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The tetrameric macrocycle $[\{P(\mu\text{-}N^tBu)\}_2NH]_4$

Alan Bashall,[a] Emma L. Doyle,[b] Catherine Tubb,[b] Sara J. Kidd,[b] Mary McPartlin,[a] Anthony D. Woods[b] and Dominic S. Wright*[b]

[a] *School of Chemistry, University of North London, London, UK N7 8DB*
[b] *Chemistry Department, University of Cambridge, Lensfield Road, Cambridge, UK CB2 1EW. E-mail: dsw1000@cus.cam.ac.uk.*

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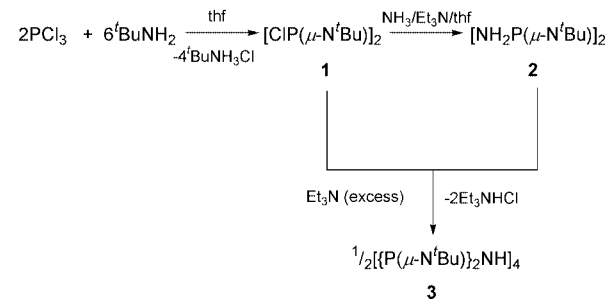
The 1:1 reaction of the symmetrical dimers $[ClP(\mu\text{-}N^tBu)]_2$ 1 and $[H_2NP(\mu\text{-}N^tBu)]_2$ 2 in thf–Et_3N gives the tetrameric macrocycle $[\{P(\mu\text{-}N^tBu)\}_2NH]_4$ 3 (67%); consisting of four $P_2(\mu\text{-}N^tBu)_2$ rings linked by *endo* N–H groups.

Although the study of macrocyclic organic ligands, such as crown ethers, calixarenes and cyclophanes,[1] is an ever-growing field of research, in comparison there are very few counterparts based on frameworks other than those of carbon. A major problem in such inorganic systems is establishing general and selective synthetic strategies to cyclic inorganic frameworks that avoid polymerisation or other undesired modes of aggregation. Mercuracarborands[2] and cyclic s-block amides[3] are two recently explored classes of inorganic ligands that behave as Lewis acids in their coordination of various anions. Particularly rare, however, are inorganic macrocycles which have the ability to act as Lewis bases; for example certain cyclophospha(v)zenes, such as $[P(NMe_2)_2N]_6$,[4] and Si/N macrocyles of the type $[(R_2Si)NH]_4$.[5] In earlier work we characterised the neutral Group 15 macrocycle $[\{Sb(\mu\text{-}NR)\}_2(\mu\text{-}NR)]_6$ (R = 2-$MeOC_6H_4$), composed of six $[Sb(\mu\text{-}NR)]_2$ rings linked into a cyclic structure by μ-NR groups.[6] Owing to the more robust nature of P–N bonds compared to other Group 15 element–nitrogen bonds, we have more recently begun to extend studies in this area to related cyclophospha(III)zanes,[7,8] with the aim of producing more generally useful and (possibly) air-stable ligand arrangements. We report here the selective, high yielding synthesis of a neutral cyclophospha(III)zane macrocycle $[\{P(\mu\text{-}N^tBu)\}_2NH]_4$ **3**, *via* the reaction of $[ClP(\mu\text{-}N^tBu)]_2$ **1** with $[NH_2P(\mu\text{-}N^tBu)]_2$ **2** (Scheme 1).

The dimer $[ClP(\mu\text{-}N^tBu)]_2$ **1** is readily prepared by the 1:3 stoichiometric reaction of PCl_3 with $^tBuNH_2$ in thf (67%).† This method is different from that reported in the literature, involving the reaction of $^tBuNH_2$, PCl_3 and Et_3N (3:2:3 equivalents, respectively).[8] However, very little of the monochloride $[^tBuNHP(\mu\text{-}N^tBu)PCl]$[7,8] is isolated after distillation of **1** from the reaction, despite the use of excess of $^tBuNH_2$. The slow addition of **1** to a saturated solution of NH_3 in thf–Et_3N at −78 °C produces $[NH_2P(\mu\text{-}N^tBu)]_2$ **2**.† Very few impurities are present in the ^1H and ^{31}P NMR spectra of the crude product (obtained in 48% yield), which can be used without further purification. The 1:1 stoichiometric reaction of **1** with **2** in thf–Et_3N was followed by variable-temperature ^1H and ^{31}P NMR spectroscopy. This study showed that the conversion to the macrocyle $[\{P(\mu\text{-}N^tBu)\}_2NH]_4$ **3** is *ca.* 100% efficient (with only minor traces of other products being generated). The selectivity of this reaction and the almost quantitative formation of **3** can be attributed to the known preference for the phosphazane dimers $[XP(\mu\text{-}NR)]_2$ to adopt the *cis* isomer in solution and in the solid state,[8,9] *i.e.* pre-organisation of the precursors. Indeed, the *cis* isomer of **1** has previously been shown to be preferred[10] and, although the structure of **2** is not known at this stage, the relatively low ^{31}P chemical shift observed (δ 100.2) is strongly indicative of a *cis* conformation (normally in the range δ 96–108; *cf.* δ 166–185 for *trans* isomers).[11] Subsequent scaling up of the reaction allows **3** to be obtained in 67% (crude) yield (the overall conversion of PCl_3 and $^tBuNH_2$ to **3** being *ca.* 30%).† Again, ^1H and ^{31}P NMR studies reveal that the crude product is extremely pure (estimated 95–100%, over several reactions). The ^{31}P NMR spectrum of **3** shows that a single species exists in solution, with a singlet resonance being observed at δ 129.5 over a wide temperature range. This chemical shift compares to δ 117.2 for the related dimer $[\{P(\mu\text{-}N^tBu)\}_2N^tBu]_2$.[12] Compound **3** is relatively air-stable, air-exposure for greater than *ca.* 6 h leading only to slight decomposition, with the appearance of minor new resonances in both the ^{31}P and ^1H NMR spectra.



Scheme 1

The low-temperature X-ray structure of **3** shows that its macrocyclic backbone arises from cyclic tetramerisation of four $[\{P(\mu\text{-}N^tBu)\}_2NH]$ units [Fig. 1(a)].‡ Although these units are crystallographically independent, the pattern of bond lengths and angles in **3** is very regular. As a result, the twelve atoms of the $(P\cdots P\text{–}N)_4$ fragment defining the macrocycle deviate by only *ca.* 0.07 Å from their mean plane, and the transannular N···N separation between opposite pairs of N centres differ by only *ca.* 0.067 Å (mean 5.221 Å). The planes of the four $[P(\mu\text{-}N^tBu)]_2$ rings are aligned almost exactly perpendicular to the macrocyclic plane (the associated dihedral angles with respect to the macrocyclic plane being in the range 87.0–93.2°), giving the ligand periphery of **3** an overall torus-shape. The only noticeable distortion in the structure of **3** arises from the steric crowding of the ^{t}Bu groups above and below the macrocycle. As a consequence, two of the four ^{t}Bu groups on either side [attached to N(1) and N(5), and N(4) and N(8)] are forced out of the planes of their P_2N_2 rings. However, this distortion has only a marginal effect on the P–N bonding within the P_2N_2 ring units; resulting in small variations in the associated P–(μ-N) bond lengths (by *ca.* 0.03 Å) and P–N–P angles (by *ca.* 2°).

The closest relatives to **3** are cyclophosphazanes of the type $[\{P(\mu\text{-}NR)\}_2NR]_2$, consisting of two $P_2(\mu\text{-}NR)_2$ rings linked into a cyclic arrangement by bridging NR groups.[12,13] The formation of a tetrameric macrocyle for **3** (as opposed to a cyclic dimer, $[\{P(\mu\text{-}N^tBu)\}_2NH]_2$) primarily results from the presence of sterically undemanding NH groups linking the $[P(\mu\text{-}N^tBu)]_2$ units; this allows the *cis* conformation of the constituent units to be retained in **3**, without producing steric congestion at the centre of the macrocylic cavity. It is interesting in this regard that the increased steric effects associated with the NR groups linking the $[Sb(\mu\text{-}NR)]_2$ units in $[\{Sb(\mu\text{-}NR)\}_2(\mu\text{-}NR)]_6$[6] (R = 2-$MeOC_6H_4$, Ph) results in the adoption of a *trans* conformation

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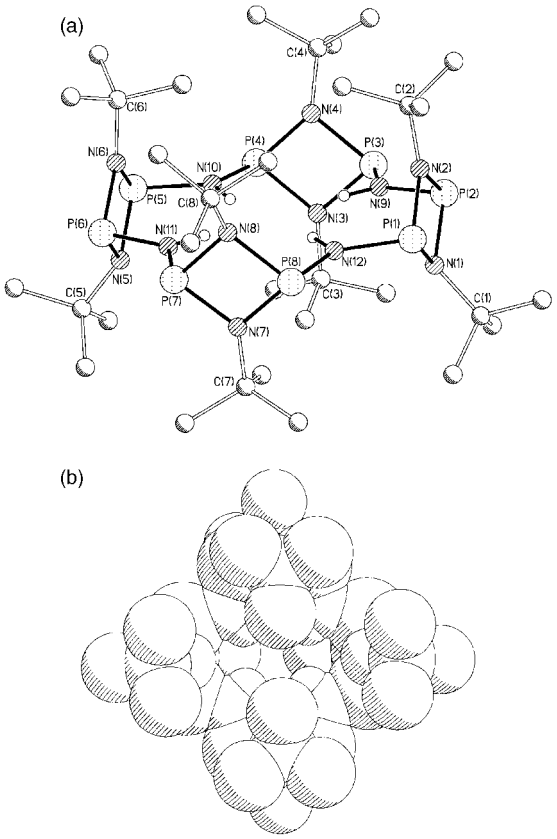

Fig. 1 (a) Structure of $[\{P(\mu\text{-}N^tBu)\}_2NH]_4$ **1** (side view). Key bond lengths (Å) and angles (°); P–N(9–12) mean 1.703 [range 1.697(2)–1.709(2)], ring P–N mean 1.725 [range 1.710(2)–1.740(2)], N(9)···N(11) 5.255(4), N(10)···N(12) 5.188(4), P–N(9,10,11,12)–P mean 127.8, endocyclic N–P(1–8)–N mean 81.4, exocyclic N–P(1–8)–N mean 103.5, P–{μ–N(1–8)}–P mean [range 97.6(1)–99.6(1)]; (b) Space-filling diagram (top view).

for these constituents. This *trans* conformation provides the most probable reason for the greater size of the macrocyles obtained in these cases, since the formation of a smaller ring composed of *trans* constituents would be more strained.

The presence of four N–H protons within the macrocyclic structure of **3** is reminiscent of a tetraazacyclotetradecane (*i.e.* based on $[CH_2CH_2NH]_4$),[14] while the molecules possess a ligand periphery that is analogous (spatially) to calixarenes.[1] Although the macrocyclic cavity of **3** is apparently sterically crowded [Fig. 1(b)], the rearrangement of the ligand framework to accommodate metal centres (upon deprotonation) may well be anticipated. This is suggested by the observed flexibility of the μ-N^{t}Bu groups within **3**. Studies of the coordination behaviour of **3** and of related P/N ligands are underway.

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Notes and references

† *Syntheses*: **1**: to a solution of freshly distilled PCl_3 (16.6 ml, 0.190 mol) in thf (300 ml) at −78 °C was added dropwise ^{t}BuNH$_2$ (60 ml, 0.571 mmol) (the addition taking *ca.* 1 h). The mixture was stirred for a further 4 h at this temperature, then allowed to stir at room temperature for 12 h. The solvent was removed under vacuum and the colourless, crystalline mass formed was carefully distilled through a 10 cm Vigreaux column under vacuum (since the product rapidly solidifies, the condenser should not be cooled). The major fraction (86 °C, 2.0 mmHg) was collected (the minor 96 °C fraction is $[^tBuNHP(\mu\text{-}N^tBu)]_2$). Yield 17.6 g (67%, based on P supplied). ^{1}H NMR (d_6-benzene, +25 °C, 400.16 MHz), δ 1.25 (s, ^{t}BuN). ^{31}P NMR (d_6-benzene, +25 °C, 161.98 MHz), δ 207.6 (s).

2: A concentrated solution of NH_3 in thf–Et_3N was produced by condensing NH_3 gas into a mixture of thf (450 ml) and Et_3N (40 ml) at 25 °C for *ca.* 40 min. To this solution (at −78 °C) was added a solution of **1** (10.0 g, 36.4 mmol) in thf (250 ml) at −78 °C. After stirring at this temperature (3 h), the mixture was allowed to warm to room temperature and stirring was continued (12 h). The solvent was removed under vacuum and to the dried solid was added *n*-pentane (400 ml). The insoluble ammonium salts were removed by filtration and the filtrate reduced under vacuum to *ca.* 120 ml, whereupon precipitation of **2** occurred. This first batch was filtered off and dried under vacuum. A second batch was obtained by further reduction of the solvent to *ca.* 50 ml. Total yield 4.15 g (48%). Mp 110–115 °C. IR (Nujol, NaCl), ν/cm^{-1} 3402 (doublet, m), 3291 (doublet, m) (N–H str.). ^{1}H NMR (d_6-benzene, +25 °C, 400.16 MHz), δ 2.41 (d, $^2J_{^{31}P-H}$ 7.9 Hz, 2H, NH_2), 1.46 (s, 9H, ^{t}BuN). ^{31}P NMR (d_6-benzene, +25 °C, 161.98 MHz), δ 100.2 (s). ^{13}C NMR (100.1 MHz, d_8-toluene, rel. 80% H_3PO_4–D_2O), δ 51.33 (t, $^1J_{C-^{31}P}$ 13.3 Hz, C_α of ^{t}Bu), 31.17 (t, $^2J_{C-^{31}P}$ 6.8 Hz, Me of ^{t}Bu). Found C 40.1, H 9.2, P 25.5, Cl 0.2; Calc. C 40.8, H 9.3, P 26.3, Cl 0.0% (satisfactory N analysis could not be obtained, despite repeated attempts). The crude reaction product is of high purity and can be used in further reactions without purification.

3: A solution of **1** (0.50 g, 2.12 mmol) in thf (20 ml) was added dropwise to a solution of **2** (0.58 g, 2.12 mmol) in thf (100 ml) and Et_3N (1 ml) at −78 °C. The mixture was stirred for 3 h at this temperature and allowed to warm to room temperature before being stirred further (12 h). The solvent was removed under vacuum and the solid extracted with *n*-pentane (100 ml) and filtered. The filtrate was reduced to dryness under vacuum to give **3** as a white powder (0.62 g, 67%). Crystals of **3** were obtained from *n*-pentane–thf at 25 °C. The following data refer to the crude material. Partial melting *ca.* 130 °C, decomp. *ca.* 170 °C. IR (Nujol, NaCl), ν/cm^{-1} 3582 (sharp, w) (N–H str.). ^{1}H NMR (d_6-benzene, +25 °C, 400.16 MHz), δ 4.86 (s, 1H, N–H), 1.54 (s, 18H, ^{t}BuN). ^{31}P NMR (d_6-benzene, +25 °C, 161.98 MHz), δ 129.5 (s) (minor impurities may be seen at *ca.* δ 120, 75 and 0). Electrospray MS (+ve ion), *m/z* = 877.4 (tetramerH$^+$) (dominant), 658.4 (trimerH$^+$) (minor) (no dimerH$^+$). Satisfactory C, H and P analysis were obtained. ^{1}H and ^{31}P NMR spectroscopy indicate that the crude product obtained from the reaction without further purification is *ca.* 95–100% pure.

‡ *Crystal data* for **3**: $C_{32}H_{76}N_{12}P_8$, M = 876.81, orthorhombic, space group $P2_12_12_1$, Z = 4, a = 13.3936(2), b = 17.1372(4), c = 21.7137(5) Å, V = 4983.92(18) Å^3, μ(Mo–Kα) = 0.315 mm^{-1}, T = 180(2) K. Data were collected on a Nonius Kappa CCD diffractometer. Of a total of 25299 reflections collected, 8699 were independent (R_{int} = 0.040). The structure was solved by direct methods and refined by full-matrix least squares on F^2.[15] Final $R1$ = 0.036 [$I > 2\sigma(I)$] and wR 2 = 0.079 (all data).

CCDC reference number 172095.

See http://www.rsc.org/suppdata/cc/b1/b107650g/ for crystallographic data in CIF or other electronic format.

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