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Selective formation of a polar incomplete coordination cage induced by remote ligand substituents[†]

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Instead of highly symmetrical *T*-symmetry cages common in self-assembly, the *p*-NMe₂-substituted triphosphine CH₃C{CH₂P(4-C₆H₄NMe₂)₃ gives open, polar C_3 symmetry cages [Ag₆(triphos)₄X₃]³⁺ which lack one of the expected facecapping anions; despite its subtlety this difference occurs selectively in solution and two examples have been crystallographically characterised.

Self-assembly tends to give rise to non-polar structures.^{1a} For example, discrete cages formed through labile metal coordination, which have been studied in solution, adopt connectivities which are often based around Platonic or Archimedean solids, $^{1b-e}$ or prisms,^{1f-i} which can be seen as approximations to spheres or cylinders.² Instances where polar structures are adopted selectively are therefore of fundamental interest. It has also been shown that polar coordination assemblies can themselves be exploited as building blocks to form still larger discrete 'clusters of clusters', *i.e.* a type of 2nd level assembly.¹ⁱ Here we describe a system which, as a result of a simple ligand modification, gives polar assemblies selectively. Specifically, whereas the unfunctionalised triphosphine CH₃C(CH₂PPh₂)₃ (L)^{3a,b} and two of its para-functionalised derivatives (with phenyl^{3c} or -CH₂N(CH₂CH₂)₂NCH₃^{3d} substituents) have previously been found to react with silver salts to give the expected type of nonpolar, T-symmetry adamantoid cages $[Ag_6(triphosphine)_4X_4]^{2+}$ (Fig. 1a), we report here that the para-NMe2-substituted derivative $CH_3C\{CH_2P(4-C_6H_4NMe_2)_2\}_3$ (L-NMe₂) gives 'incomplete' C_3 symmetry cages $[Ag_6(L-NMe_2)_4X_3]^{3+}$ which lack one of the expected face-capping anions (Fig. 1b). Although this structural difference is subtle it occurs with remarkable selectivity, as shown by solution-state ³¹P NMR for a range of anions. Two example structures have also been crystallographically characterised.



Fig. 1 High (*T*) symmetry adamantoid cages $[Ag_6(L)_4X_4]^{2+}$ and low (*C*₃) symmetry $[Ag_6(L-NMe_2)_4X_3]^{3+}$ cages missing one face-capping anion (X = tosylate).

The new *para*-NMe₂-substituted ligand **L-NMe₂** (Fig. 1) was synthesised from the secondary phosphine HP(4-C₆H₄NMe₂) and CH₃C(CH₂Cl)₃ as detailed in the ESI. It reacted in a 4:6 ligand/metal molar ratio with silver *para*-toluenesulfonate (AgOTs) in CDCl₃-CH₃CN (4:1) to give a species with a surprisingly complicated ³¹P NMR spectrum. 32 signals could be resolved at or below 25 °C (Fig. 2). At higher temperatures these signals coalesced so that at 60 °C the spectrum showed a single P environment coupled to ¹⁰⁷Ag and ¹⁰⁹Ag nuclei. This behaviour contrasts markedly with that of the unfunctionalised ligand **L**, which under the same conditions gives a spectrum with a single P environment coupled to ¹⁰⁷Ag and ¹⁰⁹Ag nuclei (as expected for a symmetrical adamantoid cage) and does not vary with temperature (Fig. 1a).

Block-shaped single crystals were grown from a CDCl₃-CH₃CN (4:1) solution of the tosylate complex by vapour diffusion of benzene and were determined by X-ray diffraction to contain a *pseudo*-adamantoid cage of the expected type but missing one face-capping anion, *i.e.* $[Ag_6(L-NMe_2)_4(OTs)_3]^{3+}$ (Fig. 3)‡ rather than the expected 'complete' cage $[Ag_6(L-NMe_2)_4(OTs)_4]^{2+}$.

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Fig. 2 Variable-temperature ${}^{31}P{}^{1}H$ NMR spectra for $[Ag_6(L-NMe_2)_4(OTs)_3]^{3+}$ in CDCl₃-CH₃CN (4:1). The coloured symbols corrrespond to the assignments shown in Fig. 4.



Fig. 3 X-ray crystal structure of $[Ag_6(L-NMe_2)_4(OTs)_3]^{3+}$. Anions are shown as spheres and the cage core as capped sticks. Ag = light blue, P = pink, S = yellow, O = red. H-atoms omitted for clarity.

This incomplete cage consists of a distorted octahedral Ag₆ core whose faces are alternately capped by the four **L-NMe₂** ligands and three tripodal anions, with one face remaining uncapped. The non-bonded Ag···Ag distances of the uncapped face are slightly greater than those in the capped faces (see ESI) due to the lack of a capping ligand. An analogous crystal structure was determined for the nitrate complex, *i.e.* $[Ag_6(L-NMe_2)_4(NO_3)_3]^{3+}$, whereas crystals of the triflate complex were found instead to be of the conventional complete adamantoid type, *i.e.* $[Ag_6(L-NMe_2)_4(OTf)_4]^{2+}$ (see ESI).

The 32-line solution-state ³¹P NMR spectrum of the AgOTs complex is fully consistent with the incomplete cage structure observed in the solid state. In particular, this idealised C_3 symmetry structure has four different P environments as indicated in Fig. 4a.



Fig. 4 Illustrative assignment of the 32-line ${}^{31}P{}^{1}H$ NMR spectrum of $[Ag_6(L-NMe_2)_4(OTs)_3]^{3+}$ which results from two pairs of mutually coupled P environments (P_A coupled to P_B and P_C to P_D) with further coupling to ${}^{107}Ag$ and ${}^{109}Ag$. J values are in Hz.

There are two types of P centre (shown in green and black) around the uncapped face because of the twisted C_3 symmetry. The remaining P centres attached to these 'rim' triphosphines (shown in blue) and the basal triphosphine (red) provide two further chemically distinct P centres. The four P centres cannot be assigned to specific signals in the NMR spectrum and so a largely arbitrary assignment has been made in Fig. 4b, for illustrative purposes, such that red = P_A , blue = P_B , black = P_C , green = P_D . Inequivalent P centres should couple via the silver centres $({}^{2}J_{PP})$ but through-backbone coupling $({}^{4}J_{PP})$ is often not observed with such ligands since it is close to the NMR resolution limit. P_A and P_B are mutually coupled (${}^2J_{PP} = 146$ Hz) as are P_{C} and P_{D} (² $J_{PP} = 133$ Hz). This P-P coupling was further confirmed by a ³¹P-COSY spectrum (Fig. S5, ESI). There are limited literature data for ${}^{2}J_{PP}$ coupling via Ag (in a related cage based on triarylphosphines 80 Hz was observed^{1a}). The resulting eight signals are all further coupled to 107 Ag $(I = \frac{1}{2})$ and ¹⁰⁹Ag $(I = \frac{1}{2})$ nuclei to produce the 32-line spectrum. The magnitudes of ${}^{1}J_{(31P-109Ag)}$ (P_A, 569 Hz; P_B, 550 Hz; P_C, 572 Hz; P_D, 584 Hz) are all characteristic of AgP₂ centres.³ Once the P-P coupling has been identified, the differences in intensities between the signals can be recognised as roofing effects $(\Delta \nu/J = 5.6 \text{ for } P_A - P_B \text{ and } 1.7 \text{ for } P_C - P_D)$. The averages of the four P chemical shifts and their silver-phosphorus coupling constants (-10.97 ppm and 568 Hz respectively at 25 °C) are in reasonable agreement with the corresponding values for the simpler spectrum seen at 60 °C (-11.50 ppm and 562 Hz), suggesting that the latter results from coalescence. This is most likely to be due to scrambling of the anions around the structure.

For the analogous system with AgNO₃, the spectrum at room temperature resembled closely the high-temperature spectrum of $[Ag_6(L-NMe_2)_4(OTs)_3]^{3+}$, *i.e.* a slightly broad single P environment (-8.95 ppm) with coupling to Ag $({}^{1}J_{31P-109Ag} = 590$ Hz, Fig. S4). Lower-temperature spectra showed a number of broad signals indicating several P environments coupled to Ag. This is consistent with similar solution state behaviour to the tosylate complex but with faster scrambling of the anions. However, precipitation prevented a full investigation at low temperatures. For AgOTf, the behaviour was again consistent with the AgOTs complex, *i.e.* it gave a single P environment at 40 °C (-9.35 ppm, 590 Hz) and more complex spectra at lower temperatures. The expected 32 lines could not be fully resolved on cooling, however, due to signal overlap (up to 27 lines could be distinguished, Fig. S2 and S3). Interestingly, at -25 °C just two of the four P signals had coalesced, before full coalescence of all four occurred by 40 °C (Fig. S3). This can be explained by flipping between C_3 enantiomeric forms becoming rapid on the NMR timescale at -25 °C (which would render equivalent all six P centres around the open rim, Fig. S3).^{1a}

Polar coordination cages identified in solution are rare, but include a saturated mixed-ligand Pd₄LL' structure⁴ (where L and L' are different tetrapodal N-donor ligands) and an unsaturated (homo-ligand) Ag₄L₃ structure (where L is a tripodal triphosphine) together with its capped derivative Ag_4L_3L' (where L' is a tripodal trinitrile).^{1a} In these cases the adoption of polar structures can be related most likely to steric effects which either induce a preference for hetero-ligand complexation (*i.e.* self-selection of one ligand is disfavoured by its steric bulk) or which prevent a complete cage from forming. In this work, a specific reason for the subtle differences between L-NMe2 and L (and previous para-functionalised analogues where the substituents are Ph or CH₂N(CH₂CH₂)₂NCH₃) is less clear-cut. We note that the behaviour is consistent with both the more electron-donating character of L-NMe₂⁵ as well as its greater steric bulk. Specifically, anion coordination may be rendered weaker in complexes of L-NMe2 because of the more basic character of the triphosphine, and the consequently lower Lewis acidity of the Ag centres. The greater steric crowding (exacerbated by the coplanarity of the C₆H₄ and NMe₂ groups) could also help to stabilise the unsaturated structure. Although selective in solution, and to a degree in the solid state, the effect does seem to rely on subtle energetics, since one of the cages investigated actually crystallised as the complete structure $[Ag_6(L-NMe_2)_4X_4]^{2+}$ (X = OTf), suggesting that crystal packing forces are of similar magnitude.

In summary we note that a remote structural change to a ligand building block switches its preferred mode of self-assembly away from the normal, saturated, non-polar *T*-symmetry coordination cage to an unusual, incomplete, polar C_3 -symmetry structure by disfavouring coordination of one of the four anions. Despite the subtlety of this structural preference, it occurs with remarkable selectivity as shown by ³¹P NMR spectroscopy. As noted above, because of their directionality, polar assemblies present interesting possibilities for 2nd level self-assembly into yet larger discrete aggregates.¹¹ Studies towards this goal are ongoing with these systems.

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Notes and references

‡ Crystal data for [Ag₆(L-NMe₂)₄(4-CH₃C₆H₄SO₃)₃][4-CH₃C₆H₄SO₃]₃: C₂₅₄H₃₁₈Ag₆N₂₄O₁₈P₁₂S₆ (excluding unmodelled disordered solvent), $M_r = 5206.68$, cubic, space group $Pa\bar{3}$, a = b = c = 39.4527(8) Å, V = 61409(2) Å³, Z = 8, $\lambda = 0.71073$ Å, $\mu = 0.53$ mm⁻¹, T = 120 K; 149637 reflections measured, 22890 unique, $R_{int} = 0.1093$; R = 0.111(F, 6751 data with $F^2 > 2\sigma$), $R_w = 0.361$ (F^2 , all data), GOF = 0.892, 1421 refined parameters, final difference map extremes +1.28 and -0.62 e Å⁻³.

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