Synthesis and Structural Characterization of a Halide-Free Rhombohedral Silver-Alkynyl Cage Complex [Ag₁₄(C₂tBu)₁₂][BF₄]₂


Keywords: Silver / Clusters / Silver alkynyls / Alkynyl cluster / Cationic silver complex / Silver cage complex / Rhombohedral silver cage

The novel cationic complex [Ag₁₄(C₂tBu)₁₂][BF₄]₂ has been synthesized by four reactions: reaction of [Ag(C₂tBu)]⁻ and AgBF₄ in acetone in a 6:1 mole ratio, that of HC≡CtBu and AgBF₄ in water in the absence of a base, treatment of [AgC₂tBu]⁻ with HBF₄ in acetone or that of [[Ag₃(C₂tBu)]²⁺ with [Ag(C₂tBu)]⁻ in a 1:4 mole ratio. Single-crystal X-ray studies showed it to be a hexacapped cube of silver(I) atoms, with twelve η¹-C₃tBu ligands.

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Introduction

Since the pioneering work of Nast[1] on acetylide complexes, dramatic developments in the field, parallel to the advances in organometallic chemistry, have been accomplished. The versatile mode of bonding of the alkynyl ligand resulted in numerous polynuclear alkynyl complexes.[2,3] Different aspects of the subject have been reviewed extensively.[2,4] Luminescence properties, particularly of mixed-metal platinum(ii)-copper(i) and -silver(i) alkynyl complexes have been studied widely.[5] In the field of pure coinage metal alkynyls, new aspects of organometallic chemistry emerged when bis(phenylethynyl) metallates [M(C₂Ph)₂] (M = Cu, Ag, Au) were treated with metal phenylacetylide polymers [M(C₂Ph)]ₙ (M = Cu, Ag, Au). Consecutive steps of ethynylation and condensation of the formed anionic and cationic moieties resulted in the formation of homonuclear [Ag₅(C₂Ph)₆] and heteronuclear [Au₂Cu(C₂Ph)₄]. [Au₃M₂(C₂Ph)₆] (M = Cu, Ag), [Ag₆Cu₄(C₂Ph)₁₄]⁻ and [AuAg₅Cu₄(C₂Ph)₁₄]⁻ complexes.[6] Extension of ethynylation reactions to neutral complexes resulted in the complexes [Au₂Ag₃(C₂Ph)(PPh₃)₂], [Ag₅Cu₃(C₂Ph)(PPh₃)₁₂], [AuAg(C₂Ph)₃]ₙ, [AuCu(C₂Ph)₃]ₙ, [AgCu(C₂Ph)₃]ₙ[6,7] Silver cages of various structures encapsulating the dianion C₃tBu₂⁻, which is isoelectronic with CN⁻, have been reported.[8] Recently anion-template, rhombohedral silver-alkynyl cages [Ag₁₄(C₂tBu)₁₂X]⁺ (X = F, Cl, Br) were synthesized and structurally identified.[9] Earlier we reported the synthesis and structure of the novel cationic silver alkynyl polymer [Ag₅(C₂tBu)]⁻[BF₄]⁻.[10] We now report new aspects of the chemistry resulting from the synthesis of halide-free rhombohedral silver alkynyl complex [Ag₁₄(C₂tBu)₁₂][BF₄]₂ and its structure.

Results and Discussion

The addition of AgBF₄ to [Ag(C₂tBu)]⁻ in a 1:6 mole ratio in acetone gave a clear solution. Normal workup resulted in the slow precipitation of colourless crystals of [Ag₁₄(C₂tBu)₁₂][BF₄]₂. Elemental analysis agrees very well with this formulation. The infrared spectrum has a strong ν(C≡C) signal at 2036 cm⁻¹. This frequency is dramatically lower than that of the linear complex [Ag(C₂Ph)]⁻[10] (by ca. 50 cm⁻¹), which indicates a bridging mode of bonding. A very strong band at 1077 cm⁻¹ was assigned to BF₄⁻.

Single-crystal X-ray structure determination showed that the fourteen silver atoms are arranged in a hexacapped cube of silver(I) atoms (rhombohedral dodecahedron) with twelve η¹-C₃tBu ligands, each pair of alkynyl groups are almost linearly bonded to each capping silver atom, and every ligand bridges two nearby silver atoms on each edge of the cube (Figure 1).

This metal cage is similar to the cage of [Ag₁₄(C₂tBu)₁₂⁻][BF₄]₂ (X = F, Cl, Br), in which the X⁻ anion is located at the centre of the cage.[9] We found, however, that halide ions are not a prerequisite to the formation and stability of the cage as claimed by other workers.[9] Unlike the case in complexes [Ag₁₄(C₂tBu)₁₂X][BF₄]⁻[9a,9b] the BF₄⁻ anions are unambiguously located here. There is a weak Ag···F interaction [2.499(4) Å]. The ¹⁹F NMR spectrum showed two reso-
nances characteristic for BF$_4^-$ at $-151.62$ and $-151.57$ ppm.$^{[9a,9b]}$

The most interesting finding that emerges from the comparison of the encapsulated halide-anion Ag$_{14}$ cages$^{[9a,9b]}$ with the present anion-free Ag$_{14}$ cage is that the encapsulated fluoride anion shrinks the Ag$_{14}$ cage, while the bromide ion expands it. The mean Ag–Ag bond length in the anion-free cage is 2.9747(7) Å, which is almost equal to the corresponding value in the chloride-encapsulated cage [2.971(2) Å], but is 0.015 Å shorter and 0.064 Å longer than the corresponding bond lengths in the bromide- and fluoride-encapsulated cages, respectively.

This cationic cluster represents the highest homoleptic finite polynuclear monosubstituted alkynyl complex to be synthesized and structurally identified. Although neutral ligands and anions$^{[11,12]}$ are known to depolymerize monosubstituted alkynyl coinage metal polymers [M(C$_2$R)$_n$] (M = Cu, Ag, Au), this reaction represents the first cationic depolymerization reaction for these polymers.

The same complex was also prepared by the reaction of HC$_2$tBu and AgBF$_4$ in water by using different mole ratios in the absence of a base. The reactions in aqueous NH$_3$, which afford [Ag(C$_2$R)$_n$]$_n$ are well known for the identification of monosubstituted alkynes; nevertheless, no report has been documented for the reaction in the absence of a base. If the above reaction is carried out in ether, the cationic polymer [Ag$_3$(C$_2$F$_3$Bu)$_2$][BF$_4$]$_n^{[10]}$ is obtained. On the other hand, using AgNO$_3$ with HC$_2$tBu in water results in the formation of the neutral polymer [Ag$_3$(C$_2$F$_3$Bu)$_2$NO$_3$]$_n$, which was reported recently.$^{[9b]}$ The other product of the above reactions is HBF$_4$ [Equation (1), Equation (2)]:

1. $7$ AgBF$_4$ + $6$ HC$_2$tBu $\rightarrow$ $\frac{1}{2} \{[Ag_{14}(C_2tBu)_{12}][BF_4]_2\} + 6$ HBF$_4$  
2. $3$ AgBF$_4$ + $2$ HC$_2$tBu $\rightarrow$ $\frac{1}{n} \{[Ag_3(C_2tBu)_2][BF_4]_n\} + 2$ HBF$_4$

The acid was determined by titration and by measuring the pH of the solution. This implies that these complexes are stable in strongly acidic media.

A third procedure for the synthesis of the same complex is the reaction of HBF$_4$ with [Ag(C$_2$F$_3$Bu)$_n$] in acetone. The product was identified by usual methods and by comparison with an authentic sample. If excess acid is used, \{[Ag$_3$(C$_2$F$_3$Bu)$_2$][BF$_4$]$_n\}$ is obtained [Equation (3), Equation (4)]:

3. HBF$_4$ + $\frac{7}{n}$ [Ag$_3$(C$_2$F$_3$Bu)$_n$] $\rightarrow$ $\frac{1}{2} \{[Ag_{14}(C_2tBu)_{12}][BF_4]_2\} + $HC$_2$Bu
4. HBF$_4$ + $\frac{3}{n}$ [Ag$_3$(C$_2$F$_3$Bu)$_n$] $\rightarrow$ $\frac{1}{n} \{[Ag_3(C_2tBu)_2][BF_4]_n\} + $HC$_2$Bu

A fourth route for the same complex involves the reaction of \{[Ag$_3$(C$_2$F$_3$Bu)$_2$][BF$_4$]$_n\}$ and [Ag(C$_2$F$_3$Bu)$_n$] in acetone in a 1:4 mole ratio [Equation (5)]:
\[
\frac{1}{n} \{[\text{Ag}(\text{t}-\text{Bu})_2]_2[\text{BF}_4]\}_n + \frac{1}{n} \{\text{Ag}(\text{t}-\text{Bu})_2\}_n \rightarrow \\
\frac{1}{2} \{[\text{Ag}_4(\text{t}-\text{Bu})_2]_2[\text{BF}_4]\}_2
\]

The cage structure of the complex indicates without doubt that a halide template is not necessary for the formation and stability of such cages. The different reactions described for the synthesis of the complex might be of general use in the synthesis of homo- and heteronuclear group 11 metal-alkynyl cluster complexes.

**Experimental Section**

**Synthesis of \{[\text{Ag}_4(\text{t}-\text{Bu})_2]_2[\text{BF}_4]\}_2**

**Method 1:** Silver tetrafluoroborate, \(\text{AgBF}_4\) (98 mg, 0.5 mmol), was added to a suspension of \(\{\text{Ag}(\text{t}-\text{Bu})_2\}_n\) (567 mg, 3.0 mmol) in acetone (20 mL). The reaction mixture was stirred for 24 h and then filtered. The solution was concentrated to a small volume and was left for crystallization. Colourless crystals of \(\{\text{Ag}_4(\text{t}-\text{Bu})_2\}_2[\text{BF}_4]\)_2 (540 mg, 81%) were obtained in two crops; m. p. 187–190 °C. IR (KBr disc): \(\tilde{\nu}\) = 3403 cm\(^{-1}\) (C=O); C\(_{72}\)H\(_{108}\)Ag\(_{14}\)B\(_2\)F\(_8\) (2657.38), triclinic, \(P1\bar{1}\), \(\alpha = 106.99(1)\), \(\beta = 13.725(1)\), \(\gamma = 13.843(1)\), \(V = 1486.3(6)\) Å\(^3\), \(Z = 2\), \(D_{calcd} = 2.012\) g cm\(^{-3}\), \(\mu = 3.10\) mm\(^{-1}\), \(\tau = 120(2)\) K, colourless.

**Method 2:** tert-Butylacetylene (1.96 mL, 16.0 mmol) was added to \(\text{AgNO}_3\) (340 mg, 2.0 mmol) in water (20 mL) in an ice bath. The mixture became turbid within a few minutes, and a white precipitate formed. After stirring for 12 h, the white precipitate of \(\{\text{Ag}_4(\text{t}-\text{Bu})_2\}_2[\text{BF}_4]\)_2 was filtered off and dried (224 mg, 59%); m. p. 190 °C. IR (KBr disc): \(\tilde{\nu}\) = 2037 (vs) cm\(^{-1}\) (C=O); \(\mu_{\text{KBr disc}} = 3036\) cm\(^{-1}\) (C=O). \(\text{C}_{72}\text{H}_{108}\text{Ag}_{14}\text{B}_{2}\text{F}_{8}\) (2657.41): calcd.: Ag 56.62; found C 32.20, H 4.12; calcd.: Ag 56.58; found C 32.58, H 4.04.

**Method 3:** A Halide-Free Rhombohedral Silver-Alkynyl Cage Complex

\[\text{C}_7\text{H}_{10}\text{AgNO}_3\ (389\ \text{mg}, \ 2.0\ \text{mmol}) \text{ in water (20 mL) in an ice bath. The mixture became turbid within a few minutes, and a white precipitate formed. After stirring for 12 h, the white precipitate of} \{\text{Ag}_4(\text{t}-\text{Bu})_2\}_2[\text{BF}_4]\)_2 \text{was filtered off and dried (224 mg, 59%); m. p. 190 °C. IR (KBr disc):} \tilde{\nu} = 2037 \text{ (vs) cm}^{-1} (\text{C=O}; \mu_{\text{KBr disc}} = 3036 \text{ cm}^{-1} (\text{C=O}). \text{C}_7\text{H}_{10}\text{AgNO}_3 (2657.41): calcd.: Ag 56.62; found C 32.20, H 4.12; calcd.: Ag 56.58; found C 32.58, H 4.04.

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**References**

SHORT COMMUNICATION

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