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Anion-Templated Syntheses of Rhombohedral Silver–Alkynyl Cage Compounds

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The interest in metal alkynyl complexes stems not only from their range of organometallic transformations, but also from their flexible structural features.[1] The linear and rigid arrangement of atoms in these compounds makes them attractive building blocks for a wide range of complex architectures.[2, 3] The alkynyl moiety has a flexible coordination environment, being able to form metal–alkynyl σ and π bonds.[4] Alkynyl complexes of the coinage metals are of particular interest since these metals can display additional noncovalent (metallophilic) M···M interactions,[5] which provide an extra degree of complexity. These metallophilic interactions are well-established for gold(I) complexes,[6] but have not been as widely studied for silver(I)[7] and copper(I).[8]

Alkynyl complexes of the coinage metals tend to form polymeric materials.[9] A potential route to oligomeric species (e.g., macrocyclic and cage-type structures) rather than polymeric products could involve the use of templating agents.[10] Most templating agents are cationic or neutral, but recently increasing interest has focused on templating anions.[11, 12]

The synthesis and novel structure of the gold(I) catenane $[\{[\mathrm{Au(C{\equiv}C}t\mathrm{Bu)}]_6\}_2]$[13] stimulated us to carry out similar studies with silver(I). Here we report the remarkable anion-templated syntheses of silver–alkynyl cage-type compounds with general formula $[\mathrm{Ag_{14}(C{\equiv}C}t\mathrm{Bu)_{12}X]Y}$ (X = Cl, Br; Y = OH, $\mathrm{BF_4}$).

When a solution of $\mathrm{AgBF_4}$ in THF is treated with a mixture of $t\mathrm{BuC{\equiv}CH}$ and $\mathrm{NEt_3}$ in THF, a white precipitate is obtained. On the basis of IR spectroscopy, $\mathrm{FAB^+}$ mass spectrometry, and elemental analyses, this solid was formulated as polymeric $[\mathrm{Ag(C{\equiv}C}t\mathrm{Bu)}]_n$ (**1**).[14] To establish the structure of **1**, attempts were made to recrystallize it. Although a wide variety of common solvents (THF, acetone, chloroform, dichloromethane, ethanol, methanol, toluene, hexane) were tried, **1** was found to dissolve only in chloroform. Addition of diethyl ether to this solution gave a white precipitate **2**, and the fact that this could then be redissolved, not only in chloroform, but also in other solvents such as acetone, ethanol, and THF (in which **1** is insoluble), suggested that a chemical modification had occurred. Crystals of this compound were obtained by slow evaporation of an ethanolic solution.

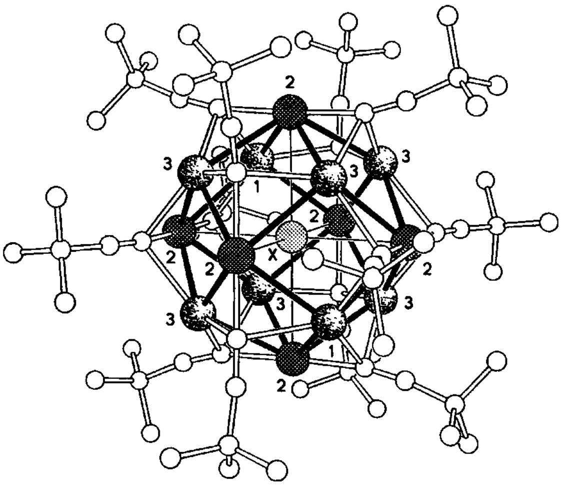

Figure 1. The structure of the silver cage complexes **2** (X = Cl) and **4** (X = Br), showing the rhombic dodecahedron of silver atoms (solid bonds) and the encapsulation of a halide anion at the center of an octahedron of type 2 silver atoms. Silver atoms of types 1 and 3 cap the faces of this octahedron and define a cubic array.

A single-crystal X-ray analysis[15, 16] showed **2** to be the novel silver cage compound $[\mathrm{Ag_{14}(C{\equiv}C}t\mathrm{Bu)_{12}Cl]OH}$ (Figure 1). The cage comprises fourteen silver atoms and twelve *tert*-butylethynyl ligands, and has a chloride anion at its center. The silver atoms are arranged so as to form a near-regular rhombic dodecahedron having crystallographic S_6 symmetry and molecular O_h symmetry, with Ag···Ag distances for the "edges" in the range of 2.953(2)–2.986(2) Å. These distances are comparable to those observed, for example, in the silver double salts reported by Mak et al. and attributed to argentophilic Ag···Ag interactions.[17] The cage contains three crystallographically unique silver centers (labeled 1, 2, and 3 in Figure 1); six of these (of type 2) can be envisaged as forming an octahedron (with the anion position at its center) which interpenetrates a cubic array made up of silver atoms of types 1 and 3 such that each silver atom of the "cube" caps a trigonal face of the octahedron. The silver atoms of the

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octahedron each bear two linearly disposed, σ-bonded *tert*-butylethynyl groups (Ag(2)–C ca. 2.07 Å, C-Ag(2)-C 175.9(6)°), the C$\equiv$C groups of which also bridge pairs of silver atoms that form the edges of the cube (C–Ag ca. 2.42 Å; Figure 2). Within the cage, the Cl ⋯ Ag distances, which range between 3.116(2) and 3.297(1) Å, are significantly longer than those of conventional silver–chlorine bonds (ca. 2.6 Å). Thus, there is clearly a small amount of residual free volume within the cage, and hence the potential for the encapsulation of larger anions.

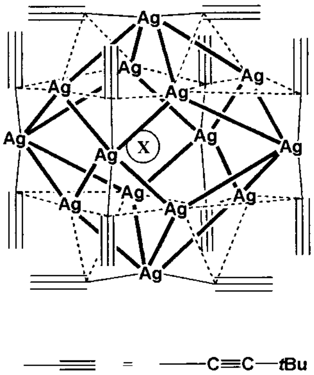

Figure 2. Schematic representation of the coordination sphere of the silver cages **2**–**4**.

The formation of the cation in **2** was confirmed by IR, FAB$^+$ mass spectrometry, and elemental analyses. These provided clear evidence for the complete transformation of the presumably polymeric species **1** into the cage-type structure **2** when the former was treated with $CHCl_3$. The IR spectrum of **2** shows a ν(C$\equiv$C) band at 2042 cm^{-1} (cf. 2053 and 2034 cm^{-1} for **1**). The FAB$^+$ mass spectrum of **2** is also consistent with this formulation: the intense molecular-ion peak at *m/z* 2519 was assigned to $[Ag_{14}(C{\equiv}CtBu)_{12}Cl]^+$. Elemental analyses were consistent with the formulation $[Ag_{14}(C{\equiv}CtBu)_{12}Cl]OH$.

A more rational route to **2** directly from $AgBF_4$ and *t*BuC$\equiv$CH in the presence of NEt_3 and stoichiometric amounts of NMe_4Cl as a chloride source in THF has now been developed. The initial precipitation but rapid redissolution of a white solid suggested that **1** was not being produced or was being rapidly converted into a soluble material. After two hours the solvent was removed under reduced pressure, and the remaining white solid washed several times with water. This solid was characterized as $[Ag_{14}(C{\equiv}CtBu)_{12}Cl]BF_4$ (**3**). Its IR spectrum shows a ν(C$\equiv$C) band at 2042 cm^{-1} and an additional strong band at 1069 cm^{-1}, characteristic of BF_4^-. In the FAB$^+$ mass spectrum, the molecular-ion peak appears at *m/z* 2519, which corresponds to $[Ag_{14}(C{\equiv}CtBu)_{12}Cl]^+$. A single-crystal X-ray analysis of this compound, however, showed only the presence of **2**, and it can be concluded that the OH^- salt crystallizes in preference to the BF_4^- salt (vide infra).

The reaction between $AgBF_4$ and *t*BuC$\equiv$CH in THF (with NEt_3 to deprotonate the alkyne) was repeated in the presence of NBu_4Br. In this reaction no solid precipitated; this suggests that **1** was not being formed. The reaction mixture was treated as described for the synthesis of **3** to give $[Ag_{14}(C{\equiv}CtBu)_{12}Br]BF_4$ (**4**). The IR spectrum of this compound showed the characteristic ν(C$\equiv$C) band at 2038 cm^{-1} together with an intense band for BF_4^- at 1068 cm^{-1}. The FAB$^+$ mass spectrum showed the expected molecular-ion peak for $[Ag_{14}(C{\equiv}CtBu)_{12}Br]^+$ at *m/z* 2564. A single-crystal X-ray study[18] revealed **4** to be isomorphous with **2** and **3**, but with a bromide ion encapsulated at its center. Again the compound crystallized more readily as an OH^- salt than as a BF_4^- salt. The dimensions of the cage differ little from those in **2** and **3**, with Ag ⋯ Ag edge distances in the rhombic dodecahedron between 2.972(2) and 3.006(2) Å. The Ag ⋯ Br distances are very similar to the Ag ⋯ Cl distances in **2**, and range between 3.148(2) and 3.313(1) Å, that is, they are longer than those of conventional Ag–Br bonds.

The rhombohedral structure of these silver cages resembles the geometry of the nickel cages $[Ni_2\{Ni(atu)_2\}_4X]X_3$ (atu = $H_2NC(NH)NHC(NH)S^-$; X = Cl, Br).[11j] The nickel atoms in these assemblies can be envisaged as forming, around the halide ion, an octahedron which interpenetrates a cubic array of NH groups. In spite of the chemical differences between the two types of cages, the M ⋯ X (M = Ag, Ni; X = Cl, Br) distances are strikingly similar and range between 3.116(2) and 3.313(1) Å for Ag ⋯ X and between 3.123(1) and 3.140(1) for Ni ⋯ X.[11j]

An anomalous feature of the silver cage structures is the apparent absence of a second counteranion in the crystals. Clearly there is insufficient space for a second anion to be located within the cage itself. The exterior of the structure is populated by the bulky, hydrophobic *tert*-butyl groups, and inspection of the packing of the molecules shows that the clefts in the region of the type 2 silver atoms in one molecule are occupied by the *tert*-butyl groups of their symmetry-related counterparts. However, the *tert*-butyl groups all exhibit rotational disorder, and it is thus possible that small cavities are formed within which the required counteranions could reside with partial occupancy (because of symmetry restraints). This scenario would be consistent with the presence of a small anion such as OH^-, which could be formed from adventitious water, distributed over several sites; a similar situation was previously reported for a gold cluster.[19] In the bromide-containing cage structure of **4**, for example, the residual electron density in the final Δ*F* map of only 0.50 e Å^{-3} indicates that the "missing" counteranion must be small, of low molecular weight, and highly disordered.[20]

The assignment of OH^- as the counteranion in **2** (i.e., the cage formed by treating **1** with chloroform) is consistent with all the spectroscopic, structural, and analytical data. However, the assignment of the counteranion for the chloride-containing cage **3** and the bromide-containing cage **4**, both of which are formed directly from $AgBF_4$, the alkyne, and stoichiometric amounts of templating halide, is more difficult. The structural analyses of both these cages again indicate that only small counteranions can be accommodated within the crystal lattice. However, spectroscopic (^{19}F, ^{11}B NMR and IR spectroscopy) and analytical data show that BF_4^- is indeed present in the bulk crystalline sample. This observation is consistent with **3** and **4** being mixtures of $[Ag_{14}(C{\equiv}CtBu)_{12}X]BF_4$ and $[Ag_{14}(C{\equiv}CtBu)_{12}X]OH$ (X = Cl, Br), from which only the OH^--containing compounds give crystals suitable for X-ray analyses. Since the analytical data of the bulk material suggest that BF_4^- is the main counteranion present in both **3** and **4**, it is possible that the required small amounts of the OH^- anion are generated in the crystallization process, which was carried out by using standard solvents that were not predried.[21]

The results presented here strongly suggest that the formation of the silver–alkynyl cage compounds **2**–**4** is templated by spherical, mono-anionic species such as chloride and bromide. When these halides are not present, the formation of the insoluble, presumably polymeric material **1**, which in turn can be converted to the cages, is favored. The ability of larger anions to act as potential templating agents is currently being explored.

Experimental Section

Synthesis of **2** from **1**: $[\mathrm{Ag(C{\equiv}C}t\mathrm{Bu)}]_n$ (0.6 g, 3.2 mmol of $\mathrm{Ag(C{\equiv}C}t\mathrm{Bu)}$) was treated with warm $CHCl_3$ to give a colorless solution. After filtration while hot, the reaction mixture was concentrated under reduced pressure, and addition of diethyl ether yielded **2** as a white powder. Yield: 45% (0.26 g). Elemental analysis (%) calcd for $Ag_{14}C_{72}ClH_{109}O$: C 34.10, H 4.32; found: C 34.36, H 4.28; IR (KBr): $\tilde{\nu} = 2042$ (vs, $C{\equiv}C$); ^1H NMR (270 MHz, $CDCl_3$): $\delta = 1.36$ (s, CCH_3); FAB^+-MS: *m/z*: 2519 $[\mathrm{Ag_{14}(C{\equiv}C}t\mathrm{Bu)_{12}Cl}]^+$, 1241 $[\mathrm{Ag_7(C{\equiv}C}t\mathrm{Bu)_6}]^+$, 1053 $[\mathrm{Ag_6(C{\equiv}C}t\mathrm{Bu)_5}]^+$, 863 $[\mathrm{Ag_5(C{\equiv}C}t\mathrm{Bu)_4}]^+$.

Synthesis of **3**: Solid $AgBF_4$ (0.5 g, 2.6 mmol) was added to a mixture of *tert*-butylacetylene (0.3 mL, 2.6 mmol), triethylamine (0.4 mL, 2.6 mmol), and tetramethylammonium chloride (0.2 g, 0.2 mmol) in THF (10 mL). A white precipitate formed but gradually redissolved, and after 10 min a clear solution was obtained. After stirring the mixture for 4 h, the solvent was evaporated under reduced pressure, and the resulting white solid was treated with water and diethyl ether to give **3** as a fine white powder. Yield: 85% (0.4 g). Elemental analysis (%) calcd for $Ag_{14}BC_{72}ClF_4H_{108}$: C 33.19, H 4.15; found: C 33.09, H 4.02; IR (KBr): $\tilde{\nu} = 2042$ (vs, $C{\equiv}C$), 1069 (vs, BF_4^-); ^1H NMR (270 MHz, $CDCl_3$): $\delta = 1.36$ (s, CCH_3); ^{11}B NMR ($CDCl_3$): $\delta = -1.83$ (s, BF_4); FAB^+-MS: *m/z*: 2519 $[\mathrm{Ag_{14}(C{\equiv}C}t\mathrm{Bu)_{12}Cl}]^+$, 1241 $[\mathrm{Ag_7(C{\equiv}C}t\mathrm{Bu)_6}]^+$, 1053 $[\mathrm{Ag_6(C{\equiv}C}t\mathrm{Bu)_5}]^+$, 863 $[\mathrm{Ag_5(C{\equiv}C}t\mathrm{Bu)_4}]^+$.

Synthesis of **4**: Solid $AgBF_4$ (1.5 g, 7.7 mmol) was added to a mixture of *tert*-butylacetylene (0.9 mL, 7.7 mmol), triethylamine (1.1 mL, 7.7 mmol), and tetrabutylammonium bromide (0.55 mmol) in THF (10 mL). A colorless solution formed immediately. After stirring the mixture for 2 h, the solvent was evaporated under reduced pressure. The resulting white solid was treated with water and subsequently recrystallized from THF/diethyl ether to give **4** as a white fine powder. Yield: 92% (0.9 g). Elemental analysis (%) calcd for $Ag_{14}BBrC_{72}F_4H_{108}$: C 32.63, H 4.08; found: C 32.62, H 4.00; IR (KBr): $\tilde{\nu} = 2038$ (vs, $C{\equiv}C$), 1068 (vs, BF_4^-); ^1H NMR (270 MHz, $[D_6]$acetone): $\delta = 1.44$ (s, CCH_3); ^{11}B NMR ($[D_6]$acetone): $\delta = -1.86$ (s, BF_4); ^{19}F NMR ($[D_6]$acetone): $\delta = -150.74$ (s, $^{11}BF_4$), -150.69 (s, $^{10}BF_4$); FAB^+-MS: *m/z*: 2564 $[\mathrm{Ag_{14}(C{\equiv}C}t\mathrm{Bu)_{12}Br}]^+$, 1287 $[\mathrm{Ag_{12}(C{\equiv}C}t\mathrm{Bu)_{10}Br}]^+$, 1241 $[\mathrm{Ag_7(C{\equiv}C}t\mathrm{Bu)_6}]^+$, 1053 $[\mathrm{Ag_6(C{\equiv}C}t\mathrm{Bu)_5}]^+$, 863 $[\mathrm{Ag_5(C{\equiv}C}t\mathrm{Bu)_4}]^+$.

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[15] Crystal data for **2**: $[C_{72}H_{108}Ag_{14}Cl]OH$, $M_r = 2536.2$, rhombohedral, space group $R\bar{3}$ (no. 148), $a = 22.438(2)$, $c = 15.601(2)$ Å, $V = 6802(1)$ Å^3, $Z = 3$ (S_6-symmetric), $\rho_{calcd} = 1.858$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 3.01$ mm^{-1}, $T = 293$ K, colorless prisms; 2618 independent measured reflections, refinement on F^2, $R_1 = 0.063$, $wR_2 = 0.144$, 1375 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 50°$], 156 parameters.

[16] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-163113 (**2**) and CCDC-163114 (**4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[17] a) G.-C. Guo, G.-D. Zhou, T. C. W. Mak, *J. Am. Chem. Soc.* **1999**, *121*, 3136; b) G.-C. Guo, G.-D. Zhou, Q.-G. Wang, T. C. W. Mak, *Angew. Chem.* **1998**, *110*, 652; *Angew. Chem. Int. Ed.* **1998**, *37*, 630; c) Q.-G. Wang, T. C. W. Mak, *J. Am. Chem. Soc.* **2001**, *123*, 1501; d) Q.-G. Wang, T. C. W. Mak, *Angew. Chem.* **2001**, *113*, 1164; *Angew. Chem. Int. Ed.* **2001**, *40*, 1130; e) Q.-M. Wang, T. C. W. Mak, *Chem. Commun.* **2001**, 807.

[18] Crystal data for **4**: $[C_{72}H_{108}Ag_{14}Br]OH$, $M_r = 2580.7$, rhombohedral, space group $R\bar{3}$ (no. 148), $a = 22.441(2)$, $c = 15.595(1)$ Å, $V = 6802(1)$ Å^3, $Z = 3$ (S_6-symmetric), $\rho_{calcd} = 1.890$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 3.42$ mm^{-1}, $T = 293$ K, colorless prisms; 2596 independent measured reflections, refinement on F^2, $R_1 = 0.054$, $wR_2 = 0.114$, 1359 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leq 50°$], 186 parameters.[16]

[19] J. W. A. van der Velden, P. T. Beurskens, J. J. Bour, W. P. Bosman, J. H. Noordik, M. Kolenbrander, J. A. K. M. Buskes, *Inorg. Chem.* **1984**, *23*, 146.

[20] The X-ray structures of the chloride-containing cage compound formed by using a range of different synthetic routes and available counteranions have been determined. In all instances the structures were isomorphous and had unit cell volumes that differed at most by only about 40 Å^3, that is, by less than 0.6%.

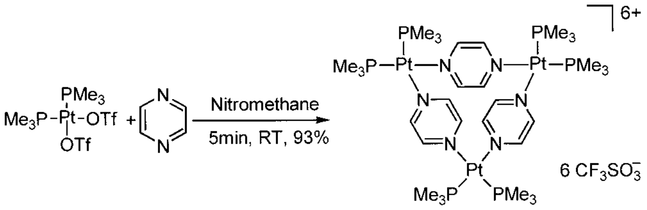
[21] The crystalline samples of **3** and **4** used for the structure determinations were uniform by simple visual inspection. However, it was found consistently that within the same sample some of the material was indeed composed of single crystals (from which the X-ray structures were obtained), whereas the remaining crystalline material was not suitable for X-ray analysis since no resolvable diffraction pattern could be obtained. This observation is consistent with the suggestion that **3** and **4** are mixtures of $[Ag_{14}(C{\equiv}C\mathit{t}Bu)_{12}X]BF_4$ and $[Ag_{14}(C{\equiv}C\mathit{t}Bu)_{12}X]OH$ (X = Cl, Br), from which only the OH^--containing compounds give crystals suitable for X-ray analyses.

The Self-Assembly of an Unexpected, Unique Supramolecular Triangle Composed of Rigid Subunits**

Manuela Schweiger, S. Russell Seidel, Atta M. Arif, and Peter J. Stang*

In recent years, coordination-driven self-assembly has been employed in the synthesis of a large assortment of supramolecular entities.[1] Among the many members of this family are a wide array of two-dimensional systems, such as rhomboids, squares, pentagons, and hexagons, and three-dimensional systems, such as truncated tetrahedra, adamantanoids, cuboctahedra, dodecahedra, and a variety of other cages.[2] In contrast, only a relatively small number of self-assembled triangles exist in the literature.[3–6] Typically, they have been either the product of rational design, where the outcome of the reaction is dictated by the relative ratios of preprogrammed building blocks, or have been in equilibrium mixtures with larger entities, such as squares. The latter usually results when flexible and/or larger subunits are employed, allowing the formation of multiple species.

Herein, we report a novel, self-assembled, unexpected supramolecular triangle **3** formed from the stoichiometric reaction of ditopic platinum acceptor unit **1**[7] and ditopic donor unit pyrazine (**2**) in nitromethane (Scheme 1).



1 **2** **3**

Scheme 1. Formation of self-assembled triangle **3** from rigid subunits **1** and **2**. ^-OTf = triflate = $CF_3SO_3^-$.

Pyrazine (**2**) is the smallest, and hence most rigid, linear aromatic linker available for self-assembly processes, while platinum corner **1**, with its two bonding sites oriented approximately 90° to one another, is also quite compact. Based solely on these considerations, the combination of **1** and **2** would be predicted to yield a square as the final aggregate, but triangle **3** instead results. This distinctive occurrence, where inflexible linkers lead to unexpected products, is rare[8] in the field of discrete molecular assembly, and we attribute it to both entropy considerations and the unique electronics incurred by having two platinum centers attached to each pyrazine ring.

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