Facile Construction of Anionic Silver(I) Aggregates with Embedded Acetylide and Cyanide Ions**

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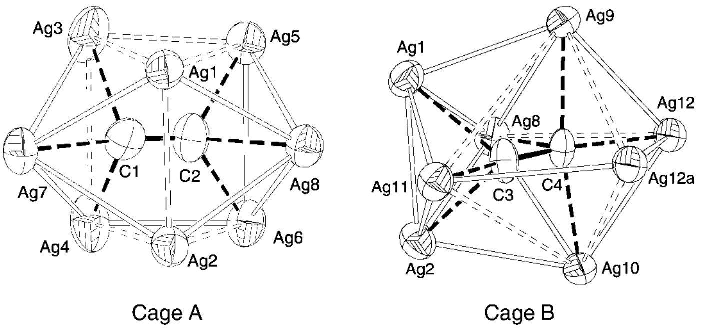
In memory of Richard K. McMullan

We have shown that the combination of Ag_2C_2 with other kinds of silver salts leads to the formation of a series of double,[1] triple,[2] and quadruple[3] salts that contain neutral or cationic silver cluster units. In addition, we have carried out exploratory studies on structural control by introducing ancillary ligands to direct the assembly process.[4] Recently, we established the generality of generating an anionic silver aggregate in a mixed-valent $Ag^{I,II}$ complex by disproportionation of silver(I) in the presence of a tetraaza macrocycle.[5] This prompted us to conduct further studies on structural diversity by incorporating hydrophobic organic cations into silver acetylide systems, thus favoring the formation of anionic silver aggregates through the attainment of overall charge balance. Proceeding on this premise, we have successfully employed a quaternary ammonium cation as the mediating agent to obtain the high-nuclearity silver complexes **1** and **2**, the latter featuring co-intercalation of cyanide and acetylide ions within a novel anionic silver column.

$(Et_4N)_6[\{(Ag_2C_2)_2(AgCF_3CO_2)_8(CF_3CO_2)_3(H_2O)_2\}_2]$ **1**

$(Et_4N)_3[(Ag_2C_2)_2(AgCN)(AgCF_3CO_2)_{11}(CF_3CO_2)_3(H_2O)_6]$ **2**

Compound **1** was prepared by dissolving Ag_2C_2 in an aqueous solution of CF_3CO_2Ag and $AgBF_4$ followed by the addition of Et_4NBF_4. X-ray structural analysis indicated that complex **1** consists of a discrete high-nuclearity cluster anion $[\{(Ag_2C_2)_2(AgCF_3CO_2)_8(CF_3CO_2)_3(H_2O)_2\}_2]^{6-}$, which is composed of two kinds of polyhedral units, a bicapped trigonal prism (cage A; Figure 1) and a triangulated dodecahedron (cage B).



Cage A Cage B

Figure 1. Cage A and cage B in **1** (35 % ellipsoids shown). Ag···Ag distances longer than 3.4 Å (twice the van der Waals radius of silver) are represented by broken open lines. Selected bond lengths [Å]: C1-C2 1.21(2), C3-C4 1.18(1), C1-Ag3 2.23(1), C1-Ag(4) 2.24(2), C1-Ag7 2.11(2), C2-Ag5 2.13(2), C2-Ag6 2.16(2), C2-Ag8 2.39(2); C3-Ag1 2.34(1), C3-Ag2 2.30(1), C3-Ag11 2.23(1), C4-Ag8 2.59(1), C4-Ag9 2.32(1), C4-Ag10 2.34(1), C4-Ag12 2.12(1). Symmetry code: a: $-x$, $-y+1$, $-z$.

For cage A, three edges Ag1···Ag2, Ag3···Ag4, and Ag5···Ag6 constitute the vertical sides of a trigonal prism, and Ag7 and Ag8 each caps a rectangular face. The mean deviation of the atoms constituting the three rectangular faces of the trigonal prism lies in the range 0.008–0.012 Å. A C_2^{2-} species is accommodated in this cage and lies closer to the uncapped rectangular face Ag3-Ag4-Ag5-Ag6.

Cage B is analogous to that found in $[Ag^I_6(C_2)(CF_3CO_2)_5(H_2O)]^{-1}_\infty$,[5a] being composed of two atom sets Ag9-Ag1-Ag2-Ag10 and Ag8-Ag12-Ag12a-Ag11, which are each coplanar within 0.019 and 0.016 Å, respectively, making a dihedral angle of 89.7°. This cage also encloses a C_2^{2-} ion, which displays an asymmetric coordination mode with C3 bound to three but C4 to four silver centers.

Cages A and B share a triangular face Ag1-Ag2-Ag8 to form a double cage, and two such double cages share an edge to generate a centrosymmetric quadruple cage comprising twenty-four silver atoms and four encapsulated acetylide ions (Figure 2). This discrete anionic cluster $[\{(Ag_2C_2)_2(AgCF_3CO_2)_8(CF_3CO_2)_3(H_2O)_2\}_2]^{6-}$ exhibits pseudosymmetry *m* with a plane passing through Ag7-Ag8-Ag11-Ag12-C1-C2-C3-C4. While single cages occur commonly and several double cages are known, this Ag_{24} quadruple cage is found for the first time and is so far the largest known cluster in the silver acetylide system.

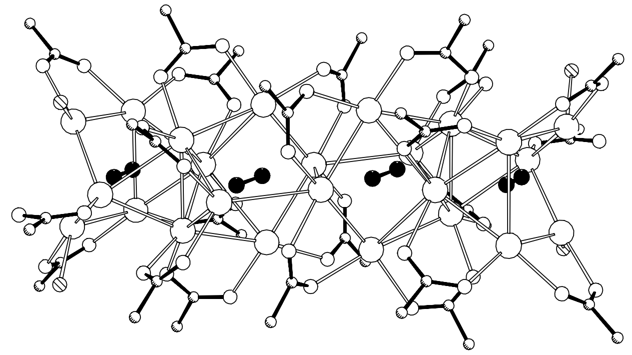


Figure 2. The centrosymmetric high-nuclearity Ag_{24} cluster (quadruple cage) in **1** generated by edge-sharing of Ag_{13} double cages with four embedded C_2^{2-} species. F atoms have been omitted for clarity, and only short Ag···Ag distances are shown. Large circles, silver; medium circles, oxygen; hatched medium circles, aqua ligands; black dumbbells, C_2^{2-} species; side-hatched small circle, carbon.

The aqua ligands are terminally coordinated to silver atoms of type Ag3 and Ag4, and the trifluoroacetate ligands each bridges an Ag···Ag edge except the one that has a monodentate carboxylate group. The rodlike clusters pack in a head-to-tail pattern along the *b* direction, and the Et_4N^+ counterions fill the space around them.

Complex **2** was synthesized in a similar manner to **1** except that AgCN was introduced as an additional component. It is a

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[**] Financial support from the Research Grants Council of the Hong Kong Special Administrative Region (Project No. CUHK 4268/00P) and a Postdoctoral Fellowship awarded to Q.-M. W. from The Chinese University of Hong Kong are gratefully acknowledged.

novel silver complex containing three kinds of anions: trifluoroacetate, acetylide, and cyanide.

The basic structural unit of **2** is a silver(I) double cage of symmetry 2, one half of which taking the shape of a triangulated dodecahedron that encapsulates a C_2^{2-} ion (Figure 3a). Two such polyhedra share an edge Ag1⋯Ag1a and have an additional vertex-to-vertex connection to generate the double cage, such that a twofold axis passes through the midpoints of Ag1⋯Ag1a and Ag7⋯Ag7a. Two pendant silver atoms of type Ag8 are each attached to a vertex of the double cage, yielding the $[(C_2)_2@Ag_{14}]Ag_2$ unit.

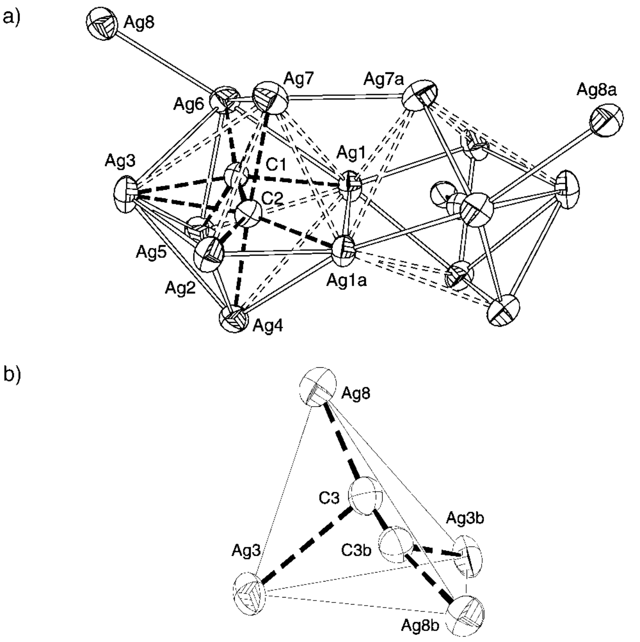

Figure 3. a) Ag_{14} double cage with two embedded C_2^{2-} species and a pair of pendant silver atoms in **2** (35% ellipsoids shown). Ag⋯Ag distances longer than 3.4 Å (twice the van der Waals radius of silver) are represented by broken open lines. The C–Ag bonds are only shown in the left half for clarity. b) Distorted Ag_4 tetrahedron with an intercalated CN^-, which is disordered over a site of symmetry 2 ($C3 = \frac{1}{2}C + \frac{1}{2}N$). Selected bond lengths [Å]: C1-C2 1.221(9), C1-Ag1 2.569(6), C1-Ag3 2.392(6), C1-Ag5 2.339(6), C1-Ag6 2.106(6), C1-Ag7 2.433(6), C2-Ag1a 2.274(6), C2-Ag2 2.211(6), C2-Ag3 2.592(6), C2-Ag4 2.308(7), C2-Ag7 2.554(6), C3-C3b 1.11(1), C3-Ag3 2.643(7), C3-Ag8 2.137(7). Symmetry codes: a: $x, -y+\frac{1}{2}, -z+\frac{1}{2}$; b: $-x+\frac{1}{2}, -y, z$.

An interesting structural feature is found in **2**, where the cyanide ion is located in a distorted tetrahedral Ag3-Ag8-Ag3b-Ag8b environment (Figure 3b). This type of coordination mode of a cyanide ligand is unprecedented, as thus far all reported μ_4-CN moieties are bound to metal centers in a nearly planar rectangular environment. The silver(I) double cages and tetrahedra link up alternately to generate an infinite anionic silver(I) column $\{[(Ag_2C_2)_2(AgCN)(AgCF_3CO_2)_{11}(CF_3CO_2)_3(H_2O)_6]^{3-}\}_\infty$ along the *b* direction (Figure 4). The presence of the CN^- ion is confirmed by the band at 2139 cm^{-1} in the IR spectrum, and also on the basis of its coordination mode. The acetylide ion is normally encapsulated in a cage comprising six or more silver atoms, while the largest ligation number of cyanide is four.

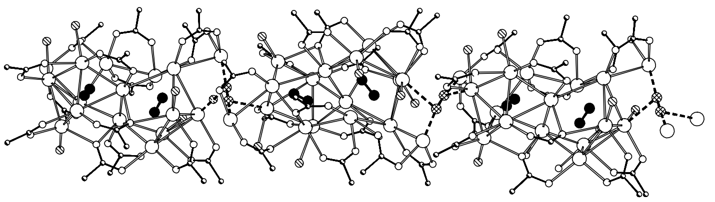

Figure 4. Infinite silver(I) column running along the *b* direction in **2** derived from linkage of silver cages with co-intercalation of cyanide and acetylide ions. F atoms have been omitted for clarity, and only short Ag⋯Ag distances are shown. Large circles, silver; medium circles, oxygen; hatched medium circles, aqua ligands; black dumbbells, C_2^{2-} species; cross-hatched dumbbells, CN^- ions; side-hatched small circle, carbon.

In **2**, the aqua ligands also act as terminal coordination groups. The trifluoroacetate ligands function as μ_2 bridges across Ag⋯Ag edges except one in the μ_3 mode. The silver(I) columns pack parallel to one another with Et_4N^+ ions located between them.

Under the induction of argentophilicity,[6] namely the d^{10}–d^{10} closed-shell attraction[7] between silver(I) ions, Ag_2C_2 readily dissolves in a concentrated aqueous solution of a silver salt to generate polynuclear $[Ag_n(C_2)]^{(n-2)+}$ moieties, the assembly of which may be affected by coexisting ions and solvent molecules to afford novel crystal structures that exhibit unprecedented geometries of silver polyhedra each enclosing a C_2^{2-} species. Further study on the synthesis of a variety of anionic silver acetylide aggregates by variation of quaternary ammonium counterions and coexisting halide/pseudohalide is in progress.

Experimental Section

Ag_2C_2 was prepared as described previously.[1] **Caution**: thoroughly dried Ag_2C_2 detonates easily upon mechanical shock or heating, and only a small quantity should be used in any chemical reaction.

1: Ag_2C_2 was added to 1 mL of a concentrated aqueous solution of $AgCF_3CO_2$ (0.442 g, 2 mmol) and $AgBF_4$ (0.195 g, 1 mmol) in a plastic beaker with stirring until saturated. The excess amount of Ag_2C_2 was filtered off, and Et_4NBF_4 (0.108 g) was added to the filtrate. The colorless solution was placed in a desiccator charged with P_2O_5, and colorless platelike crystals of **1** were deposited in about 32% yield (based on Et_4NBF_4) after a few hours. Elemental analysis (%): calcd: C 19.94, H 2.14, N 1.39; found: C 19.80, H 1.90, N 1.21.

2: Excess AgCN was added to 1 mL of a concentrated aqueous solution of $AgCF_3CO_2$ (0.442 g, 2 mmol) and $AgBF_4$ (1.17 g, 6 mmol) in a plastic beaker with stirring until saturated. Then Ag_2C_2 was added and stirred until equilibrium was reached. The undissolved amount of Ag_2C_2 and AgCN was filtered off, and Et_4NBF_4 (0.108 g) was added to the filtrate. The resulting clear solution was placed in a desiccator charged with P_2O_5. Colorless prismatic crystals of **2** were obtained in about 30% yield. Elemental analysis (%): calcd: C 17.64, H 1.87, N 1.44; found: C 17.82, H 1.62, N 1.21. Both compounds **1** and **2** readily decompose in common solvents such as water and ethanol. Complexes **1** and **2** are unstable to heat; **1** decomposes to a black residue at about 145 °C and **2** melts at 105 °C.

Crystal data for **1**: $C_{100}H_{128}Ag_{24}F_{66}N_6O_{48}$, $M_r = 6024.96$, $P\bar{1}$ (no. 2), $a = 17.0844(5)$, $b = 19.6091(6)$, $c = 27.3695(8)$ Å, $\alpha = 79.490(1)$, $\beta = 81.743(1)$, $\gamma = 74.041(1)°$, $V = 8625.3(4)$ Å^3, $Z = 2$, $\lambda = 0.71073$ Å, $\rho_{calcd} = 2.320\ g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 2.795\ mm^{-1}$, $R1 = 0.0740$, $wR2 = 0.1749$ for 13663 observed reflections ($I > 2\sigma(I)$). Crystal data for **2**: $C_{57}H_{72}Ag_{16}F_{42}N_4O_{34}$, $M_r = 3881.11$, *Pnna* (no. 52), $a = 15.0738(7)$, $b = 25.747(1)$, $c = 27.088(1)$ Å, $V = 10514.4(9)$ Å^3, $Z = 4$, $\lambda = 0.71073$ Å, $\rho_{calcd} = 2.452\ g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 3.051\ mm^{-1}$. $R1 = 0.0460$, $wR2 = 0.1304$ for 7909 observed reflections ($I > 2\sigma(I)$). Data collection was performed at 20 °C on a Bruker SMART 1000 CCD diffractometer using frames of oscillation range 0.3°, $1 < \theta < 28°$. The structures were solved by direct methods and refined by full-matrix least-squares on F^2. The cyanide group in **2** is disordered over a site of symmetry 2, and the independent carbon atom is represented by $^1/_2$C + $^1/_2$N.

CCDC-184663 (**1**) and CCDC-184664 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

Received: July 24, 2002 [Z19812]

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Cobalt-Catalyzed Coupling Reaction of Alkyl Halides with Allylic Grignard Reagents**

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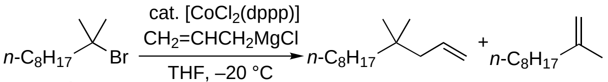
Nickel- and palladium-catalyzed cross-coupling reactions of organic halides with organometallic reagents is one of the most versatile carbon–carbon bond-forming reactions in organic synthesis.[1] In most cases, aryl and vinyl halides are employed as organic halides, yielding sp^2–sp, sp^2–sp^2, and sp^2–sp^3 linkages. The connection of two sp^3 carbon atoms under transition metal catalysis is also important, and a variety of retrosynthetic analyses are conceivable in which an arbitrary carbon–carbon bond in an alkyl chain is cleaved. However, coupling with alkyl halides is difficult for two main reasons: 1) Oxidative addition of alkyl halides is much slower than that of aryl and vinyl halides. 2) β-Hydride elimination of the alkylpalladium and -nickel compound is problematic. Thus, novel and efficient methods for alkyl–alkyl coupling are currently under intense investigation.[2,3]

We are interested in cobalt-catalyzed reactions[4,5] and report herein the cobalt-catalyzed cross-coupling reaction of alkyl halides with allylic Grignard reagents. Allylation of various alkyl halides proceeds smoothly, and even quaternary carbon atoms have become readily accessible by transition-metal-catalyzed coupling reactions.

Allylmagnesium chloride (1.0 M solution in THF, 1.5 mmol) was added to a solution of 2-bromo-2-methyldecane (**1a**; 0.50 mmol) in THF in the presence of [$CoCl_2$(dppp)] (0.05 mmol) at −20 °C (Scheme 1; dppp = 1,3-bis(diphenylphosphanyl)propane). Stirring for 2 h at −20 °C provided the allylated product **2a**, which contains a quaternary carbon center (90% yield), and **3a** (8%). No allylated product was obtained when the [$CoCl_2$(dppp)] catalyst was omitted. The yield of **2a** was lower when 1,4-bis(diphenylphosphanyl)butane (DPPB), 1,2-bis(diphenylphosphanyl)ethane (DPPE), and bis(diphenylphosphanyl)methane (DPPM) were employed in place of DPPP. Reaction at −40 °C led to recovery of **1a**, whereas reaction at 0 °C resulted in a lower ratio of **2a**/**3a** (82:18).



1a **2a** **3a**

Scheme 1. Cobalt-catalyzed cross-coupling reaction of alkyl halide **1a** with allylmagnesium chloride.

Allylation of a variety of alkyl halides proceeded smoothly, although tuning of reaction conditions was necessary for the different substrates (Table 1). Benzylic allylation of **1d** required DPPE in place of DPPP to attain a satisfactory result. Primary and secondary bromides were less reactive. Instead, use of alkyl iodides such as **1g-I** led to high yields at −40 °C. It is worth noting that halides **1h**, **1h-I**, and **1i-I**, which have alkoxy groups at the β position to the halide atom, participated in the allylation.

Other allylic Grignard reagents were available for this reaction (Scheme 2). Regioselective coupling was observed to yield methyl-branched product **5b** upon treatment of **1g-I** with crotyl Grignard reagent. Unfortunately, reaction of prenyl Grignard reagent was unsuccessful.

Substrates having proper carbon–carbon double bonds were then subjected to the cobalt-catalyzed allylation (Scheme 3). Consequently, tandem cyclization/allylation occurred, thereby affording 3-butenyl-substituted lactones after Jones oxidation of the cyclic acetals. For example, iodoacetal **7c** was converted to lactone **9c** bearing a quaternary center, and cyclization of **7d** provided the *trans* isomer **9d** exclusively.

Interestingly, treatment of **7e** with the allyl Grignard reagent CH_2=$CHCH_2MgCl$ in the presence of [$CoCl_2$(dppp)] furnished the ring-opening product **9e** (Scheme 4). Given that intramolecular carbocobaltation proceeds to yield cyclopropylmethylcobalt species, β-carbon elimination would provide a route to **9e**. However, β-carbon elimination seems unlikely

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[**] This work was supported by Grants-in-Aid for Scientific Research (Nos. 12305058 and 10208208) from the Ministry of Education, Culture, Sports, Science and Technology, Government of Japan. H.Y. acknowledges JSPS for financial support.

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