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Assembly of Heterometallic Silver(I)-Copper(I) Alkyl-1,3-diynyl Clusters via Inner-Core Expansion

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ABSTRACT

New tetranuclear supramolecular precursors $[(\mathrm{R{-}C{\equiv}C{-}C{\equiv}C})\mathrm{Ag}]_4$ (R = ^{i}Pr, ^{t}Bu and chx) are employed to construct a series of heterometallic silver(I)-copper(I) alkyl-1,3-diynyl cluster complexes (**1**–**9**) that bear a common $CuAg_3$ core (normally trigonal-planar, but can be distorted to pyramidal) consolidated by cupro-argentophilic interaction under 3.12 Å, as found in **1** and **2**. The photophysical properties of the multinuclear supramolecular precursors and selected complexes have been investigated. The present results strongly suggest that the assembly of medium-nuclearity clusters **3** to **9** is initiated by accretion of additional Ag(I) ions by the ubiquitous $CuAg_3$ template through argentophilic (< 3.4 Å) interaction, with cooperative cuprophilic enhancement (< 2.76 Å) in the case of compound **9**. To our knowledge, the present study provides the first report of conversion of a Group 11 homonuclear cluster into a heteronuclear one of higher nuclearity *via* inner-core expansion.

INTRODUCTION

Monovalent group 11 metal alkynyl complexes have been actively investigated over the past decade owing to their ubiquitous metallophilic interactions and variable metal-carbon interactions,[1-4] which account for their rich structural diversity and remarkable photophysical and photochemical properties.[5-6] In particular, tetranuclear cuboidal complexes of d^{10} electronic configuration are well-known and a number of their analogs have been shown to exhibit desirable luminescence properties.[7] In addition, extension of studies on the alkynyl ligands to homologous diynyl systems showed significant effect on the luminescence behavior of their corresponding complexes.[7b,8-9] On the contrary, heteronuclear alkynyl complexes have been much less explored because of the difficulty in controlling assembly of heterometallic systems, in contrast to the relative strong tendency to form homonuclear arrays.[10-17]

In a previous study, we employed the multinuclear supramolecular synthon $R{-}C{\equiv}C \supset Ag_n$ (R = ^{t}Bu and chx) to construct two Ag_{38} high-nuclearity silver ethynide cluster complexes which bear the same novel Cl_6Ag_8 central core.[18] The formation of these clusters is suggested to involve transformation of the encapsulated chloride template within a Ag_{14} cage into a Cl_6Ag_8 central core within a much expanded Ag_{38} cluster, which provided the first example of conversion of a silver cluster into one of high nuclearity *via* inner-core transformation.

Herein, we describe the synthesis, structural characterization and photophysical properties of a series of novel heteronuclear Ag(I)···Cu(I) molecular cluster complexes obtained from the reaction between designed $[(RC{\equiv}C{-}C{\equiv}C)Ag]_4(PPh_3)_4$ (R = ^{i}Pr, ^{t}Bu and chx) precursors and $[Cu(MeCN)_4]X$ (X = PF_6 and ClO_4) *via* $CuAg_3$ core expansion, stabilization of the products being provided by peripheral alkyl-1,3-diynyl and triphenylphosphine ligands.

RESULTS and DISCUSSION

General procedure to prepare synthetic precursors $[(RC{\equiv}C{-}C{\equiv}C)Ag]_4(PPh_3)_4$ *(R =* ^{i}*Pr,* ^{t}*Bu and chx)*

CAUTION. Silver ethynides are potentially explosive and should be handled in small amounts with extreme care!

Polymeric silver ethynides $[(RC{\equiv}C{-}C{\equiv}C)Ag]_n$ (0.1 mmol)[18] was first dissolved in a mixed solution of dichloromethane (3.0 mL) and methanol (0.5 mL); triphenylphosphine (0.1 mmol) was then added with vigorous stirring to achieve complete dissolution. The resulting solution was filtered and left to stand in the dark at room temperature. After two days, colorless block-like crystals of $[(^iPrC{\equiv}C{-}C{\equiv}C)Ag]_4(PPh_3)_4$, $[(^tBuC{\equiv}C{-}C{\equiv}C)Ag]_4(PPh_3)_4{\cdot}2MeCN$ and $[(chxC{\equiv}C{-}C{\equiv}C)Ag]_4(PPh_3)_4{\cdot}2MeOH$ were each deposited in *ca.* 80 % yield.

Description of Crystal and Molecular Structure

$[(chxC{\equiv}C{-}C{\equiv}C)Ag]_4(PPh_3)_4{\cdot}2MeOH$

There are two independent and isostructural $[(chxC{\equiv}C{-}C{\equiv}C)Ag]_4(PPh_3)_4$ molecular clusters each occupying an inversion center in its crystalline methanol solvate. The core of each molecule consists of two nearly isosceles Ag_3 triangles sharing a common edge, with the resulting parallelogram-like Ag_4 array consolidated by two pairs of bridging $chxC{\equiv}C{-}C{\equiv}C^-$ groups, whereas the PPh_3 ligands are attached only to the outer Ag1 centers (Figure 1). In the two independent cluster molecules, the observed argentophilic Ag···Ag distances range from 2.962(5) to 3.008(5) Å, and the Ag1-Ag2-Ag1A and Ag2-Ag1-Ag2A angles are 120.3(1)° and 59.5(1)°, respectively. The two methanol molecules are linked together by a weak hydrogen bond of length 2.67 Å.

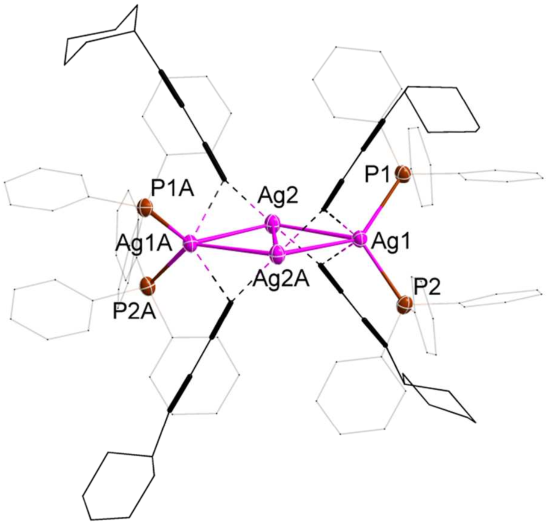

Figure 1. Coordination environment of the silver(I) atoms in the discrete molecule [(chxC≡C–C≡C)Ag]$_4$(PPh$_3$)$_4$. The C≡C triple bonds in the alkyl-1,3-diynyl ligands are shown as thick rods. Silver atoms are drawn as thermal ellipsoids (50% probability level) with atom labeling. (Color scheme: purple, silver atoms; broken lines, Ag–C bonds) The argentophilic Ag···Ag distances lie in the range 2.70–3.40 Å. Symmetry code: A: 0.5–*x*, 1.5–*y*, *z*.

As expected, single-crystal X-ray analysis established that the tetranuclear molecular clusters [(RC≡C–C≡C)Ag]$_4$(PPh$_3$)$_4$ (R = ^{i}Pr and ^{t}Bu) are structural analogs of [(chxC≡C–C≡C)Ag]$_4$(PPh$_3$)$_4$, with each *i*-propyl or *tert*-butyl group replacing the corresponding peripheral cyclohexyl group, the only difference between them is that crystalline [(^{i}PrC≡C–C≡C)Ag]$_4$(PPh$_3$)$_4$ is solvent-free, and there are two co-crystallized acetonitrile molecules in [(^{t}BuC≡C–C≡C)Ag]$_4$(PPh$_3$)$_4$·2MeCN.

*[CuAg$_3$(chxC≡C–C≡C)$_3$(PPh$_3$)$_6$]PF$_6$·2Et$_2$O (**1**) and [CuAg$_3$(^{i}PrC≡C–C≡C)$_3$(PPh$_3$)$_6$]PF$_6$ (**2**)*

The reaction between 1.0 equiv. of [(chxC≡C–C≡C)Ag]$_4$(PPh$_3$)$_4$ and 0.7 equiv. of [Cu(MeCN)$_4$]PF$_6$ in CH$_2$Cl$_2$ gave complex **1** in *ca*. 50% yield. In the crystal structure of **1**, the Cu(I) ion is bound by three Ag(I) atoms through cupro-argentophilic interactions

(2.684(1)–2.739(3) Å) to yield a trigonal-planar $CuAg_3$ core (Figure 2a), which is stabilized by three μ_3–coordinated chxC≡C–C≡C$^-$ groups on one side and a pair of η^1–triphenylphosphine ligands on the other. As expected, single-crystal X-ray analysis established that **2** is a structural analog of **1**, with each *iso*-propyl group replacing the corresponding peripheral cyclohexyl group (Figure 2b), the only difference between them being the incorporation of two co-crystallized diethyl ether molecules in **1**.

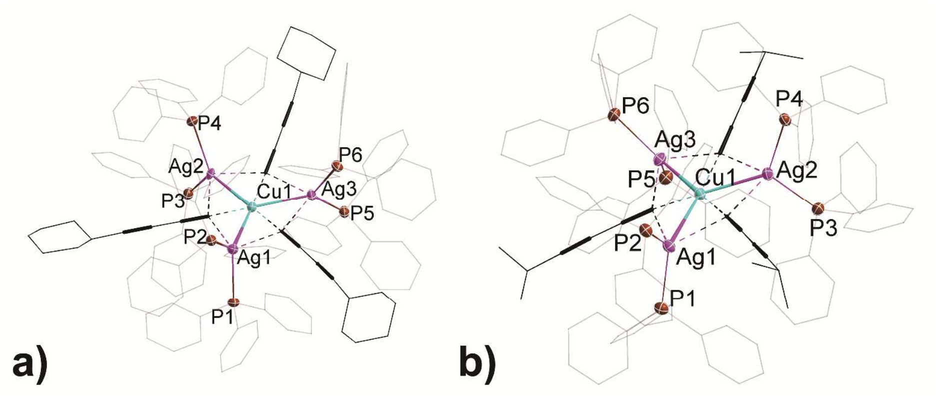

Figure 2. a) Coordination environment of the silver(I) and copper(I) atoms in the discrete molecule $[CuAg_3(chxC{\equiv}C{-}C{\equiv}C)_3(PPh_3)_6]PF_6$ in (**1**). b) Perspective view of the analogous cluster structure of $[CuAg_3({}^iPrC{\equiv}C{-}C{\equiv}C)_3(PPh_3)_6]PF_6$ (**2**). The hexafluorophosphate ions, diethyl ether solvate molecules and hydrogen atoms are omitted for clarity. Silver and copper atoms are drawn as thermal ellipsoids (50% probability level) with atom labeling. (Color scheme: purple, silver atoms; turquoise, copper atoms; broken lines, Ag–C and Cu–C bonds; the same color scheme for atoms and bonds applies to all other figures.) The argentophilic Ag(I)···Ag(I) distances lie in the range 2.70–3.40 Å, and the cupro–argentophilic Cu(I)···Ag(I) distances lie in the range 2.40–3.12 Å.

*$[\{CuAg_3\}Ag_4(chxC{\equiv}C{-}C{\equiv}C)_7(PPh_3)_5]PF_6{\cdot}1.5Et_2O$ (**3**), $[\{CuAg_3\}Ag_4({}^tBuC{\equiv}C{-}C{\equiv}C)_7(PPh_3)_5]ClO_4$ (**4**) and $[\{CuAg_3\}Ag_3({}^iPrC{\equiv}C{-}C{\equiv}C)_6(PPh_3)_5]PF_6$ (**5**)*

Yellow complex **3** was prepared by the reaction of 2 equiv. of $[(chxC{\equiv}C{-}C{\equiv}C)Ag]_4(PPh_3)_4$ and 1.5 equiv. of $[Cu(MeCN)_4]PF_6$ in CH_2Cl_2 (3 mL) at room temperature. Recrystallization by layering diethyl ether afforded yellow crystals in 25% yield. As illustrated in Figure 3a, seven Ag(I) and Cu(I) ions are aggregated to form a distorted augmented triangular prism through argentophilic interaction with Ag(I)···Ag(I) bond distances in the range 2.844(1)–3.343(1) Å, which are comparable to those observed in a wide variety of silver double and multiple salts.[19] Silver atoms Ag1, Ag2 and Ag3 are bound to the Cu1 atom (Ag(I)···Cu(I) bond distances: 2.641(1)–2.932(1) Å) in trigonal-planar fashion, and also to the non-planar tetragon formed by the remaining four silver atoms Ag4 to Ag7 on one side. The seven chxC≡C–C≡C^{-} ligands can be divided into four groups based on their different ligation behavior: two each in $\mu_4–\eta^1,\eta^1,\eta^2,\eta^2$, $\mu_3–\eta^1,\eta^1,\eta^2$ and $\mu_3–\eta^1,\eta^1,\eta^1$, and one in $\mu_2–\eta^1,\eta^1$ mode (Figure 3b). Silver atoms Ag1, Ag2, Ag3, Ag5 and Ag7 are each stabilized by a peripheral η^1–triphenylphosphine ligand. Of the two solvated diethyl ether molecules, one was found to have 50% site occupancy.

Notably, addition of a polar protic solvent like methanol (0.5 mL) to the reaction mixture is detrimental to the formation of complex **3**.

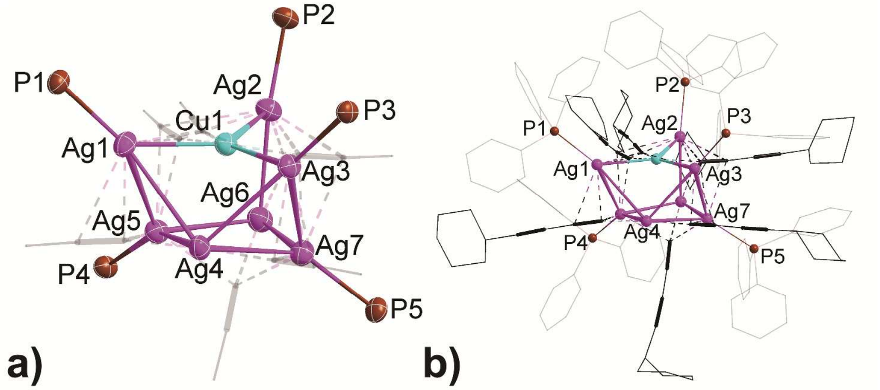

Figure 3. a) Thermal ellipsoid plot (50% probability level) of the $\{CuAg_3\}Ag_4$ core in $[\{CuAg_3\}Ag_4(chxC{\equiv}C–C{\equiv}C)_7(PPh_3)_5]PF_6{\cdot}1.5Et_2O$ (**3**) with atom labeling. b) Perspective view of the cluster structure including all peripheral ligands.

The reaction between $[(^t\mathrm{BuC{\equiv}C{-}C{\equiv}C})\mathrm{Ag}]_4(\mathrm{PPh_3})_4$ and $[\mathrm{Cu(MeCN)_4}]\mathrm{ClO_4}$ was conducted in $\mathrm{CH_2Cl_2}$ to obtain crystalline complex **4**, which is isostructural with **3**. In its $\mathrm{CuAg_7}$ core, the argentophilic Ag(I)···Ag(I) distances lie in the range of 2.876(1)–3.368(1) Å and the cupro-argentophilic interactions ranging from 2.650(1)–2.989(1) Å (Figure S1a in Supporting Information). The seven peripheral $^t\mathrm{BuC{\equiv}C{-}C{\equiv}C^-}$ ligands in **4** can be divided into five groups based on their different ligation behavior: two each in $\mu_4{-}\eta^1,\eta^1,\eta^2,\eta^2$ and $\mu_3{-}\eta^1,\eta^1,\eta^1$; one each in $\mu_3{-}\eta^1,\eta^2,\eta^2$, $\mu_3{-}\eta^1,\eta^1,\eta^2$ and $\mu_2{-}\eta^1,\eta^1$ mode (Figure S1b in Supporting Information).

Using a less bulky $^i\mathrm{PrC{\equiv}C{-}C{\equiv}C^-}$ ligand to react with $[\mathrm{Cu(MeCN)_4}]\mathrm{PF_6}$ in $\mathrm{CH_2Cl_2}$ yielded a smaller heterometallic $\mathrm{CuAg_6}$ core (Figure 4a). The six peripheral $^i\mathrm{PrC{\equiv}C{-}C{\equiv}C^-}$ ligands in **5** can be divided into four groups based on their different ligation behavior: one $\mu_4{-}\eta^1,\eta^1,\eta^1,\eta^2$, one $\mu_4{-}\eta^1,\eta^1,\eta^1,\eta^1$, two $\mu_3{-}\eta^1,\eta^1,\eta^1$ and two $\mu_3{-}\eta^1,\eta^1,\eta^2$ (Figure 4b).

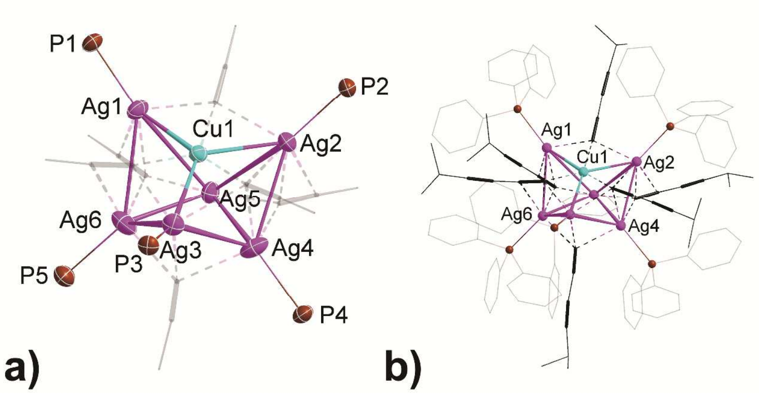

Figure 4. a) Thermal ellipsoid plot (50% probability level) of the $\{\mathrm{CuAg_3}\}\mathrm{Ag_3}$ core with atom labeling. b) Perspective view of the cluster structure of $[\{\mathrm{CuAg_3}\}\mathrm{Ag_3}(^i\mathrm{PrC{\equiv}C{-}C{\equiv}C})_6(\mathrm{PPh_3})_5]\mathrm{PF_6}$ (**5**).

*$[\{\mathrm{CuAg_3}\}\mathrm{Ag_4}\{\mathrm{CuAg_3}\}(\mathrm{chxC{\equiv}C{-}C{\equiv}C})_{10}(\mathrm{PPh_3})_6](\mathrm{PF_6})_2$ (**6**) and*

$[\{\mathrm{CuAg_3}\}\mathrm{Ag_4}\{\mathrm{CuAg_3}\}(^i\mathrm{PrC{\equiv}C{-}C{\equiv}C})_{10}(\mathrm{PPh_3})_6](\mathrm{PF_6})_2$ (7)

Yellow block-like crystals of complex **6** were obtained in 15% yield from crystallization by layering diethyl ether over the reaction between 1.0 equiv. of $[(chxC{\equiv}C{-}C{\equiv}C)Ag]_4(PPh_3)_4$ and 0.9 equiv. of $[Cu(MeCN)_4]PF_6$ in CH_2Cl_2. Copper(I) atom Cu1 is surrounded by silver(I) atoms Ag3, Ag4 and Ag5 in trigonal-planar fashion with Cu(I)···Ag(I) interactions in the range 2.680(1)–2.837(7) Å (Figure 5a). Atoms Ag1 and Ag2 and their inversion-related counterparts constitute a Ag_4 rhombus, which unsymmetrically bridge a pair of $CuAg_3$ aggregates through argentophilic interaction to engender a $\{CuAg_3\}Ag_4\{CuAg_3\}$ core structure. The different cyclohexyl-1,3-diynyl ligand coordination modes that stabilize the heterometallic core can be divided into three groups: four $\mu_4{-}\eta^1,\eta^1,\eta^1,\eta^2$, two $\mu_4{-}\eta^1,\eta^1,\eta^1,\eta^1$ and four $\mu_3{-}\eta^1,\eta^1,\eta^2$ (Figure 5b). The six symmetry-related triphenylphosphine ligands are each attached to one silver atom in the normal $\mu_1{-}P$ ligation mode.

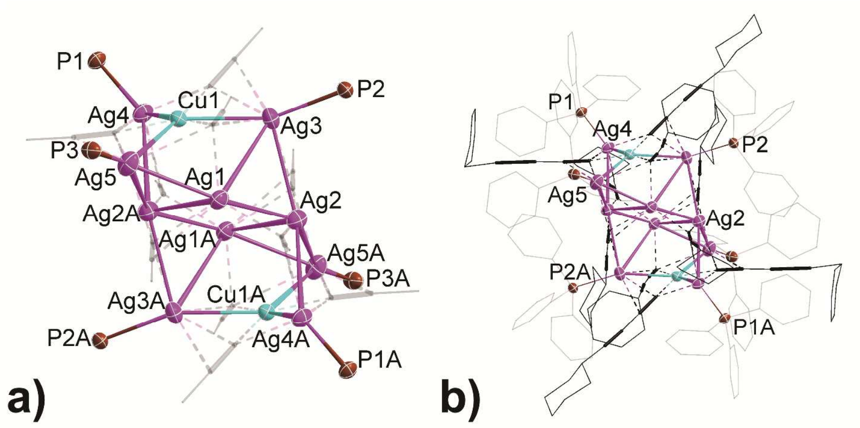

Figure 5. a) Thermal ellipsoid plot (50% probability level) of the centrosymmetric $\{CuAg_3\}Ag_4\{CuAg_3\}$ core of $[\{CuAg_3\}Ag_4\{CuAg_3\}(chxC{\equiv}C{-}C{\equiv}C)_{10}(PPh_3)_6](PF_6)_2$ (**6**) with atom labeling. b) Perspective view of the cluster structure showing all peripheral ligands. Symmetry code: A: $-x$, $1-y$, $1-z$.

Similar reaction using an analogous $[(^iPrC{\equiv}C{-}C{\equiv}C)Ag]_4(PPh_3)_4$ precursor produced iso-structural complex **7** in 15% yield. In its $\{CuAg_3\}Ag_4\{CuAg_3\}$ core, the Cu(I)···Ag(I) interaction distances lie in the range of 2.639(1)–2.679(1) Å, and argentophilic Ag(I)···Ag(I) distances between shell silver atoms range from 2.871(1) to 3.396(1) Å (Figure S2a in

Supporting Information). The ten peripheral iso-propyl-1,3-diynyl ligands can be divided into three groups based on their different ligation behavior: two $\mu_4{-}\eta^1,\eta^1,\eta^1,\eta^2$, two $\mu_3{-}\eta^1,\eta^1,\eta^2$, and six $\mu_3{-}\eta^1,\eta^1,\eta^1$ (Figure S2b in Supporting Information).

*[$Cu_2Ag_{10}({}^tBuC{\equiv}C{-}C{\equiv}C)_{12}(PPh_3)_2$] (**8**)*

When the reaction between 1.0 equiv. of [(^{t}BuC≡C–C≡C)Ag]$_4$(PPh$_3$)$_4$ and 0.8 equiv. of [Cu(MeCN)$_4$]ClO$_4$ was carried out in a more concentrated condition (2 mL CH$_2$Cl$_2$), well-formed yellow rhombus-like crystals of **8** were obtained in 30% yield. Two inversion-related pyramidal CuAg$_3$ segments, in which the central Cu1 atom is displaced from the least-squares plane of atoms Ag1, Ag1A and Ag4A by 0.435(6) Å, coalesce through argentophilic interaction to generate a heterometallic {CuAg$_3$}Ag$_2$Ag$_2${CuAg$_3$} core through vertex (Ag5 and Ag5A) and segment (Ag2–Ag3 and Ag2A–Ag3A) sharing (Figure 6a). The twelve peripheral ^{t}BuC≡C–C≡C$^-$ ligands exhibit three kinds of coordination modes: two $\mu_4{-}\eta^1,\eta^1,\eta^1,\eta^2$, four $\mu_3{-}\eta^1,\eta^1,\eta^1$, and six $\mu_2{-}\eta^1,\eta^1$ (Figure 6b). Silver atoms Ag5 and Ag5A are each further protected by a η^1–triphenylphosphine ligand.

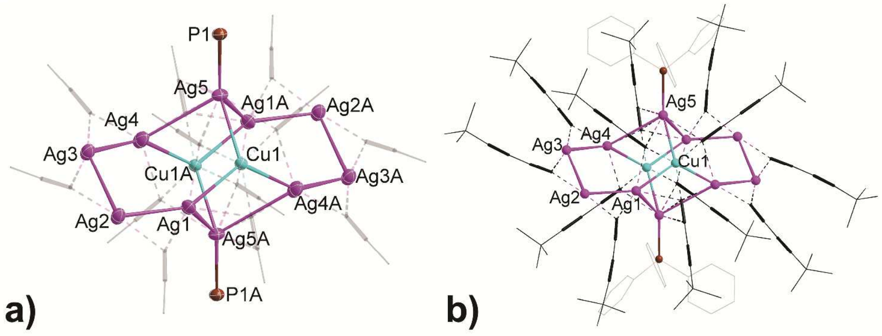

Figure 6. a) Thermal ellipsoid plot (50% probability level) of the {CuAg$_3$}Ag$_6${CuAg$_3$} core with atom labeling. b) Perspective view of the cluster structure of [Cu$_2$Ag$_{10}$(^{t}BuC≡C–C≡C)$_{12}$(PPh$_3$)$_2$] (**8**). Symmetry code: A: 2–*x*, 2–*y*, 2–*z*.

$[\{CuAg_3\}CuAg_6\{CuAg_3\}(^tBuC{\equiv}C{-}C{\equiv}C)_{12}(PPh_3)_6]$ $[\{CuAg_3\}Cu_2Ag_2\{CuAg_3\}(^tBuC{\equiv}C{-}C{\equiv}C)_{10}(PPh_3)_6]$ $(PF_6)_4{\cdot}(OH){\cdot}3Et_2O$ (**9**)

Orange block-like crystals of **9** were obtained in 10% yield by layering diethyl ether over a mixed solution of dichloromethane (3 mL) and methanol (0.5 mL) used in the reaction between 1.0 equiv. of $[(^tBuC{\equiv}C{-}C{\equiv}C)Ag]_4(PPh_3)_4$ and 1.0 equiv. of $Cu(MeCN)_4PF_6$. It is notable that only a yellowish oily substance was obtained when $[Cu(MeCN)_4]ClO_4$ replaced $[Cu(MeCN)_4]PF_6$ in the reaction.

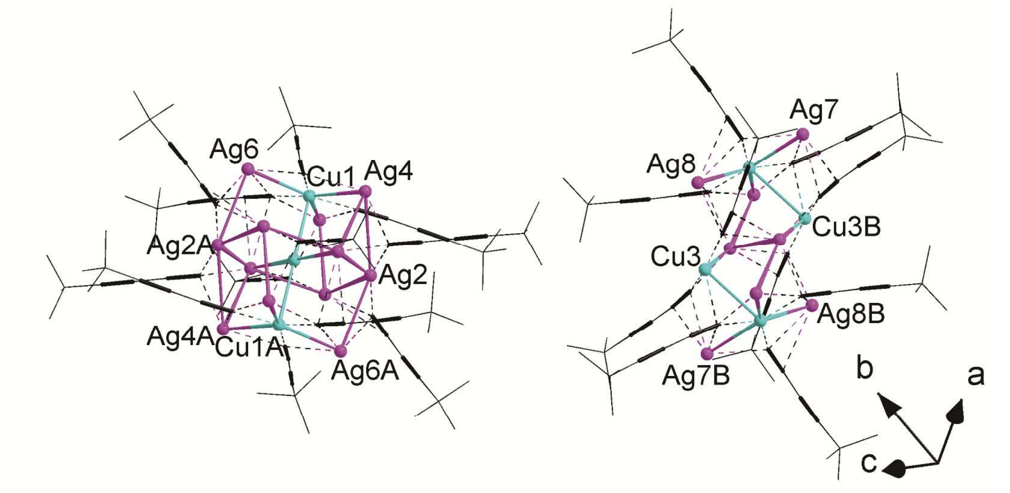

Figure 7. Perspective view of the structure of cationic clusters $[\{CuAg_3\}CuAg_6\{CuAg_3\}(^tBuC{\equiv}C{-}C{\equiv}C)_{12}(PPh_3)_6]^{3+}$ (left) and $[\{CuAg_3\}Cu_2Ag_2\{CuAg_3\}(^tBuC{\equiv}C{-}C{\equiv}C)_{10}(PPh_3)_6]^{3+}$ (right) in complex **9**. Symmetry code: A: $-x$, $2-y$, $2-z$; B: $1-x$, $1-y$, $1-z$.

There are two discrete centrosymmetric heterometallic molecular cations in the crystal structure, and charge balance is provided by four hexafluorophosphate anions and one hydroxide anion. In the larger cation $[\{CuAg_3\}CuAg_6\{CuAg_3\}(^tBuC{\equiv}C{-}C{\equiv}C)_{12}(PPh_3)_6]^{3+}$ (Figure 7, left side), a central Cu_3 rod-shaped segment (Cu(I)···Cu(I) distance = 2.752(8)Å, which indicates the presence of significant cuprophilic interaction in the range 2.46–3.42 Å.[20]) is surrounded by a quasi-cuboctahedral shell of twelve Ag(I) ions through cupro-argentophilic Cu(I)···Ag(I) interactions in the range 2.682(1)–2.898(7) Å and argentophilic Ag(I)···Ag(I) interactions ranging from 2.909(1) to 3.327(1) Å. The six symmetry-related pairs of peripheral ^{t}BuC≡C–C≡C¯ ligands are bound to such heterometallic core *via* different coordination modes, which can be divided into three groups: two μ_4–η^1,η^1,η^1,η^2, four μ_3–η^1,η^1,η^2 and six μ_3–η^1,η^1,η^1. The six triphenylphosphine ligands are each chelated on one silver atom via the μ_1–*P* ligation mode (Figure 8a).

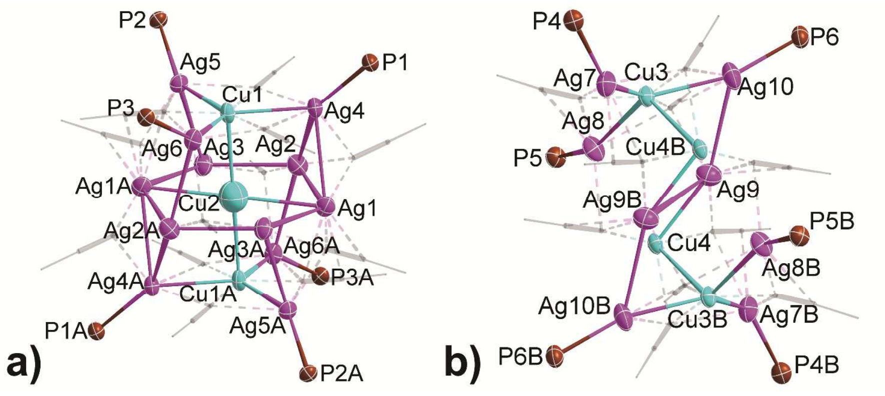

Figure 8. a) Thermal ellipsoid plot (50% probability level) of the core structure in the [{CuAg$_3$}CuAg$_6${CuAg$_3$}(^{t}BuC≡C–C≡C)$_{12}$(PPh$_3$)$_6$]$^{3+}$ cationic cluster molecule. b) Thermal ellipsoid plot (50% probability level) of the core structure in [{CuAg$_3$}Cu$_2$Ag$_2${CuAg$_3$}(^{t}BuC≡C–C≡C)$_{10}$(PPh$_3$)$_6$]$^{2+}$ cationic cluster molecule. Symmetry code: A: –*x*, 2–*y*, 2–*z*; B: 1–*x*, 1–*y*, 1–*z*.

In the smaller heterometallic cation [{CuAg$_3$}Cu$_2$Ag$_2${CuAg$_3$}(^{t}BuC≡C–C≡C)$_{10}$(PPh$_3$)$_6$]$^{2+}$ (Figure 7, right side), a central Cu$_2$Ag$_2$ zigzag segment is linked by a pair of trigonal-planar CuAg$_3$ aggregates through Cu(I)···Cu(I) (2.861(1) Å) and Ag(I)···Ag(I) interactions to engender a Cu$_4$Ag$_8$ heterometallic core. The ten peripheral symmetry-related pairs of ^{t}BuC≡C–C≡C¯ ligands are each bonded to either three or four Ag(I) centers in different ligation modes: four in μ_4–η^1,η^1,η^1,η^1 and six in μ_3–η^1,η^1,η^2 mode, and the three independent triphenylphosphine groups are each chelated on one silver atom (Figure 8b).

Complex **9** is unique as it is the only one in the series that contains two different cationic silver(I)-copper(I) clusters that are consolidated by cuprophilic Cu(I)···Cu(I) interactions.

Photophysical Properties

The photophysical data for the three synthetic precursors and complexes **1**–**3** and **5**–**8** are summarized in Table 1. Figure 9 illustrates the electronic absorption spectra of the $[(\text{chxC}\equiv\text{C}-\text{C}\equiv\text{C})\text{Ag}]_4(\text{PPh}_3)_4$ precursor and **1** in CH_2Cl_2 at room temperature, while Figure 10 depicts the emission spectra of **7** in the solid state at room temperature and 77 K.

The electronic absorption spectra of the three precursors and complexes **1**–**3** and **5**–**8** show an intense high-energy absorption band at *ca*. 240–295 nm, while **1**–**3** and **5**–**8** show an additional lower-energy absorption shoulder at *ca*. 320 nm. The high-energy absorption band can be assigned as the intra-ligand transition of the triphenylphosphine and diynyl ligands while the lower-energy absorption shoulder can be tentatively assigned as the metal-perturbed intraligand $[\pi\rightarrow\pi^*(\text{RC}\equiv\text{C}-\text{C}\equiv\text{C}-)]$ transition.[7,22,23]

Excitation of the three precursors and complexes **1**–**3** and **5**–**8** in ethanol-methanol glass and in the solid state at 77 K, the solid samples of $[(\text{chxC}\equiv\text{C}-\text{C}\equiv\text{C})\text{Ag}]_4(\text{PPh}_3)_4$, **1** and **6**–**8**, and the fluid solutions of **2**, **5**–**7** at room temperature at $\lambda > 320$ nm results in long-lived emission. Their emission lifetimes in the microsecond range suggest the triplet parentage of the emission origins.

Highly structured emission bands are obtained for all the complexes in ethanol-methanol glass at 77 K with vibrational progressional spacings of *ca.* 1350–1450 cm^{-1} and 1800–2100 cm^{-1}, which are typical of the ν(C–H) and ν(C≡C) stretching modes in the ground state. Similar vibronic-structured emission bands have also been observed for the solid samples of the three synthetic precursors, **1**–**3**, **5** and **8** at 77 K, $[(\text{chxC}\equiv\text{C}-\text{C}\equiv\text{C})\text{Ag}]_4(\text{PPh}_3)_4$ precursor and **1** at room temperature, and the fluid solution of **2**, **5**–**7** at room temperature. These observations are suggestive of the involvement of the diynyl unit in the emissive excited state.[7,22,23] Structure-less emission bands have been obtained for the solid samples of **6** and **7** at room temperature and 77 K, which can be tentatively assigned as the metal centered d→s state, mixing with the ligand-to-metal charge-transfer (LMCT) character modified by the Ag(I)···Ag(I) and/or Ag(I)···Cu(I) interactions.[7,22,23] These findings are in line with the crystal structures obtained for **6** and **7**, which consist of more compact $\{CuAg_3\}Ag_4\{CuAg_3\}$cores with more extended Ag(I)···Ag(I) and Ag(I)···Cu(I) interactions, and are different from the relatively open $CuAg_3$ cores of **3** and **5** and $\{CuAg_3\}Ag_2Ag_2\{CuAg_3\}$ core of **8** that mainly lead to vibronic-structured ligand-centered emission bands.

Table 1. Photophysical data for the synthetic precursors and selected complexes.

Complex	Absorption λ / nm (ε / dm^3 mol^{-1} cm^{-1})[a]	Medium (T / K)	Emission λ_{em} / nm (τ / μs)
$[(chxC{\equiv}C{-}C{\equiv}C)Ag]_4(PPh_3)_4$	248 sh (99,120),	CH_2Cl_2 (298)	–[e]
	274 sh (39,680),	Solid (298)[b]	485 (258)
	295 sh (12,710)	Solid (77)[b]	483 (495)
		Glass (77)[b–d]	472 (107)
$[(^iPrC{\equiv}C{-}C{\equiv}C)Ag]_4(PPh_3)_4$	246 sh (90,950),	CH_2Cl_2 (298)	–[e]
	276 sh (35,230),	Solid (298)	–[e]
	291 sh (13,780)	Solid (77)[b,c]	476 (380)
		Glass (77)[b–d]	468 (109)
$[(^tBuC{\equiv}C{-}C{\equiv}C)Ag]_4(PPh_3)_4$	247 sh (102,340),	CH_2Cl_2 (298)	–[e]
	276 sh (38,610),	Solid (298)	–[e]

	294 sh (13,720)	Solid (77)^{b,c}	465 (503)
		Glass (77)$^{b\text{–}d}$	473 (118)
$[CuAg_3(chxC{\equiv}C{-}C{\equiv}C)_3(PPh_3)_6]PF_6{\cdot}2Et_2O$ (**1**)	247 (134,910), 256 sh (107,690), 276 sh (73,740), 321 sh (10,210)	CH_2Cl_2 (298) Solid (298)^{b,c} Solid (77)^{b,c} Glass (77)$^{b\text{–}d}$	–^{e} 464 (10.6) 468 (51.6) 465 (38.7)

Complex	**Absorption λ / nm (ε / dm^3 mol^{-1} cm^{-1})^a**	**Medium (T / K)**	**Emission λ_{em} / nm (τ / μs)**
$[CuAg_3(^{i}PrC{\equiv}C{-}C{\equiv}C)_3(PPh_3)_6]PF_6$ (**2**)	244 (125,000), 256 sh (104,520), 276 sh (74,190), 319 (12,070)	CH_2Cl_2 (298)^{b,c} Solid (298) Solid (77)^{b,c} Glass (77)$^{b\text{–}d}$	506 (9.37) –^{e} 486 (71.9) 466 (45.5)
$[\{CuAg_3\}Ag_4(chxC{\equiv}C{-}C{\equiv}C)_7(PPh_3)_5]PF_6{\cdot}1.5Et_2O$ (**3**)	244 sh (170,820), 254 sh (143,860), 276 sh (94,470), 322 sh (16,060)	CH_2Cl_2 (298) Solid (298) Solid	–^{e} –^{e} 462 (17.9) 484

		(77)^{b,c}	(31.4)
		Glass (77)$^{b–d}$	
$[\{CuAg_3\}Ag_3(^iPrC{\equiv}C{-}C{\equiv}C)_6(PPh_3)_5]PF_6$ (**5**)	243 (125,130), 253 sh (109,520), 277 sh (69,140), 318 (13,020)	CH_2Cl_2 (298)^{b,c}	501 (10.1)
		Solid (298)	–^{e}
		Solid (77)^{b,c}	484 (64.0)
		Glass (77)$^{b–d}$	465 (39.2)
$[\{CuAg_3\}Ag_4\{CuAg_3\}(chxC{\equiv}C{-}C{\equiv}C)_{10}(PPh_3)_6](PF_6)_2$ (**6**)	245 sh (189,500), 264 sh (141,300), 278 sh (104,310), 318 sh (19,360)	CH_2Cl_2 (298)^{b,c}	501 (10.2)
		Solid (298)	705 (1.05)
		Solid (77)	725 (7.81)
		Glass (77)$^{b–d}$	483 (28.8)

Complex	**Absorption λ / nm (ε / dm^3 mol^{-1} cm^{-1})^a**	**Medium (T / K)**	**Emission λ_{em} / nm (τ / μs)**

$[\{CuAg_3\}Ag_4\{CuAg_3\}(^iPrC{\equiv}C{-}C{\equiv}C)_{10}(PPh_3)_6](PF_6)_2$ (**7**)	244 (229,010), 252 sh (199,270), 278 sh (125,170), 318 (25700)	CH_2Cl_2 (298)^{b,c}	505 (10.4) 634 (5.16)
		Solid (298)	650 (35.5)
		Solid (77)	458 (10.9)
		Glass (77)$^{b–d}$	
$[Cu_2Ag_{10}(^tBuC{\equiv}C{-}C{\equiv}C)_{12}(PPh_3)_2]$ (**8**)	242 sh (236,160), 254 sh (164,220), 263 sh (131,450), 277 sh (95,900), 293 sh (54,800), 318 sh (22,160)	CH_2Cl_2 (298)	–^{e}
		Solid (298)	498 (0.98)
		Solid (77)^{b,c}	474 (12.4)
		Glass (77)$^{b–d}$	478 (26.0)

[a] Measured in CH_2Cl_2

[b] Vibrational progressional spacing of *ca*. 2100 cm^{-1}

[c] Vibrational progressional spacing of *ca*. 1350 cm^{-1}

[d] Measured in ethanol-methanol-dichloromethane (4:1:0.1, v/v) glass

[e] Non-emissive

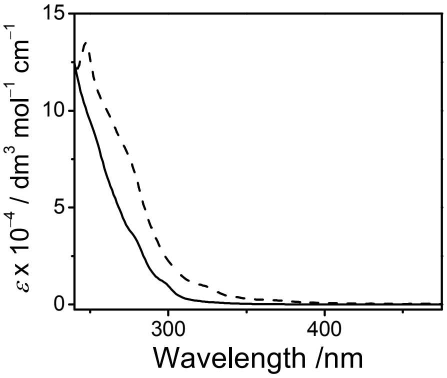

Figure 9. Electronic absorption spectra of $[(chxC{\equiv}C{-}C{\equiv}C)Ag]_4(PPh_3)_4$ (solid line) and **1** (dashed line) in CH_2Cl_2 at 298 K.

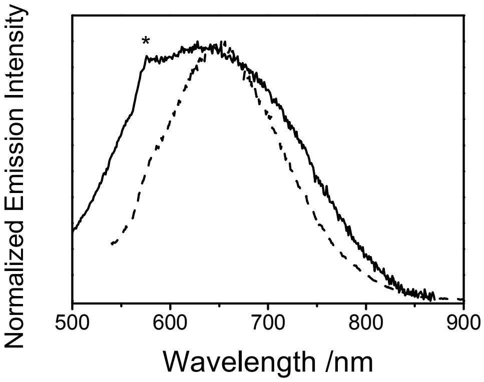

Figure 10. Emission spectra of **7** in the solid state at 298 K (solid line) and 77 K (dashed line) (* denotes instrumental artefact).

Assembly Mechanism

Design of the three synthetic precursors was based on the anticipation that bulky alkyl 1,3-diyn-1-ide and triphenylphosphine could play complementary roles in serving as peripheral protective ligands for the generation and stabilization of heteropolynuclear Cu(I)-Ag(I) clusters. In either $[Cu(MeCN)_4]PF_6$ or $[Cu(MeCN)_4]ClO_4$, the Cu(I) ion is isolated by four linear acetonitrile ligands from poorly-coordinating PF_6^- and ClO_4^- groups. The argentophilic Ag_4 aggregate of all three precursors $[(RC{\equiv}C{-}C{\equiv}C)Ag]_4(PPh_3)_4$ (R = ^{i}Pr, ^{t}Bu and chx) may be envisaged to partially degrade upon dissolution in CH_2Cl_2 in the presence of Cu(I) ions, thereby freeing it for condensation with the abundant supply of Cu(I) ions. As a result, the central Cu(I) ion is encapsulated by three Ag(I) alkyl diynyls through cupro-argentophilic interaction to yield **1** and **2**, which serve as a core structural element in the formation of complexes **3–9**. Attempts to isolate the structural analog of **1** using $[(^tBuC{\equiv}C{-}C{\equiv}C)Ag]_4(PPh_3)_4$ as a synthetic precursor were unsuccessful, but existence of complexes **4**, **8** and **9** indicated the *in-situ* formation of $Cu[Ag(^tBuC{\equiv}C{-}C{\equiv}C)]_3$ during synthesis.

Generation of heteronuclear cluster complexes **3**–**9** presumably materializes from the choice of, and proper stoichiometric balance between, silver(I) alkyl-1,3-diynyl and acetonitrile-coordinated copper(I) salts in CH_2Cl_2. A plausible assembly mechanism for the series of cluster complexes **3**–**9** is illustrated in Figure 11. It is proposed that each assembly is first initiated by the formation of a $CuAg_3(C{\equiv}C{-}C{\equiv}CR)_3$ central core from the reaction between $[(RC{\equiv}C{-}C{\equiv}C)Ag]_4$ and $[Cu(MeCN)_4]X$ ($X = PF_6$ or ClO_4). For complex **3** and **4**, the $\{CuAg_3\}Ag_4$ core is assembled through argentophilic interaction between *in-situ* generated $CuAg_3(C{\equiv}C{-}C{\equiv}CR)_3$ and remaining neighbor $[(RC{\equiv}C{-}C{\equiv}C)Ag]_4$ clusters. The decreased bulkiness of the *iso*-propyl group with respect to the *tert*-butyl or cyclohexyl group accounts for the fact that only a smaller $\{CuAg_3\}Ag_3$ core exists in **5**.

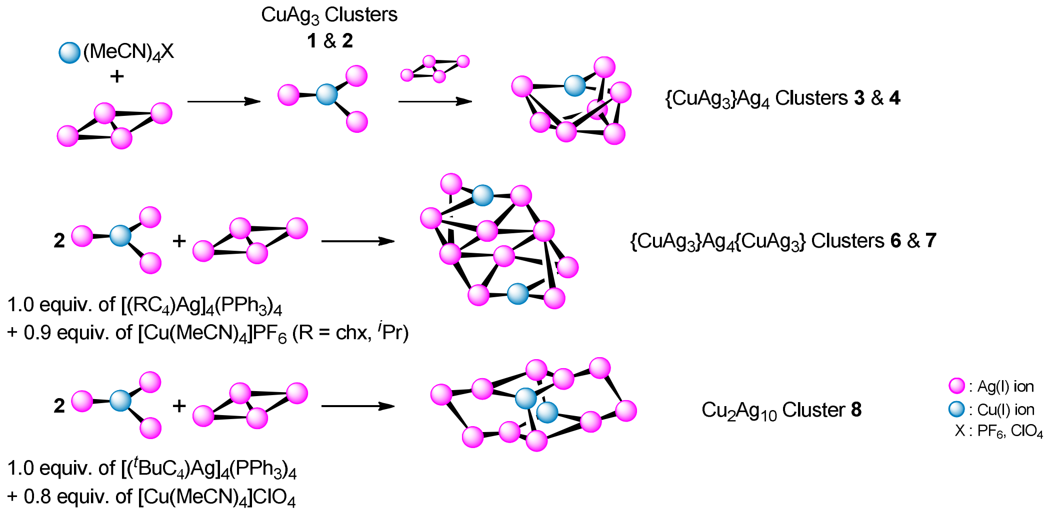

Figure 11. Proposed assembly mechanism for complexes **1**–**9**, showing only the connection between monovalent Group 11 cations.

As the concentration of Cu(I) ions in the reaction mixture increases, the corresponding $CuAg_3(C{\equiv}C{-}C{\equiv}CR)_3$ complex is expected to be generated in a relatively higher content, in which case the ratio of $CuAg_3$ complex and unreacted $[(RC{\equiv}C{-}C{\equiv}C)Ag]_4$ clusters reaches 2:1. For both the *iso*-propyl and cyclohexyl groups, which are considered to be less sterically hindered, two $CuAg_3$ units sandwich a Ag_4 aggregate through argentophilic interaction to yield a $\{CuAg_3\}Ag_4\{CuAg_3\}$ structural core (complexes **6** and **7**). When either the *iso*-propyl or cyclohexyl peripheral group is replaced by the more bulky *tert*-butyl group in **8**, two pyramidal $CuAg_3$ units are connected by a pair of Ag_2 rods to yielded a $\{CuAg_3\}Ag_2Ag_2\{CuAg_3\}$ cluster core. In the synthesis of **9**, the reaction mechanism presumably involves multiple steps when molar ratio of the precursor and Cu(I) salt becomes 1:1. There are two discrete molecules in one asymmetric unit, in which $CuAg_3(^tBuC{\equiv}C{-}C{\equiv}C)_3$ is found to be their common structural unit.

Among the seven heterometallic clusters, the peripheral triphenylphosphine ligands play a key role to stabilize each core structure. Complexes **1**–**7** are slightly soluble in dichloromethane, while complexes **8** and **9** are insoluble in different polar organic solvents. The solution properties of **1**–**7** were investigated using ESI-MS and NMR spectroscopy. Unfortunately, attempts to record the molecular weight signals of all complexes were unsuccessful, as the highly charged cluster cation was labile during the ESI process, in which the molecular ions of the corresponding clusters or fragments generated could not be detected. It is worthy of note that although the re-assembly process that results in the synthesis of **1**–**9** takes a long time to accomplish at room temperature, it is nonetheless energetically feasible and reproducible.

CONCLUSION

In summary, we have employed designed tetranuclear precursors $[(R{-}C{\equiv}C{-}C{\equiv}C)Ag]_4$ (R = ^{i}Pr, ^{t}Bu and chx) to construct a series of heteropolynuclear silver(I)-copper(I) diynyl complexes (**1**–**9**) that bear a common trigonal-planar $CuAg_3$ cluster core. The tetranuclear precursors and selected complexes are found to exhibit long-lived emission upon photo-excitation in various media at room temperature and 77 K.

The present study strongly suggests that the formation of medium-nuclearity Group 11 heterometallic clusters **3–9** is initiated by accretion of additional Ag(I) ions by the ubiquitous trigonal-planar $CuAg_3$ template through argentophilic interaction, with cooperative cuprophilic enhancement in the case of compound **9**. To our knowledge, the synthesis and structural characterization of clusters **3-9** provides the first example of conversion of a homonuclear coinage-metal cluster into a heteronuclear one of higher nuclearity *via* inner-core transformation.

ASSOCIATED CONTENT

Supporting Information

Experimental details, additional figures, NMR spectra, and X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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Table of Contents

New tetranuclear supramolecular precursors [(R–C≡C–C≡C)Ag]$_4$ (R = ^{i}Pr, ^{t}Bu and chx) are employed to construct a series of heterometallic silver(I)-copper(I) alkyl-1,3-diynyl cluster complexes (**1**-**9**) that bear a common CuAg$_3$ core (normally trigonal-planar, but can be distorted to pyramidal) consolidated by cupro-argentophilic interaction.