Synthesis and crystal structure of [tBu$_3$SiPAg$_2$]$_8$: A novel Ag$_{16}$-cluster featuring a remarkable symmetrical structure

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The synthesis of [tBu$_3$SiPAg$_2$]$_8$ which features an Ag$_{16}$-cluster in the solid state was achieved by metathesis reaction of AgOCN with tBu$_3$SiPNa$_2$.

In a number of recent studies, bulk silyl chalcogenolate ligands of the type R$_3$SiE$^-$ (E = O, S, Se, Te) have been used to stabilize transition metal centres.[1–5] Such ligands have attracted interest for a number of reasons. The chalcogen donor atoms are often found to bridge metal centres, suggesting possible applications in the stabilization of transition metal clusters.[1–4] Such metal clusters with subnanometre core dimensions may be useful as building blocks for nanoscale devices because they are small enough to possess discrete electronic states.[6] Otherwise, it has been suggested that bulky siloxides such as tri-*tert*-butylsiloxide (supersiloxide), tBu$_3$SiO$^-$, can function as analogs of the ubiquitous cyclopentadienyl (Cp) ligand.[4] Previous investigations have indicated that supersiloxide possesses a cone angle greater than 120° (cyclopentadienide ~ 130°).[5] The supersilyl monophosphanediide anion tBu$_3$SiP^{2-} also has the ability to stabilize metal clusters as the isoelectronic supersilyl chalcogenolate ligands do.[7–9]

Several synthetic routes to transition metal complexes with chalcogenolate and monophosphanediide ligands are known. These compounds can be prepared (i) by the reaction of transition metal halides MX with R–P(SiMe$_3$)$_2$ or (ii) by metathesis reactions of MX with monophosphanediide derivatives R$_3$SiPM$'_2$ (M$'$ = Li, Na, K). Transition metal clusters with chalcogenolate and monophosphanediide ligands are normally synthesized by Me$_3$SiX elimination from MX and R–E(SiMe$_3$)$_n$.[7,10,11]

Since only few alkali metal or alkaline earth metal monophosphanediides are known,[9,12,13] it is almost impossible to carry out metathesis reactions of MX with monophosphanediides. However, the synthesis of the copper phosphanediide [tBu$_3$SiPCu$_2$]$_6$ (**1[Cu]**) was achieved by the reaction of CuI with tBu$_3$SiPNa$_2$.[9] Recently, we have reported that the degradation of P$_4$ with tBu$_3$SiM$'$ (M$'$ = Li, Na, K) cleanly leads to the monophosphanediides tBu$_3$SiPM$'_2$ (M$'$ = Li, Na, K).[15–17] As noted earlier, the alkali metal phosphanediides, Mes(iPr)$_2$SiPLi$_2$ and tBu$_3$SiPM$'_2$ (M$'$ = Li, Na, K), can be also generated by deprotonation of the corresponding phosphanes[14] with nBuLi and tBu$_3$SiM$'$ (M$'$ = Na, K).[9,12]

$$\begin{matrix} 8\ t\mathrm{Bu_3Si-PNa_2} \\ + \\ 16\ \mathrm{AgOCN} \end{matrix} \xrightarrow[\mathrm{(THF)}]{-16\ \mathrm{NaOCN}} \begin{matrix} [t\mathrm{Bu_3Si-PAg_2}]_8 \\ \mathbf{1[Ag]} \end{matrix} \qquad (1)$$

Continuing our investigations,[4,15–18] we were interested in the synthesis and properties of the silver monophosphanediide [tBu$_3$SiPAg$_2$]$_8$ (**1[Ag]**). As shown in eqn (1), the reaction of AgOCN and tBu$_3$SiPNa$_2$, which has been generated by P$_4$-degradation with tBu$_3$SiNa,[19] conveniently produces **1[Ag]** in THF at ambient temperature.

Single crystals of **1[Ag]** suitable for X-ray crystallography were grown from a toluene filtrate of the reaction mixture at −25 °C.† The structure of the silver supersilylphosphanediide **1[Ag]** is shown in Fig. 1–3. In contrast to the silver chalcogenide and phosphanide clusters that have been structurally characterized so far, the supersilylphosphanediide **1[Ag]** shows a remarkably symmetrical structure in the solid state (molecular symmetry: 4*mm*). Surprisingly, however, the Ag atoms in the supersilylphosphanediide **1[Ag]** do not occupy the vertices of a regular cuboctahedron like the Cu atoms in the phosphanediide **1[Cu]**,[9] but the vertices of a novel Ag$_{16}$-polyhedron as it is depicted in Fig. 2 and 3.

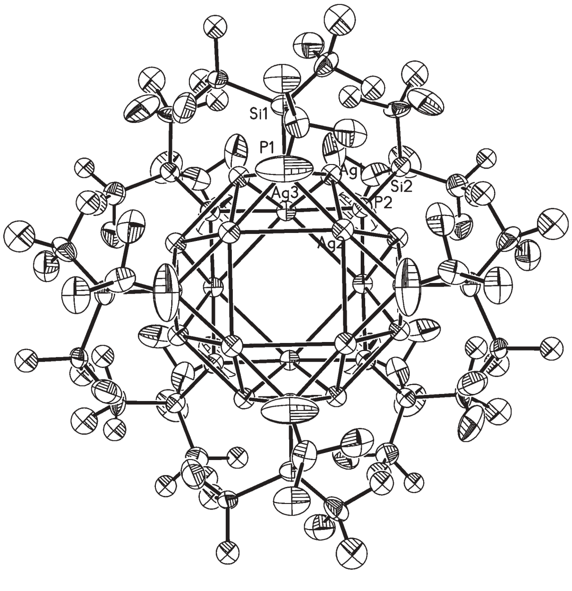

Fig. 1 Thermal ellipsoid plot of **1[Ag]** showing the atom numbering scheme. The displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity. One position is shown for each of the disordered tBu groups.

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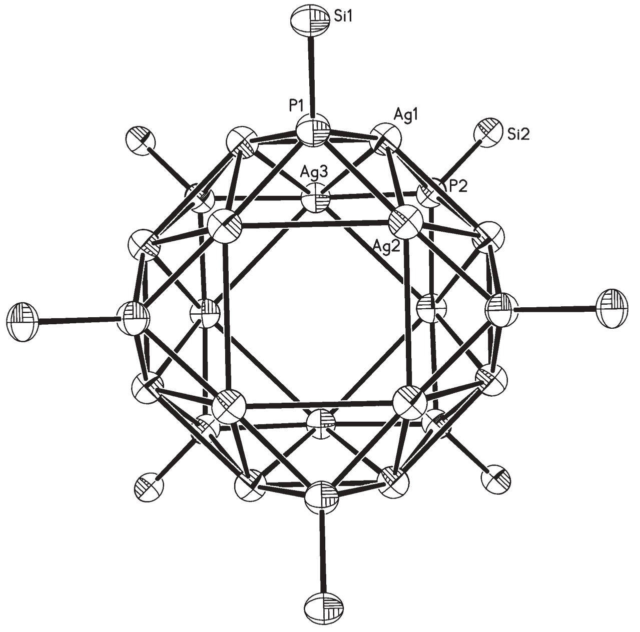

Fig. 2 Positions of the Ag, P and Si atoms in **1[Ag]**; orientation along the *c*-axis.

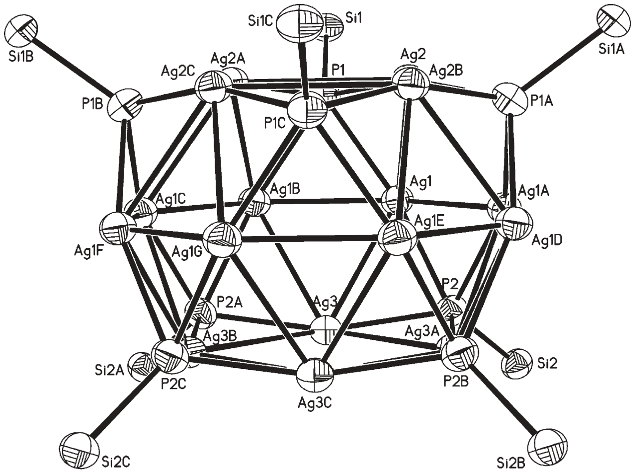

Fig. 3 Positions of the Ag, P and Si atoms in **1[Ag]**; orientation along the [1 1 0]-axis. The displacement ellipsoids are drawn at the 50% probability level. *t*Bu groups have been omitted for clarity. Selected bond lengths/Å and angles/°: P–Si 2.261(4) [av], Ag(1)–P(1) 2.478(2), Ag(1)–P(2) 2.479(2), Ag(1)–Ag(1)#1 2.7827(11), Ag(1)–Ag(1)#2 2.7914(11), Ag(1)–Ag(3) 2.9424(8), Ag(1)–Ag(2) 2.9524(8), Ag(2)–P(1) 2.427(2), Ag(2)–Ag(1)#1 2.9524(8), Ag(2)–Ag(2)#4 3.2990(11), Ag(2)–Ag(2)#3 3.2991(11), Ag(3)–P(2) 2.424(2), Ag(3)–Ag(1)#2 2.9425(8) Ag(3)–Ag(3)#3 3.3502(11) Ag(3)–Ag(3)#4 3.3502(11), P(2)–Ag(3)#3 2.424(2), P(2)–Ag(1)#1 2.479(2), P(1)–Ag(2)#4 2.427(2), P(1)–Ag(1)#2 2.478(2), Ag(1)#1–Ag(1)–Ag(1)#2 135.0, Ag(1)#1–Ag(1)–Ag(3) 95.536(15), Ag(1)#2–Ag(1)–Ag(3) 61.685(12), Ag(1)#1–Ag(1)–Ag(2) 61.884(12), Ag(1)#2–Ag(1)–Ag(2) 94.932(15), Ag(3)–Ag(1)–Ag(2) 120.19(3), Ag(1)–Ag(2)–Ag(1)#1 56.23(2), Ag(1)–Ag(2)–Ag(2)#4 85.068(15), Ag(1)#1–Ag(2)–Ag(2)#4 125.485(16), Ag(1)–Ag(2)–Ag(2)#3 125.484(16), Ag(1)#1–Ag(2)–Ag(2)#3 85.066(15), Ag(2)#4–Ag(2)–Ag(2)#3 90.001(1), Ag(1)–Ag(3)–Ag(1)#2 56.63(2), Ag(1)–Ag(3)–Ag(3)#3 84.464(15), Ag(1)#2–Ag(3)–Ag(3)#3 125.055(16), Ag(1)–Ag(3)–Ag(3)#4 125.054(17), Ag(1)#2–Ag(3)–Ag(3)#4 84.466(15), Ag(3)#3–Ag(3)–Ag(3)#4 90.0. Symmetry transformations used to generate equivalent atoms: #1 x, $3/2 - y$, z; #2 y, x, z; #3 y, $3/2 - x$, z; #4 $3/2 - y$, x, z.

The Ag_{16}-polyhedron can be described as consisting of annelated Ag_3- and Ag_4-rings. On the one hand, the Ag_3-rings are connected solely to the edges of those Ag_4-rings that are capped by tBu$_3$SiP groups. On the other hand, these Ag_4-rings, which are equatorially oriented in Fig. 3, are connected by three common edges with three adjacent Ag_3-rings and additionally by a common edge with another Ag_4-ring that is not capped by a tBu$_3$SiP unit. Both the polyhedron found in the Ag_{16}-cluster and the cuboctahedron that is a structural feature of **1[Cu]** can be constructed of the same geometrical forms, equilateral triangles and squares. Moreover, the three- and four-membered rings in both polyhedra have nearly identical connectivity. In contrast to **1[Cu]** in **1[Ag]** there are eight rather than six metal atoms arranged on an equatorial plane. The central eight-membered ring in **1[Ag]** that is visible in this case is surrounded from above and below by four metal atoms arranged in a square, while the central six-membered ring in **1[Cu]** is surrounded by three metal atoms arranged in an equilateral triangle. The metal centres that surround the planar Ag_8-ring in **1[Ag]** feature a square antiprism and the metal centres that surround the planar Cu_6-ring in **1[Cu]** form a trigonal antiprism. For **1[Ag]** the polyhedron shows Ag–Ag bond lengths between 2.783(1) and 3.350(1) Å. The short Ag–Ag contacts are located between the Ag atoms of the central eight-membered Ag-ring, shown equatorially in Fig. 3, whereas the square antiprismatically arranged Ag atoms show long Ag–Ag bonds in the Ag_4-ring. The Si–P distances, averaging 2.261(4) Å, are in the normal range for Si–P single bonds. Remarkably, there is a hollow space inside the Ag_{16}-cluster, in which no further atom or molecule has been found, although the Ag_{16}-cluster has an equatorial inner diameter of 7.283 Å. The structural comparison between **1[Ag]** and **1[Cu]** shows in an exemplary manner how, given the equal bonding principles of both molecules in the solid state, the dimensions of the cluster are exclusively determined by the ratio of ligand size to the size of the central atom. The molecules are separated in the crystal structure by large solvate regions. There are no direct intermolecular contacts between the molecules.

It is interesting to note that the photolysis reaction of **1[Ag]** ($h\nu$ = 366 nm; t = 2 h) in a mixture of toluene and d_6-benzene at ambient temperature leads to silver and the supersilylphosphane tBu$_3$SiPH$_2$[14] in quantitative yield (further investigations into the photolysis reaction of **1[Ag]** are currently under way).‡

Notes and references

† Crystal structure analysis of **1[Ag]**: $C_{96}H_{216}Ag_{16}P_8Si_8$, M = 3569.09, tetragonal, a = 22.826(2), c = 14.8258(16) Å, V = 7724.8(13) Å^3, T = 162(2) K, space group $P4/nmm$, Z = 2, μ(Mo Kα) = 2.153 mm^{-1}, 89397 reflections measured, 5037 unique (R_{int} = 0.1269). $R1$ = 0.056 $wR2$ = 0.147 (data $I > 2\sigma(I)$). Data were collected on a Siemens-SMART-CCD three-circle diffractometer. The structure was determined by direct methods using program SHELXS. The positions of the t-butyl groups are disordered about mirror planes. The H atoms were geometrically positioned and were constrained. The unit cell contains two symmetry-related channels filled with disordered solvate groups. No discrete atoms could be located in the solvate regions. Program PLATON/SQUEEZE was used to model the solvate density. The volume of the solvate region was estimated as 1420 Å^3 cell^{-1}, while the electron count in the solvate region was about 960 e cell^{-1}. The electron density within the Ag_{16}-cluster was less than 1.0 e Å^{-3}. CCDC 254881. See http://dx.doi.org/10.1039/b507833d for crystallographic data in CIF or other electronic format.

‡ Synthesis of **1[Ag]**: A mixture of AgOCN (0.172 g, 1.15 mmol) and 0.58 mmol tBu$_3$SiPNa$_2$ in 3 mL THF was stirred for 12 h at room

temperature. All volatile components were removed *in vacuo*. The remaining solid was extracted with toluene. The obtained solution was filtered off. Single crystals suitable for X-ray structure determination were grown from the filtrate at −25 °C. Yield: 0.108 g (41%). **1[Ag]**: ^{1}H NMR (250 MHz, C_6D_6, 25 °C, int. TMS): $\delta = 1.42$ (br, 27 H *t*Bu). $^{13}C\{^1H\}$NMR (62.9 MHz, C_6D_6, 25 °C, int. TMS): $\delta = 26.6$ (br; *C*Me$_3$), $\delta = 32.4$ (br; C*Me*$_3$). $^{31}P\{^1H\}$NMR (162 MHz, C_6D_6, 25 °C, ext. H_3PO_4): $\delta = -327.0$ (br). $^{29}Si\{^1H\}$NMR (49.7 MHz, C_6D_6, 25 °C, ext. TMS): δ 35.3 0 (m; Si*t*Bu3). MS (MALDI-TOF): *m*/*z* = 3568.10 (calcd.: 3568.13) $[M - H]^+$, 3512.63 $[M - t\text{Bu}]^+$, 3371.26 $[M - \text{Si}t\text{Bu}_3]^+$, 3329.84 (calcd.: 3329.86; 100%) $[M - \text{AgPHSi}t\text{Bu}_3]^+$. Anal. Calcd. for $C_{103}H_{224}Ag_{16}P_8Si_8$: C, 33.77; H, 6.22. Found: C, 34.45; H, 6.04.

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