

Assembly of a coordination cage with four aromatic channel receptors on the outside

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Silver salts and triphosphine ligands with biphenyl substituents assemble to give coordination cages with four external aromatic channel receptors in a pseudo-tetrahedral arrangement.

The last ten years have seen great advances in the synthesis of nanoscale multimetallic ring and cage coordination complexes.¹ These could now be used as scaffolds on which to build new large structures, able, for example, to act as new types of receptors. An interesting possibility is the preparation of single species that contain several receptors, since they could show cooperative or anticooperative guest inclusion. Also, whilst some attention has been given to guest inclusion within metallogages,¹ relatively little study has been made of assemblies with binding sites on their exteriors.² This sort of functionalisation could allow such species to be used as construction units in still larger discrete assemblies or extended networks, by using guests as linkers.

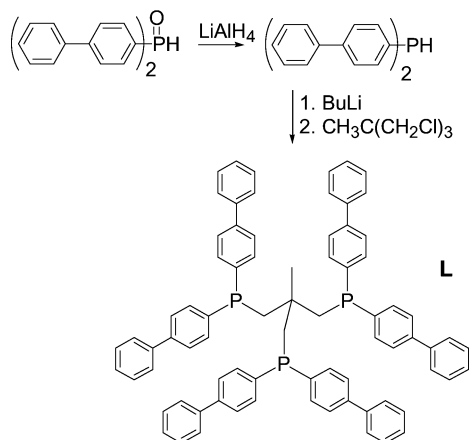
We are investigating multidentate phosphines as ligands for generating metal cages and polymers.³ For example, we reported the triphosphine–silver cage [Ag₆(triphos)₄(OTf)₄]²⁺ (triphos = CH₃C(CH₂Ph)₃, OTf = triflate, CF₃SO₃[−]),^{3a} an interesting feature of which is its arrangement of twenty-four phenyl groups in four short (*ca.* 5 Å) C₃-symmetry aromatic channels on the exterior. Most of the short channel space is occupied by triflate anions, coordinated to the silver ions at the core, and so no inclusion behaviour in the channels would be expected. However, the *para*-hydrogen atoms of the phenyl groups all point directly away from the cage core, so that *para* substituents *could* extend these channels into effective receptors, particularly in combination with smaller anions. To test this idea, the 4-biphenyl-substituted triphosphine **L**[†] was synthesised (Scheme 1).

Addition of 4 equivalents of **L** to six equivalents of AgX gave the hexasilver cages [Ag₆L₄X₄]²⁺ (X = NO₃, **1a**; CF₃SO₃, **1b**; or 4-CH₃C₆H₄SO₃, **1c**) instantly and quantitatively. ³¹P NMR data (δ/ppm and ¹J_{P–¹⁰⁹Ag}/Hz: **1a** –6.3, 555; **1b** –6.2, 586; **1c** –8.9, 570) were similar to those of the phenyl-substituted

triphos cages.^{3a,b} The nitrate complex **1a** was chosen for inclusion studies since its non-bulky anions should have left the channel space free for guests. When CHCl₃–CH₃CN solutions were layered with benzene, crystals were obtained for which the molecular structure, determined by single crystal X-ray diffraction,[†] is shown in Fig. 1. The cage core, similar to that of [Ag₆(triphos)₄(triflate)₄]²⁺,^{3a} was confirmed, with all bond lengths and angles within normal ranges. The Ag⁺ ions define a distorted octahedron whose faces are alternately capped by nitrates and back-flipped or 'endo-methyl'^{3a} **L**.

The twenty-four biphenyl groups form the expected four aromatic channels, each of length *ca.* 9.5 Å, in a pseudo-tetrahedral arrangement, and three of the channels were found to contain single benzene guests. The structure has crystallographically imposed C₃ symmetry about an axis though the centre of the vacant channel, making the filled channels symmetry-equivalent. Interestingly, the vacant channel has a distinctly different 'closed' conformation compared to the other three, with three of its six biphenyl groups pointing inwards and resulting in a (shortest) cross-channel C⋯C distance of *ca.* 4.2 Å, compared to *ca.* 8.6 Å in the filled channels (Fig. 2). The atomic displacement parameters indicate that there is some disorder associated with the biphenyls and the guests, therefore detailed comments on specific host–guest interactions are not possible, although C⋯C distances appear to be in the expected range of 3.5–4.0 Å. The nitrate anion of the unfilled channel sits on the crystallographic C₃ axis and weakly bridges between three silver ions (O⋯Ag distances = 2.62 Å). The nitrates in the filled channels are not actually tripodal but instead bond to only two silver ions each (O12A⋯Ag1B = 2.43 and O13A⋯Ag2B = 2.84 Å) with the distance to the third silver centre being too far for a significant contact (O11A⋯Ag1A = 3.77 Å).

Interestingly, when a similar solution of **1a** was layered with pentafluorobenzene, in anticipation of stronger binding of an



Scheme 1

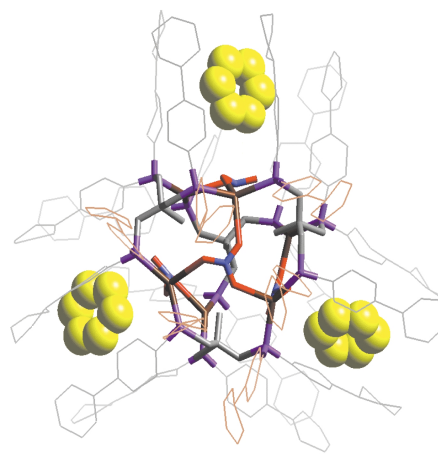


Fig. 1 Crystal structure of **1a**·(C₆H₆)₃: benzene-filled channels are in grey, unfilled channel in light brown. P = purple, O = red, N = blue, Ag = brown. Hydrogen atoms omitted for clarity, space-filling spheres set at 0.70 van der Waals radius. The biphenyl groups show evidence of disorder and have not all been constrained to planarity.

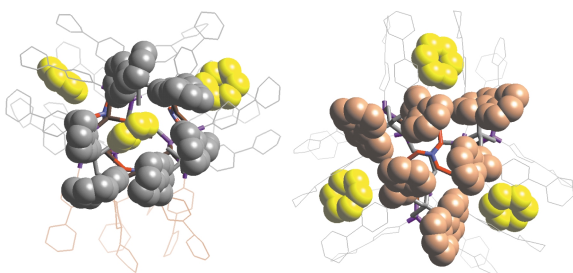


Fig. 2 Comparison of the conformations of filled (grey, left) and unfilled (light brown, right) channels in **1a**·(C₆H₆)₃. Hydrogen atoms are omitted for clarity.

electron deficient aromatic,⁴ crystals of another trisolvate were obtained, but single crystal X-ray diffraction† revealed that pentafluorobenzene had not in fact been incorporated. The disordered guests could only be modelled as a mixture of chloroform and water. This surprising result may have been due to the slightly greater size of pentafluorobenzene, or unavoidable edge-to-face interactions with the biphenyls, which could be unfavourable.⁵ It suggests, interestingly, that **1a** can discriminate between differently substituted aromatics, similarly to *p*-tert-butylcalix[4]arenes.⁶

Several receptors connected together, as in **1a–c**, can potentially exhibit cooperative or anticooperative guest inclusion. In **1a–c**, the receptors are mechanically coupled to each other *via* the cage core, since the biphenyls of a given channel are connected to those in adjacent channels *via* shared P atoms. It is therefore possible that the closing up of the fourth channel is caused by guest inclusion in the other three. Alternatively, it may be that the isolation of trisolates is simply due to their favourable crystal packing. It would be necessary to measure stepwise association constants in the solution state to determine which is the case. However, for aromatic guests such as benzene, toluene and phenol we have not observed significant changes in ¹H NMR chemical shifts on titration with **1a**, possibly due to competition with the organic solvents necessary to dissolve the cage. Use of water as a solvent, with a water-soluble version of the cage, might give measurable solution state association, as found for water-soluble calixarenes.⁷

In summary, a unique arrangement of four connected receptors has been assembled on the exterior of a coordination cage by rational ligand design. Future work will concentrate on detailed studies of guest binding and the connecting together of cages with bridging guests such as oligoaromatics, toward higher-level assemblies.

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Notes and references

† Characterising data for 1,1,1-tris[bis(4-biphenyl)phosphinomethyl]ethane **L**: ¹H NMR (300 MHz, CDCl₃): δ 7.25–7.46 (m, 54 H_{aromatic}), 2.47 (s, 6 H, CH₂), 1.11 (s, 3 H, CH₃); ³¹P{¹H} NMR (121 MHz, CDCl₃): δ –27.12 (s); FAB MS: *m/z* (%): 1081 (12) [M⁺], 307 (100); microanalysis: calc. C 85.53, H 5.87; found C 84.25, H 5.60%.

Synthesis of cage complexes **1a–c**: typically, a solution of **L** (100 mg, 0.092 mmol) in CDCl₃ or CHCl₃ (4 ml) was added to a solution of the appropriate silver salt (0.138 mmol) in CH₃CN (1 ml) and ³¹P NMR spectra were obtained. For **1a**, the solution was layered with either benzene or pentafluorobenzene to obtain **1a**·(C₆H₆)₃ or **1a**·(CHCl₃)₂(H₂O), respectively.

Crystal structure determinations: data for both structures were collected on a Bruker SMART diffractometer using the SAINT-NT⁸ software with graphite monochromated Mo-Kα radiation using phi/omega scans. A crystal was mounted on to the diffractometer at low temperature under nitrogen at *ca.* 120 K. Crystal stabilities were monitored and there were no significant variations (< ±2%). Lorentz and polarisation corrections were applied.

The structures were solved using direct methods and refined with the SHELXTL program package.⁹ The absolute configurations of **1a**·(C₆H₆)₃ and **1a**·(CHCl₃)₂(H₂O) were assigned using the Flack parameter¹⁰ (0.03(11) and 0.05(10) for **1a**·(C₆H₆)₃ and **1a**·(CHCl₃)₂(H₂O) respectively). The complexes exhibit higher than expected atomic displacement parameters this is indicative of disorder which we were unable to model because the crystals exhibited weak diffraction. However we were able to establish the atomic connectivity and the presence of solvent within the ‘channels’. The function minimised was Σ[w(|F_o|² – |F_c|²)] with reflection weights $w^{-1} = [\sigma^2|F_o|^2 + (g_1P)^2 + (g_2P)]$ where $P = [\max(|F_o|^2 + 2|F_c|^2)/3]$.

Crystal data for C₃₀₈H₂₅₂O₁₈N₆P₁₂Ag₆·3(C₆H₆) (**1a**·(C₆H₆)₃): *M* = 5578.34, cubic, space group P2₁3, *a* = 30.564(5) Å, *U* = 28553(8) Å³, *Z* = 4, μ = 0.534 mm^{–1}. A total of 42984 reflections were measured for the angle range 4 < 2θ < 40 and 8890 independent reflections were used in the refinement. The final parameters were *w*R² = 0.3419 and *R*1 = 0.1159 [*I* > 2σ(*I*)]. CCDC 178938.

Crystal data for C₃₀₈H₂₅₂O₁₈N₆P₁₂Ag₆·3{2/3(H₂O) + 1/3(CHCl₃)} (**1a**·(CHCl₃)₂(H₂O)): *M* = 5607.51, cubic, space group P2₁3, *a* = 30.7586(10) Å, *U* = 29100.4(16) Å³, *Z* = 4, μ = 0.553 mm^{–1}. A total of 74941 reflections were measured for the angle range 4 < 2θ < 40 and 9086 independent reflections were used in the refinement. The final parameters were *w*R² = 0.3296 and *R*1 = 0.1141 [*I* > 2σ(*I*)]. CCDC 178939. See <http://www.rsc.org/suppdata/cc/b2/b204260f/> for crystallographic files in .cif or other electronic format. For both structures, the silver and phosphorus atoms have been refined anisotropically, all other non-hydrogen atoms were refined isotropically. The biphenyl substituents were restrained to have a chemically feasible geometry and the thermal parameters have been modelled using SIMU constraints.

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