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Silver(I)−Ethynide Clusters Constructed with Phosphonate-Functionized Polyoxovanadates

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S *Supporting Information*

ABSTRACT: Two neutral silver(I)−phenylethynide clusters incorporating the $[(^t\mathrm{BuPO_3})_4\mathrm{V_4O_8}]^{4-}$ unit as an integral shell component, namely $\{(\mathrm{NO_3})_2@\mathrm{Ag_{16}}(\mathrm{C{\equiv}CPh})_4[(^t\mathrm{BuPO_3})_4\mathrm{V_4O_8}]_2(\mathrm{DMF})_6(\mathrm{NO_3})_2\}\cdot\mathrm{DMF}\cdot\mathrm{H_2O}$ and $\{[(\mathrm{O_2})\mathrm{V_2O_6}]_3@\mathrm{Ag_{43}}(\mathrm{C{\equiv}CPh})_{19}[(^t\mathrm{BuPO_3})_4\mathrm{V_4O_8}]_3(\mathrm{DMF})_6\}\cdot 5\mathrm{DMF}\cdot 2\mathrm{H_2O}$, have been isolated and characterized by X-ray crystallography. The central cavities of the $\mathrm{Ag_{16}}$ and $\mathrm{Ag_{43}}$ clusters are occupied by two $\mathrm{NO_3}^-$ and three $[(\mathrm{O_2})\mathrm{V_2O_6}]^{4-}$ template anions, respectively.

Polyoxometalates (POMs) are of interest due to their structural variety and desirable properties in catalysis, materials science, and medicine.[1] Much progress has been made on the synthesis of spherical and bowl-shaped POMs displaying very interesting host−guest and encapsulation properties.[2] Of the POMs, polyoxovanadates (POVs) constitute a fascinating family of polynuclear oxo-anions, attributable to the fact that vanadium can adopt variable coordination geometries and has a strong tendency to exhibit mixed-valent states.[3] Recent research on POVs mainly focused on the incorporation of group 15 elements, and a number of P−V−O, As−V−O, and Sb−V−O clusters have been synthesized by different methods.[4] Furthermore, it is expected that a second transition metal can be integrated into the POV skeleton, which may generate a new class of mixed-metal clusters with novel structures and useful properties.

The conventional way to assemble molecular nanosized POM architectures is through the ligation of hetero-POM lacunary clusters by complexation with electrophiles or additional heteroatoms.[5] However, few investigations have been carried out to achieve this goal because it is hard to obtain lacunary POV precursors. Hence new synthetic routes, especially those conducted in organic media with soluble vanadium precursors, are worthy of exploration because they may lead to the assembly and construction of POVs exhibiting novel cluster structures.

tert-Butyl and phenyl ethynide ligands adopting μ_3, μ_4, or μ_5 ligation modes have been employed as versatile precursors for the synthesis of a vast variety of silver(I) double, triple, and quadruple salts, thereby confirming the general utility of the multinuclear silver(I)−ethynide[6] $\mathrm{R{-}C{\equiv}C{\supset}Ag}_n$ ($n = 3, 4, 5$; R = alkyl, aryl, heteroaryl) supramolecular synthon in coordination network assembly. Recently, using polymeric $\mathrm{RC_2Ag}$ as precursors, we and other groups have reported a new and growing number of high-nuclearity silver(I)−ethynide clusters, whose size and shape can be controlled by the introduction of various templating anions.[7] Now we present a new synthetic approach employing silver(I)−ethynide, POV precursor, and *tert*-butylphosphonic acid in the assembly of a novel type of high-nuclearity silver(I)−phenylethynide clusters.

In this work, two unprecedented mixed-metal giant clusters with silver(I)−phenylethynide moieties and phosphonate-functionalized POVs as their surface components, $\{(\mathrm{NO_3})_2@\mathrm{Ag_{16}}(\mathrm{C{\equiv}CPh})_4[(^t\mathrm{BuPO_3})_4\mathrm{V_4O_8}]_2(\mathrm{DMF})_6(\mathrm{NO_3})_2\}\cdot\mathrm{DMF}\cdot\mathrm{H_2O}$ (**1**) and $\{[(\mathrm{O_2})\mathrm{V_2O_6}]_3@\mathrm{Ag_{43}}(\mathrm{C{\equiv}CPh})_{19}[(^t\mathrm{BuPO_3})_4\mathrm{V_4O_8}]_3(\mathrm{DMF})_6\}\cdot 5\mathrm{DMF}\cdot 2\mathrm{H_2O}$ (**2**), have been isolated. Their cluster architectures have been elucidated. They are both neutral molecular materials, in which different numbers and kinds of template anionic species are encapsulated.

The reaction of $(\mathrm{Me_4N})_3(\mathrm{H_3V_{10}O_{28}})$ with $\mathrm{AgC{\equiv}CPh}$, $\mathrm{AgNO_3}$ and $^t\mathrm{BuPO_3H_2}$ in dimethyl formamide (DMF) yielded $\{(\mathrm{NO_3})_2@\mathrm{Ag_{16}}(\mathrm{C{\equiv}CPh})_4[(^t\mathrm{BuPO_3})_4\mathrm{V_4O_8}]_2(\mathrm{DMF})_6(\mathrm{NO_3})_2\}\cdot\mathrm{DMF}\cdot\mathrm{H_2O}$ (**1**).[8] Single-crystal X-ray analysis[9] revealed that complex **1** is a solvated, neutral centrosymmertic ellipsoidal $\mathrm{Ag_{16}}$ cluster encapsulating a pair of template nitrate anions (Figures 1 and S1). Within the $\mathrm{NO_3}^-$ anion, only one oxygen atom coordinates to two silver atoms by the μ_2-η^1,η^1 ligation mode, with Ag−O bond distances of 2.299(1) and 2.431(1) Å. The structure of the cationic cluster shell can be described as consisting of two $[(^t\mathrm{BuPO_3})_4(\mathrm{V_4O_8})]^{4-}$ caps symmetrically bridged by four mid-section butterfly-shaped $\mathrm{Ag_4}$-(μ_4-η^1,η^1,η^1,η^2-$\mathrm{C{\equiv}CPh}$) units (Figure 1b). In the $[(^t\mathrm{BuPO_3})_4(\mathrm{V_4O_8})]^{4-}$ building unit, the tetranuclear $[\mathrm{V_4O_8}]^{4+}$ fragment comprises a boat-shaped eight-membered $\mathrm{V_4O_4}$ ring bearing four exocyclic V═O groups (Figure 2a). Hence, each vanadium(V) atom has a square-pyramidal coordination environment, with V−O bond lengths of 1.794(6)−1.998(6) Å and V═O bond lengths of 1.572(6)−1.600(6) Å, which are in good agreement with structural data reported for similar polyoxovanadium clusters.[10] Eight *tert*-butylphosphonate ligands, each adopting the μ_6 bridging mode to bind two vanadium and four silver atoms, consolidate the mixed-metal cluster shell via $\mathrm{Ag{-}O_P}$ ($\mathrm{O_P}$ = oxygen atom of the *tert*-butylphosphonate ligand) bond lengths ranging from 2.257(6) to 2.516(6) Å. The argentophilic Ag···Ag bond distances lie in the range 2.845(2)−3.100(2) Å. Additionally, six DMF molecules and two nitrate anions each coordinate to one silver atom, and the crystal structure also contains another DMF and a water molecule in the unit cell.

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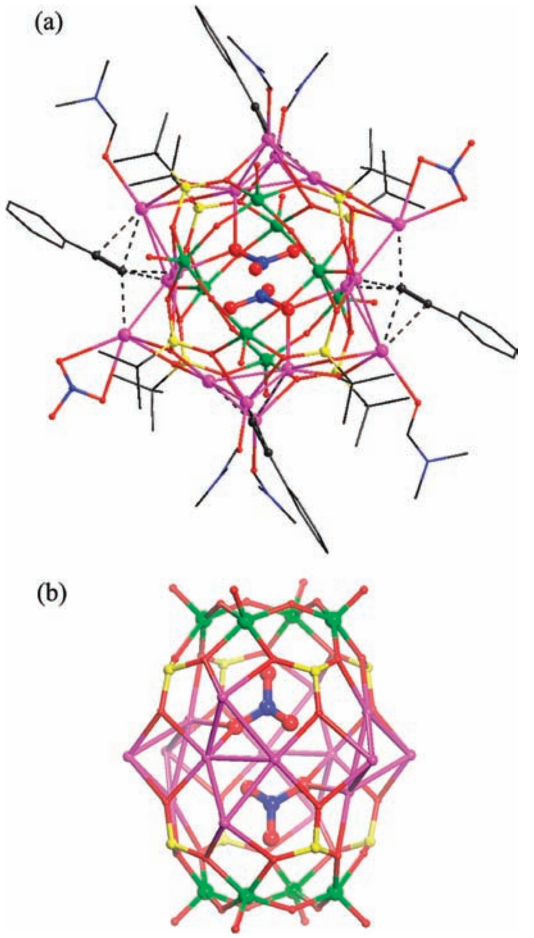

Figure 1. (a) Top-down view of the centrosymmetric Ag_{16} cluster molecule in complex **1**. H atoms are omitted for clarity. Color code: Ag, pink; C, black; O, red; N, blue; V, green; P, yellow. The C atoms of the ethynide group are represented as small black balls, and their bonds to silver atoms are indicated by broken lines. The encapsulated NO_3^- anions are represented by larger ball-and-stick models. (b) Side view showing the ellipsoidal cluster core with all peripheral ligands removed.

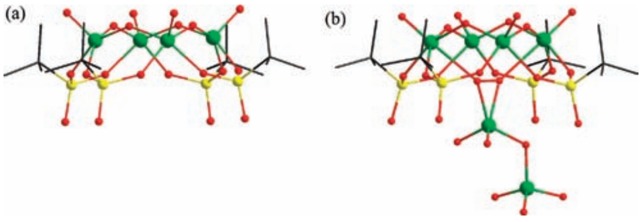

Figure 2. (a) The $[(^tBuPO_3)_4(V_4O_8)]^{4-}$ peripheral structural unit in **1**. (b) Bonding between $[(^tBuPO_3)_4(V_4O_8)]^{4-}$ and encapsulated $[(O_2)(V_2O_6)]^{4-}$ anion in **2**. H atoms are omitted for clarity. Color code: C, black; O, red; V, green; P, yellow.

Peroxo-POMs are known to be effective oxidizing agents, and examples in which the peroxo group is bound to addenda atoms of the POM skeleton have been reported.[11] Accordingly, we decided to investigate in detail the interaction of POVs with $AgC\equiv CPh$, $AgNO_3$, and $^tBuPO_3H_2$ in the presence of hydrogen peroxide.

The synthesis procedure used to obtain $\{[(O_2)V_2O_6]_3@Ag_{43}(C\equiv CPh)_{19}[(^tBuPO_3)_4V_4O_8]_3(DMF)_6\}\cdot 5DMF\cdot 2H_2O$ (**2**) is similar to that used for **1**, except that aqueous H_2O_2 (30%) and $Ph_2PCH_2PPh_2$ were added to the reaction mixture.[8] Complex **2** exhibits a neutral, pseudo-C_3-symmetric cluster shell composed of 43 silver(I) ions consolidated by 3 $[(^tBuPO_3)_4(V_4O_8)]^{4-}$ units, 19 peripheral $PhC\equiv C^-$ ligands, and 6 DMF ligands (Figure S2). The structure of the $[(^tBuPO_3)_4(V_4O_8)]^{4-}$ moiety is identical to that found in **1**, with each *tert*-butylphosphonate ligand adopting a μ_6-bridging mode to coordinate to two vanadium and four silver atoms. On the other hand, the Ag_{43} cluster cavity in **2** is sufficiently large to accommodate three template $[(O_2)V_2O_6]^{4-}$ anions (Figure 3). The peroxo group in each $[(O_2)V_2O_6]^{4-}$ moiety is connected to a $[(^tBuPO_3)_4(V_4O_8)]^{4-}$ surface unit, whereas the other six oxygen atoms are bound to silver atoms by μ_1,μ_2-η^1,η^1 or μ_3-η^1,η^1,η^1 ligation modes (Figure 2b). The three independently measured peroxo $O_{po}-O_{po}$ bond lengths lie in the range of 1.484(9)−1.493(9) Å, and the $V-O_{po}$ bond lengths of 1.894(7)−2.461(7) Å are significantly longer than the V−O (1.646(7)−2.056(7) Å) and V=O (1.578(7)−1.614(7) Å) bond lengths. If the peroxo group were regarded as occupying a single ligand site, both vanadium(V) atoms in $[(O_2)V_2O_6]^{4-}$ would be in a tetrahedral coordination environment. As compared to **1**, more silver triangles, tetragons, and pentagons are present in **2**. Of the 19 $PhC\equiv C$ ligands that hold the Ag_{43} cluster together, 10 adopt μ_3-η^1,η^1,η^1 or μ_3-η^1,η^1,η^2 ligation modes to link different silver triangles, 8 use the μ_4-$\eta^1,\eta^1,\eta^1,\eta^1$ or μ_4-$\eta^1,\eta^1,\eta^1,\eta^2$ mode to coordinate to planar or butterfly silver tetragons, and the remaining 1 takes a μ_5-$\eta^1,\eta^1,\eta^1,\eta^1,\eta^2$ ligation mode within a square-pyramidal Ag_5 basket. Additionally, six DMF ligands each coordinate to only one silver atom. The crystal structure is further stabilized by five DMF and two water solvate molecules.

The syntheses of **1** and **2** indicate that large silver(I) ethynide clusters can be built up by a disassembly−reassembly solution process. In this work, under suitable reaction conditions the POV precursor $(Me_4N)_3(H_3V_{10}O_{28})$ can be transformed into polyoxovanadium phosphonate building blocks, which tend to induce the formation of large silver clusters via Ag−O bonding interactions. It is noteworthy that the same $[(^tBuPO_3)_4(V_4O_8)]^{4-}$ structure building component occurs in constructing the different cluster shells of **1** and **2**. In contrast, all previously reported high-nuclearity silver(I)−ethynide cluster compounds have shells composed of Ag(I) vertices only,[7a−e] and those that incorporate POMs have the latter component either occupying interior cavities[7e,f] or attached to the cluster surface.[7g] Furthermore, hitherto most synthetic studies were carried out with polymeric $^tBuC\equiv CAg$, but here we used $PhC\equiv CAg$. In **1**, the Ag_{16} cluster cavity accommodates two template nitrate anions, whereas in **2** the much larger Ag_{43} cluster cavity encloses three $[(O_2)V_2O_6]^{4-}$ template anions. Alternatively, as the peroxo group in $[(O_2)V_2O_6]^{4-}$ is connected to a surface $[(^tBuPO_3)_4(V_4O_8)]^{4-}$ unit to form a $[(^tBuPO_3)_4(V_4O_8)(O_2)(V_2O_6)]^{8-}$ entity, complex **2** may be regarded as assembled directly from this enlarged POV and the silver(I)−phenylethynide supramolecular synthon $Ph-C\equiv C\supset Ag_n$ (n = 3, 4, 5).

Attempts to prepare analogous complexes of **1** with other small inorganic anions as templates were unsuccessful and always yielded yellow intractable solids. It is evident that $AgNO_3$ plays a critical role in the formation of **1**.

The synthesis of **2** involving dropwise addition of aqueous hydrogen peroxide could present a general procedure for incorporating peroxo groups into POVs, thereby yielding an enlarged Ag(I)−POV cluster. As compared to **1**, more oxygen atoms in **2** are available for coordination to the surface silver(I) atoms via Ag−O bonding interactions. On the other hand, although $Ph_2PCH_2PPh_2$ was not incorporated in complex **2**, we were unable

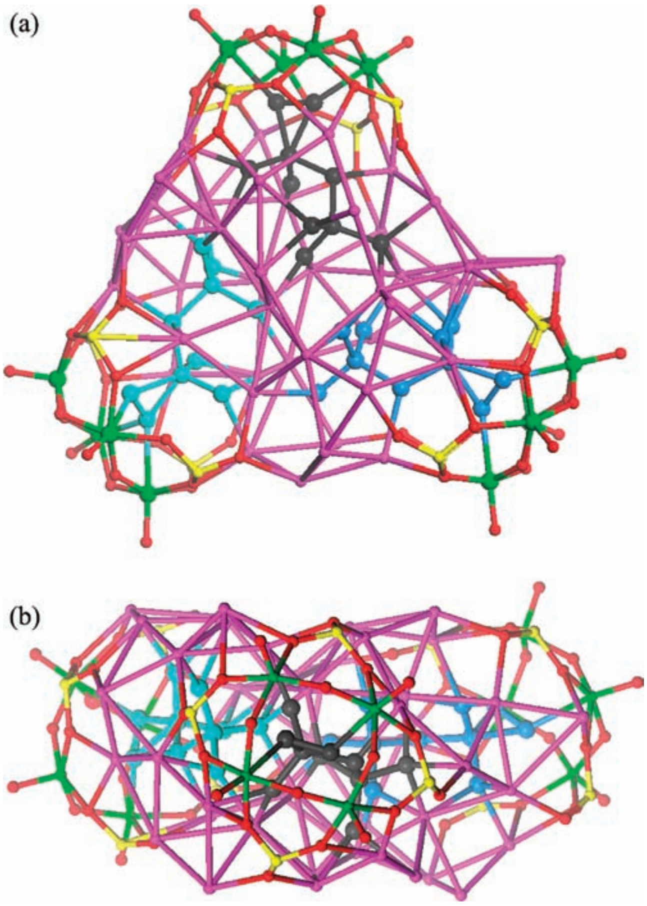

Figure 3. (a) Top-down view and (b) side view of the core structure of the pseudo-C_3 Ag_{43} cluster in complex **2**. All peripheral PhC≡C, ^{t}Bu, and DMF groups are omitted for clarity. Color code: V, green; P, yellow; O, red; Ag, pink. For enhanced visibility, the three independent encapsulated $[(O_2)(V_2O_6)]^{4-}$ species are represented by larger gray, turquoise, and sky-blue ball-and-stick models. Figure S2 in the Supporting Information shows the molecular structure of this giant Ag_{43} cluster, including all peripheral ligands.

to generate the Ag_{43} cluster in its absence. The role of $Ph_2PCH_2PPh_2$ is not yet clear, but it is conceivable that its chelating and bridging capability facilitates the stabilization of certain intermediates in the molecular assembly process.

In summary, we have synthesized and structurally characterized two neutral high-nuclearity silver(I)−ethynide clusters based on polyoxovanadium(V) phosphonate building blocks. For the first time, the $[(^tBuPO_3)_4(V_4O_8)]^{4-}$ species is demonstrated to be a robust structural component for building up multinuclear silver (I)−ethynide cluster shells. Compound **1** represents the first well-characterized neutral Ag(I)−POM cluster encapsulating two nitrate anions. Compound **2** provides a precedent of a giant silver (I)−ethynide cluster that accommodates three POV template anions. Further investigation of various factors that influence the formation of silver(I)−ethynide clusters based on POMs as shell components and/or template anions is in progress.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Experimental details, additional figures, and X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) (a) Jeannin, Y. P. *Chem. Rev.* **1998**, *98*, 51–76. (b) Gouzerh, P.; Proust, A. *Chem. Rev.* **1998**, *98*, 77–111. (c) Rhule, J. T.; Hill, C. L.; Judd, D. A. *Chem. Rev.* **1998**, *98*, 327–357. (d) Mizuno, N.; Yamaguchi, K.; Kamata, K. *Coord. Chem. Rev.* **2005**, *249*, 1944–1956. (e) Müller, A.; Kögerler, P.; Dress, A. W. M. *Coord. Chem. Rev.* **2001**, *222*, 193–218. (f) Katsoulis, D. E. *Chem. Rev.* **1998**, *98*, 359–387. (g) Yamase, T. *Chem. Rev.* **1998**, *98*, 307–325. (h) Streb, C.; Ritchie, C.; Long, D. -L.; Kögerler, P.; Cronin, L. *Angew. Chem., Int. Ed.* **2007**, *46*, 7579–7582. (i) AlDamen, M. A.; Clemente-Juan, J. M.; Coronado, E.; Martí-Gastaldo, C.; Gaita-Ariño, A. *J. Am. Chem. Soc.* **2008**, *130*, 8874–8875. (j) Pichon, C.; Dolbecq, A.; Mialane, P.; Marrot, J.; Rivière, E.; Goral, M.; Zynek, M.; McCormac, T.; Borshch, S. A.; Zueva, E.; Sécheresse, F. *Chem.—Eur. J.* **2008**, *14*, 3189–3199. (k) Giusti, A.; Charron, G.; Mazerat, S.; Compain, J.; Mialane, P.; Dolbecq, A.; Rivière, E.; Wernsdorfer, W.; Biboum, R. N.; Keita, B.; Nadjo, L.; Filoramo, A.; Bourgoin, J.; Mallah, T. *Angew. Chem., Int. Ed.* **2009**, *48*, 4949–4952. (l) *Polyoxometalate Chemistry: From Topology via Self-Assembly to Applications*; Pope, M. T., Müller, A., Eds.; Kluwer: Dordrecht, 2001.

(2) (a) Hölscher, M.; Englert, U.; Zibrowius, B.; Hölderich, W. F. *Angew. Chem., Int. Ed. Engl.* **1995**, *33*, 2491–2493. (b) Long, D.-L.; Burkholder, E.; Cronin, L. *Chem. Soc. Rev.* **2007**, *36*, 105–121.

(3) (a) Hamilton, E. E.; Fanwick, P. E.; Wilker, J. J. *J. Am. Chem. Soc.* **2002**, *124*, 78–82. (b) Day, V. W.; Klemperer, W. G.; Yaghi, O. M. *J. Am. Chem. Soc.* **1989**, *111*, 4518–4519. (c) Hegetschweiler, K.; Morgenstern, B.; Zubieta, J.; Hagrman, P. J.; Lima, N.; Sessoli, R.; Totti, F. *Angew. Chem., Int. Ed.* **2004**, *43*, 3436–3439. (d) Chen, L.; Jiang, F. L.; Lin, Z. Z.; Zhou, Y. F.; Yue, C. Y.; Hong, M. C. *J. Am. Chem. Soc.* **2005**, *127*, 8588–8589.

(4) (a) Finn, R. C.; Zubieta, J.; Haushalter, R. C. *Prog. Inorg. Chem.* **2003**, *51*, 421. (b) Salta, J.; Chen, Q.; Zubieta, J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 757–760. (c) Zhang, Y. P.; Clearfield, A.; Haushalter, R. C. *Chem. Mater.* **1995**, *7*, 1221–1225. (d) Khanra, S.; Kloth, M.; Mansaray, H.; Muryn, C. A.; Tuna, F.; Sañudo, E. C.; Helliwell, M.; McInnes, E. J. L.; Winpenny, R. E. P. *Angew. Chem., Int. Ed.* **2007**, *46*, 5568–5571. (e) Dong, B.; Peng, J.; Gómez-García, C. J.; Benmansour, S.; Jia, H.; Hu, N. *Inorg. Chem.* **2007**, *46*, 5933–5941. (f) Kiebach, R.; Näther, C.; Köerlerb, P.; Bensch, W. *Dalton Trans.* **2007**, 3221–3223.

(5) (a) Fang, X. K.; Kögerler, P. *Angew. Chem., Int. Ed.* **2008**, *47*, 8123–8126. (b) Fang, X. K.; Kögerler, P. *Chem. Commun.* **2008**, 3396–3398. (c) Hussain, F.; Gable, R. W.; Speldrich, M.; Kögerler, P.; Boskovic, C. *Chem. Commun.* **2009**, 328–330. (d) Sokolov, M. N.; Korenev, V. S.; Izarova, N. V.; Peresypkina, E. V.; Vicent, C.; Fedin, V. P. *Inorg. Chem.* **2009**, *48*, 1805–1807. (e) Mal, S. S.; Dickman, M. H.; Kortz, U. *Chem.—Eur. J.* **2008**, *14*, 9851–9855.

(6) (a) Mak, T. C. W.; Zhao, L. *Chem. Asian J.* **2007**, *2*, 456–467. (b) Mak, T. C. W.; Zhao, X.-L.; Wang, Q.-M.; Guo, G.-C. *Coord. Chem. Rev.* **2007**, *251*, 2311–2333. (c) Zhao, L.; Wan, C.-Q.; Han, J.; Chen, X.-D.; Mak, T. C. W. *Chem.—Eur. J.* **2008**, *14*, 10437–10444. The term "silver(I)−ethynide" is preferred to "silver(I)−ethynyl" because in the supramolecular synthon R−C≡C⊃Ag_n (n = 3, 4, 5) the silver−carbon bonding interaction is considered to be mainly ionic with minor covalent

σ and π components; the negative charge residing mainly on the terminal C atom draws neighboring Ag(I) atoms close to one another to facilitate the onset of argentophilic interactions.

(7) (a) Rais, D.; Yau, J.; Mingos, D. M. P.; Vilar, R.; White, A. J. P.; Williams, D. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 3464–3467. (b) Bian, S.-D.; Wang, Q.-M. *Chem. Commun.* **2008**, 5586–5588. (c) Bian, S.-D.; Wu, H.-B.; Wang, Q.-M. *Angew. Chem., Int. Ed.* **2009**, *48*, 5363–5365. (d) Bian, S.-D.; Jia, J.-H.; Wang, Q.-M. *J. Am. Chem. Soc.* **2009**, *131*, 3422–3423. (e) Qiao, J.; Shi, K.; Wang, Q.-M. *Angew. Chem., Int. Ed.* **2010**, *49*, 1765–1767. (f) Gao, G. G.; Cheng, P.-S.; Mak, T. C. W. *J. Am. Chem. Soc.* **2009**, *131*, 18257–18259. (g) Gruber, F.; Jansen, M. *Angew. Chem., Int. Ed.* **2010**, *49*, 4924–4926.

(8) Synthesis of complex **1**: $(Me_4N)_3[H_3V_{10}O_{28}]$ (0.012 g, 0.010 mmol) and $^tBuPO_3H_2$ (0.011 g, 0.080 mmol) were dissolved is DMF (4 mL), and then $PhC{\equiv}CAg$ (0.070 g, 0.335 mmol) was added under stirring to form an orange suspension. After 6 h, $AgNO_3$ (0.010 g, 0.059 mmol) was added. After a further 3 h, an orange-red solution was collected by filtration. The orange-red crystals were obtained by diffusion of Et_2O into the reaction mixture. Yield: ca. 8% (based on V). Elemental analysis (%) calcd for $C_{84}H_{134}Ag_{16}N_{11}O_{60}P_8V_8$: C, 21.75; H, 2.91; N, 3.32. Found: C, 21.86; H, 2.99; N, 3.45. Selected IR data (KBr): 2020 ($C{\equiv}C$), 1050, 969, 780, 754, 696, 546, 508 cm^{-1} ($[(V_4O_8)(PO_3)_4]$). Synthesis of complex **2**: $(Me_4N)_3[H_3V_{10}O_{28}]$ (0.012 g, 0.010 mmol), $^tBuPO_3H_2$ (0.011 g, 0.080 mmol), and 0.3 mL of aqueous H_2O_2 (30%) were dissolved in DMF (4 mL), and then $PhC{\equiv}CAg$ (0.070 g, 0.335 mmol) was added under stirring to form an orange suspension. After 6 h, $Ph_2PCH_2PPh_2$ (0.015 g, 0.040 mmol) and $AgNO_3$ (0.010 g, 0.059 mmol) were added. After a further 3 h, an orange-red solution was collected by filtration. The orange-red crystals were obtained by diffusion of Et_2O into the reaction mixture. Yield: ca. 12% (based on V). Elemental analysis (%) calcd for $C_{233}H_{284}Ag_{43}N_{11}O_{97}P_{12}V_{18}$: C, 26.11; H, 2.67; N, 1.44. Found: C, 26.24; H, 2.55; N, 1.57. Selected IR data (KBr): 2023 ($C{\equiv}C$) 1057, 958, 916, 882, 865, 787, 755, 628, 602, 541, 516 cm^{-1} ($[(V_4O_8)(V_2O_6)(O_2)(PO_3)_4]$).

(9) Crystallographic data for complex **1**: monoclinic, $a = 17.396(4)$, $b = 25.696(6)$, and $c = 22.829(4)$ Å, $\beta = 130.765(11)$, $V = 7729(3)$ Å^3, $T = 293$ K, space group $P2_1/c$, $Z = 2$, 120 189 reflections measured, 18 362 unique ($R_{int} = 0.0680$) which were used in all calculations, $R_1 = 0.0675$, $wR_2 = 0.1773$ for $I > 2\sigma(I)$. Crystallographic data for complex **2**: monoclinic, $a = 23.597(7)$, $b = 23.139(7)$, and $c = 33.025(10)$ Å, $\beta = 99.636(6)$, $V = 17777(9)$ Å^3, $T = 293$ K, space group $P2_1$, $Z = 2$, 312 311 reflections measured, 85 247 unique ($R_{int} = 0.0595$) which were used in all calculations, $R_1 = 0.0506$, $wR_2 = 0.1235$ for $I > 2\sigma(I)$. CCDC 802119 for **1** and 802120 for **2**.

(10) (a) Wulff-Molder, D.; Meisel, M. *Acta Crystallogr., Sect. C* **2000**, *C56*, 33–34. (b) Konar, S.; Clearfield, A. *Inorg. Chem.* **2008**, *47*, 3492–3494.

(11) (a) Hussain, F.; Bassil, B. S.; Kortz, U.; Kholdeeva, O. A.; Timofeeva, M. N.; de Oliveira, P.; Keita, B.; Nadjo, L. *Chem.—Eur. J.* **2007**, *13*, 4733–4742. (b) Suzuki, H.; Hashimoto, M.; Okeya, S. *Eur. J. Inorg. Chem.* **2004**, 2632–2634. (c) Sakai, Y.; Kitakoga, Y.; Hayashi, K.; Yoza, K.; Nomiya, K. *Eur. J. Inorg. Chem.* **2004**, 4646–4652.