

Anion-templated formation of a unique inorganic 'super-adamantoid' cage [Ag₆(triphos)₄(O₃SCF₃)₄]²⁺ [triphos = (PPh₂CH₂)₃CMe]

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In the presence of templating anions, 2:3 molar mixtures of triphos and silver(I) cations unexpectedly give novel hexanuclear cages, which result from an unusual 'endo-methyl' geometry of the triphos ligands.

Multidentate ligands in general tend to promote the formation of metal clusters or aggregates by forming radial metal–ligand bonds which place the metal atoms at the centre of the molecule. For example, 2:2 (ligand:metal) diphosphine complexes of silver(I) or copper(I) generally form dinuclear rings shown in Fig. 1(a) and (b), with terminal or bridging anions.¹ Metallo-cage assembly is receiving increasing attention,² and the use of appropriate tripodal phosphines in a 2:3 ratio might be expected to give trinuclear cages of the type shown in Fig. 1(c). The only triphos [MeC(CH₂PPh₂)₃] silver(I) complex to be structurally characterised so far is the mononuclear 1:1 complex [Ag(triphos)I].³ Here we report our unexpected observation that a 2:3 molar mixture of triphos and silver(I) ions in fact gives a novel hexanuclear cage of formula [Ag₆(triphos)₄X₄]²⁺. The triphosphine ligands assemble with their methyl groups concentrating in the central region of the molecule, and the dative bonds to the complexed phosphino substituents lead to an aggregate of silver ions on the surface. Anions are further complexed to the outside of the cage and appear to play an important templating role.

When solutions of triphos are titrated against a silver(I) salt of an oxo anion [AgX] (X = SO₃CF₃, ClO₄, NO₃) and monitored by ³¹P{¹H} NMR spectroscopy, broad featureless signals are seen until a molar ratio of 2:3 (triphos: silver) is reached, when only a very sharp pattern with well defined ¹⁰⁹Ag–³¹P and ¹⁰⁷Ag–³¹P coupling is observed. Crystals of the 2:3 adduct **1** (X = SO₃CF₃ **1a**, ClO₄ **1b**, NO₃ **1c**)[†] suitable for X-ray analysis were grown by diffusion of hexane into a tetrachloroethane–acetonitrile solution of the complex.[‡] The molecular structure (Fig. 2) is based on a cage of stoichiometry [Ag₆(triphos)₄(O₃SCF₃)₄]²⁺ with approximate *T* symmetry.[§] It may be simply represented as a truncated tetrahedron in which the four triphos ligands define the truncated apices and the six silver ions occupy the edges (Fig. 3). The four faces of the cage correspond to fused 18-membered rings each having local *C*₃ symmetry, containing six phosphorus atoms and three silver(I) centres. Approaching each facial trio of silver(I) atoms is a triflate ion with its oxygen atoms directed inwards. A novel feature is the

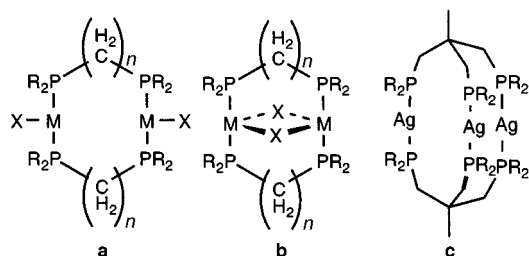


Fig. 1 Macrocyclic diphosphine silver(I) and copper(I) complexes with terminal (a) or bridging (b) anions and postulated trinuclear cages based on triphos ligands (c).

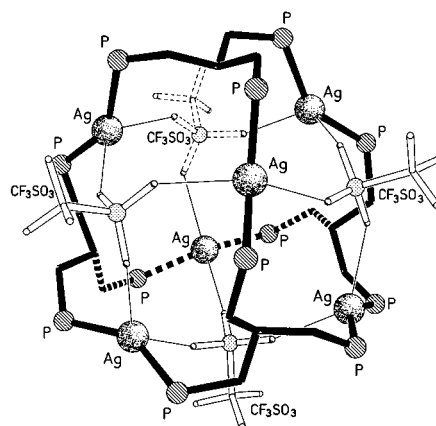


Fig. 2 The central core of complex **1a**. The phenyl and methyl groups on the triphos ligands have been omitted for clarity.

'endo-methyl' conformation of the triphos ligands, in which their methyl groups point toward the centre of the cage, leaving only a small cavity of van der Waals radius *ca.* 2.4 Å at the centre. This arrangement differs markedly from the 'exo-methyl' conformation observed when triphos acts as a face capping ligand.⁴ As a consequence, the in-pointing methyls generate an ordered hydrophobic interior and the Ag⁺ and O₃SCF₃⁻ ions form a polar spherical surface.

The average Ag–O distance is 2.66 Å indicating a significant degree of interaction [*cf.* 2.639(4), 2.712(6) and 2.74(2) in [Ag₂{μ-Ph₂P(CH₂)₆PPh₂}₂{μ-ClO₄}]^{1a}]. The resulting geometry at each Ag(I) centre can best be described as distorted tetrahedral, the angles subtended at the two independent metal centres by the phosphorus atoms being 144.6(1) and 147.9(1)°, and by the oxygen atoms 128.2(5) and 126.8(5)° respectively. The O–Ag–O and P–Ag–P planes at each silver ion are essentially orthogonal (between 88 and 90°). The Ag–P

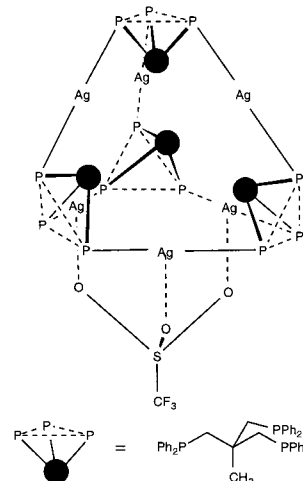


Fig. 3 Truncated tetrahedral representation of complex **1a**.

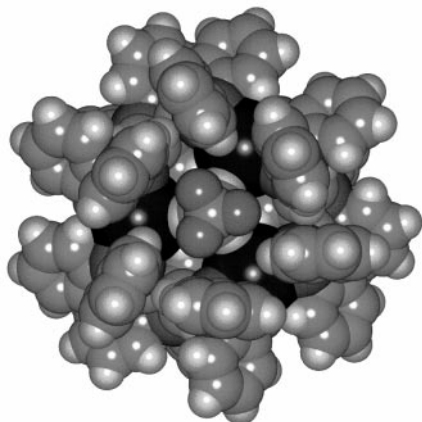


Fig. 4 Space-filling representation of the solid state structure of **1a** viewed along the crystallographic C_3 axis.

distances are in the range 2.405(4)–2.416(4) Å. The ability of triflate to coordinate to the cage is perhaps surprising given the steric bulk of the triphos phenyl substituents. However, the space filling representation of **1a** (Fig. 4) reveals how the phenyl groups are arranged in such a way as to provide channels through which the triflate anions can approach the silver ions. These channels are chiral and could potentially discriminate between enantiomeric anions.

The presence of four faces which are tetrahedrally disposed, each with approximate C_3 symmetry (as in adamantane) but composed of 18-membered rings (*cf.* six-membered as in adamantane) suggests the description 'super-adamantoid' for the cage. In the super-adamantoid cage, bridgehead atoms are replaced by tridentate triphos ligands, and the bridging atoms are replaced by silver ions.

As mentioned above, in solution, sharp ^{31}P NMR spectra are observed at room temperature which indicate chemically equivalent phosphorus atoms. The silver–phosphorus coupling constants $^1J_{^{109}\text{Ag}-^{31}\text{P}}$ for **1a–c** lie in the range 588–561 Hz which is consistent with the silver(I) centres being coordinated to two phosphine groups.^{5,6} In addition the, albeit small, variations in chemical shift and silver–phosphorus coupling constants between **1a**, **1b** and **1c** imply that some degree of anion coordination occurs at the silver(I) centres in solution. This is further supported by the ^{19}F NMR spectrum of the triflate complex **1a**, which consists of two singlets at δ –77.9 and –78.6 in a 4 : 2 intensity ratio, as expected for four coordinated and two free triflate anions. On the basis of the closely related NMR spectra of complexes **1a–c**, we assume that similar cage structures are formed, at least in solution, for complexes **1b** ($\text{X} = \text{ClO}_4$) and **1c** ($\text{X} = \text{NO}_3$). By contrast, under similar conditions, a mixture of triphos and AgBF_4 gave a solution whose ^{31}P NMR spectrum consisted for the main part (98% of the total intensity) of a broad signal lacking any evidence of $^{109}\text{Ag}-^{31}\text{P}$ couplings. The remaining 2% consisted of sharp signals indicative of cage formation. With AgSbF_6 , only the broad featureless signal was observed. It therefore seems that the less nucleophilic BF_4^- and SbF_6^- anions are unable to promote the selective formation of the cage structure in solution.

The anion-specific behaviour noted above, *i.e.* selective formation of a rigid cage when $\text{X} = \text{SO}_3\text{CF}_3$, ClO_4 or NO_3 *vs.* more labile species in which phosphine dissociation occurs on the NMR timescale at room temperature when $\text{X} = \text{BF}_4^-$ or SbF_6^- , may be related to the μ_3 -face-capping coordination mode of the anion in the structure. The anion is required to be tridentate and reasonably nucleophilic. These criteria are satisfied by the O_3SCF_3 , ClO_4 and NO_3 anions, but not BF_4^- and SbF_6^- .

In conclusion, complexes **1** have a unique super-adamantoid structure which results from the phosphines adopting a novel tetramer at the centre of the molecule, providing an outer surface which enables the coordination of six silver ions in an octahedral aggregate. This unusual geometry is stabilised by

tridentate anions capable of capping the faces of the octahedron.

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Notes and references

† *Experimental*: in a typical preparation, a solution of triphos (70 mg, 0.122 mmol) in tetrachloroethane (4 cm³) was added to a solution of $[\text{AgX}]$ (0.183 mmol) in MeCN (1 cm³) and the resulting solution layered with hexane to give the product as colourless crystals. ^{31}P NMR (110 MHz, $\text{CD}_3\text{CN}-\text{CDCl}_3$, 4 : 1, 25 °C, 85% H_3PO_4) δ –5.95 ($^1J_{^{109}\text{Ag}-^{31}\text{P}}$ 588 Hz) **1a**; –4.49 ($^1J_{^{109}\text{Ag}-^{31}\text{P}}$ 587 Hz) **1b**; –4.75 ($^1J_{^{109}\text{Ag}-^{31}\text{P}}$ 561 Hz) **1c**. Reactions between triphos and AgBF_4 or AgSbF_6 were conducted similarly. ^{31}P NMR (110 MHz, $\text{CD}_3\text{CN}-\text{CDCl}_3$, 4 : 1, 25 °C, 85% H_3PO_4); AgBF_4 : 98% of total intensity is a broad signal from δ –5 to –12, 2% is sharp, with δ –3.67 ($^1J_{^{109}\text{Ag}-^{31}\text{P}}$ 588 Hz); AgSbF_6 : broad signal from δ –5 to –12.

‡ *Crystal data* for **1a**: $[(\text{C}_{164}\text{H}_{156}\text{P}_{12}\text{Ag}_6)(\text{CF}_3\text{SO}_3)_4](\text{CF}_3\text{SO}_3)_2 \cdot 6(\text{C}_2\text{H}_2\text{Cl}_4)$, $M = 5047.2$, rhombohedral, space group $R\bar{3}$ (no. 148), $a = 24.454(2)$, $c = 70.832(6)$ Å, $V = 36684(5)$ Å³, $Z = 6$ (the complex has crystallographic C_3 symmetry), $D_c = 1.371$ g cm^{–3}, $\mu(\text{Cu}-\text{K}\alpha) = 79.5$ cm^{–1}, $F(000) = 15\,192$, $T = 183$ K, clear prisms, $0.53 \times 0.53 \times 0.37$ mm, Siemens P4 rotating anode diffractometer, ω -scans, 11 915 independent reflections. The structure was solved by direct methods and all of the non-hydrogen atoms of the complex and its associated counter-ions were refined anisotropically. The solvent molecules and the remaining counter-ions were found to be highly disordered and could not be resolved. They were thus modelled by the assignment of appropriate partial occupancy atoms to fit the electron density throughout the diffuse area. Refinements were by full matrix least-squares based on F^2 to give $R_1 = 0.109$, $wR_2 = 0.283$ for 5962 independent observed absorption corrected [semiempirical based on ψ -scans, max. and min. transmission factors 0.23 and 0.08 respectively] reflections $[|F_o| > 4\sigma(F_o)]$, $2\theta \leq 120^\circ$ and 720 parameters. CCDC 182/1030.

§ The crystallographic symmetry is C_3 only about an axis passing through one of the triflate anions, though the departures from this symmetry about the other three anions are only slight.

- (a) S. Kitagawa, M. Kondo, S. Kawata, S. Wada, M. Maekawa and M. Munakata, *Inorg. Chem.*, 1995, **34**, 1455; (b) E. R. T. Tiekink, *Acta Crystallogr., Sect. C*, 1990, **46**, 1933; (c) D. M. Ho and R. Bau, *Inorg. Chem.*, 1983, **21**, 4073; (d) S. P. Neo, Z.-Y. Zhou, T. C. W. Mak and T. S. A. Hor, *ibid.*, 1995, **34**, 520; (e) A. F. M. J. van der Ploeg, G. van Koten and A. L. Spek, *ibid.*, 1979, **18**, 1052; (f) A. F. M. J. van der Ploeg and G. van Koten, *Inorg. Chim. Acta*, 1981, **51**, 225; (g) Y. Ruina, Y. M. Hou, B. Y. Xue, D. M. Wang and D. M. Jin, *Transition Met. Chem.*, 1996, **21**, 28; (h) *Acta Crystallogr., Sect. B*, 1976, **32**, 2521; (i) F. Caruso, M. Camalli, H. Rimml and L. M. Venanzi, *Inorg. Chem.*, 1995, **34**, 673; (j) *J. Org. Chem.*, 1980, **45**, 2995; (k) *Inorg. Chim. Acta*, 1997, **69**, 262.
- R. W. Saalfrank, R. Burak, A. Breit, D. Stalke, R. Hirbstirmer, J. Daub, M. Porsch, E. Bill, M. Muther and A. X. Trautwein, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1621; D. L. Caulder, R. E. Powers, T. N. Parac and K. N. Raymond, *ibid.*, 1998, **37**, 1840; T. Beissel, R. E. Powers and K. N. Raymond, *ibid.*, 1996, **35**, 1084; C. Bruckner, R. E. Powers and K. N. Raymond, *ibid.*, 1998, **37**, 1837; A. J. Amoroso, J. C. Jeffrey, P. L. Jones, J. A. McCleverty, P. Thornton and M. D. Ward, *ibid.*, 1995, **34**, 1443; J. S. Fleming, K. L. V. Mann, C. A. Carraz, E. Psillakis, J. C. Jeffrey, J. A. McCleverty and M. D. Ward, *ibid.*, 1998, **37**, 1279; R. Vilar, D. M. P. Mingos, A. J. P. White and D. J. Williams, *ibid.*, 1998, **37**, 1258.
- M. Camalli and F. Caruso, *Inorg. Chim. Acta*, 1990, **169**, 189.
- H. Zimmerman, M. Gomm, E. Kock and J. Ellerman, *Acta Crystallogr., Sect. C*, 1988, **44**, 48; M. R. Churchill, C. H. Lake, W. G. Feighery and J. B. Keister, *Organometallics*, 1991, **10**, 2384.
- Methods in Stereochemical Analysis, Volume 8, Phosphorus-31 NMR spectroscopy in Stereochemical Analysis*, ed. J. G. Verkade and L. D. Quin, VCH Publishers Inc., Deerfield Beach, FL, 1987; M. Barrow, H. B. Buergi, M. Camalli, F. Caruso, E. Fischer, L. M. Venanzi and L. Zambonelli, *Inorg. Chem.*, 1983, **22**, 2356.
- Camalli *et al.* (ref. 3), in broad agreement with our observations, report that reaction between triphos and $[\text{AgX}]$ ($\text{X} = \text{ClO}_4$ or NO_3) was found to give complexes with silver–phosphorus coupling constants 'higher than expected for complexes of the type AgP_3^+ ($\text{P} = \text{phosphine}$). While noting that definitive structure assignments could not be made, it was postulated that these complexes were two-coordinate with one arm of the triphos ligand non-coordinate. We suggest that they were in fact observing the cages **1b** and **1c** respectively.