Synthesis and structure of the calixarene-like phosph(III)azane macrocycle $[\{P(\mu\text{-}N^tBu)\}_2\{1,5\text{-}(NH)_2C_{10}H_6\}]_3$

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The reaction of $[ClP(\mu\text{-}N^tBu)]_2$ with 1,5-diamino-naphthalene $[1,5\text{-}(NH_2)_2C_{10}H_6]$ in Et_3N–thf gives the trimeric macrocycle $[\{P(\mu\text{-}N^tBu)\}_2\{1,5\text{-}(NH)_2C_{10}H_6\}]_3$ (1); the X-ray structure of the toluene solvate 1·3toluene reveals a cone-shaped (calixarene-like) arrangement in which toluene guest molecules are trapped within the cavity.

The coordination chemistry of calixarenes is an extensive and ongoing area of research (Fig. 1).[1,2] Such ligands are capable of coordinating both cations and neutral molecules, using π-arene interactions with the aromatic units as well as by bonding to Lewis base donor substituents on the aromatic rings. In addition, the cone-shaped conformations of these ligands can provide specific coordination environments for the accommodation of hosts. For example, a recent development in this area has been the selective coordination and separation of fullerenes (such as C_{60} and C_{70}) *via* the formation of π-arene bonded, host–guest complexes with calixarenes.[2] Much current interest is focused on the synthesis of a range of inorganic macrocycles based on phosphorus–nitrogen frameworks that have coordination and spatial characteristics related to well known organic counterparts.[3–7] Recent studies have shown that macrocyclic phosphorus–nitrogen ligands of this type can be prepared far more readily than many of those based on carbon. The reactions of the phosphazane dimers $[ClP(\mu\text{-}NR)]_2$ with bifunctional organic acids (LL) potentially provide general access to a broad range of highly versatile macrocycles of the type $[\{P(\mu\text{-}NR)\}_2\{LL\}]_n$ (Scheme 1). However, until recently only simple monomers (n = 1) of this type had been reported with a broad range of bifunctional spacers.[5] The realisation that dimers (n = 2) can be readily prepared (depending on the reaction conditions and spacer employed)[6] has lead us to explore the possibility of obtaining larger macrocycles, possessing viable cavities for the potential coordination of hosts. We report here the synthesis of trimeric $[\{P(\mu\text{-}N^tBu)\}_2\{1,5\text{-}(NH)_2C_{10}H_6\}]_3$ (**1**), the first macrocycle of this type larger than a dimer. The cone-shaped conformation of the trimer and the structure of the toluene solvate **1**·3toluene illustrate a close relation with the characteristics of calixarenes.

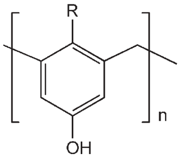
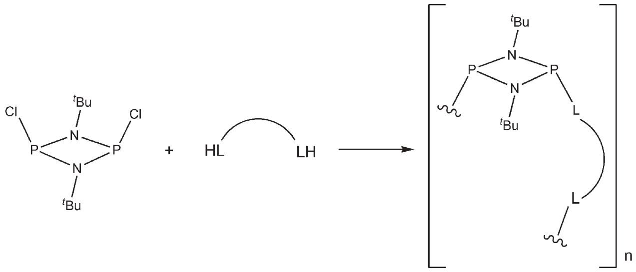
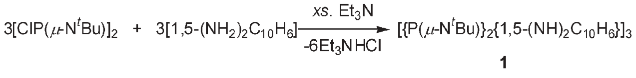


Fig. 1 General formula of calixarenes.



Scheme 1

Dropwise addition of a dilute solution of the dimer $[ClP(\mu\text{-}N^tBu)]_2$ in thf to a dilute solution of the 1,5-diamino-naphthalene $[1,5\text{-}(NH_2)_2C_{10}H_6]$ in Et_3N–thf gives **1** in 46% yield after workup (Scheme 2).† *In situ* $^{31}P\{^1H\}$ studies of the reaction mixture (using d_6-acetone capillary to obtain a lock) reveal that *no* other macrocyclic homologues of **1** (*e.g.*, monomers or dimers) are formed and that **1** is the only soluble P-containing product of this reaction. Key NMR spectroscopic features of **1** are summarised in Fig. 2. The presence of two 1 : 1 singlets in the room temperature $^{31}P\{^1H\}$ NMR spectrum of **1** (δ 100.2 and 98.7) provided an initial indication of the rigidity of its structure in solution. The inequivalence of the two P centres within each of the P_2N_2 ring units of **1** is the result of their bonding to *exo*- and *endo*-NH groups in the macrocyclic arrangement. The large difference in the environments of these N–H protons is seen in the ^{31}P, ^1H-coupled NMR spectrum in which only the resonance at δ 98.7 splits into a 1 : 1 doublet ($^2J_{PH}$ = 38.3 Hz), while the coupling constant for the other is too small to be observed owing to the line width of the resonance. The rigidity of the structure of **1** is also apparent in the observation of two distinct N–H resonance [δ 6.01 (d., $^2J_{P–H}$ = 4.6 Hz) and 5.55 (d., $^2J_{P–H}$ = 38.3 Hz)] in the ^1H NMR spectrum.[8] Similar spectroscopic features were found previously for the dimer



$$3[ClP(\mu\text{-}N^tBu)]_2 + 3[1,5\text{-}(NH_2)_2C_{10}H_6] \xrightarrow[-6Et_3NHCl]{xs.\ Et_3N} \underset{\mathbf{1}}{[\{P(\mu\text{-}N^tBu)\}_2\{1,5\text{-}(NH)_2C_{10}H_6\}]_3}$$

Scheme 2

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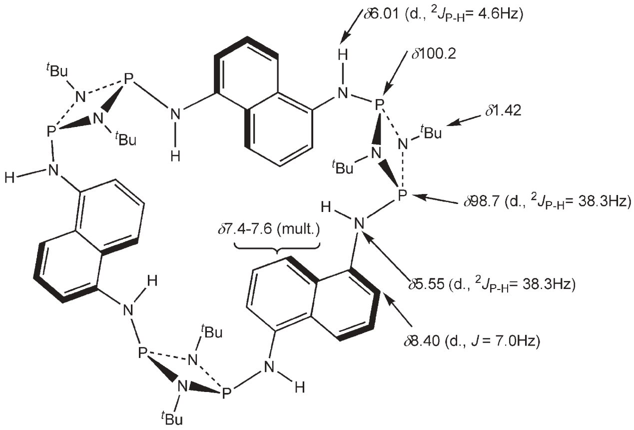
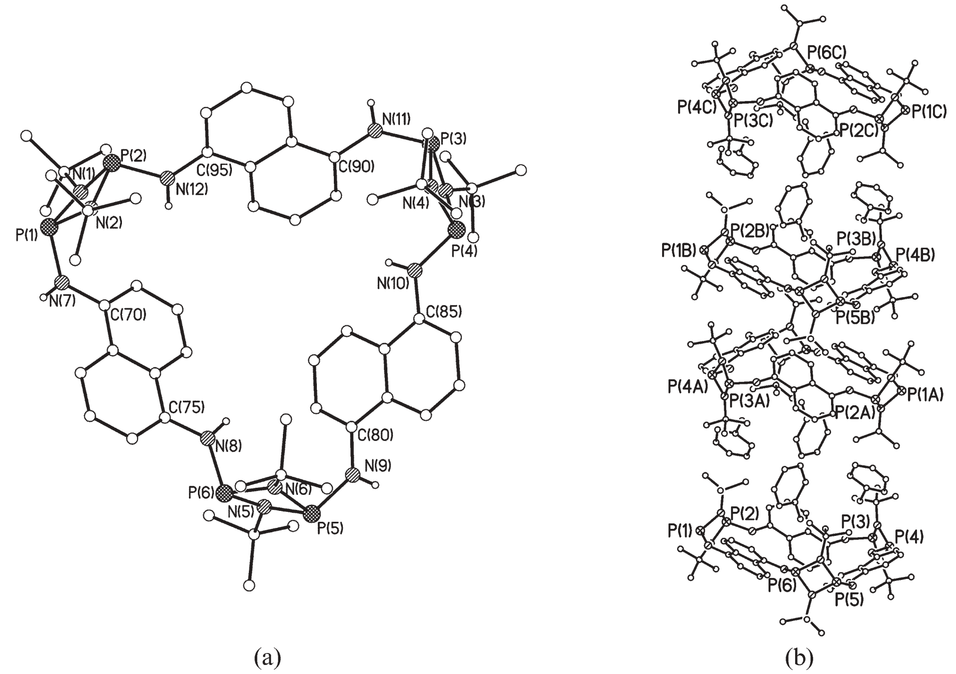


Fig. 2 ^{1}H and ^{31}P NMR spectroscopic assignments for **1**.

$[\{P(\mu\text{-}N^tBu)\}_2\{2,6\text{-}(NH)_2C_5H_3N\}]_2$,[6b] also containing *exo*- and *endo*-N–H groups.

Crystals of the toluene solvate **1**·3toluene were grown from a saturated solution of **1** in toluene at −5 °C. The low-temperature X-ray structure‡ is consistent with the initial spectroscopic analysis of the compound. Trimeric macrocycles of **1** are constructed from bridging of the 1,5-diamido-naphthalene groups between the P_2N_2 ring units (Fig. 3a). The cavity radius of **1**, which measures *ca.* 4.4 Å, is defined by the mean distance from the three *endo*-N centres [N(8), N(10) and N(12)] to their centroid; all six of the *exo*- and *endo*-N atoms are co-planar to within *ca.* 0.26 Å. The planes of the naphthyl groups are inclined by a mean dihedral angle of *ca.* 35.5° with respect to the N mean plane of **1**, resulting in a cone-shaped cavity that is reminiscent of coordinated and uncoordinated calixarenes.[1,2] A further similarity with the behaviour of calixarenes is seen in the manner of toluene inclusion in the crystal lattice. Molecules of **1** are associated into pairs in the crystal lattice *via* the interpenetration of their ^{t}Bu and naphthyl groups in the manner shown in Fig. 3b (molecules A and B). This association is related conceptually to the sextuple embrace found in phosphonium compounds,[9] and involves relatively short C···C contacts between carbon atoms within the arene rings and those of the ^{t}Bu groups (range 3.50–3.74 Å). The aggregation of these supramolecular dimers into infinite columns parallel to the *c*-axis creates ellipsoidal voids (*ca.* 11.1 Å long[10]) in the crystal lattice, which are bound on either side by the open faces of two molecules (**1**, **1A** and **1B**, **1C**, Fig. 3b). Interestingly, two toluene molecules are located within the cavities of each molecule of **1**, so that each void has two pairs of symmetry-related guests. The Me group of one of these molecules is orientated towards the centroids of each of the macrocycles, forming long-range C–H···arene contacts with the naphthylene rings (*ca.* 3.20–3.39 Å). This inclusion is similar to that found previously in the structures of toluene clathrates of calix[4]arenes, *e.g.*, in the [*p*-^{t}Bu-MeO-calix[4]arene·Na·toluene]$^+$ cation[11] and in [*p*-^{t}Bu-OH-calix[4]arene·toluene].[12]

In summary, the study presented here reports the synthesis of the largest macrocycle of the type $[\{P(\mu\text{-}NR)\}_2\{LL\}]_n$ so far



(a) (b)

Fig. 3 (a) Structure of trimeric macrocycles of **1**. H-atoms (except those attached to N) and lattice-bound toluene molecules have been omitted for clarity. Selected bond lengths (Å) and angles (°); P(1)–N(1) 1.719(6), P(1)–N(2) 1.716(6), P(1)–N(7) 1.694(7), N(7)–C(70) 1.416(9), P(2)–N(1) 1.729(6), P(2)–N(2) 1.721(6), P(2)–N(12) 1.691(7), C(95)–N(12) 1.405(9), P(3)–N(4) 1.712(6), P(3)–N(3) 1.719(6), P(3)–N(11) 1.697(6), N(11)–C(90) 1.420(8), P(4)–N(3) 1.732(6), P(4)–N(4) 1.713(6), P(4)–N(10) 1.692(6), C(85)–N(10) 1.407(9), P(5)–N(6) 1.707(6), P(5)–N(5) 1.727(6), P(5)–N(9) 1.696(6), N(9)–C(80) 1.405(9), P(6)–N(5) 1.728(6), P(6)–N(6) 1.712(6), P(6)–N(8) 1.696(7), C(75)–N(8) 1.398(10), N(^{t}Bu)–P–N(^{t}Bu) mean 80.5, P–N(^{t}Bu)–P mean 98.0, *endo*-P–N(8,10,12)–C mean 133.0 (range [131.9(5)–134.4(5)], *exo*-P–N(7,9,11)–C mean 127.7 [range 127.4(5)–128.1(6)], fold of P_2N_2 rings av. 17.6° about the P···P vector; (b) 'back-to-back' interpenetration of molecules (**1A** and **1B**) and the ellipsoidal voids (**1**, **1A** and **1B**, **1C**) formed by chains running parallel to the *c*-axis showing the calixarene-like inclusion of toluene molecules into the cavities of the molecules of **1**. Symmetry relating the molecules A: $1 - x, 2 - y, -z$; B: $x, y, 1 + z$; C $1 - x, 2 - y, 1 - z$.

reported. The cone-like spatial arrangement of **1** and the presence of a hydrophobic interior makes **1** similar to a calixarene. This similarity is stressed by the inclusion behaviour of **1** with toluene, which is closely related to previously reported calixarene clathrates. In view of the large size of the cavity of **1** and its potential multifunctional ligand characteristics (*i.e.*, hydrophobic character and presence of N–H functional groups), further studies on the coordination behaviour of this type of macrocycle with various cationic and neutral hosts as well as metal bases should be of future interest.

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Notes and references

† *Synthesis of* **1**: To a solution of 1,5-diamino-naphthalene (0.237 g, 1.5 mmol) (freshly sublimed; 24 h, 10^{-1} atm, 120 °C) in Et_3N (6.0 ml, large excess) and thf (70 ml) at −78 °C (under argon in a 100 ml round bottomedflask fitted with a water condenser) was added dropwise (*via* a pressure-equalised dropping funnel) to a mixture of $[ClP(\mu\text{-}N^tBu)]_2$ (0.413 g, 1.5 mmol) in thf (70 ml) (over the course of *ca.* 1 h). The reaction mixture was allowed to warm to room temperature and then brought to reflux (16 h). The reaction mixture was cooled and filtered through Celite. An *in situ* ^{31}P NMR spectrum of the filtrate at this stage (d_6-acetone capillary) showed that **1** is the only P-containing product (commonly with minor hydrolysis products being found at *ca.* δ 0– −10 ppm). The solvent was removed under vacuum. The residue was extracted with toluene (60 ml) and filtered through Celite. The solvent was removed from the filtrate under vacuum and the residue washed with *n*-pentane (50 ml) to remove any hydrolysis products. A fine white powder of **1** was produced. This powder does not contain any toluene solvation. Yield 0.25 g (46%). ^1H NMR (500.2 MHz, +25 °C, d_8-toluene), δ = 8.40 [d., 1H, J_{HH} = 7.0 Hz, C(2)–H], 7.4–7.6 [mult., 5H, C(3,4,6,7,8)–H], 5.55 [d., 1H, $^2J_{PH}$ = 38.3 Hz, *endo*-N–H], 6.01 [d., $^2J_{PH}$ = 4.6 Hz, *exo*-N–H], 1.42 [s., 18H, ^{t}Bu]. ^{31}P NMR (202.5 MHz, +25 °C, d_8-toluene), δ = 100.2 (s., P next to *exo*-N–H), 98.7 (s., P next to *endo*-N–H) (no interconversion between *exo* and *endo* P environments was observed in toluene up to 60 °C). Elemental analysis: despite repeated attempts, satisfactory C analysis could not be obtained (possibly suggesting the formation of carbides during combustion); found (typical) C 55.3, H 7.4, N 14.5, P 15.9, calcd. for **1**, C 60.0, H 7.3, N 15.6, P 17.2 (the absence of toluene in samples after isolation under vacuum was confirmed by ^1H NMR spectroscopy). Crystals of **1**·3toluene were grown from a saturated toluene solution at −5 °C. Drying the toluene solvate under vacuum (10^{-1} atm) results in complete loss of the toluene solvent (as shown by ^1H NMR spectroscopy).

‡ *Crystal data for* **1**·3toluene: $C_{75}H_{102}N_{12}P_6$, M = 1357.51, triclinic, space group $P\bar{1}$, $Z = 2$, a = 16.803(3), b = 16.913(3), c = 17.229(3) Å, α = 61.92(3), β = 77.82(3), γ = 64.56(3)°, V = 3900.9(14) Å^3, μ(Mo-Kα) = 0.186 mm^{-1}, ρ_{calc} = 1.156 Mg m^{-3}, T = 180(2) K. Data were collected on a Nonius KappaCCD diffractometer. Of a total of 27209 reflections collected, 10417 were unique (R_{int} = 0.0614). The structure was solved by direct methods and refined by full-matrix least squares on F^2 (G. M. Sheldrick, *SHELX-97*, Göttingen, Germany, 1997). Final $R1$ = 0.068 [$I > 2\sigma(I)$] and w$R2$ = 0.187 (all data). Relatively high atomic displacement parameters indicated some rotational disorder of the ^{t}Bu ligands in **1**. This was resolved for two of the Me groups bonded to C(6) and all three Me groups bonded to C(4). There was evidence of disorder for all of the toluene molecules in the lattice. The disorder in two of these molecules was resolved, each into two components related by a small displacement. In all cases of disorder isotropic atomic parameters were constrained to be of 50 : 50 occupancy. CCDC 268852. See http://dx.doi.org/10.1039/b504686f for crystallographic data in CIF or other electronic format.

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