Supporting Information

Assembly of high-symmetry silver(I) alkyl-1,3-diynyl cluster complexes via core transformation

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1. *X-ray crystallography*

Selected crystals were used for intensity data collection on a Bruker AXS Kappa Apex II Duo diffractometer at 173K using frames of oscillation range 0.3°, with 2° < θ < 28°. An empirical absorption correction was applied using the SADABS program.[1] The structures were solved by the direct method and refined by full-matrix least-squares on F^2 using the SHELXTL program package.[2]

The crystal structures of synthetic precursors $[(RC{\equiv}C{-}C{\equiv}C)Ag]_4(PPh_3)_4$ (R = ^{i}Pr, ^{t}Bu, chx and Ph), $[(chxC{\equiv}C{-}C{\equiv}C{-}C{\equiv}C)Ag]_4(PPh_3)_4$ and complexes **1-3** were determined by single-crystal X-ray analysis. The crystal data of complexes **7** and **8** and refinement parameters are presented in Table S1.

Table S1. Crystallographic data and structure refinement parameters of synthetic precursors **7** and **8**.

Complex	$[(PhC{\equiv}C{-}C{\equiv}C)Ag]_4(PPh_3)_4{\cdot}1.5MeCN$ (**7**)	$[(chxC{\equiv}C{-}C{\equiv}C{-}C{\equiv}C)Ag]_4(PPh_3)_4{\cdot}MeOH{\cdot}5H_2O$ (**8**)
Structural Formula	$C_{230}H_{169}Ag_8N_3P_8$	$C_{121}H_{107}Ag_4O_9P_4$
Formula Wt.	4085.40	2260.43
Crystal System	Monoclinic	Monoclinic
Space Group	$P2_1/n$	$P2/n$
a [Å]	16.305(1)	16.805(1)
b [Å]	34.222(2)	21.229(3)
c [Å]	17.656(1)	16.900(1)
α [Å]	90.0	90.0
β [Å]	102.069(1)	101.531(2)
γ [Å]	90.0	90.0
V [Å^3]	9633.8(11)	5907.5(12)
Z	2	2
ρ_c[gcm^{-3}]	1.408	1.271
μ [mm^{-1}]	0.917	0.759
R_1[a] (I>2σ)	0.0711	0.0971
wR_2[b] (all data)	0.1347	0.2114
GOF	1.128	1.093

[a] $R_1 = \Sigma||F_o| - |F_c|| \,/\, \Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] \,/\, \Sigma[w(F_o^2)^2]\}^{1/2}$.

* Space group $P2_1/n$ is equivalent to standard $P2_1$/c by an axial transformation.

*2. Description of Synthetic Precursors **7** and **8***

*[(PhC≡C–C≡C)Ag]$_4$(PPh$_3$)$_4$·1.5MeCN (**7**)*

The cluster core of [(PhC≡C–C≡C)Ag]$_4$(PPh$_3$)$_4$ 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≡C–C≡C$^-$ groups. The PPh$_3$ ligands are attached only to the outer Ag1 and Ag3 centers (Figure S1). In the cluster molecule, the observed argentophilic Ag···Ag distances range from 2.924(7) to 3.449(8) Å, and the Ag2–Ag1–Ag4, Ag1–Ag2–Ag3, Ag2–Ag3–Ag4 and Ag1–Ag4–Ag3 angles are 52.7(1)˚, 130.7(1)˚, 58.9(1)˚ and 117.4(2)˚, respectively.

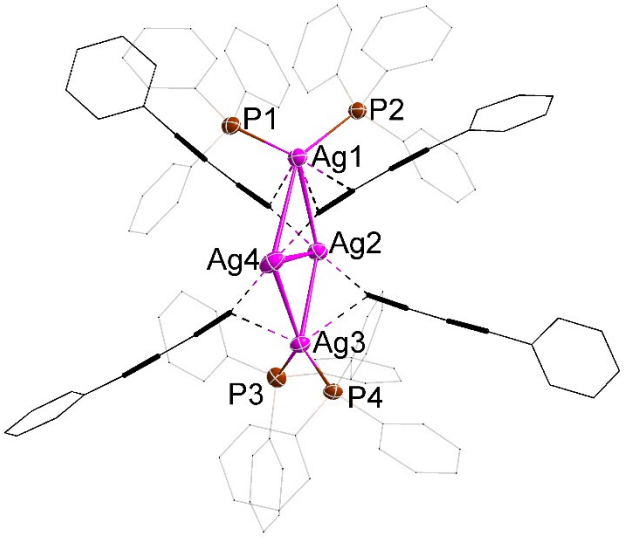

Figure S1. Coordination environment of the silver(I) atoms in the discrete molecule [(PhC≡C–C≡C)Ag]$_4$(PPh$_3$)$_4$·2MeCN. The C≡C triple bonds in the aryl-1,3-diynyl ligands are shown as thick rods. Silver atoms are drawn as thermal ellipsoids (50% probability level) with atom labeling. The argentophilic Ag···Ag distances lie in the range 2.70–3.40 Å. Color scheme: purple, silver atoms; broken lines, Ag–C bonds.

*[(chxC≡C–C≡C–C≡C)Ag]$_4$(PPh$_3$)$_4$·5H$_2$O·MeOH (**8**)*

There are two independent cluster molecules in the

$[(chxC{\equiv}C{-}C{\equiv}C{-}C{\equiv}C)Ag]_4(PPh_3)_4{\cdot}5H_2O{\cdot}MeOH$ complex. The cluster core of $[(chxC{\equiv}C{-}C{\equiv}C{-}C{\equiv}C)Ag]_4(PPh_3)_4$ 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 $chxC{\equiv}C{-}C{\equiv}C{-}C{\equiv}C^-$ groups, whereas the PPh_3 ligands are attached only to the outer inversion-related Ag1 centers (Figure S2). In the cluster molecule, the observed argentophilic Ag···Ag distances range from 2.889(7) to 3.214(8) Å, and the Ag2–Ag1–Ag2A and Ag1–Ag2–Ag1A angles are 55.0(2)° and 124.9(2)°, respectively. The methanol molecule (O1) in the lattice is linked with an aqua ligand O5W by a weak hydrogen bond of length 2.84 Å. The remaining aqua ligands are connected together by weak hydrogen bonds ranging from 2.45 to 2.79 Å.

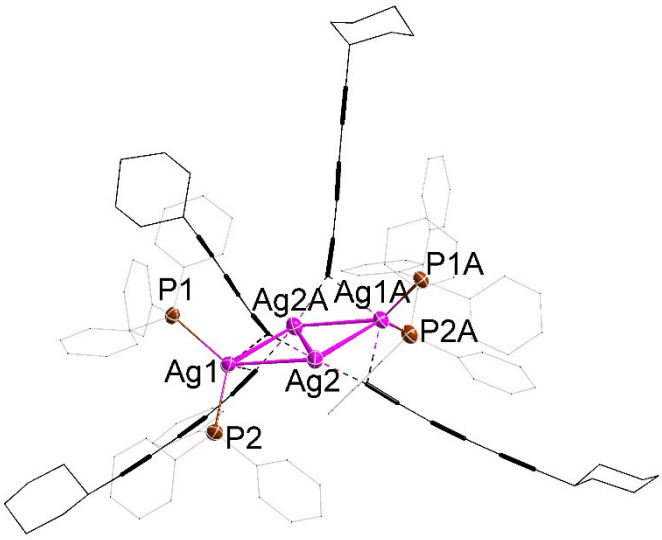

Figure S2. Coordination environment of the silver(I) atoms in the discrete molecule $[(chxC{\equiv}C{-}C{\equiv}C{-}C{\equiv}C)Ag]_4(PPh_3)_4{\cdot}5H_2O{\cdot}MeOH$. The C≡C triple bonds in the alkyl-1,3,5-triynyl ligands are shown as thick rods. Silver atoms are drawn as thermal ellipsoids (50% probability level) with atom labeling.

3. General procedure to prepare synthetic precursors [(RC≡C–C≡C)Ag]$_4$(PPh$_3$)$_4$ (R = ^{i}Pr, ^{t}Bu, chx and Ph) and [(chxC≡C–C≡C–C≡C)Ag]$_4$(PPh$_3$)$_4$

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

Polymeric silver ethynide [(RC≡C–C≡C)Ag]$_n$[3] (0.1 mmol) was first dissolved in a mixed solution of dichloromethane (3.0 mL) and methanol (0.5 mL) or acetonitrile (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 [(chxC≡C–C≡C)Ag]$_4$(PPh$_3$)$_4$·2MeOH (**4**), [(^{i}PrC≡C–C≡C)Ag]$_4$(PPh$_3$)$_4$ (**5**), [(^{t}BuC≡C–C≡C)Ag]$_4$(PPh$_3$)$_4$·2MeCN (**6**) and [(PhC≡C–C≡C)Ag]$_4$(PPh$_3$)$_4$·1.5MeCN (**7**) were each deposited in *ca.* 80 % yield. [(chxC≡C–C≡C–C≡C)Ag]$_4$(PPh$_3$)$_4$·5H$_2$O·MeOH (**8**) was similarly prepared and obtained in *ca.* 60% yield.

References

1. Sheldrick, G. M. *SADABS: Program for Empirical Absorption Correction of Area Detector Data*; University of Göttingen: Göttingen, Germany (**1996**).
2. Sheldrick, G. M. *SHELXTL 5.10 for Windows Structure Determination Software Programs*; Bruker Analytical X-ray Systems, Inc.; Madison, WI, **1997**.
3. Hau, S. C. K.; Cheng, P.-S.; Mak, T. C. W. *J. Am. Chem. Soc.* **2012**, *134*, 2922.

4. NMR plots

Due to the poor solubility of high weighted complexes in either polar or non-polar organic solvents, the ^{13}C NMR of some complexes could not be recorded.

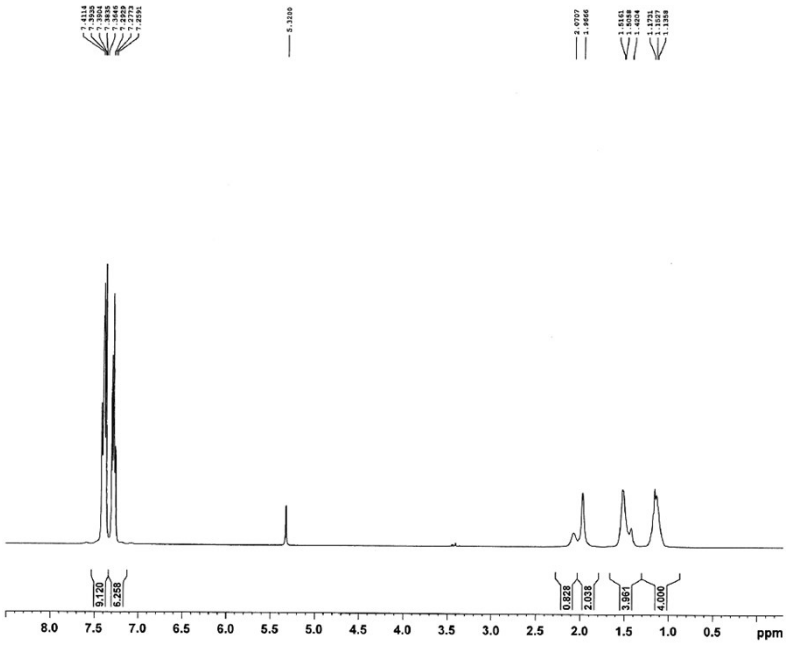

Figure S3. ^{1}H NMR of $[Ag_5@(chxC{\equiv}C{-}C{\equiv}C)_6Ag_3(PPh_3)_8]\cdot 2NO_2\cdot 8MeOH\cdot 4H_2O$ (**1**).

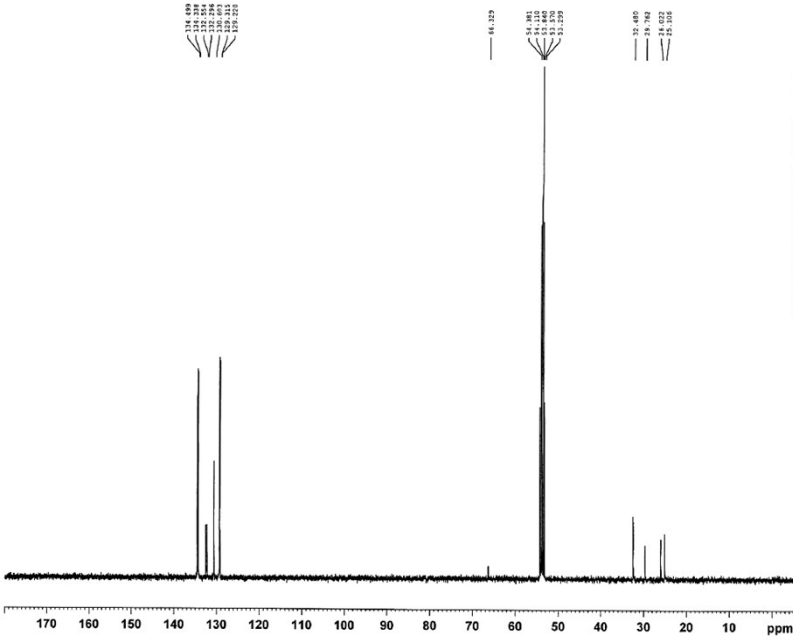

Figure S4. ^{13}C NMR of $[Ag_5@(chxC{\equiv}C{-}C{\equiv}C)_6Ag_3(PPh_3)_8]\cdot 2NO_2\cdot 8MeOH\cdot 4H_2O$ (**1**).

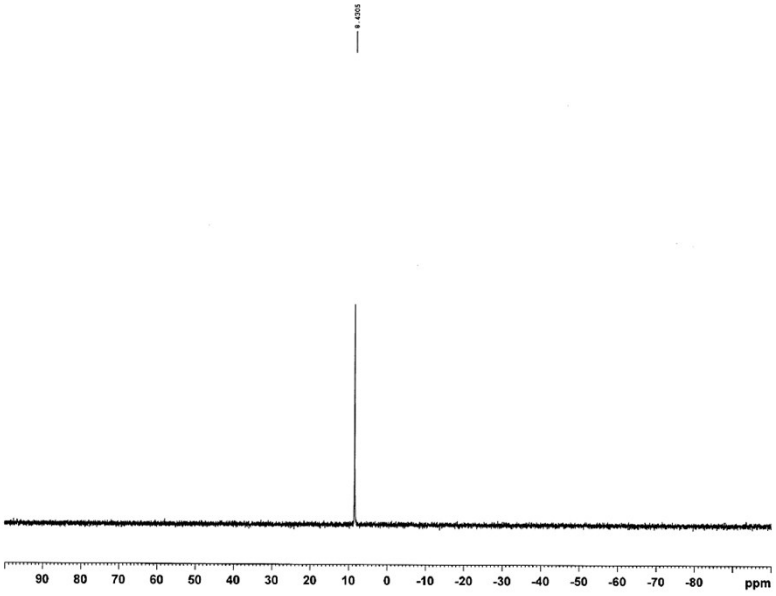

Figure S5. ^{31}P NMR of $[Ag_5@(chxC{\equiv}C{-}C{\equiv}C)_6Ag_3(PPh_3)_8]\cdot 2NO_2\cdot 8MeOH\cdot 4H_2O$ (**1**).

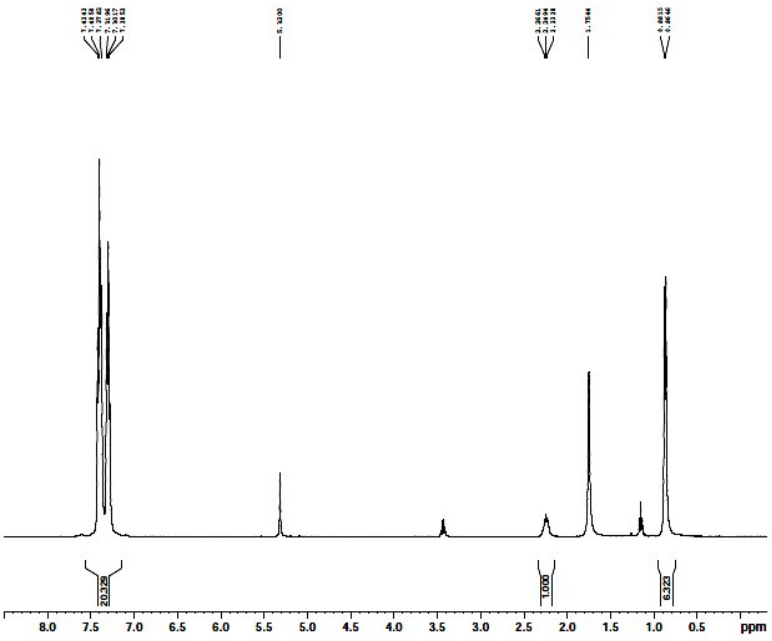

Figure S6. ^{1}H NMR of $[Ag_5@(i\text{PrC}{\equiv}C{-}C{\equiv}C)_6Ag_3(PPh_3)_8]\cdot 2NO_3\cdot MeOH\cdot H_2O$ (**3**).

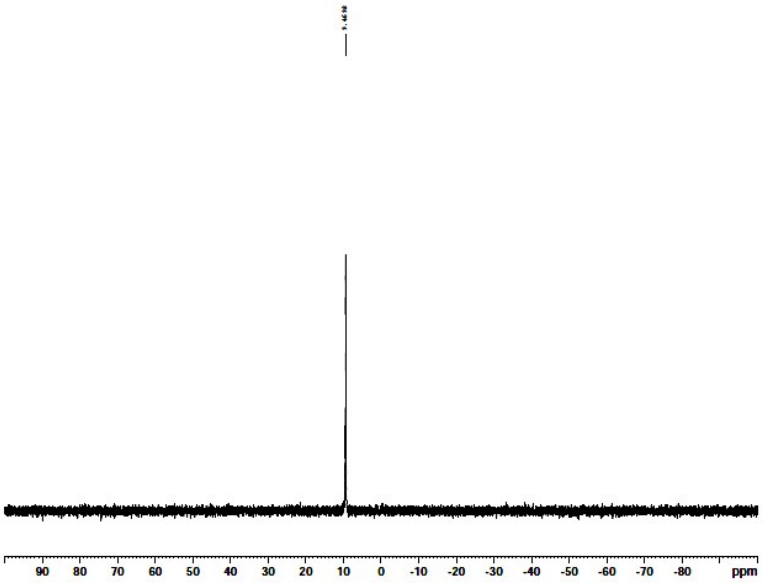

Figure S7. ^{31}P NMR of $[Ag_5@(i\text{PrC}{\equiv}\text{C}{-}\text{C}{\equiv}\text{C})_6Ag_3(PPh_3)_8]\cdot 2NO_3\cdot MeOH\cdot H_2O$ (**3**).

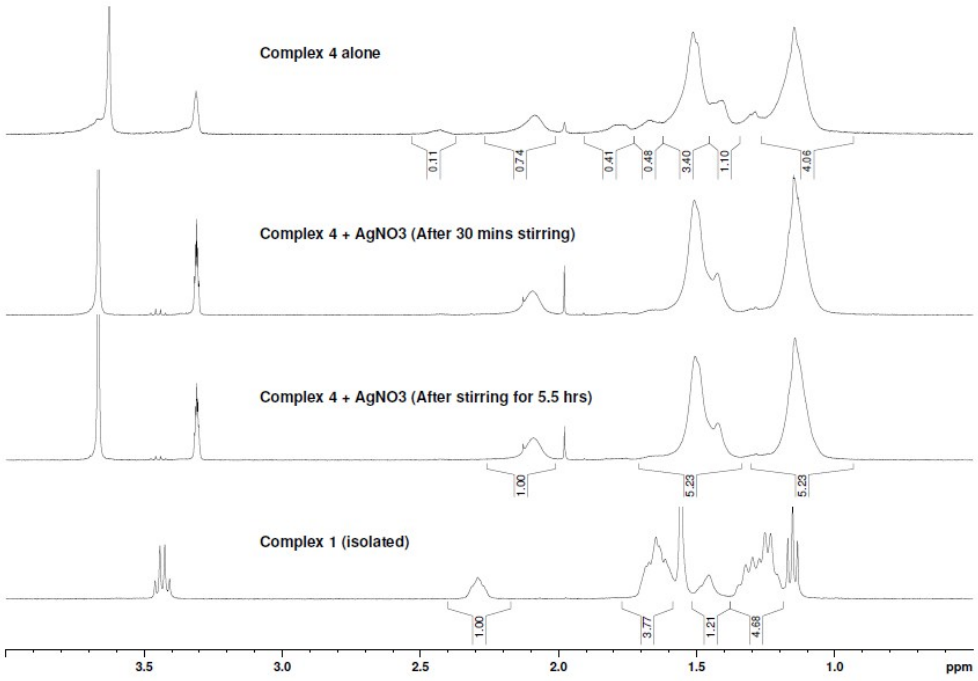

Figure S8. ^{1}H NMR monitoring for the transformation of **1**.

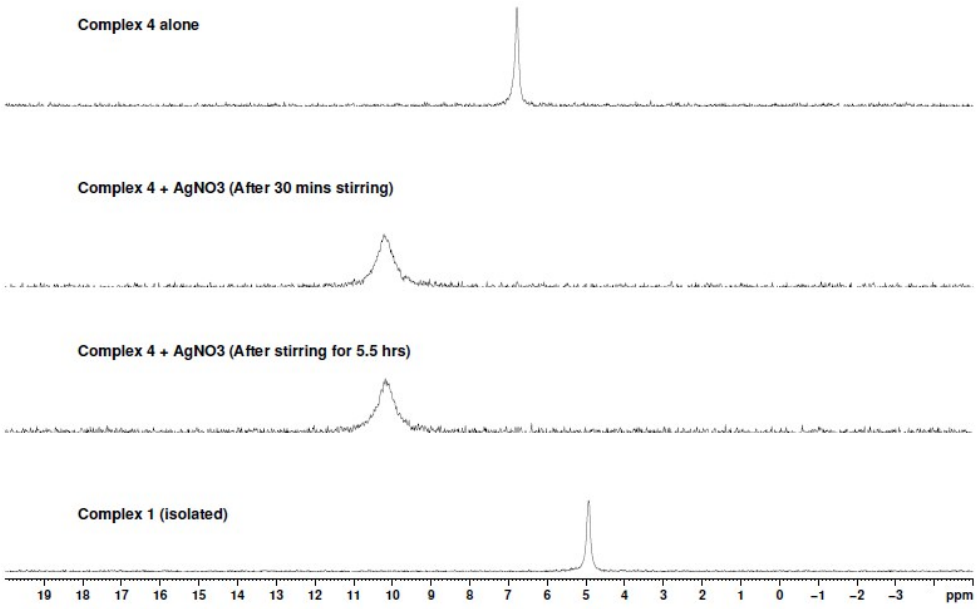

Figure S9. ^{31}P NMR monitoring for the transformation of **1**.