COMMUNICATION

ChemComm
www.rsc.org/chemcomm

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

Philip W. Miller, Mark Nieuwenhuyzen, Xingling Xu and Stuart L. James*
School of Chemistry, The Queen's University of Belfast, David Keir Building, Stranmillis Road, Belfast, Northern Ireland, UK BT9 5AG. E-mail: s.james@qub.ac.uk

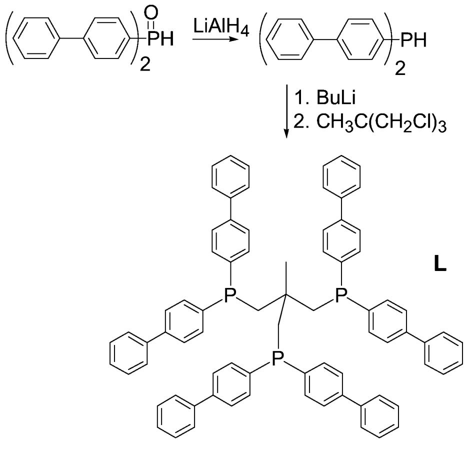
Received (in Cambridge, UK) 7th May 2002, Accepted 24th July 2002
First published as an Advance Article on the web 8th August 2002

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 metallocages,[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 $[Ag_6(triphos)_4(OTf)_4]^{2+}$ (triphos = $CH_3C(CH_2PPh_2)_3$, OTf = triflate, $CF_3SO_3^-$),[3a] an interesting feature of which is its arrangement of twenty-four phenyl groups in four short (*ca*. 5 Å) C_3-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 $[Ag_6\mathbf{L}_4X_4]^{2+}$ (X = NO_3, **1a**; CF_3SO_3 **1b**; or 4-$CH_3C_6H_4SO_3$ **1c**) instantly and quantitatively. ^{31}P NMR data (δ/ppm and $^1J_{^{31}P\_^{109}Ag}$/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 $CHCl_3$–CH_3CN 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 $[Ag_6(triphos)_4(triflate)_4]^{2+}$,[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**.



Scheme 1

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 C_3 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 C_3 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

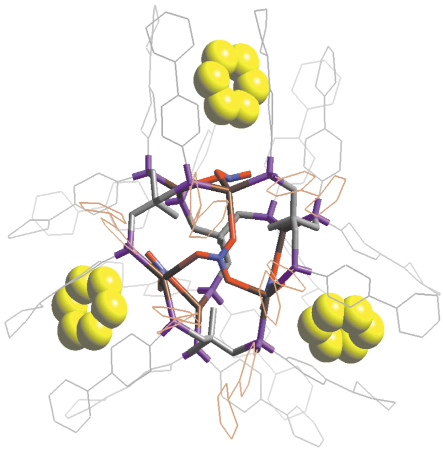


Fig. 1 Crystal structure of **1a**·$(C_6H_6)_3$: benzene-filled channels are in grey, unfilled channel in light brown. P = purple, O = red, N = blue, Ag = brown. Hydrogen atoms omitted for clarity, space-filling spheres set at 0.70 van der Waals radius. The biphenyl groups show evidence of disorder and have not all been constrained to planarity.

DOI: 10.1039/b204260f

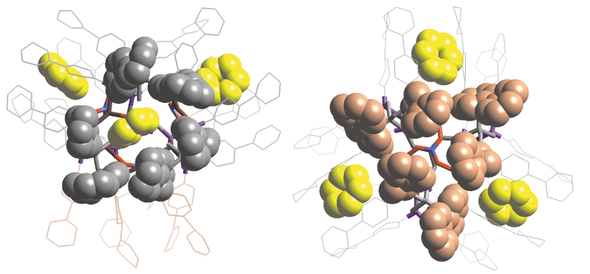


Fig. 2 Comparison of the conformations of filled (grey, left) and unfilled (light brown, right) channels in **1a**·(C_6H_6)$_3$. Hydrogen atoms are omitted for clarity.

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 trisolvates 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 ^{1}H 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.

We are grateful to EPSRC, the McClay Trust and the Northern Ireland Department of Education and Learning for funding, and to the referees for valuable comments.

Notes and references

† *Characterising data* for 1,1,1-tris{bis(4-biphenyl)phosphinomethyl}ethane **L**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.25–7.46 (m, 54 $H_{aromatic}$), 2.47 (s, 6 H, CH_2), 1.11 (s, 3 H, CH_3): $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): 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 $CDCl_3$ or $CHCl_3$ (4 ml) was added to a solution of the appropriate silver salt (0.138 mmol) in CH_3CN (1 ml) and ^{31}P NMR spectra were obtained. For **1a**, the solution was layered with either benzene or pentafluorobenzene to obtain **1a**·(C_6H_6)$_3$ or **1a**·($CHCl_3$)$_2$(H_2O), respectively.

Crystal structure determinations: data for both structures were collected on a Bruker SMART diffractometer using the SAINT-NT[8] 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 ($< \pm 2\%$). 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**·(C_6H_6)$_3$ and **1a**·($CHCl_3$)(H_2O) were assigned using the Flack parameter[10] (0.03(11) and 0.05(10) for **1a**·(C_6H_6)$_3$ and **1a**·($CHCl_3$)$_2$(H_2O) 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 $\Sigma[w(|F_o|^2 - |F_c|^2)]$ 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 $C_{308}H_{252}O_{18}N_6P_{12}Ag_6{\cdot}3(C_6H_6)$ (**1a**·(C_6H_6)$_3$): $M = 5578.34$, cubic, space group $P2_13$, $a = 30.564(5)$ Å, $U = 28553(8)$ Å^3, $Z = 4$, $\mu = 0.534$ mm^{-1}. A total of 42984 reflections were measured for the angle range $4 < 2\theta < 40$ and 8890 independent reflections were used in the refinement. The final parameters were $wR2 = 0.3419$ and $R1 = 0.1159$ [$I > 2\sigma I$]. CCDC 178938.

Crystal data for $C_{308}H_{252}O_{18}N_6P_{12}Ag_6{\cdot}3\{2/3(H_2O) + 1/3(CHCl_3)\}$ (**1a**·($CHCl_3$)(H_2O)): $M = 5607.51$, cubic, space group $P2_13$, $a = 30.7586(10)$ Å, $U = 29100.4(16)$ Å^3, $Z = 4$, $\mu = 0.553$ mm^{-1}. A total of 74941 reflections were measured for the angle range $4 < 2\theta < 40$ and 9086 independent reflections were used in the refinement. The final parameters were $wR2 = 0.3296$ and $R1 = 0.1141$ [$I > 2\sigma I$]. 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.

1 D. L. Caulder and K. N. Raymond, *Acc. Chem. Res.*, 1999, **32**, 975–982; P. J. Stang, *Chem.–Eur. J.*, 1998, **4**, 19–27; M. Fujita, *Chem. Soc. Rev.*, 1998, **27**, 417–425; C. J. Jones, *Chem. Soc. Rev.*, 1998, **27**, 289–299; Transition Metals in Supramolecular Chemistry R. W. Saalfrank and B. Demleitner, in *Perspectives in Supramolecular Chemistry*, ed. J. P. Sauvage, Wiley-VCH, Weinheim, 1999, vol. 5, pp. 1–51; S. Leininger, B. Olenyuk and P. J. Stang, *Chem. Rev.*, 2000, **100**, 853–908.

2 Y. L. Cho, H. Uh, S.-Y. Chang, H.-Y. Chang, M.-G. Choi, I. Shin and K.-S. Jeong, *J. Am. Chem. Soc.*, 2001, **123**, 1258–1259; H. Abourahma, A. W. Coleman, B. Moulton, B. Rather, P. Shahgaldian and M. J. Zaworotko, *Chem. Commun.*, 2001, 2380.

3 (*a*) S. L. James, D. M. P. Mingos, A. J. P. White and D. J. Williams, *Chem. Commun.*, 1998, 2323; (*b*) X. Xu, E. J. MacLean, S. J. Teat, M. Nieuwenhuyzen, M. Chambers and S. L. James, *Chem. Commun.*, 2002, 78; (*c*) E. Lozano, M. Niewenhuyzen and S. L. James, *Chem.–Eur. J.*, 2001, **12**, 1644; (*d*) X. Xu, M. Niewenhuyzen and S. L. James, *Angew. Chem., Int. Ed.*, 2002, **41**, 764.

4 C. R. Patrick and G. S. Prosser, *Nature*, 1960, **187**, 1021; T. Dahl, *Acta Chem. Scand., Ser. A*, 1988, **42**, 1–7; C. A. Hunter, X.-J. Lu, G. M. Kapteijn and G. van Koten, *J. Chem. Soc., Faraday Trans.*, 1995, **91**, 2009–2015.

5 N. Hayashi, T. Mori and K. Matsumoto, *Chem. Commun*, 1998, 1905; I. S. Neretin, K. A. Lyssenko, M. Y. Antipin, Y. L. Slovokhotov, O. V. Boltalina, P. A. Troshin, A. Y. Lukonin, L. N. Sidorov and R. Taylor, *Angew. Chem., Int. Ed.*, 2000, **39**, 3273; attraction between C_6F_6 and electron *donors*: I. Alkorta, I. Rozas and J. Elguero, *J. Org. Chem.*, 1997, **62**, 1997.

6 A. Pochini and R. Ungaro, in *Comprehensive Supramolecular Chemistry*, ed. F. Vögtle, Pergamon Press, Oxford, 1996, vol. 2, p. 103.

7 S. Shinkai, *Tetrahedron*, 1993, **49**, 8933 and references therein.

8 SAINT-NT, program for data collection and data reduction, Bruker-AXS, Madison, WI, 1998.

9 G. M. Sheldrick, SHELXTL Version 5.0, A System for Structure Solution and Refinement, Bruker-AXS, Madison WI, 1998.

10 H. D. Flack, *Acta Crystallogr., Sect. A*, 1983, **39**, 876.