

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

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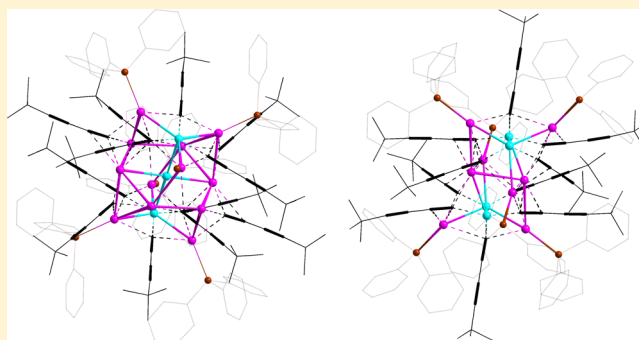
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Supporting Information

ABSTRACT: New tetranuclear supramolecular precursors $[(R-C\equiv C-C\equiv C)Ag]_4$ ($R = ^iPr, ^tBu,$ 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 cupro-philic 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 $R-C\equiv C\equiv Ag_n$ ($R = ^iBu$ 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 $Ag(I)\cdots Cu(I)$ molecular cluster complexes obtained from the reaction between designed $[(RC\equiv C-C\equiv C)Ag]_4(PPh_3)_4$ ($R = ^iPr, ^tBu$ 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 $[(RC\equiv C-C\equiv C)Ag]_4(PPh_3)_4$ ($R = ^iPr, ^tBu,$ 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 dichloro-methane (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 2 days, colorless block-like crystals of $[(^iPrC\equiv C-C\equiv C)-$

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$\text{Ag}]_4(\text{PPh}_3)_4$, $[(^t\text{BuC}\equiv\text{C}-\text{C}\equiv\text{C})\text{Ag}]_4(\text{PPh}_3)_4 \cdot 2\text{MeCN}$ and $[(\text{chxC}\equiv\text{C}-\text{C}\equiv\text{C})\text{Ag}]_4(\text{PPh}_3)_4 \cdot 2\text{MeOH}$ were each deposited in ca. 80% yield.

Description of Crystal and Molecular Structure. $[(\text{chxC}\equiv\text{C}-\text{C}\equiv\text{C})\text{Ag}]_4(\text{PPh}_3)_4 \cdot 2\text{MeOH}$. There are two independent and isostructural $[(\text{chxC}\equiv\text{C}-\text{C}\equiv\text{C})\text{Ag}]_4(\text{PPh}_3)_4$ 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 $\text{chxC}\equiv\text{C}-\text{C}\equiv\text{C}^-$ groups, whereas the PPh_3 ligands are attached only to the outer Ag1 centers (Figure 1). In the two independent cluster molecules, the observed

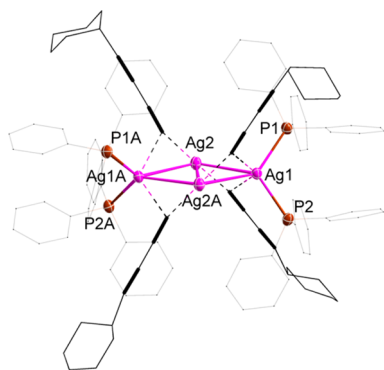
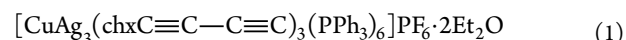


Figure 1. Coordination environment of the silver(I) atoms in the discrete molecule $[(\text{chxC}\equiv\text{C}-\text{C}\equiv\text{C})\text{Ag}]_4(\text{PPh}_3)_4$. The $\text{C}\equiv\text{C}$ triple bonds in the alkyl-1,3-diyne ligands are shown as thick rods. Silver atoms are drawn as thermal ellipsoids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

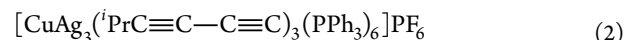
argentophilic $\text{Ag}\cdots\text{Ag}$ distances range from 2.962(5) to 3.008(5) Å, and the $\text{Ag1}-\text{Ag2}-\text{Ag1A}$ and $\text{Ag2}-\text{Ag1}-\text{Ag2A}$ angles are 120.3(1)° and 59.5(1)°, respectively. The two methanol molecules are linked together by a weak hydrogen bond of length 2.67 Å.

As expected, single-crystal X-ray analysis established that the tetranuclear molecular clusters $[(\text{RC}\equiv\text{C}-\text{C}\equiv\text{C})\text{Ag}]_4(\text{PPh}_3)_4$ ($\text{R} = ^i\text{Pr}$ and ^tBu) are structural analogs of $[(\text{chxC}\equiv\text{C}-\text{C}\equiv\text{C})\text{Ag}]_4(\text{PPh}_3)_4$,

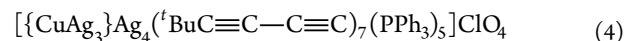
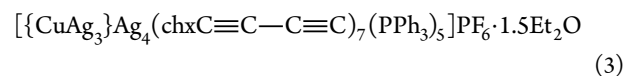
with each *i*-propyl or *tert*-butyl group replacing the corresponding peripheral cyclohexyl group, the only difference between them is that crystalline $[(^i\text{PrC}\equiv\text{C}-\text{C}\equiv\text{C})\text{Ag}]_4(\text{PPh}_3)_4$ is solvent-free, and there are two cocrystallized acetonitrile molecules in $[(^t\text{BuC}\equiv\text{C}-\text{C}\equiv\text{C})\text{Ag}]_4(\text{PPh}_3)_4 \cdot 2\text{MeCN}$.



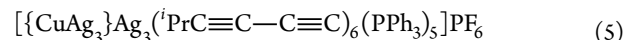
and



The reaction between 1.0 equiv of $[(\text{chxC}\equiv\text{C}-\text{C}\equiv\text{C})\text{Ag}]_4(\text{PPh}_3)_4$ and 0.7 equiv of $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$ in CH_2Cl_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 $\text{chxC}\equiv\text{C}-\text{C}\equiv\text{C}^-$ 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 cocrystallized diethyl ether molecules in **1**.



and



Yellow complex **3** was prepared by the reaction of **2** equiv of $[(\text{chxC}\equiv\text{C}-\text{C}\equiv\text{C})\text{Ag}]_4(\text{PPh}_3)_4$ and 1.5 equiv of $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$ 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 $\text{Ag}(\text{I})\cdots\text{Ag}(\text{I})$ bond distances in the range 2.844(1)–3.343(1) Å, which are comparable to those observed in a wide variety of silver

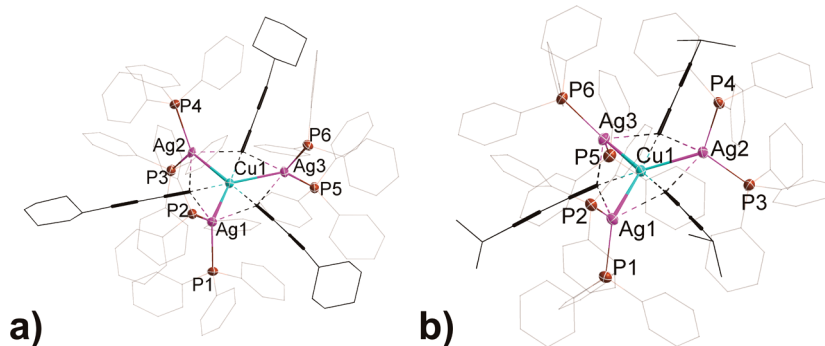


Figure 2. a) Coordination environment of the silver(I) and copper(I) atoms in the discrete molecule $[\text{CuAg}_3(\text{chxC}\equiv\text{C}-\text{C}\equiv\text{C})_3(\text{PPh}_3)_6]\text{PF}_6$ (**1**). b) Perspective view of the analogous cluster structure of $[\text{CuAg}_3(^i\text{PrC}\equiv\text{C}-\text{C}\equiv\text{C})_3(\text{PPh}_3)_6]\text{PF}_6$ (**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, $\text{Ag}-\text{C}$ and $\text{Cu}-\text{C}$ bonds; the same color scheme for atoms and bonds applies to all other figures.) The argentophilic $\text{Ag}(\text{I})\cdots\text{Ag}(\text{I})$ distances lie in the range 2.70–3.40 Å, and the cupro-argentophilic $\text{Cu}(\text{I})\cdots\text{Ag}(\text{I})$ distances lie in the range 2.40–3.12 Å.

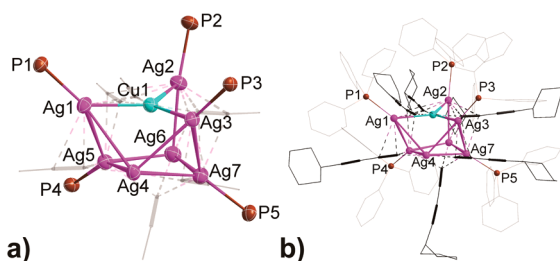


Figure 3. a) Thermal ellipsoid plot (50% probability level) of the $\{\text{CuAg}_3\}\text{Ag}_4$ core in $[\{\text{CuAg}_3\}\text{Ag}_4(\text{chxC}\equiv\text{C}-\text{C}\equiv\text{C})_7(\text{PPh}_3)_5]\text{PF}_6 \cdot 1.5\text{Et}_2\text{O}$ (**3**) with atom labeling. b) Perspective view of the cluster structure including all peripheral ligands.

double and multiple salts.¹⁹ Silver atoms Ag1, Ag2, and Ag3 are bound to the Cu1 atom ($\text{Ag(I)}\cdots\text{Cu(I)}$ bond distances: 2.641(1)–2.932(1) Å) in trigonal-planar fashion, and also to the nonplanar tetragon formed by the remaining four silver atoms Ag4 to Ag7 on one side. The seven $\text{chxC}\equiv\text{C}-\text{C}\equiv\text{C}^-$ 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**.

The reaction between $[(^t\text{BuC}\equiv\text{C}-\text{C}\equiv\text{C})\text{Ag}]_4(\text{PPh}_3)_4$ and $[\text{Cu}(\text{MeCN})_4]\text{ClO}_4$ was conducted in CH_2Cl_2 to obtain crystalline complex **4**, which is isostructural with **3**. In its CuAg_7 core, the argentophilic $\text{Ag(I)}\cdots\text{Ag(I)}$ 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 the Supporting Information). The seven peripheral $^t\text{BuC}\equiv\text{C}-\text{C}\equiv\text{C}^-$ 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).

Using a less bulky $^i\text{PrC}\equiv\text{C}-\text{C}\equiv\text{C}^-$ ligand to react with $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$ in CH_2Cl_2 yielded a smaller heterometallic CuAg_6 core (Figure 4a). The six peripheral $^i\text{PrC}\equiv\text{C}-\text{C}\equiv\text{C}^-$ 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).

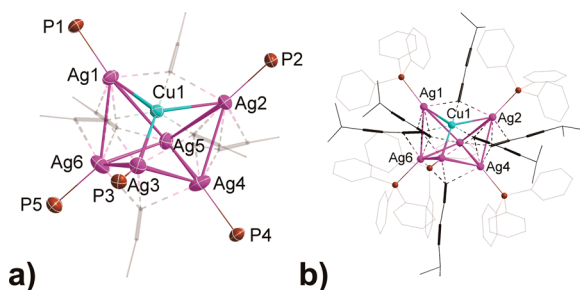
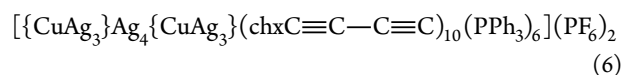
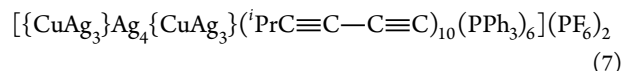


Figure 4. a) Thermal ellipsoid plot (50% probability level) of the $\{\text{CuAg}_3\}\text{Ag}_3$ core with atom labeling. b) Perspective view of the cluster structure of $[\{\text{CuAg}_3\}\text{Ag}_3(^i\text{PrC}\equiv\text{C}-\text{C}\equiv\text{C})_6(\text{PPh}_3)_5]\text{PF}_6$ (**5**).



and



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 $[(\text{chxC}\equiv\text{C}-\text{C}\equiv\text{C})\text{Ag}]_4(\text{PPh}_3)_4$ and 0.9 equiv of $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$ in CH_2Cl_2 . Copper(I) atom Cu1 is surrounded by silver(I) atoms Ag3, Ag4, and Ag5 in trigonal-planar fashion with $\text{Cu(I)}\cdots\text{Ag(I)}$ interactions in the range 2.680(1)–2.837(7) Å (Figure 5a).

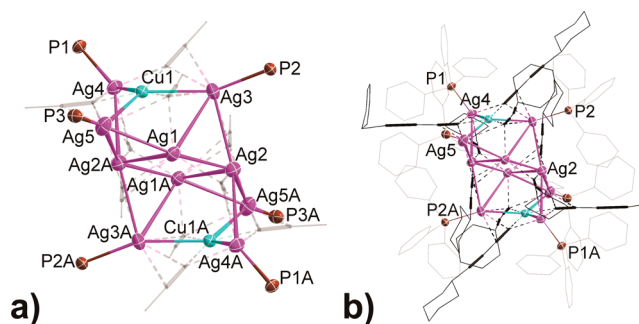
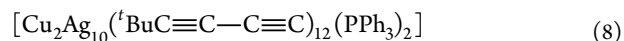


Figure 5. a) Thermal ellipsoid plot (50% probability level) of the centrosymmetric $\{\text{CuAg}_3\}\text{Ag}_4\{\text{CuAg}_3\}$ core of $[\{\text{CuAg}_3\}\text{Ag}_4\{\text{CuAg}_3\}(\text{chxC}\equiv\text{C}-\text{C}\equiv\text{C})_{10}(\text{PPh}_3)_6](\text{PF}_6)_2$ (**6**) with atom labeling. b) Perspective view of the cluster structure showing all peripheral ligands. Symmetry code: A: $-x, 1-y, 1-z$.

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 $\{\text{CuAg}_3\}\text{Ag}_4\{\text{CuAg}_3\}$ 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 μ_1-P ligation mode.

Similar reaction using an analogous $[(^i\text{PrC}\equiv\text{C}-\text{C}\equiv\text{C})\text{Ag}]_4(\text{PPh}_3)_4$ precursor produced iso-structural complex **7** in 15% yield. In its $\{\text{CuAg}_3\}\text{Ag}_4\{\text{CuAg}_3\}$ core, the $\text{Cu(I)}\cdots\text{Ag(I)}$ interaction distances lie in the range of 2.639(1)–2.679(1) Å, and argentophilic $\text{Ag(I)}\cdots\text{Ag(I)}$ distances between shell silver atoms range from 2.871(1) to 3.396(1) Å (Figure S2a). 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).



When the reaction between 1.0 equiv of $[(^t\text{BuC}\equiv\text{C}-\text{C}\equiv\text{C})\text{Ag}]_4(\text{PPh}_3)_4$ and 0.8 equiv of $[\text{Cu}(\text{MeCN})_4]\text{ClO}_4$ was carried out in a more concentrated condition (2 mL CH_2Cl_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

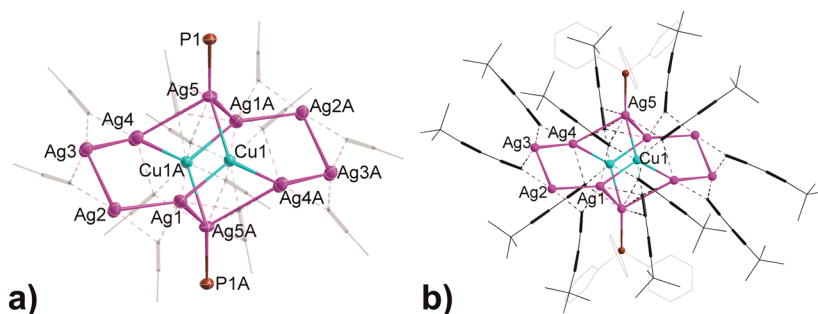
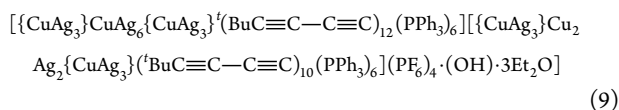


Figure 6. a) Thermal ellipsoid plot (50% probability level) of the $\{\text{CuAg}_3\}\text{Ag}_2\{\text{CuAg}_3\}$ core with atom labeling. b) Perspective view of the cluster structure of $[\text{Cu}_2\text{Ag}_{10}(\text{}^t\text{BuC}\equiv\text{C}-\text{C}\equiv\text{C})_{12}(\text{PPh}_3)_2]$ (**8**).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

$\{\text{CuAg}_3\}\text{Ag}_2\{\text{CuAg}_3\}$ core through vertex (Ag5 and Ag5A) and segment (Ag2–Ag3 and Ag2A–Ag3A) sharing (Figure 6a). The 12 peripheral $\text{}^t\text{BuC}\equiv\text{C}-\text{C}\equiv\text{C}$ 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.



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 $[(\text{}^t\text{BuC}\equiv\text{C}-\text{C}\equiv\text{C})\text{Ag}]_4(\text{PPh}_3)_4$ and 1.0 equiv of $\text{Cu}(\text{MeCN})_4\text{PF}_6$. It is notable that only a yellowish oily substance was obtained when $[\text{Cu}(\text{MeCN})_4]\text{ClO}_4$ replaced $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$ in the reaction.

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 $[\{\text{CuAg}_3\}\text{CuAg}_6\{\text{CuAg}_3\}-(\text{}^t\text{BuC}\equiv\text{C}-\text{C}\equiv\text{C})_{12}(\text{PPh}_3)_6]^{3+}$ (Figure 7, left side), a central

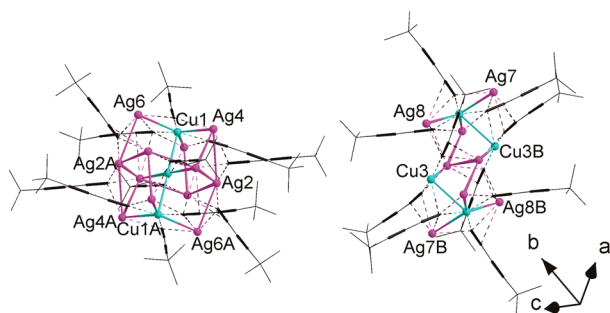


Figure 7. Perspective view of the structure of cationic clusters $[\{\text{CuAg}_3\}\text{CuAg}_6\{\text{CuAg}_3\}(\text{}^t\text{BuC}\equiv\text{C}-\text{C}\equiv\text{C})_{12}(\text{PPh}_3)_6]^{3+}$ (left) and $[\{\text{CuAg}_3\}\text{Cu}_2\text{Ag}_2\{\text{CuAg}_3\}(\text{}^t\text{BuC}\equiv\text{C}-\text{C}\equiv\text{C})_{10}(\text{PPh}_3)_6]^{3+}$ (right) in complex **9**. Symmetry code: A: $-x, 2-y, 2-z$; B: $1-x, 1-y, 1-z$.

Cu_3 rod-shaped segment ($\text{Cu(I)}\cdots\text{Cu(I)}$ distance = $2.752(8)\text{Å}$, which indicates the presence of significant cuprophilic interaction in the range $2.46\text{--}3.42\text{Å}$.^{20,21}) is surrounded by a quasi-cuboctahedral shell of 12 Ag(I) ions through cuproargentophilic $\text{Cu(I)}\cdots\text{Ag(I)}$ interactions in the range $2.682(1)\text{--}2.898(7)\text{Å}$ and argentophilic $\text{Ag(I)}\cdots\text{Ag(I)}$ interactions ranging from $2.909(1)$ to $3.327(1)\text{Å}$. The six symmetry-related pairs of peripheral $\text{}^t\text{BuC}\equiv\text{C}-\text{C}\equiv\text{C}$ ligands are bound to such

heterometallic core via different coordination modes, which can be divided into three groups: two $\mu_4-\eta^1, \eta^1, \eta^1, \eta^2$, four $\mu_3-\eta^1, \eta^1, \eta^2$, and six $\mu_2-\eta^1, \eta^1$. The six triphenylphosphine ligands are each chelated on one silver atom via the μ_1-P ligation mode (Figure 8a).

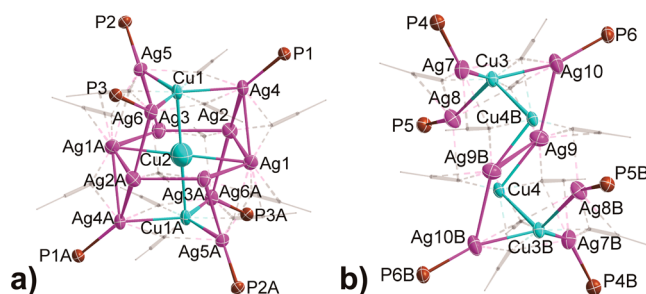


Figure 8. a) Thermal ellipsoid plot (50% probability level) of the core structure in the $[\{\text{CuAg}_3\}\text{CuAg}_6\{\text{CuAg}_3\}(\text{}^t\text{BuC}\equiv\text{C}-\text{C}\equiv\text{C})_{12}(\text{PPh}_3)_6]^{3+}$ cationic cluster molecule. b) Thermal ellipsoid plot (50% probability level)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

In the smaller heterometallic cation $[\{\text{CuAg}_3\}\text{Cu}_2\text{Ag}_2\{\text{CuAg}_3\}(\text{}^t\text{BuC}\equiv\text{C}-\text{C}\equiv\text{C})_{10}(\text{PPh}_3)_6]^{2+}$ (Figure 7, right side), a central Cu_2Ag_2 zigzag segment is linked by a pair of trigonal-planar CuAg_3 aggregates through $\text{Cu(I)}\cdots\text{Cu(I)}$ ($2.861(1)\text{Å}$) and $\text{Ag(I)}\cdots\text{Ag(I)}$ interactions to engender a Cu_4Ag_8 heterometallic core. The ten peripheral symmetry-related pairs of $\text{}^t\text{BuC}\equiv\text{C}-\text{C}\equiv\text{C}$ ligands are each bonded to either three or four Ag(I) centers in different ligation modes: four in $\mu_4-\eta^1, \eta^1, \eta^1, \eta^1$ and six in $\mu_3-\eta^1, \eta^1, \eta^2$ 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 $\text{Cu(I)}\cdots\text{Cu(I)}$ 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 $[(\text{chx}\text{C}\equiv\text{C}-\text{C}\equiv\text{C})\text{Ag}]_4(\text{PPh}_3)_4$ 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. $240\text{--}295\text{nm}$, while **1–3** and **5–8** show an additional lower-energy absorption shoulder at ca. 320

Table 1. Photophysical Data for the Synthetic Precursors and Selected Complexes

complex	absorption λ/nm ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) ^a	medium (T/K)	emission $\lambda_{\text{em}}/\text{nm}$ ($\tau / \mu\text{s}$)
[(chxC≡C—C≡C)Ag] ₄ (PPh ₃) ₄	248 sh (99 120),	CH ₂ Cl ₂ (298)	^e
	274 sh (39 680),	solid (298) ^b	485 (258)
	295 sh (12 710)	solid (77) ^b glass (77) ^{b-d}	483 (495) 472 (107)
[(^t PrC≡C—C≡C)Ag] ₄ (PPh ₃) ₄	246 sh (90 950),	CH ₂ Cl ₂ (298)	^e
	276 sh (35 230),	solid (298)	^e
	291 sh (13 780)	solid (77) ^{b,c} glass (77) ^{b-d}	476 (380) 468 (109)
[(^t BuC≡C—C≡C)Ag] ₄ (PPh ₃) ₄	247 sh (102 340),	CH ₂ Cl ₂ (298)	^e
	276 sh (38 610),	solid (298)	^e
	294 sh (13 720)	solid (77) ^{b,c} glass (77) ^{b,d}	465 (503) 473 (118)
[CuAg ₃ (chxC≡C—C≡C) ₃ (PPh ₃) ₆]PF ₆ ·2Et ₂ O (1)	247 (134 910), 256	CH ₂ Cl ₂ (298)	^e
	sh (107 690), 276	solid (298) ^{b,c}	464 (10.6)
	sh (73 740), 321 sh	solid (77) ^{b,c}	468 (51.6)
	(10 210)	glass (77) ^{b-d}	465 (38.7)
complex	absorption λ/nm ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) ^a	medium (T/K)	emission $\lambda_{\text{em}}/\text{nm}$ ($\tau / \mu\text{s}$)
[CuAg ₃ (^t PrC≡C—C≡C) ₃ (PPh ₃) ₆]PF ₆ (2)	244 (125 000),	CH ₂ Cl ₂	506 (9.37)
	256 sh	(298) ^{b,c}	^e
	(104 520), 276	solid	486 (71.9)
	sh (74 190), 319	(298)	466 (45.5)
	(12 070)	solid (77) ^{b,c} glass (77) ^{b,d}	
[CuAg ₃ Ag ₄ (chxC≡C—C≡C) ₇ (PPh ₃) ₅]PF ₆ ·1.5Et ₂ O (3)	244 sh	CH ₂ Cl ₂	^e
	(170 820), 254	(298)	^e
	sh (143 860),	solid	462
	276 sh (94 470),	(298)	(17.9)
	322 sh (16 060)	solid (77) ^{b,c} glass (77) ^{b,d}	484 (31.4)
[CuAg ₃ Ag ₃ (^t PrC≡C—C≡C) ₆ (PPh ₃) ₅]PF ₆ (5)	243 (125 130),	CH ₂ Cl ₂	501
	253 sh	(298) ^{b,c}	(10.1)
	(109 520), 277	solid	^e
	sh (69 140), 318	(298)	484
	(13 020)	solid (77) ^{b,c} glass (77) ^{b,d}	(64.0) 465 (39.2)
[CuAg ₃ Ag ₄ {CuAg ₃ }(chxC≡C—C≡C) ₁₀ (PPh ₃) ₆](PF ₆) ₂ (6)	245 sh	CH ₂ Cl ₂	501
	(189 500), 264	(298) ^{b,c}	(10.2)
	sh (141 300),	solid	705
	278 sh	(298)	(1.05)
	(104 310), 318	solid	725
	sh (19 360)	(77) glass (77) ^{b,d}	(7.81) 483 (28.8)
complex	absorption λ/nm ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) ^a	medium (T/K)	emission $\lambda_{\text{em}}/\text{nm}$ ($\tau / \mu\text{s}$)
[CuAg ₃ Ag ₄ {CuAg ₃ }(^t PrC≡C—C≡C) ₁₀ (PPh ₃) ₆](PF ₆) ₂ (7)	244 (229 010),	CH ₂ Cl ₂	505 (10.4)
	252 sh	(298) ^{b,c}	634 (5.16)
	(199 270), 278	solid (298)	650 (35.5)
	sh (125 170),	solid (77)	458 (10.9)
[Cu ₂ Ag ₁₀ (^t BuC≡C—C≡C) ₁₂ (PPh ₃) ₂] (8)	242 sh	CH ₂ Cl ₂	^e
	(236 160), 254	(298)	498
	sh (164 220),	solid (298)	(0.98)

Table 1. continued

complex	absorption λ/nm ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) ^a	medium (T/K)	emission $\lambda_{\text{em}}/\text{nm}$ ($\tau / \mu\text{s}$)
	263 sh	solid	474
	(131 450), 277	(77) ^{b,c}	(12.4)
	sh (95 900), 293	glass	478
	sh (54 800), 318	(77) ^{b,d}	(26.0)
	sh (22 160)		

^aMeasured in CH_2Cl_2 . ^bVibrational progressional spacing of ca. 2100 cm^{-1} . ^cVibrational progressional spacing of ca. 1350 cm^{-1} . ^dMeasured in ethanol–methanol–dichloromethane (4:1:0.1, v/v) glass. ^eNonemissive.

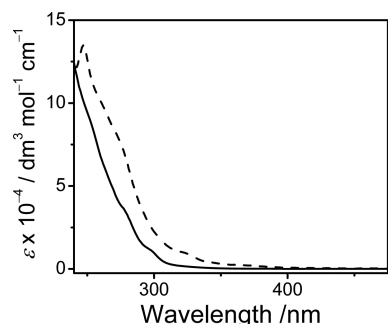


Figure 9. Electronic absorption spectra of $[(\text{chxC}\equiv\text{C}-\text{C}\equiv\text{C})\text{-Ag}]_4(\text{PPh}_3)_4$ (solid line) and **1** (dashed line) in CH_2Cl_2 at 298 K.

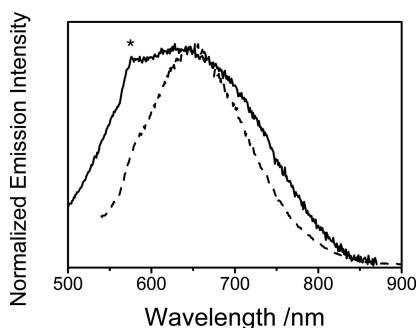


Figure 10. Emission spectra of **7** in the solid state at 298 K (solid line) and 77 K (dashed line) (* denotes instrumental artifact).

nm. The high-energy absorption band can be assigned as the intraligand 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 $\lambda > 320 \text{ nm}$ 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. $1350\text{--}1450 \text{ cm}^{-1}$ and $1800\text{--}2100 \text{ cm}^{-1}$, which are typical of the $\nu(\text{C}-\text{H})$ and $\nu(\text{C}\equiv\text{C})$ 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 $d \rightarrow s$ state, mixing with the ligand-to-metal charge-transfer (LMCT) character modified by the $\text{Ag}(\text{I})\cdots\text{Ag}(\text{I})$ and/or $\text{Ag}(\text{I})\cdots\text{Cu}(\text{I})$ interactions.^{7,22,23} These findings are in line with the crystal structures obtained for **6** and **7**, which consist of more compact $\{\text{CuAg}_3\}\text{Ag}_4\{\text{CuAg}_3\}$ cores with more extended $\text{Ag}(\text{I})\cdots\text{Ag}(\text{I})$ and $\text{Ag}(\text{I})\cdots\text{Cu}(\text{I})$ interactions, and are different from the relatively open CuAg_3 cores of **3** and **5** and $\{\text{CuAg}_3\}\text{-Ag}_2\text{Ag}_2\{\text{CuAg}_3\}$ core of **8** that mainly lead to vibronic-structured ligand-centered emission bands.

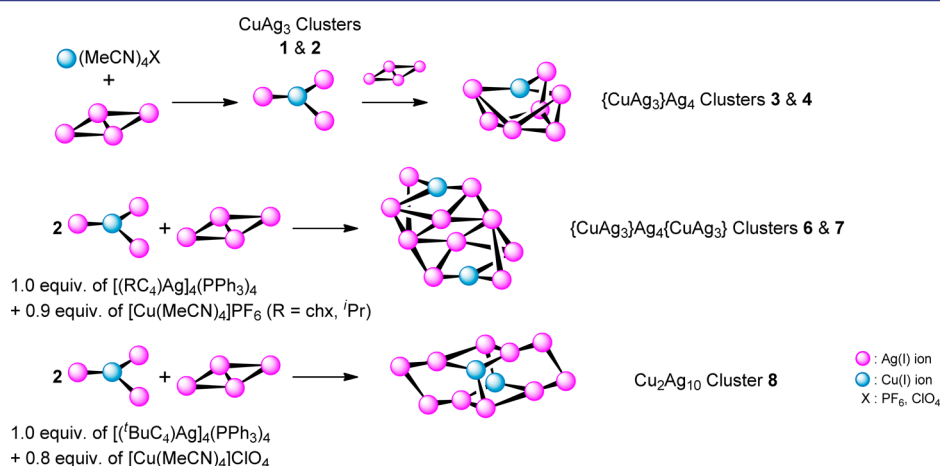


Figure 11. Proposed assembly mechanism for complexes **1–9**, showing only the connection between monovalent Group 11 cations.

Assembly Mechanism. Design of the three synthetic precursors was based on the anticipation that bulky alkyl 1,3-diyne-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 $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$ or $[\text{Cu}(\text{MeCN})_4]\text{ClO}_4$, 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 $[(\text{RC}\equiv\text{C}-\text{C}\equiv\text{C})\text{Ag}]_4(\text{PPh}_3)_4$ ($\text{R} = \text{tPr}, \text{tBu}, \text{and chx}$) 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 $[(\text{tBuC}\equiv\text{C}-\text{C}\equiv\text{C})\text{Ag}]_4(\text{PPh}_3)_4$ as a synthetic precursor were unsuccessful, but existence of complexes **4**, **8**, and **9** indicated the in situ formation of $\text{Cu}[\text{Ag}(\text{tBuC}\equiv\text{C}-\text{C}\equiv\text{C})]_3$ 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-diyne 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 $\text{CuAg}_3(\text{C}\equiv\text{C}-\text{C}\equiv\text{CR})_3$ central core from the reaction between $[(\text{RC}\equiv\text{C}-\text{C}\equiv\text{C})\text{Ag}]_4$ and $[\text{Cu}(\text{MeCN})_4]\text{X}$ ($\text{X} = \text{PF}_6$ or ClO_4). For complex **3** and **4**, the $\{\text{CuAg}_3\}\text{Ag}_4$ core is assembled through argentophilic interaction between in situ generated $\text{CuAg}_3(\text{C}\equiv\text{C}-\text{C}\equiv\text{CR})_3$ and remaining neighbor $[(\text{RC}\equiv\text{C}-\text{C}\equiv\text{C})\text{Ag}]_4$ 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 $\{\text{CuAg}_3\}\text{Ag}_3$ core exists in **5**.

As the concentration of Cu(I) ions in the reaction mixture increases, the corresponding $\text{CuAg}_3(\text{C}\equiv\text{C}-\text{C}\equiv\text{CR})_3$ complex is expected to be generated in a relatively higher content, in which case the ratio of CuAg_3 complex and unreacted $[(\text{RC}\equiv\text{C}-\text{C}\equiv\text{C})\text{Ag}]_4$ 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 $\{\text{CuAg}_3\}\text{Ag}_4\{\text{CuAg}_3\}$ 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 $\{\text{CuAg}_3\}\text{Ag}_2\{\text{CuAg}_3\}$ 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 $\text{CuAg}_3(\text{tBuC}\equiv\text{C}-\text{C}\equiv\text{C})_3$ 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 reassembly 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.

CONCLUSIONS

In summary, we have employed designed tetranuclear precursors $[(\text{R}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C})\text{Ag}]_4$ ($\text{R} = \text{tPr}, \text{tBu}, \text{and chx}$) to construct a series of heteropolynuclear silver(I)–copper(I) diyne 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 photoexcitation 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

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b08674.

Experimental details, additional figures, and NMR spectra (PDF)

X-ray crystallographic data in CIF format (CIF)

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Notes

The authors declare no competing financial interest.

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