.3%
Allyl iodide	Absolute rate, $k_{\text{experimental}}$	2.54E−9	3.18E−9	1.19E−9	3.77E−9
	$k_{\text{theoretical}}$[b]	1.15E−9	1.02E−9	1.06E−9	0.99E−9
	Reaction efficiency[c]	69.0%	97.4%	35.1%	119.0%

[a] Units of $cm^3\ molecule^{-1}\ s^{-1}$.

[b] Calculated using the theory of Chesnavich et al. [W.J. Chesnavich, T. Su, M.T. Bowers, Journal of Chemical Physics 72 (1980) 2641]. The calculation was done using the program COLRATE [K.F. Lim, Quantum Chemistry Program Exchange 14 (1994) 3].

[c] Reaction efficiency = $k_{\text{experimental}}/k_{\text{theoretical}} \times 100$.

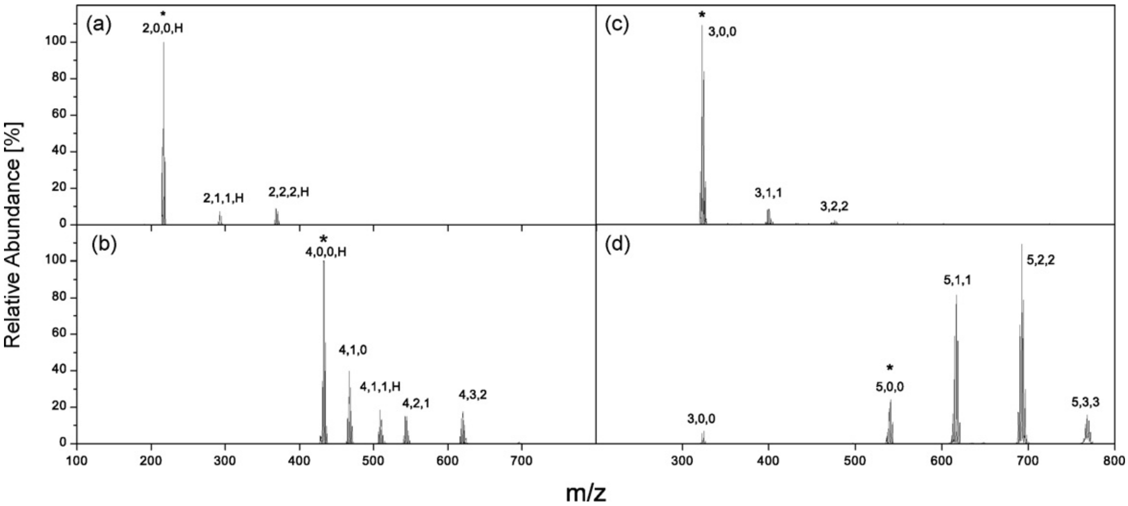


Fig. 1. Ion-molecule reactions of allylchloride (concentration of neutral = ca. 3×10^9 molecules cm^{-3}) with: (a) Ag_2H^+ (reaction time = 300 ms); (b) Ag_4H^+ (reaction time = 300 ms); (c) $Ag_3{}^+$ (reaction time = 300 ms); (d) $Ag_5{}^+$ (reaction time = 300 ms). The mass selected precursor ion is designated with a *.

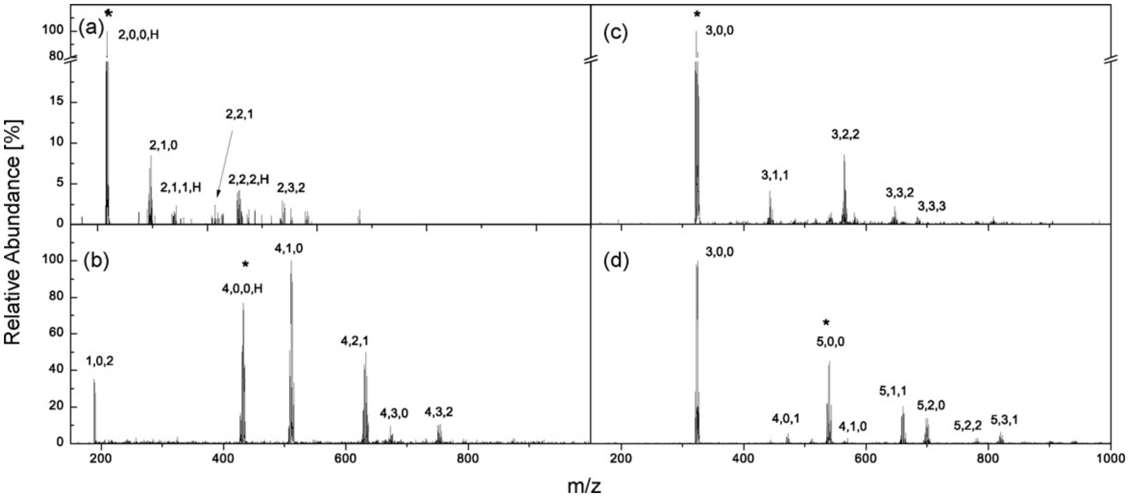


Fig. 2. Ion-molecule reactions of allylbromide (concentration of neutral = ca. 3.5×10^9 molecules cm^{-3}) with: (a) Ag_2H^+ (reaction time = 100 ms); (b) Ag_4H^+ (reaction time = 100 ms); (c) $Ag_3{}^+$ (reaction time = 100 ms); (d) $Ag_5{}^+$ (reaction time = 100 ms). The mass selected precursor ion is designated with a *.

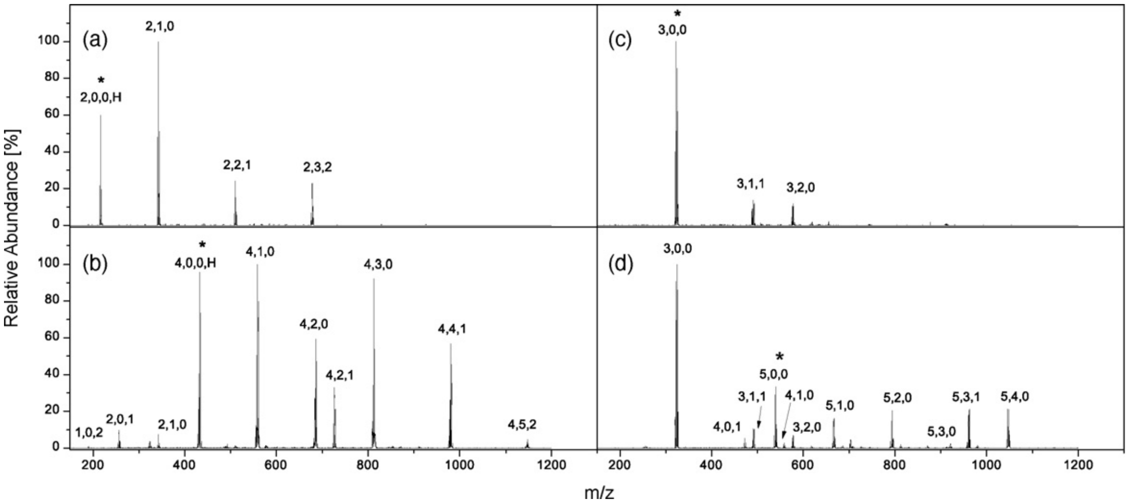


Fig. 3. Ion-molecule reactions of allyliodide (concentration of neutral = ca. 4×10^9 molecules cm^{-3}) with: (a) Ag_2H^+ (reaction time = 60 ms); (b) Ag_4H^+ (reaction time = 60 ms); (c) $Ag_3{}^+$ (reaction time = 60 ms); (d) $Ag_5{}^+$ (reaction time = 60 ms). The mass selected precursor ion is designated with a *.

further reactions as described in Section 3.1.3.1.

$$Ag_{n-1}H^{+} + C_3H_5X \rightarrow Ag_{n-1}H(C_3H_5X)^{+} \quad (6a)$$

$$Ag_{n-1}H^{+} + C_3H_5X \rightarrow Ag_{n-1}X^{+} + C_3H_6 \quad (6b)$$

3.1.2.2. Primary products arising from Ag_3^+ and Ag_5^+. The Ag_n^+ clusters undergo a more diverse set of reactions with the allylhalides, including: adduct formation (Eq. (7a)); halide atom abstraction with concomitant formation of the allyl radical (Eq. (7b)); and two addition reactions that proceed via cluster fragmentation. The first addition/cluster fragmentation reaction results in the formation of the organometallic cluster, $Ag_{n-1}(C_3H_5)^+$, and presumably the silver halide (Eq. (7c)). The second yields the silver cluster cation, Ag_3^+ (Eq. (7d)). Since the neutrals of these reactions are not detected, the neutral(s) associated with Eq. (7d) may either be an organometallic silver dimer or two monomers: allylsilver and the silver halide. Which of the four reactions (Eqs. (7a)–(7d)) are observed depends on both the size of the cluster as well as the substrate. Adduct formation (Eq. (7a)) is observed in all cases except for $n = 5$ and allyliodide, and is the only primary pathway observed for the smaller cluster cation, Ag_3^+. Halide atom abstraction (Eq. (7b)) is only observed for Ag_5^+ reacting with allyliodide (Fig. 3d). Formation of the organometallic cation, $Ag_{n-1}(C_3H_5)^+$ (Eq. (7c)), mainly occurs for allyliodide (Fig. 3d), although it is also observed for allylbromide (Fig. 2d). The Ag_3^+ product is observed in all the reactions of Ag_5^+ with the allylhalides (Eq. (7d), Figs. 1d, 2d and 3d). Each of these primary products can undergo subsequent reactions with the allylhalide as described in Section 3.1.3.2.

$$Ag_n^{+} + C_3H_5X \rightarrow Ag_n(C_3H_5X)^{+} \quad (7a)$$

$$Ag_n^{+} + C_3H_5X \rightarrow Ag_nX^{+} + C_3H_5^{\bullet} \quad (7b)$$

$$Ag_n^{+} + C_3H_5X \rightarrow Ag_{n-1}(C_3H_5)^{+} + AgX \quad (7c)$$

$$Ag_n^{+} + C_3H_5X \rightarrow Ag_{n-2}^{+} + [Ag_2, C_3H_5, X] \quad (7d)$$

3.1.3. Subsequent reactions of the primary products

Here we solely consider the product ions of Eqs. (6) and (7) undergoing further reactions with the allylhalides. In some cases addition reactions with background ESI solvent molecules (water and methanol) are observed, but these tend to be very minor products and are thus not discussed further. Our approach to unravelling the sequential reactions has been twofold: (i) the reaction time has been varied to see how the primary product ions change and what new product ions appear; (ii) the various primary product ions have been mass selected to directly establish how they react with the allylhalide. In order to help navigate the reader through the discussions below on the diverse number of subsequent reactions, we have summarized which reactions occur for the allylhalides reacting with Ag_2H^+ and Ag_4H^+ (Table 2) and with Ag_3^+ and Ag_5^+ (Table 3).

3.1.3.1. Subsequent reactions arising from the primary products formed in Eqs. (6) from Ag_2H^+ and Ag_4H^+. The products of the reactions shown in Eqs. (6a) and (6b) undergo a series of further reactions with the allyl halides as laid out in Table 2 (Eqs. (8)–(12)). The key secondary reactions are described by Eqs. (8) and (9). Bis-adduct formation (Eq. (8)) only occurs in the case of $n = 3$ and X = Cl, Br (Figs. 1a and 2a).

$$Ag_{n-1}H(C_3H_5X)^{+} + C_3H_5X \rightarrow Ag_{n-1}H(C_3H_5X)_2^{+} \quad (8)$$

The metathesis product, $Ag_{n-1}X^+$, can undergo three possible reactions. Adduct formation (Eq. (9a)) occurs in all cases except in the cases of $n = 3$ and X = Cl, Br (Figs. 1a and 2a). Addition and cluster fragmentation (Eq. (9b)) only occurs in the case of $n = 5$ and X = I (Fig. 3b). Related cluster fragmentation reactions have been observed for Aluminium cluster anions reacting with Chlorine [55]. Similarly, the abstraction of another halide (Eq. (9c)) only occurs in the case of $n = 5$ and X = I (Fig. 3b).

$$Ag_{n-1}X^{+} + C_3H_5X \rightarrow Ag_{n-1}X(C_3H_5X)^{+} \quad (9a)$$

$$Ag_{n-1}X^{+} + C_3H_5X \rightarrow Ag_{n-3}(C_3H_5)^{+} + [Ag_2, X_2] \quad (9b)$$

$$Ag_{n-1}X^{+} + C_3H_5X \rightarrow Ag_{n-1}X_2^{+} + C_3H_5^{\bullet} \quad (9c)$$

The secondary products formed in Eqs. (9) can undergo further reactions with the allylhalide (Table 2, Eqs. (10)–(12)). For example, the $Ag_{n-1}X(C_3H_5X)^+$ product ion (formed in Eq. (9a)) can undergo a further addition reaction (Eq. (10a)) in the case of $n = 5$ with X = Cl (Fig. 1b), Br (Fig. 2b) and $n = 3$ with X = Br (Fig. 2a), I (Fig. 3a). Interestingly, two related C—C bond formation reactions (Eqs. (10b) and (10c)) can also be observed in the case of $n = 5$ and with both X = Br (Fig. 2b) and X = I (Fig. 3b). Note also, that Eq. (10b) is a generalized version of Eq. (3). Since the focus of this work is on C—C bond coupling, the occurrence of these reactions was directly confirmed by mass selecting the $Ag_{n-1}X(C_3H_5X)^+$ product ions and allowing them to react with the allylhalide (Fig. 4). In the case of X = Br (Fig. 4a), the main C—C bond coupled product is bound to Ag^+ (Eqs. (3) and (10b)), while in the case of X = I (Fig. 4b), the presumed 1,5-hexadiene coupled product is lost as a neutral (Eq. (10c)).

$$Ag_{n-1}X(C_3H_5X)^{+} + C_3H_5X \rightarrow Ag_{n-1}X(C_3H_5X)_2^{+} \quad (10a)$$

$$Ag_{n-1}X(C_3H_5X)^{+} + C_3H_5X \rightarrow Ag_{n-2}X_3 + Ag_{n-4}(C_3H_5)_2^{+} \quad (10b)$$

$$Ag_{n-1}X(C_3H_5X)^{+} + C_3H_5X \rightarrow Ag_{n-1}X_3^{+} + (C_3H_5)_2 \quad (10c)$$

The organometallic ion formed in Eq. (9b) can undergo further reactions that presumably involve C—C bond coupling (Eqs. (11a) and (11b), Fig. 3b). These reactions only occur in the case of $n = 5$ and X = I, and were directly confirmed by mass selecting $Ag_2(C_3H_5)^+$ and allowing it to react with allyliodide (Fig. 5a).

$$Ag_{n-3}(C_3H_5X)^{+} + C_3H_5X \rightarrow Ag_{n-3}X^{+} + (C_3H_5)_2 \quad (11a)$$

$$Ag_{n-3}(C_3H_5X)^{+} + C_3H_5X \rightarrow Ag_{n-4}(C_3H_5)_2^{+} + AgX \quad (11b)$$

Finally, the product of Eq. (9c) can undergo further reaction by abstracting a halide with concomitant allyl radical formation (Eq. (12)) in the case of $n = 5$ and X = I. Since the possible structures of $Ag_4I_2^+$ and $Ag_4I_3^+$ have been described in a previous publication [49], they are not discussed further here.

$$Ag_{n-1}X_2^{+} + C_3H_5X \rightarrow Ag_{n-1}X_3^{+} + C_3H_5^{\bullet} \quad (12)$$

3.1.3.2. Subsequent reactions arising from the primary products formed in Eqs. (7) from Ag_3^+ and Ag_5^+. The primary products formed in the reactions of the allylhalides with the silver cluster cations (Eq. (7)) undergo a series of other reactions with the allyl halides, as laid out in Table 3 (Eqs. (13)–(19)). The $Ag_n(C_3H_5X)^+$ product ion (formed in Eq. (7a)) undergoes, amongst others, a further addition reaction (Eq. (13a)) in the cases of: $n = 3$ and X = Cl (Fig. 1c); $n = 3$ and X = Br (Fig. 2c); $n = 5$ and X = Cl (Fig. 1d); $n = 5$ and X = Br (Fig. 2d). Interestingly, $Ag_n(C_3H_5X)^+$ also undergoes a C—C bond coupling reaction (Eq. (13b)), which occurs for $n = 3$, X = I and $n = 5$, X = Br. This C—C bond coupling reaction was confirmed by mass selecting $Ag_3(C_3H_5I)^+$ and allowing it to react with the allyliodide, and the resultant spectrum is shown in Fig. 6. Other minor products are evident in this figure and may be due to halide abstraction with concomitant formation of an allyl radical (Eq. (13c)) and an addition/cluster fragmentation reaction (Eq. (13d)).

$$Ag_n(C_3H_5X)^{+} + C_3H_5X \rightarrow Ag_n(C_3H_5X)_2^{+} \quad (13a)$$

$$Ag_n(C_3H_5X)^{+} + C_3H_5X \rightarrow Ag_nX_2^{+} + (C_3H_5)_2 \quad (13b)$$

$$Ag_n(C_3H_5X)^{+} + C_3H_5X \rightarrow Ag_nX(C_3H_5X)^{+} + C_3H_5^{\bullet} \quad (13c)$$

Table 2

Summary of the branching ratios (%) of the reaction channels occurring in the ion-molecule reactions of the silver hydride cluster cations $Ag_{n-1}H^+$ (where $n = 3$ and 5) reacting with the allylhalides, $CH_2=CHCH_2X$ (where X = Cl, Br, I). Note that Eqs. (6) is a primary reaction, Eqs. (8) and (9) are secondary and Eqs. (10)–(12) are tertiary reactions. Branching ratios were calculated as described in Section 2.

n	X	Eq. (6a)	Eq. (6b)	Eq. (8)	Eq. (9a)	Eq. (9b)	Eq. (9c)	Eq. (10a)	Eq. (10b)	Eq. (10c)	Eq. (11a)	Eq. (11b)	Eq. (12)
3	Cl	100	0	100	0	0	0	0	0	0	0	0	0
3	Br	50	50	100	100	0	0	100	0	0	0	0	0
3	I	0	100	0	100	0	0	100	0	0	0	0	0
5	Cl	31	69	0	000	0	0	000	0	0	0	0	0
5	Br	0	100	0	100	0	0	20	76	4	100	0	0
5	I	0	100	0	30	13	57	0	2	98	99	1	100

Table 3

Summary of the branching ratios (%) of the reaction channels occurring in the ion-molecule reactions of the silver cluster cations Ag_n^+ (where $n = 3$ and 5) reacting with the allylhalides, $CH_2{=}CHCH_2X$ (where X = Cl, Br, I). Note that Eq. (7) is a primary reaction, Eqs. (13)–(15) are secondary and Eqs.) are tertiary reactions. Branching ratios were calculated as described in Section 2.

n	X	Eq. (7a)	Eq. (7b)	Eq. (7c)	Eq. (7d)	Eq. (13a)	Eq. (13b)	Eq. (13c)	Eq. (13d)	Eq. (14)	Eq. (15)	Eq. (16a)	Eq. (16b)	Eq. (16c)	Eq. (17)
3	Cl	100	0	0	0	100	0	0	0	0	0	0	0	0	0
3	Br	100	0	0	0	100	0	0	0	0	0	0	0	0	100
3	I	100	0	0	0	0	53	3	44	0	0	100	0	0	0
5	Cl	99	0	0	1	100	0	0	0	0	0	0	0	0	100
5	Br	49	2	8	41	14	86	0	0	0	100	98	0	2	0
5	I	2	48	7	43	0	0	0	0	100	100	83	15	2	0

$$Ag_n(C_3H_5X)^+ + C_3H_5X \rightarrow Ag_{n-1}(C_3H_5)(C_3H_5X)^+ + AgX \qquad (13d)$$

The Ag_nX^+ product ion (formed in Eq. (7b)) also undergoes a further reaction, which involves halide abstraction and formation of an allyl radical (Eq. (14)) and only occurs in the case of $n = 5$ and X = I (Fig. 3d). Since the possible structures of the reactant and product ions have been described in a previous publication [49], they are not discussed further here.

$$Ag_nX^+ + C_3H_5X \rightarrow Ag_nX_2^+ + C_3H_5^{\bullet} \qquad (14)$$

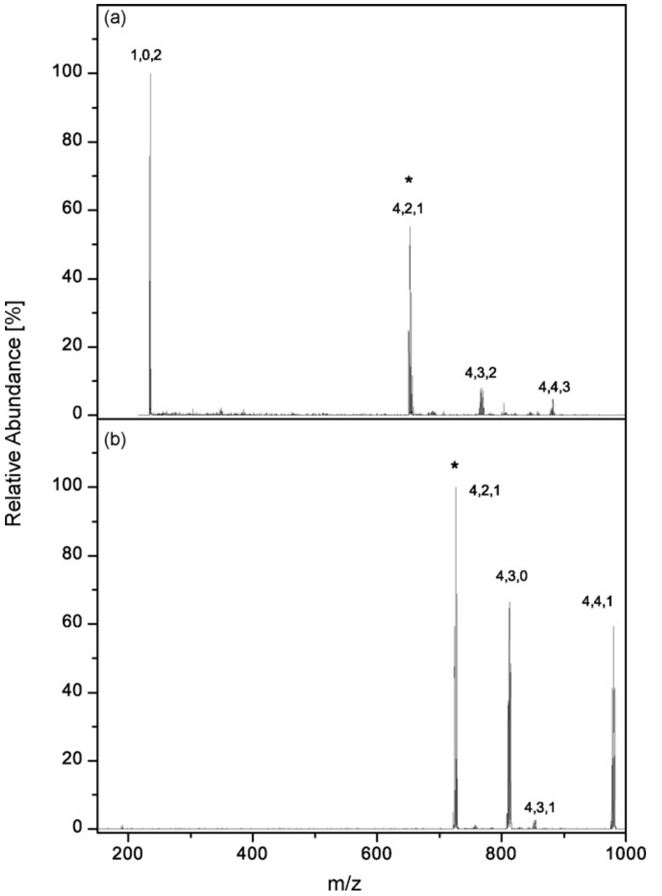


Fig. 4. Ion-molecule reactions of mass selected: (a) $Ag_4Br(C_3H_5Br)^+$ with allylbromide (concentration of neutral = ca. 3.5×10^9 molecules cm^{-3}; reaction time = 30 ms); (b) $Ag_4I(C_3H_5I)^+$ with allyliodide (concentration of neutral = ca. 3.5×10^9 molecules cm^{-3}; reaction time = 30 ms). The mass selected precursor ion is designated with a *.

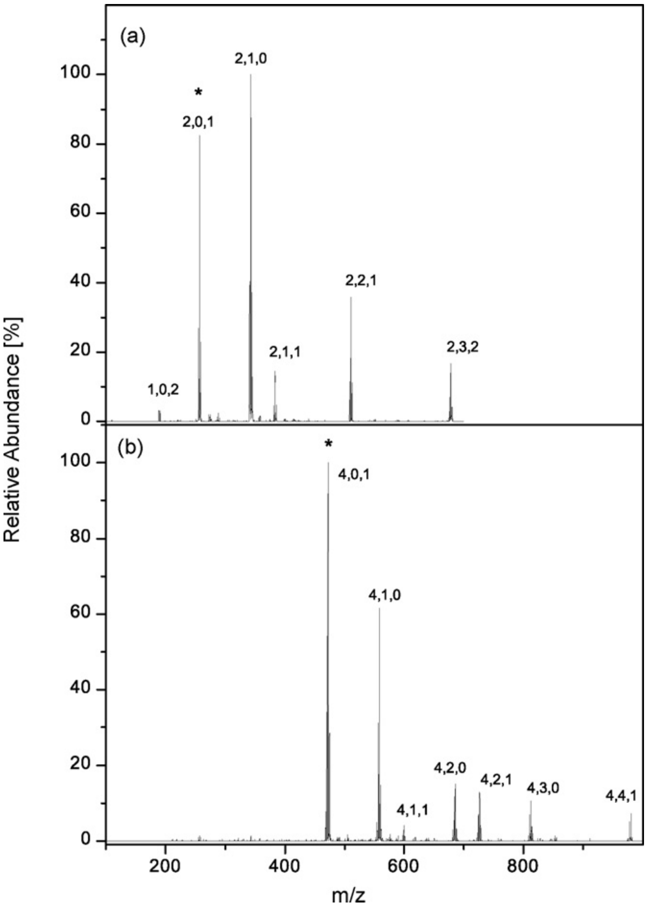
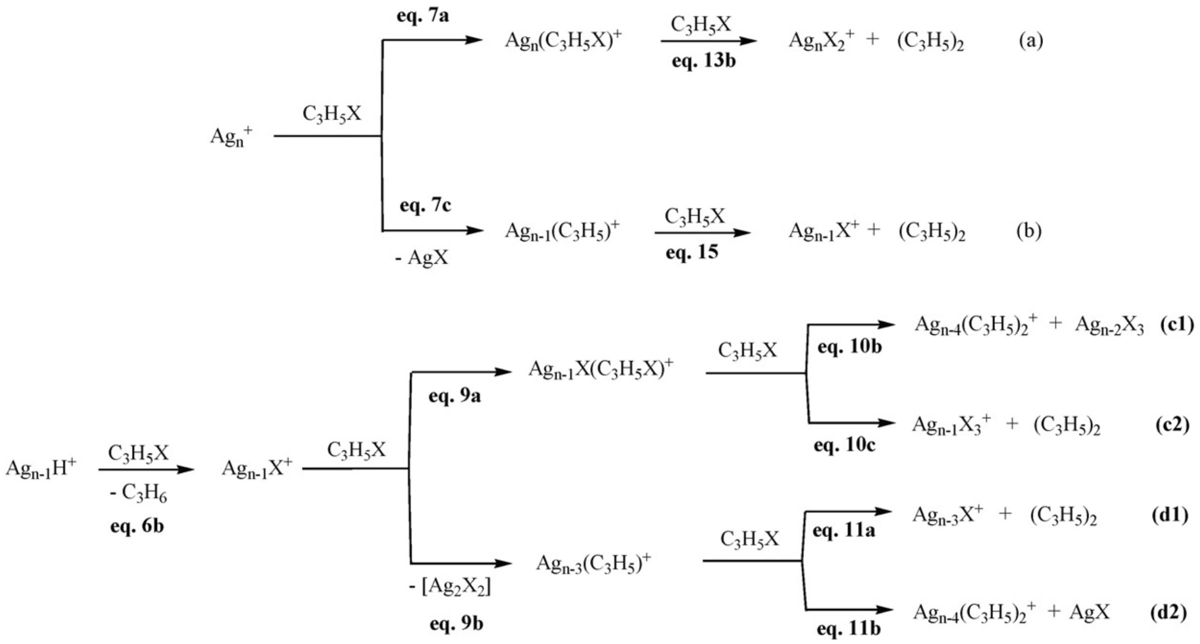


Fig. 5. Ion-molecule reactions of mass selected: (a) $Ag_2(C_3H_5)^+$ with allyliodide (concentration of neutral = ca. 3.3×10^9 molecules cm^{-3}; reaction time = 10 ms); (b) $Ag_4(C_3H_5)^+$ with allyliodide (concentration of neutral = ca. 4.3×10^9 molecules cm^{-3}; reaction time = 10 ms). The mass selected precursor ion is designated with a *.



Scheme 2. The key C—C bond coupling pathways available for the reactions of silver hydride and silver cluster cations with allylhalides: (a) adduct pathway starting from Ag_n^+; (b) organometallic pathway via $Ag_{n-1}(C_3H_5)^+$ intermediate; (c1) and (c2) metathesis – adduct pathways starting from $Ag_{n-1}H^+$; (d1) and (d2) metathesis – organometallic pathways via $Ag_{n-3}(C_3H_5)^+$ intermediate.

Interestingly, the organometallic product ion $Ag_{n-1}(C_3H_5)^+$ (formed in Eq. (7c)) and related to that formed in Eq. (9b), also undergoes a C—C bond coupling reaction with the allyl halide (Eq. (15)) in the case of $n = 5$ and both X = Br and I (Figs. 2d and 3d). To confirm this C—C bond coupling reaction, the organometallic ion $Ag_4(C_3H_5)^+$ was mass selected and allowed to react with the allylhalide, with Fig. 5b being a representative spectrum (where X = I).

$$Ag_{n-1}(C_3H_5)^+ + C_3H_5X \rightarrow Ag_{n-1}X^+ + (C_3H_5)_2 \quad (15)$$

Finally in this series, the cluster fragmentation product ion formed in Eq. (7d) undergoes further addition reaction (cf. Eq. (7a)). Indeed, Ag_3^+ is formed in all the reactions of Ag_5^+ with all the allylhalides (Figs. 1d, 2d and 3d) and exhibits the same reactivity as Ag_3^+ directly formed via Scheme 1c.

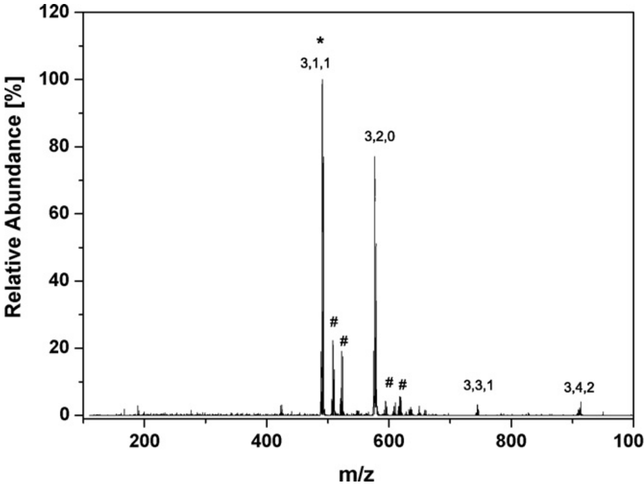


Fig. 6. Ion-molecule reactions of mass selected $Ag_3(C_3H_5I)^+$ with allyliodide (concentration of neutral = ca. 3.5×10^9 molecules cm^{-3}; reaction time = 30 ms). The mass selected precursor ion is designated with a *. A # represents the addition of background ESI solvent molecules.

The product ions of these secondary reactions undergo further reactions in the presence of the allyl halide. These include further addition (Eqs. (16a), (17), cf. (9a) and (13a)), halide abstraction (Eq. (16b)) and stable neutral loss (Eq. (16c)) reactions. Since none of these appear to lead to C—C bond coupling reactions, they are not discussed any further.

$$Ag_nX_2^+ + C_3H_5X \rightarrow Ag_nX_2(C_3H_5X)^+ \quad (16a)$$

$$Ag_nX_2^+ + C_3H_5X \rightarrow Ag_nX_3^+ + C_3H_5^\bullet \quad (16b)$$

$$Ag_nX_2^+ + C_3H_5X \rightarrow Ag_{n-3}(C_3H_5)^+ + Ag_{n-2}X_3 \quad (16c)$$

$$Ag_n(C_3H_5X)_2^+ + C_3H_5X \rightarrow Ag_n(C_3H_5X)_3^+ \quad (17)$$

4. Discussion

Based on the data presented above, there are four main sequences of C—C bond coupling reactions, and these are summarized in Scheme 2. Sequences (a) and (b) of Scheme 2 involve two reactions steps starting from the silver cluster cations Ag_n^+ and are thus the shortest of all the sequences. Sequence (a) involves the following reactions: the initial adduct, which is formed in Eq. (7a) and whose structure is unknown, reacts with a second molecule of the allylhalide to form $Ag_nX_2^+$ (Eq. (13b)). This sequence of reactions only occurs for: Ag_3^+ reacting with allyliodide (recall Fig. 6); and Ag_5^+ reacting with allylbromide.

Sequence (b) involves the C—C bond coupling (Eq. (15)) of the organometallic intermediate, $Ag_{n-1}(C_3H_5)^+$, formed via a ligand addition/cluster fragmentation reaction (Eq. (7c)). This sequence of reactions only occurs in the reactions of Ag_5^+ with allylbromide and allyliodide (recall Fig. 5b).

Sequences (c1), (c2), (d1) and (d2) of Scheme 2 all involve three reactions steps and start from the silver hydride cluster cations $Ag_{n-1}H^+$. All of these reactions involve the same first step, which is the metathesis reaction given by Eq. (6b). In sequences (c1) and (c2), the metathesis product $Ag_{n-1}X^+$ reacts further to form an adduct, $Ag_{n-1}X(C_3H_5X)^+$ (Eq. (9a)), whose structure is unknown. This adduct reacts with a third molecule of the allylhalide in the final step, which results in C—C bond coupling. The only difference

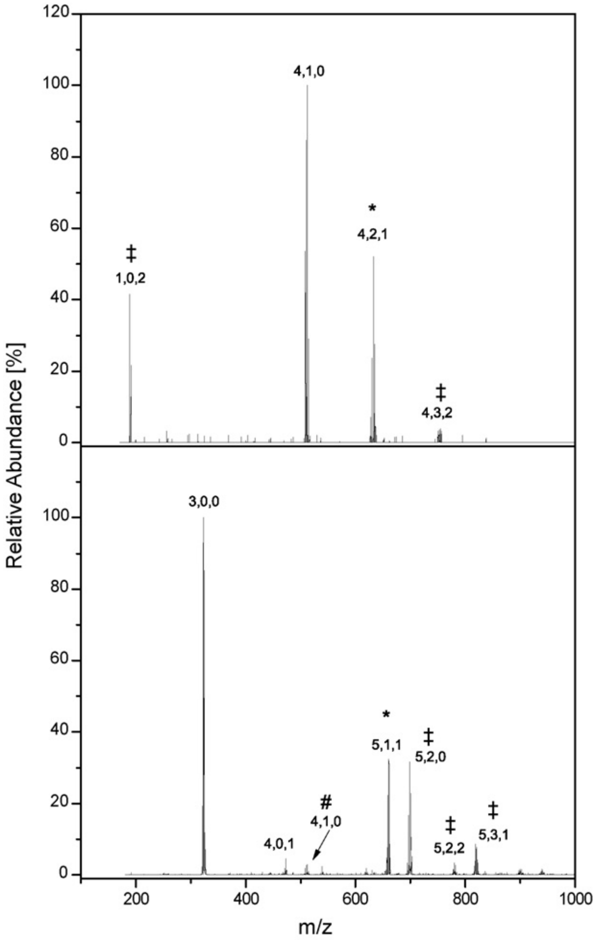


Fig. 7. CID reactions of mass selected: (a) $Ag_4Br(C_3H_5Br)^+$; (b) $Ag_5(C_3H_5Br)^+$. The mass selected precursor ion is designated with a *. Peaks marked with a ‡ are due to ion-molecule reactions between the mass selected precursor ion and allylbromide, while those marked with a # are due to ion-molecule reactions between a CID product ion and allylbromide.

between sequences (c1) and (c2) is whether the C—C bond coupled product remains bond to a cation (sequence (c1)) or is lost as a neutral (sequence (c2)). Both sequences only occur for the cases of Ag_4H^+ reacting with allylbromide and allyliodide.

Sequences (d1) and (d2) differ from (c1) and (c2) in that the initially formed metathesis product $Ag_{n-1}X^+$ reacts via ligand addition/cluster fragmentation to the organometallic intermediate, $Ag_{n-3}(C_3H_5)^+$ (Eq. (9b)). The organometallic intermediate undergoes C—C bond coupling with a third molecule of the allylhalide in the final step. Once again, the only difference between sequences (d1) and (d2) is whether the C—C bond coupled product remains bond to a cation (sequence (d2)) or is lost as a neutral (sequence (d1)). Both sequences only occur for the cases of Ag_4H^+ reacting with allyliodide (Fig. 5a).

Although we cannot provide detailed mechanistic insights into these C—C bond coupling reactions, several comments are waranted:

(i) Only the more reactive halides undergo these C—C bond coupling reactions, with allylchoride giving no appreciable products that might be ascribed to the C—C bond coupling sequences shown in Scheme 2.

(ii) The nature of initial ligation in the sequential additions of two allyhalide molecules to $Ag_n{}^+$ and $Ag_{n-1}X^+$ that subsequently give rise to C—C bond coupling (sequences a and c of Scheme 2) is unclear. Thus the addition of the first molecule of the allylhalide may simply give rise to an adduct in which the C—X bond is intact, or it might be an oxidative addition reaction in which the C—X bond is reductively cleaved and two Ag atoms of the cluster are oxidized. In the case of $Ag_n{}^+$, the products of these two scenarios would be formulated as the metallic cluster $Ag_n(C_3H_5X)^+$ and the mixed metallic/ionic cluster $Ag_{n-2}(AgX)(AgC_3H_5)^+$ respectively. To gain insights into which of these two different structures may be important, we have carried out CID on two different adducts: $Ag_4Br(C_3H_5Br)^+$ (Fig. 7a) and $Ag_5(C_3H_5Br)^+$ (Fig. 7b). These experiments are complicated by the fact that CID is done in the presence of allylbromide and thus the CID fragments can undergo further reaction. Nonetheless, some interesting observations can be made. $Ag_4Br(C_3H_5Br)^+$ fragments via loss of the allylbromide (Eq. (18)), suggesting it has the ligated structure. In contrast, $Ag_5(C_3H_5Br)^+$ fragments via the losses of (Eq. (19a)) and (Eq. (19b)), which suggests it has the mixed metallic/ionic structure $Ag_3(AgX)(AgC_3H_5)^+$. Thus it would appear that both types of structures may play a role in C—C bond coupling.

$$Ag_4Br(C_3H_5Br)^+ \rightarrow Ag_4Br^+ + (CH_2{=}CHCH_2Br) \tag{18}$$

$$Ag_5(C_3H_5Br)^+ \rightarrow Ag_3{}^+ + [Ag_2C_3H_5Br] \tag{19a}$$

$$Ag_5(C_3H_5Br)^+ \rightarrow Ag_4(C_3H_5)^+ + AgBr \tag{19b}$$

(iii) The reactions of the allylhalides with the organometallic ions $Ag_2(C_3H_5)^+$ and $Ag_4(C_3H_5)^+$ (sequences b and d of Scheme 2) are reminisent of solution phase organometallic chemistry [33] and the coupling of a surface bound allyl to an allylhalide [28]. Given the smaller size of these organometallic clusters, current experimental and theoretical studies are underway to model the reaction of $Ag_2(CH_3)^+$ with allyliodide.

5. Conclusions

Twelve different systems involving ion-molecule reactions between the cluster cations Ag_2H^+, Ag_4H^+, $Ag_3{}^+$ and $Ag_5{}^+$ and allylchloride, allylbromide and allyliodide have been studied in detail. The following trends have emerged:

(i) As the cluster size becomes larger, the clusters become more reactive. Thus Ag_4H^+ is more reactive than Ag_2H^+ and $Ag_5{}^+$ is more reactive than $Ag_3{}^+$.
(ii) The reactivity order for the allyhalides is as follows: allyliodide > allylbromide > allylchloride.
(iii) Although Ag_2H^+ is more reactive than $Ag_3{}^+$, Ag_4H^+ is less reactive than $Ag_5{}^+$.
(iv) C—C bond coupling does not occur for the substrate allylchloride.
(v) Four different reaction sequences can result in C—C bond coupling, as outlined in Scheme 2.

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