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Directing role of anions in the syntheses of the silver–alkynyl cages $[Ag_{14}(C{\equiv}C^tBu)_{12}X][BF_4]$ (X = F, Cl, Br) and silver–alkynyl polymers $[Ag_3(C{\equiv}C^tBu)_2(X)]_n$ (X = Tos, NO_3)

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Abstract

The reactions between silver(I) salts and *tert*-butylacetylene in the presence of different anions (i.e. F^-, Cl^-, Br^-, BF_4^- Tos^- and NO_3^-) are reported. When fluoride, chloride or bromide salts are present, $AgBF_4$ reacts with *tert*-butylacetylene to yield the rhombic dodecahedral silver-alkynyl cages $[Ag_{14}(C{\equiv}C^tBu)_{12}X][BF_4]$ (X = Cl, **1**; Br, **2**; F, **3**). The crystal structure of the fluoride-containing cage is presented in this paper and compared to the previously reported structures of the chloride and bromide-containing cages. In the three structures, the silver atoms are held together by a combination of bridging alkynyl groups and Ag···Ag metallophilic interactions. A remarkable feature in the syntheses of these cages is the templating role played by the halide anions. Solution IR spectroscopy and ESI mass spectrometry experiments have demonstrated that the cage structure of compounds **1**–**3** is retained in solution. When AgTos (Tos = *p*-toluenesulfonate) and $AgNO_3$ are reacted with *tert*-butylacetylene (in the absence of halides) the formation of the organometallic polymers $[Ag_3(C{\equiv}C^tBu)_2X]_n$ (X = Tos, **4**; NO_3, **5**) is observed. The crystal structure of **4** is here reported. © 2002 Published by Elsevier Science B.V.

Keywords: Alkynyl ligands; Cage compounds; Metallophilic interactions; Silver; Template synthesis; Organometallic polymers; Anions

1. Introduction

The chemistry of metal alkynyl complexes has attracted much attention both in view of the unusual structural and chemical properties of these derivatives and because of their wide use as organometallic reagents [1]. Although the study of their chemistry can be traced back to the work of Nast nearly 40 years ago [2], metal alkynyls have not yet ceased to reveal new intriguing properties and potential applications. The alkynyl ligand itself has proved to be remarkably versatile in its co-ordination abilities, with the capacity of not only forming strong terminal σ-bonds but also to co-ordinate to other Lewis acid centres through its π-system [3].

Simple coinage metal alkynyls have usually been formulated ambiguously as polymeric materials $[M(C{\equiv}CR)]_n$ (M = Cu, Ag, Au) because their insolubility in common organic solvents [4,5] has prevented a detailed structural elucidation of their polymeric nature [2b]. Recently, interest in alkynyl complexes of the coinage metals has experienced a renaissance thanks to the increasing number of reports regarding the ability of these metal centres to display non-covalent, metallophilic M···M interactions. Although well documented in the chemistry of gold [6], metallophilic interactions are less common for gold's lighter congeners, silver [7] and copper [8]. However, recent work by Mak [9] and other research groups [10] has highlighted the importance of 'argentophilic' interactions in promoting the solid state aggregation of silver compounds. Mak's work, in particular, has demonstrated how a range of structurally diverse silver polyhedra, encapsulate the ethynide dianion $(C{\equiv}C)^{2-}$. The formation of these compounds relies in part on a large number of non-covalent metal···metal contacts.

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Metallophilic interactions have also been shown to play an important role in influencing the self-assembly of the $\{[Au(C{\equiv}C^tBu)]_6\}_2$ catenane structure [11]. The seemingly simple isoleptic compound $[Au(C{\equiv}C^tBu)]_n$ aggregates into a catenane comprising two interlocking Au_6 rings, the alkynyl ligands displaying a range of bonding modes that involve both σ and π interactions. In an attempt to form an analogous silver–catenane, we have recently explored the reactivity of silver salts towards *tert*-butylacetylene, demonstrating that the assembly of the $[Ag(C{\equiv}C^tBu)]$ units is extremely sensitive to the presence of halide anions. Upon addition of chloride or bromide ions to $[Ag(C{\equiv}C^tBu)]_n$, the novel silver–alkynyl cage-type compounds $[Ag_{14}(C{\equiv}C^tBu)_{12}X][BF_4]$ (where X = Cl, **1**; Br, **2**) [12] are formed (see Fig. 1).

In order to extend our investigation on the templating role played by anions in the formation of this type of alkynyl cage, the previous reaction has been repeated in the presence of several other simple anions. Here we report the fluoride-templated synthesis of $[Ag_{14}(C{\equiv}C^tBu)_{12}F][BF_4]$ (**3**) and the formation of the polymeric materials $[Ag_3(C{\equiv}C^tBu)_2(Tos)]_n$ (**4**) and $[Ag_3(C{\equiv}C^tBu)_2(NO_3)]_n$ (**5**). The structural characterisation of the hydroxide salt of **3** and of the polymer **4** are also described. Both these silver–alkynyl systems further demonstrate the crucial role of anionic species in promoting the assembly process.

2. Results and discussion

2.1. Synthesis of $[Ag_{14}(C{\equiv}C^tBu)_{12}X]^+$ (X = Cl, 1; Br, 2; F, 3)

We have recently reported the preparation of the novel rhombohedral silver cages $[Ag_{14}(C{\equiv}C^tBu)_{12}Cl][BF_4]$ (**1**) and $[Ag_{14}(C{\equiv}C^tBu)_{12}Br][BF_4]$ (**2**) from the reaction of $AgBF_4$ and $^tBuC{\equiv}CH$ in the presence of NEt_3 and stoichiometric amounts of the appropriate alkylammonium halide [12]. Further proof of the generality of this anion-templated strategy has now come from the synthesis of the analogous fluoride-containing cage $[Ag_{14}(C{\equiv}C^tBu)_{12}F][BF_4]$ (**3**). When solid $AgBF_4$ was added to a solution of $^tBuC{\equiv}CH$, NEt_3 and stoichiometric amounts of $[NBu_4]F$ in THF, a white precipitate of $[Ag(C{\equiv}C^tBu)]_n$ was immediately formed which gradually re-dissolved to yield a clear, colourless solution after ca. 15 min. From the reaction mixture, the new silver-cage complex $[Ag_{14}(C{\equiv}C^tBu)_{12}F][BF_4]$ (**3**) could be isolated quantitatively. IR spectroscopy showed the (C≡C) stretching frequency at 2045 cm^{-1}, in the same region as the ones reported for **1** and **2** (Table 1), with a strong band at 1073 cm^{-1} that confirmed the presence of the BF_4 anion. As for cages **1** and **2**, FAB(+)-MS was diagnostic in indicating the successful synthesis of the fluoride-containing structure; the molecular ion peak was observed at 2503 a.m.u., which corresponds to $[Ag_{14}(C{\equiv}C^tBu)_{12}F]^+$.

The formulation of the new fluoride-templated cage was further confirmed by elemental analyses and by single crystal X-ray crystallography. The structure of the fluoride complex **3** (Fig. 2) is virtually identical to that of the already reported chloride and bromide analogues **1** and **2**, respectively [12]. Apart from differences in the orientations of the peripheral *tert*-butyl substituents, the most noticeable change on reducing the size of the encapsulated anion from chloride to fluoride is a commensurate shrinking of the overall cage dimensions (Table 2). The structure still has the same crystallographic S_6 and molecular O_h symmetries, the 'type 1' and 'type 3' silver atoms describing a cubic arrangement with those of 'type 2' forming an interpenetrating octahedron with the fluoride anion being positioned at its centre. The shortest silver···silver edge distances range between 2.898(2) and 2.920(2) Å, values ca. 0.06 Å less than seen in the chloride species **1**. The F···Ag separations [2.949(2)–3.292(1) Å] are, as expected, slightly shorter than their counterparts in **1**, and are at the longer end of the range of interacting distances observed between silver and fluoride containing anions [13].

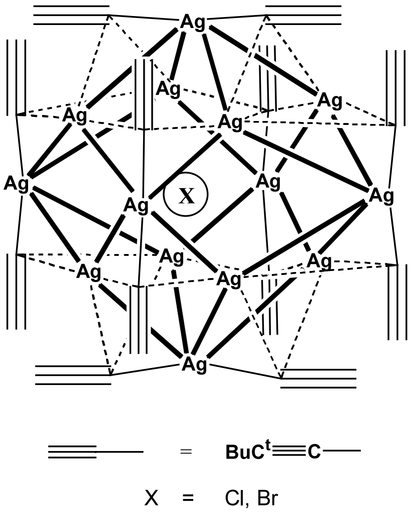

Fig. 1. Schematic representation of cages **1** and **2**.

Table 1
ν(C≡C) stretching frequencies for $[Ag_{14}(C{\equiv}C^tBu)_{12}X][BF_4]$ (X = F, Cl, Br)

Compound	ν(C≡C), KBr pellets (cm^{-1})	ν(C≡C), CH_2Cl_2 sol. (cm^{-1})
$[Ag_{14}(C{\equiv}C^tBu)_{12}Cl][BF_4]$ (**1**)	2042	2042
$[Ag_{14}(C{\equiv}C^tBu)_{12}Br][BF_4]$ (**2**)	2038	2035
$[Ag_{14}(C{\equiv}C^tBu)_{12}F][BF_4]$ (**3**)	2045	2036
$[Ag_3(C{\equiv}C^tBu)_2Tos]$ (**4**)	2023	2023

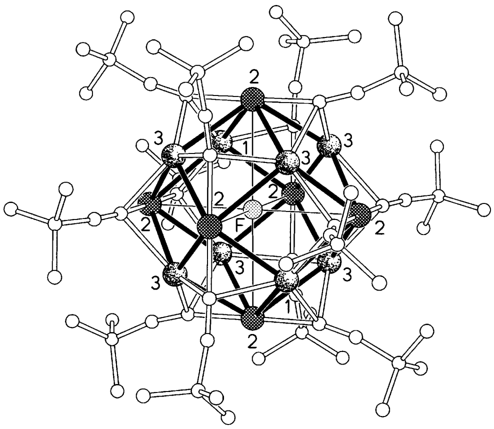

Fig. 2. The rhombohedral cage complex **3** showing the mutually interpenetrating octahedral and cubic arrangements of silver atoms of type 2 and of types 1 and 3, respectively, and the positioning of the fluoride at the centre.

Table 2
Comparative Ag···X and Ag···Ag edge contacts (Å) in complexes **1** (X = Cl), **2** (X = Br) and **3** (X = F)

	3 (X = F)	**1** (X = Cl)	**2** (X = Br)
Ag(1)···X	2.949(2)	3.116(2)	3.148(2)
Ag(2)···X	3.292(1)	3.297(1)	3.313(1)
Ag(3)···X	3.042(2)	3.174(1)	3.200(1)
Ag(1)···Ag(2)	2.914(2)	2.978(1)	2.997(1)
Ag(2)···Ag(3)	2.898(2)	2.953(2)	2.972(2)
	2.913(2)	2.966(2)	2.985(2)
	2.920(2)	2.986(2)	3.006(2)

The presence of the fluoride anion in **3** was also revealed by ^{19}F-NMR spectroscopy. The ^{19}F-NMR spectrum showed the presence of the BF_4 anion as two broad singlets at δ −150.64 and −150.59 due to coupling to the ^{11}B and ^{10}B isotopes respectively, and a singlet at −65.70 that was assigned to the fluoride anion present in **3**. Interestingly, ^{19}F-NMR spectroscopy did not show any coupling between the fluoride anion and the surrounding silver centres thus suggesting the absence of any strong bonding interactions between the ions.

An important question that needed to be addressed about the three silver cages **1**–**3** regarded whether they retained their structure in solution. Consequently solution studies were carried out by means of solution IR spectroscopy and electrospray mass spectrometry. The results of these studies strongly suggest that the cage-type structure observed in the solid state is indeed retained in solution. The IR spectra of the three samples in CH_2Cl_2 solution demonstrated the presence of the characteristic (C≡C) stretching frequency for cages **1**–**3** (see Table 1). The small differences between the solid and solution state measurements can be attributed to solvent effects. To further confirm these results, the cages were also analysed by ES$^+$ mass spectrometry. Electrospray has been successfully used to characterise a wide range of weakly-associated systems in solution [14]. The mass spectrum for the chloride cage **1** showed the molecular ion peak at 2519 a.m.u. with the pattern accurately matching the simulation for $[Ag_{14}(C{\equiv}C^tBu)_{12}Cl]^+$ (see Fig. 3), demonstrating the retention of the cage in solution (methanol). Analogous results were obtained for a sample of **2** (with a molecular peak at 2563 a.m.u.) but not for **3** which failed to show the molecular peak (although various peaks at lower molecular weight were observed). This suggests that, while the chloride and bromide cages are very stable in solution, the fluoride analogue is not.

2.2. Synthesis of $[Ag_{14}(C{\equiv}C^tBu)_{12}F][BF_4]$ from TlOAc

Since the formation of the cages relies on the templating ability of spherical halides and on metallophilic interactions, it was decided to explore the possibility of using spherical cationic templates for the formation of analogous structures. Hence, the reaction of $[Ag(C{\equiv}C^tBu)]_n$ with thallium salts was investigated, the rationale behind this strategy being the use of Tl^I–Ag^I (s^2–d^{10}) metallophilic interactions as a driving force towards the self–assembly of a closed system [15]. When solid TlOAc was added to a mixture of $AgBF_4$, *tert*-butylacetylene and triethylamine in THF, the initial white suspension (due to the presence of $[Ag(C{\equiv}C^tBu)]_n$) gradually yielded a clear solution suggesting the formation of a new species. After work-up of the reaction mixture, a white solid was obtained which, surprisingly, analysed correctly for $[Ag_{14}(C{\equiv}C^tBu)_{12}F]$-$[BF_4]$ (**3**). The presence of the fluoride anion was detected by ^{19}F-NMR spectroscopy, which gave an identical response to the one obtained for **3**. IR spectroscopy, FAB(+)-MS and elemental analyses all confirmed the formulation of the new species to be that of **3**. Since no obvious source of fluoride ions had been added to the reaction mixture, it had to be concluded that the halide had come from the silver starting material, i.e. $AgBF_4$. Decomposition of the BF_4^- anion into F^- and hydrolysed species such as $[BF_3(OH)]^-$ and $[BF_2(OH)_2]^-$ has been reported previously in the presence of heavy metals [16]. Therefore, it seems plausible to suggest that the presence of thallium induces the decomposition of BF_4^- which releases the fluoride anion that can then act as a templating agent for the synthesis of cage **3**.

*2.3. Synthesis of $[Ag_3(C{\equiv}C^tBu)_2(Tos)]_n$ (**4**)*

The potential decomposition of anions such as BF_4^-, PF_6^- and $CF_3SO_3^-$ and the consequent formation of free fluoride anions, constitutes a serious disadvantage for

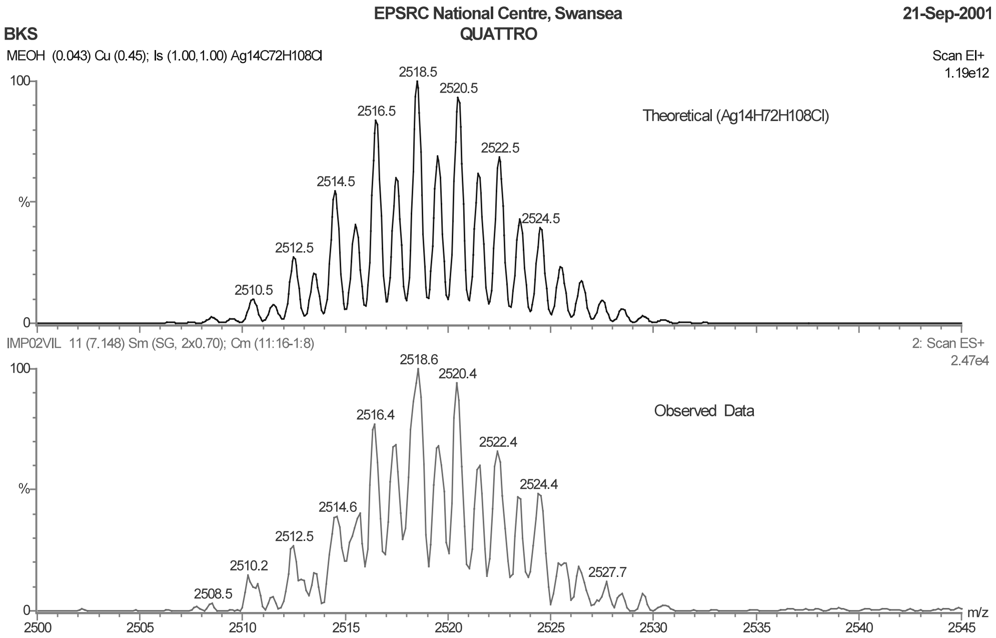

Fig. 3. Observed and simulated ES$^+$-MS pattern for $[Ag_{14}(C{\equiv}C^tBu)_{12}Cl]^+$.

the understanding of these systems. Hence, it was decided to explore the use of other silver salts as starting materials for the formation of cages **1**–**3**. Specifically AgTos (where Tos = *p*-toluenesulfonate) and $AgNO_3$ were investigated. Once again, unexpected results were obtained that demonstrated the crucial role played by the anions in the present systems. When a mixture of AgTos, *tert*-butylacetylene and triethylamine (in a 1:1:1 ratio) was reacted, a white precipitate was obtained which was formulated as $[Ag(C{\equiv}C^tBu)]_n$ on the basis of IR spectroscopy and elemental analyses. Addition of TlOAc to this material in THF did not lead to any apparent change. However, when the mixture was warmed up a clear solution was obtained which eventually yielded a white microcrystalline solid. Analytical data, however, did not indicate the presence of Tl in the new compound. These results prompted a further investigation into the nature of the product resulting from mixing AgTos, *tert*-butylacetylene and triethylamine in warm THF. As soon as the reagents were mixed in THF at room temperature, $[Ag(C{\equiv}C^tBu)]_n$ formed as a white precipitate; however, upon warming, the solid re-dissolved to yield a clear colourless solution from which a white crystalline material separated out. IR spectroscopy, elemental analyses and structural characterisation led to a formulation of this solid as the polymeric $[Ag_3(C{\equiv}C^tBu)_2(Tos)]_n$ (**4**). IR spectroscopy (as KBr pellets) showed the (C≡C) stretching frequency at 2023 cm^{-1}, with strong bands at 1119, 1010, 678, 568 cm^{-1} that confirmed the presence of the tosylate anion. Elemental analyses were also consistent with the formulation. In contrast to the case of the silver alkynyl cages, FAB(+)-MS failed to provide accurate evidence for the formation of the polymeric species. Various peaks at high *m*/*z* values were observed but none of them corresponded to a predictable aggregation of the $[Ag_3(C{\equiv}C^tBu)_2(Tos)]$ units.

The structure of **4** was determined by a single crystal X-ray study which showed the compound to be polymeric with a ladder-like assemblage (Figs. 4 and 5) very similar to that of the related polymer $\{[Ag_3(C{\equiv}C^tBu)_2][BF_4]\}_n$ reported by Al-Farhan et al. [17] In **4**, however, the tosylate 'anion' is O-bonded to one of the three unique silver centres [Ag(1)–O(1) 2.503(6) Å], whereas in the literature structure the disordered BF_4

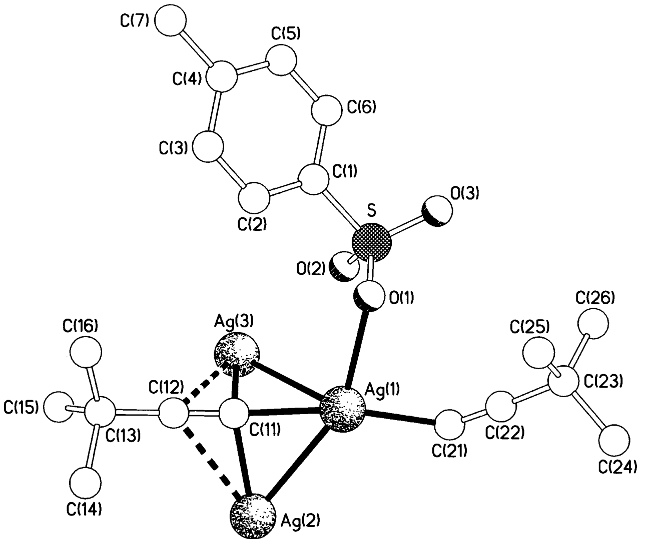

Fig. 4. The asymmetric unit and atom numbering in **4**. The 'non-bonded' Ag(2)···Ag(3) and Ag(1)···C(22) distances are 3.394(1) and 3.106(9) Å, respectively.

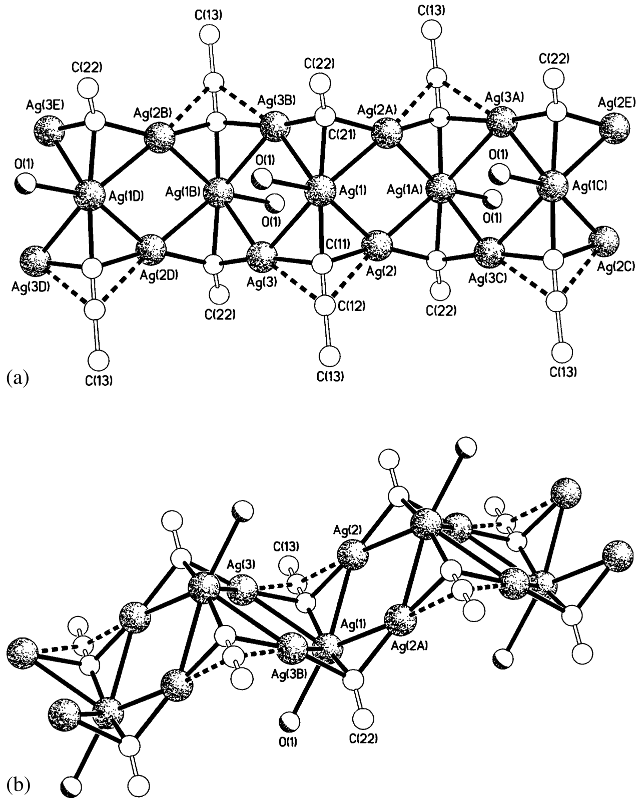

Fig. 5. (a) Plan and (b) perspective views of the polymer chain structure of **4**; peripheral portions of the acetylide and tosyl units have been omitted for clarity.

counter-anion makes only long F···Ag approaches (ca. 2.8 Å) from partial occupancy fluoride centres. The pattern of bonding to the two unique acetylide moieties is different (Table 3). In the case of the C(11)≡C(12) linkage the pi-bonding approaches from Ag(2) and Ag(3) are 2.235(9), 2.778(10) and 2.193(9), 2.687(9) Å to C(11), C(12), respectively. By contrast the C(21)≡C(22) acetylide, whilst again bridging adjacent silver centres, does so only via the terminal carbon atom C(21) [Ag(2)–C(21) 2.175(9), Ag(3)–C(21) 2.167(9) Å]; the contacts to C(22) are both in excess of 3 Å. There is strong evidence for argentophilic interactions analogous to those seen in the cage structures **1**–**3**; here the Ag···Ag separations between nearest neighbour metal centres in the polymer chain are in the range 2.901(1)–3.035 (1) Å [the adjacent 'non-bonded' Ag···Ag distances range between 3.298(1) and 3.866(2) Å]. The tosylate moieties lie symmetrically above and below the zig–zag profile of the silver–acetylide polymer chain (Fig. 5b), and the only interchain interactions are van der Waals contacts between the *tert*-butyl and tolyl substituents; there are no π-stacking interactions.

The same reaction that had led to the isolation of the $[Ag_3(C{\equiv}C^tBu)_2(Tos)]_n$ polymer was also carried out using $AgNO_3$ as the silver starting material. Addition of $AgNO_3$ to a mixture of *tert*-butylacetylene and triethylamine in THF led to the initial formation of $[Ag(C{\equiv}C^tBu)]_n$. Upon heating the mixture under reflux the white solid re-dissolved yielding a colourless solution which eventually afforded $[Ag_3(C{\equiv}C^tBu)_2(NO_3)]_n$ (**5**) as a white precipitate. IR spectroscopy showed the (C≡C) stretch at 2022 cm^{-1}, in virtually an identical position to the one observed for **4**. Strong bands at 1373 and 1297 cm^{-1} indicated the presence of the nitrate anion. The formulation was also confirmed by elemental analyses.

3. Conclusions

The results presented in this paper show the important role played by anionic species in the assembly of different silver–alkynyl structures. The rhombohedral cages $[Ag_{14}(C{\equiv}C^tBu)_{12}X][BF_4]$ are formed from $[Ag(C{\equiv}C^tBu)]_n$ through the templating action of $X = F^-, Cl^-, Br^-$, whereas the polymeric compounds $[Ag_3(C{\equiv}C^tBu)_2(X)]_n$ are synthesised from the initial $[Ag(C{\equiv}C^tBu)]_n$ when X = Tos^- or NO_3^- anions are present in the system. In all these silver–alkynyl systems, weak argentophilic interactions are observed between the silver centres, which provide a significant contribution to the assembly and the stability of the structures.

4. Experimental

4.1. General procedures and instrumentation

All reactions involving silver salts were carried with exclusion of light. All reagents used during the syntheses were purchased from Aldrich and used as received. IR spectra were recorded in a Perkin–Elmer 1720 IR Fourier transform spectrometer between 4000 and 250 cm^{-1} as KBr pellets or as CH_2Cl_2 solutions using solution-IR-cells with KBr plates. FAB-Mass spectra were recorded by J. Barton at Imperial College on a VG AutoSpec-Q as FAB using 3-NBA as matrix while ES-Mass spectra were recorded at the EPSRC National Mass Spectrometry Service Centre, Department of Chemistry, University of Wales, Swansea. Microanalyses (C, H, N) were carried out by S. Boyer at University of North London. The compounds $[Ag_{14}(C{\equiv}C^tBu)_{12}X][BF_4]$ (X = Cl, Br) were prepared as described by us previously in the literature [12].

4.2. Preparations

4.2.1. $[Ag_{14}(C{\equiv}C^tBu)_{12}F][BF_4]$ (*3*)

Solid $AgBF_4$ (1 g, 5.14 mmol) was added to a mixture of *tert*-butylacetylene (0.63 ml, 5.14 mmol), triethylamine (0.72 ml, 5.14 mmol) and tetrabutylammonium fluoride (0.096 g, 0.37 mmol) in THF (10 ml). A white solid formed immediately but gradually re-dissolved

Table 3
Selected bond lengths (Å) for **4**

Ag(1)–C(11)	2.131(9)	Ag(1)–C(21)	2.176(10)	Ag(1)–O(1)	2.503(6)
Ag(1)–Ag(2)	2.9014(11)	Ag(1)–Ag(2A)	2.9399(12)	Ag(1)–Ag(3B)	2.9598(12)
Ag(1)–Ag(3)	3.0349(12)	Ag(2)–C(11)	2.235(9)	Ag(2)–C(12)	2.778(10)
Ag(2)–C(21)	2.175(9)	Ag(3)–C(11)	2.193(9)	Ag(3)–C(12)	2.687(9)
Ag(3)–C(21)	2.167(9)	C(11)–C(12)	1.202(13)	C(21)–C(22)	1.181(12)

yielding a colourless solution after ca. 5 min. After stirring the mixture for 2 h, the solvent was evaporated under reduced pressure. The resulting white solid was treated with water. The remaining solid insoluble in water was filtered and washed several times with pentane yielding **3** as a white fine powder (0.938 g, 98%). Anal. Found: C, 33.3; H, 4.2. $Ag_{14}BC_{72}F_5H_{108}$ requires: C, 33.4; H, 4.2%. ^{1}H-NMR (d_6-acetone): $\delta = 1.42$ (s, $-CCH_3$); ^{19}F-NMR (d_6–acetone): $\delta = -150.64$ (s, $^{11}BF_4$), -150.59 (s, $^{10}BF_4$), -65.70 (s, F); IR (KBr disc): $\nu = 2045$ (vs) (C≡C), 1073 (vs) (BF_4^-); IR (CH_2Cl_2 solution): $\nu = 2036$ (vs) (C≡C), 1062 (s) (BF_4^-) FAB$^+$-MS: $m/z = 2503$ $\{[Ag_{14}(C{\equiv}C^tBu)_{12}F]\}^+$, 1747 $\{[Ag_{10}(C{\equiv}C^tBu)_8F]\}^+$, 1241 $\{[Ag_7(C{\equiv}C^tBu)_6]\}^+$, 1053 $\{[Ag_6(C{\equiv}C^tBu)_5]\}^+$, 863 $\{[Ag_5(C{\equiv}C^tBu)_4]\}^+$.

4.2.2. Synthesis of $[Ag_{14}(C{\equiv}C^tBu)_{12}F][BF_4]$ (3) from TlOAc

Solid $AgBF_4$ (1 g, 5.14 mmol) was added to a mixture of *tert*-butylacetylene (0.63 ml, 5.14 mmol) and triethylamine (0.72 ml, 5.14 mmol) in THF (10 ml). A white solid formed immediately and was stirred for 30 min at room temperature (r.t.). Solid TlOAc (0.097 g, 0.37 mmol) was then added and the suspension gradually turned into a clear colorless solution. After 1 h the solvent was evaporated under reduced pressure and the resulting white solid was treated with water. The white solid insoluble in water was filtered and washed several times with diethyl ether yielding **3** as a white fine powder (0.940 g, 98%). Anal. Found: C, 33.3; H, 4.3. $Ag_{14}BC_{72}F_5H_{108}$ requires: C, 33.4; H, 4.2%. ^{1}H-NMR (d_6-acetone): $\delta = 1.42$ (s, $-CCH_3$); ^{19}F-NMR (d_6-acetone): $\delta = -150.65$ (s, $^{11}BF_4$), -150.60 (s, $^{10}BF_4$), -65.66 (s, F); IR (KBr): $\nu = 2045$ (vs) (C≡C), 1073 (vs) (BF_4^-); FAB$^+$-MS: $m/z = 2503$ $\{[Ag_{14}(C{\equiv}C^tBu)_{12}F]\}^+$, 1747 $\{[Ag_{10}(C{\equiv}C^tBu)_8F]\}^+$, 1241 $\{[Ag_7(C{\equiv}C^tBu)_6]\}^+$, 1053 $\{[Ag_6(C{\equiv}C^tBu)_5]\}^+$, 863 $\{[Ag_5(C{\equiv}C^tBu)_4]\}^+$.

4.2.3. Synthesis of $[Ag_3(C{\equiv}C^tBu)_2(Tos)]_n$ (4)

Solid AgTos (1 g, 3.58 mmol) was added to a mixture of *tert*-butylacetylene (0.44 ml, 3.58 mmol) and triethylamine (0.5 ml, 3.58 mmol) in THF (10 ml). A white solid formed immediately. The mixture was heated under reflux yielding a colourless solution from which white needle-like crystals separated after ca. 15 min. The microcrystalline solid **4** (0.361g, 46%) was then filtered and washed with diethyl ether. Anal. Found: C, 34.8; H, 3.8. $Ag_3C_{19}H_{25}O_3S$ requires: C, 34.7; H 3.8%. ^{1}H-NMR (CD_3OD): $\delta = 7.73$ (d, $^3J = 4.21$ Hz, 2H), 7.24 (d, $^3J = 4.21$ Hz, 2H), 2.37 (s, 3H), 1.41 (s, 18H, ^{t}Bu); IR (KBr disc): $\nu = 2023$ (vs) (C≡C), 1119 (s), 1010 (m) 678 (s) 568 (m), (Tos); IR (CH_2Cl_2 solution) $\nu = 2023$ (vs) (C≡C), 1119 (s), 1010 (m) 678 (s) 568 (m), (Tos).

4.2.4. Synthesis of $[Ag_3(C{\equiv}C^tBu)_2(NO_3)]_n$ (5)

Solid $AgNO_3$ (1 g, 5.89 mmol) was added to a mixture of *tert*-butylacetylene (0.72 ml, 5.89 mmol) and triethylamine (0.82 ml, 5.89 mmol) in THF (10 ml). A white solid formed immediately. The mixture was heated under reflux yielding a colourless solution from which a white solid separated soon afterwards. The solid **5** (1.02 g, 95%) was then filtered and washed with diethyl ether. Anal. Found: C, 26.3; H, 3.2; N, 2.5. $Ag_3C_{12}H_{18}NO_3$ requires: C, 26.3; H, 3.3; N, 2.6%. ^{1}H-NMR (CD_3OD): $\delta = 1.42$ (s, ^{t}Bu); IR (KBr disc): $\nu = 2022$ (vs) (C≡C), 1373 (vs), 1297 (vs) (NO_3).

4.3. Crystallography

Crystal data for **3**: $[C_{72}H_{108}Ag_{14}F][OH]$, $M = 2519.8$, rhombohedral, $R\bar{3}$ (no. 148), $a = 22.449(2)$, $c = 15.544(1)$ Å, $V = 6784.0(8)$ Å^3, $Z = 3$ (S_6 symmetric), $D_{calc} = 1.850$ g cm^{-3}, μ(Mo–K$_\alpha$) = 2.99 mm^{-1}, $T = 293$ K, colourless rhombs; 2607 independent measured reflections, F^2 refinement, $R_1 = 0.066$, $wR_2 = 0.155$, 1277 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 50°$], 156 parameters.

Crystal data for **4**: $\{C_{19}H_{25}O_3SAg_3\}_n$, $M = 657.1$, monoclinic, $P2_1/c$ (no. 14), $a = 6.643(1)$, $b = 15.349(3)$, $c = 21.955(4)$ Å, $\beta = 94.49(2)°$, $V = 2231.7(8)$ Å^3, $Z = 4$, $D_{calc} = 1.956$ g cm^{-3}, μ(Mo–K$_\alpha$) = 2.71 mm^{-1}, $T = 293$ K, colourless needles; 3918 independent measured reflections, F^2 refinement, $R_1 = 0.049$, $wR_2 = 0.102$, 2564 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 50°$], 259 parameters.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 178209 for compound **3** and CCDC 178210 for compound **4**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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