Synthesis and structure of the Li_{13} cage $[\{[O\overset{\cdots}{-}P(\mu\text{-}N^tBu)]_2Li_2\}_3(LiCl)_6Li(Cl/O^nBu)_{0.5}(thf)_7]$, containing a $[O\overset{\cdots}{-}P(\mu\text{-}N^tBu)]_2^{2-}$ dianion†

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The hydrolysis of $[ClP(\mu\text{-}N^tBu)]_2$ with H_2O–Et_3N in thf, followed by *in situ* lithiation with ^nBuLi gives the Li_{13} cage $[\{[O\overset{\cdots}{-}P(\mu\text{-}N^tBu)]_2Li_2\}_3(LiCl)_6Li(Cl/O^nBu)_{0.5}(thf)_7]$, containing a $[O\overset{\cdots}{-}P(\mu\text{-}N^tBu)]_2^{2-}$ dianion that is isoelectronic with ligands of the type $[(RN)P(\mu\text{-}NR)]_2^{2-}$.

Recently there has been considerable interest in inorganic macrocycles and the potential parallel of their host–guest chemistry with organic counterparts.[1] Macrocyclic phosph(III)azane ring systems of the type $[\{P(\mu\text{-}NR)\}_2(\mu\text{-}Y)]_n$ (Y = NH,[2] O,[3] Se[4]) have been our major area of study. Like organic systems, the formation of different cyclic oligomers of this type can be controlled by templating. For example, the tetramer $[\{P(\mu\text{-}N^tBu)\}_2(\mu\text{-}NH)]_4$ (Fig. 1a) or the pentamer $[\{P(\mu\text{-}N^tBu)\}_2(\mu\text{-}NH)]_5$ can be obtained from the condensation of $[ClP(\mu\text{-}N^tBu)]_2$ and $[(NH_2)P(\mu\text{-}N^tBu)]_2$ in the presence of Et_3N,[2a,b] depending on the presence or the absence of iodide ions as the template.[2c]

More recently we showed that a Wurtz-type coupling reaction of $[(Se{=})ClP(\mu\text{-}N^tBu)]_2$ with Na metal results in the hexameric macrocyclic $[\{Se{=}P(\mu\text{-}N^tBu)_2P\}(\mu\text{-}Se)]_n$ comprising of alternating P^{III}/P^{V} centres in its backbone (Fig. 1b).[4] Although this procedure can be used for the corresponding S-precursor macrocycles,[5] it fails to produce the oxygen counterparts. We report here a key potential precursor to (crown ether-like) O-bridged macrocycles of the type $[\{P(\mu\text{-}N^tBu)\}_2(\mu\text{-}O)]_n$, the dianion $[O\overset{\cdots}{-}P(\mu\text{-}N^tBu)]_2^{2-}$ (**A**, Fig. 2). Interestingly, this dianion is isoelectronic with the group 15 dianions $[(RN)E(\mu\text{-}NR)]_2^{2-}$ (E = P,[6] As,[7] Sb,[8] Bi[9]) (**B**, Fig. 2), which have been applied extensively in the coordination chemistry of a range of main group and transition elements.

In previous investigations we reported that the hydrolysis of $[ClP(\mu\text{-}N^tBu)]_2$ at room temperature in the presence of excess of Et_3N afforded the dimer $[\{(O{=})HP(\mu\text{-}N^tBu)_2P\}_2(\mu\text{-}O)]$.[10] However, *in situ* ^{31}P NMR spectroscopic studies undertaken as part of the current work now show that the immediate precursor $[(O{=})HP(\mu\text{-}N^tBu)]_2$ is formed exclusively if short reaction times are employed (*ca.* 10 min), two equivalents of Et_3N are used in the reaction and the temperature is maintained below 10 °C. This species can be isolated at room temperature in the form of the dianion $[O\overset{\cdots}{-}P(\mu\text{-}NR)]_2^{2-}$ after it is effectively trapped *in situ* by treatment with ^nBuLi. This strategy requires 4 equivalents of ^nBuLi in order to deprotonate $[(O{=})HP(\mu\text{-}N^tBu)]_2$ *and* the $Et_3N{\cdot}HCl$ which is formed as a by-product during the hydrolysis step (Scheme 1).‡

The product crystallized reproducibly from this reaction is the thf solvate $[\{[O\overset{\cdots}{-}P(\mu\text{-}N^tBu)]_2Li_2\}_3(LiCl)_6Li(Cl/O^nBu)_{0.5}(thf)_7]{\cdot}0.25thf$ (**1**·0.25thf) (in 40% yield).‡ The elaborated structure of this complex was established later by single-crystal X-ray analysis (Fig. 3a).§ The complex is composed of a

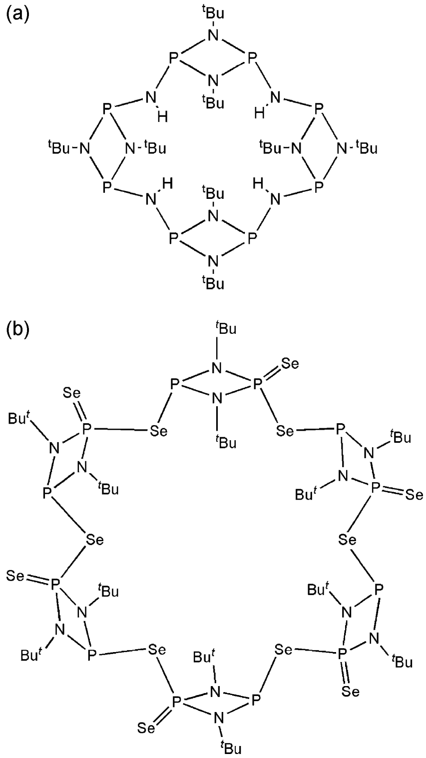

Fig. 1 Structures of (a) the NH-bridged tetramer and (b) the Se-bridged hexamer.

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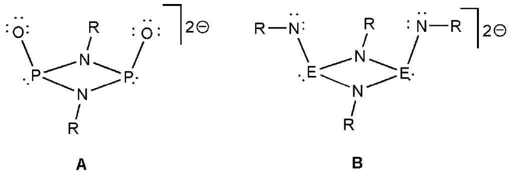


Fig. 2 The isoelectronic anions $[\text{O⎓P}(\mu\text{-NR})]_2^{2-}$ (**A**) and $[(\text{RN})\text{E}(\mu\text{-NR})]_2^{2-}$ (**B**).

central '$[\text{Li}_{13}\text{Cl}_6(\text{Cl/O}^n\text{Bu})_{0.5}]^{6+}$' cage fragment, which is co-ordinated by three $[\text{O⎓P}(\mu\text{-N}^t\text{Bu})]_2^{2-}$ dianions. The structure exhibits extensive disorder. Most significantly, Cl(7X) exhibits apparent 50 : 50 disordering with an $^n\text{BuO}^-$ ion [O(1X), Fig. 3a]. The reproducible formation of the same cage was shown by several unit cell analyses and by ^{31}P, ^{1}H and ^{7}Li NMR spectroscopic studies of separately-prepared crystalline samples of **1**. In addition, all of the disorder [including that of Cl(7X) and O(1X)] was found to be reproducible, as shown by two *full* data collections on separately-prepared crystalline samples of **1**. The origin of the apparent O^nBu group is, however, unclear at this stage but is possibly the result of ring-opening of thf[11] or alternatively adventitious oxidation of ^{n}BuLi with O_2 during storage of the reaction prior to crystallisation.[12]

Viewed in another way, complex **1** can be seen to be constructed from a highly distorted $[\text{Li}_8\text{X}_7]^+$ double-cubane fragment (X = Cl or ^{n}OBu) coordinated within a macrocyclic $[\{[\text{O⎓P}(\mu\text{-N}^t\text{Bu})]_2\}_3\text{Li}_7]^-$ arrangement (Fig. 3b). Related 'inverse-crown' arrangements to that found for **1** have been identified in a number of other s-block and Group 2 amide complexes.[13] Although this description is largely semantic in this case, the *cis* conformation of the O-atoms within the $[\text{O⎓P}(\mu\text{-N}^t\text{Bu})]_2^{2-}$ dianions in **1** and the overall arrangement of these anions in an equatorial belt at the periphery of the cage provides an indication of the potential importance of templating in the selective formation of species like the Se macrocycle shown in Fig. 1b. Of particular interest, the $[\text{O⎓P}(\mu\text{-N}^t\text{Bu})]_2^{2-}$ dianion in **1** is the first of its type to be reported. A similar *cis*-arrangement of the ^{t}BuN ligands is found in all of the isoelectronic dianions $[(\text{RN})\text{E}(\mu\text{-NR})]_2^{2-}$ (E = P–Bi).[6–9] Apart from the presence of P–O bonds within the $[\text{O⎓P}(\mu\text{-N}^t\text{Bu})]_2^{2-}$ dianion of **1** (mean 1.56 Å),[14] the remaining bond lengths and all of the angles present are very similar to those found in lithium complexes of the $[(\text{RN})\text{P}(\mu\text{-NR})]_2^{2-}$ dianions.[6] Despite the shortness of the P⎓O bonds, the P–O stretching band in the IR spectrum of solid **1** (1049 cm^{-1}) is in fact more typical of single P–O bonds, *e.g.*, the

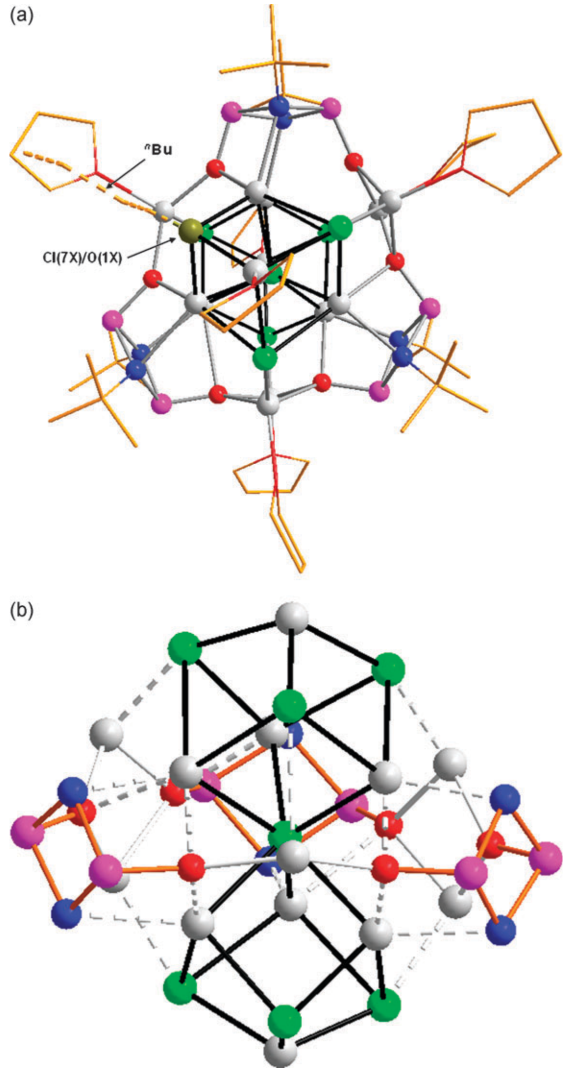
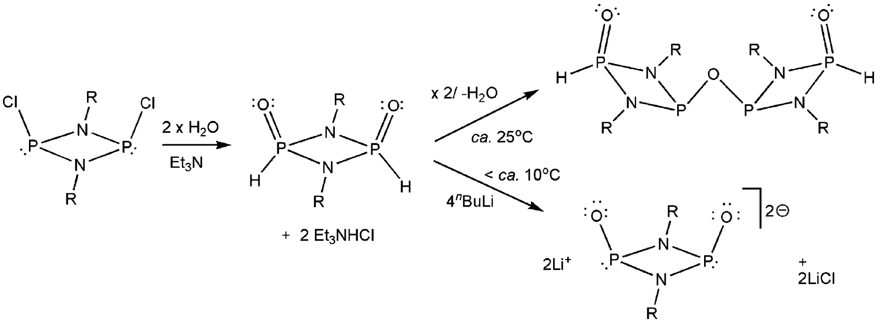


Fig. 3 (a) Molecular structure of **1** viewed down the major axis of the double-cubane core, showing the 50 : 50 disordering of Cl(1X) and O(1X) (lattice thf, the disorder of Li(7) and the Li-bonded thf ligands have been omitted for clarity), (b) side-view of the core, drawn as an inverse-crown structure involving coordination of a central $[\text{Li}_8\text{X}_7]^+$ cation [P (magenta), N (blue), O (red), Cl (green), Li (silver), disorder of Cl(7X)/O(1X) (brown)]. Selected bond lengths (Å) and angles (°); P⎓O range 1.555(4)–1.568(4) [mean 1.56], P–N range 1.756(4)–1.779(5) [mean 1.76], Li–N range 2.19(1)–2.41(1), Li–O(1–6) range 1.85(1)–2.28(1), Li–Cl range 2.16(1)–2.74(1), N–P–N range 82.7(2)–83.8(2) [mean 83.1], P–N–P range 96.2(2)–96.8(2) [mean 96.6], N–P–O range 100.6(2)–104.4(2) [mean 102.5].



Scheme 1

P–O–P and P=O stretching bands in $[\{(\text{O}{=})\text{HP}(\mu\text{-N}^t\text{Bu})_2\text{P}\}_2(\mu\text{-O})]$ are found at 936 and 1209 cm^{-1}, respectively.[10] Although cubane arrangements containing Li_4X_4 units are well-known,[15] the double-cubane arrangement found in **1** is apparently unique in alkali metal chemistry and represents a new fragment of the parent salt lattice of $[\text{LiCl}]_\infty$.[16]

As far as its solution structure is concerned, the $^{31}\text{P}\{^1\text{H}\}$, ^{1}H and ^{7}Li NMR spectra of **1** exhibit complicated concentration- and temperature-dependent behavior, suggesting the presence of a dynamic equilibrium between various closely-related solution species. For example, roughly four broad overlapping resonances are found in the ^{7}Li NMR spectrum irrespective of temperature (in the region δ 0.74–1.64, rel. to LiCl–D_2O), the intensities of which vary with concentration, while the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum consists of essentially three major resonances (δ = 140.5, 123.0 and 120.0), again varying in intensity with concentration and temperature. Although we are unable to assign any of these resonances to individual species, it is clear that **1** dissociates significantly in solution.

In conclusion, we have prepared the first $[\text{O}\overset{\cdots}{-}\text{P}(\mu\text{-NR})]_2{}^{2-}$ dianion (isoelectronic with well-known $[(\text{RN})\text{P}(\mu\text{-NR})]_2{}^{2-}$ dianions). Explorations of the applications of **1** as a source of the $[\text{O}\overset{\cdots}{-}\text{P}(\mu\text{-N}^t\text{Bu})]_2{}^{2-}$ dianion in coordination chemistry (with various main group and transition metals) and as a pre-organised precursor to O-bridged macrocyles are underway.

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Notes and references

‡ Synthesis of **1**·0.25thf: $[\text{ClP}(\mu\text{-N}^t\text{Bu})]_2$ (0.83 g, 3.00 mmol) was dissolved in toluene (40 ml) and Et_3N (1.00 ml, 6.00 mmol) was added. The mixture was cooled to −78 °C and H_2O (108 μL, 6.00 mmol) was added dropwise. It was allowed to warm up to 5–7 °C and stirred for 10 min at this temperature. The turbid mixture was cooled again to −78 °C and ^{n}BuLi (8.2 ml, 1.6 mol dm^{-3} in hexanes, 13.00 mmol) was added followed by stirring at room temperature for 8 h. After removal of all volatiles under vacuum the solid residue was extracted with *n*-hexane (40 ml) and thf (4 ml). The clear filtrate was stored at −28 °C to afford colourless crystals in 2 days. The mother liquor, after being concentrated to 15 ml, gave another crop of **1**. Crystals were isolated after drying under vacuum (10^{-1} atm, 15 min), resulting in the loss of *ca*. 1.25 thf molecule for each formula unit. The following data refer to this material. Total yield (0.62 g, 0.40 mmol, 40% with respect to $[\text{ClP}(\mu\text{-N}^t\text{Bu})]_2$). Mp 270 °C. IR spectrum (Nujol, NaCl), ν/cm^{-1} = 1073(s), 1049(vs) (P$\overset{\cdots}{-}$O str.), other bands at 1261(m), 1243(m), 955(m), 917(w), 825(s), 801(ms), 722(m) [air-exposure leads to the P$\overset{\cdots}{-}$O str. band shifting to 1096 cm^{-1}]. $^1\text{H}\{^{31}\text{P}\}$ (+25 °C, 500.12 MHz, D_8-toluene) δ = 2.0–1.0 (overlapping s); $^{31}\text{P}\{^1\text{H}\}$ NMR (+25 °C, 161.95 MHz, D_8-toluene, rel. to 85% H_3PO_4–D_2O) δ = 140.5, 123.0 (s), 120.0 (s); ^{7}Li NMR (+25 °C, 194.40 MHz, D_8-toluene, rel. to saturated LiCl–D_2O) δ = 1.64–0.74 (overlapping s). Anal. found: C, 40.2; H, 7.2; N, 5.4%, Calcd for **1**–thf C, 40.7; H, 7.4; N, 5.7%.

§ *Crystal data for* **1**·0.25thf; empirical formula $\text{C}_{55}\text{H}_{116.50}\text{Cl}_{6.50}\text{Li}_{13}\text{N}_6\text{O}_{13.75}\text{P}_6$, FW = 1588.51, crystal system orthorhombic, space group *Pbca*, a = 19.906(4), b = 21.982(4), c = 39.230(8) Å, V = 17166(6) Å^3, Z = 8, ρ_calcd = 1.215 Mg m^{-3}, μ(Mo-Kα) = 0.380 mm^{-1}, reflections collected 77 200, independent reflections 12 471 [R_int = 0.068]. $R1$ = 0.070, $wR2$ = 0.185. Data for **1** were collected on a Nonius KappaCCD diffractometer at 180(2)K, solved by direct methods and refined by full-matrix least squares on F^2.[17] The complex exhibited extensive disordering of the Li^+ cations and Li-bonded thf molecules. All of the Li-bonded thf molecules, except that bonded to Li(1), are disordered over two 50 : 50 sites. Li(7) and its associated thf molecule are disordered over two 50 : 50 sites. The disorder of Cl(1X) was modelled as a 50 : 50 site disorder with an *n*-BuO group. In addition, $\frac{1}{4}$ of an uncoordinated thf molecule is present in the crystal lattice.†

1 E. L. Doyle, L. Riera and D. S. Wright, *Eur. J. Inorg. Chem.*, 2003, 3279; M. S. Balakrishna, D. J. Eisler and T. Chivers, *Chem. Soc. Rev.*, 2006, **36**, 650; T. Chivers, *Angew. Chem., Int. Ed.*, 2007, **46**, 4610.

2 (*a*) E. L. Doyle, C. Tubb, S. J. Kidd, M. McPartlin and D. S. Wright, *Chem. Commun.*, 2001, 2542; (*b*) A. Bashall, A. D. Bond, E. L. Doyle, F. García, S. J. Kidd, G. T. Lawson, M. C. Parry, M. McPartlin, A. D. Wood and D. S. Wright, *Chem.–Eur. J.*, 2002, **8**, 3377; (*c*) F. García, J. M. Goodman, R. A. Kowenicki, I. Kuzu, M. McPartlin, M. A. Silva, L. Riera and D. S. Wright, *Chem.–Eur. J.*, 2004, **10**, 6066; (*d*) F. García, R. A. Kowenicki, I. Kuzu, M. McPartlin, L. Riera and D. S. Wright, *Inorg. Chem. Commun.*, 2005, **8**, 1060.

3 A. D. Bond, E. L. Doyle, F. García, R. A. Kowenicki, M. McPartlin, L. Riera and D. S. Wright, *Chem. Commun.*, 2003, 2990.

4 S. González-Calera, D. J. Eisler, J. V. Morey, M. McPartlin, S. Singh and D. S. Wright, *Angew. Chem., Int. Ed.*, 2008, **47**, 1111.

5 S. Singh and D. S. Wright, unpublished results.

6 I. Schranz, L. Stahl and R. J. Staples, *Inorg. Chem.*, 1998, **37**, 1493; J. K. Brask, T. Chivers, M. L. Krahn and M. Parvez, *Inorg. Chem.*, 1999, **38**, 290.

7 M. A. Beswick, E. A. Harron, A. D. Hopkins, P. R. Raithby and D. S. Wright, *J. Chem. Soc., Dalton Trans.*, 1998, 1389.

8 R. A. Alton, D. Barr, A. J. Edwards, M. A. Paver, M.-A. Rennie, C. A. Russell and P. R. Raithby, *J. Chem. Soc., Chem. Commun.*, 1994, 1481.

9 D. Barr, M. A. Beswick, A. J. Edwards, J. R. Galsworthy, M. A. Paver, M.-A. Rennie, C. A. Russell, P. R. Raithby, K. L. Verhorevoort and D. S. Wright, *Inorg. Chim. Acta*, 1996, **248**, 9.

10 E. L. Doyle, F. García, S. M. Humphrey, R. Kowenicki, L. Riera, A. D. Woods and D. S. Wright, *Dalton Trans.*, 2004, 807.

11 For similar ring-opening thf cleavage, see: S. M. Kunnari, R. Oilunkaniemi, R. S. Laitinen and Markku Ahlgrén, *J. Chem. Soc., Dalton Trans.*, 2001, 3417; R. F. Moreira, E. Y. Tshuva and S. J. Lippard, *Inorg. Chem.*, 2004, **43**, 4427; G. C. Welch, J. D. Masuda and D. W. Stephan, *Inorg. Chem.*, 2006, **45**, 478; T. Beweries, U. Jäger-Fiedler, M. A. Bach, V. V. Burlakov, P. Arndt, W. Baumann, A. Spannenberg and U. Rosenthal, *Organometallics*, 2007, **26**, 3000; H. C. Lo, H. Han, L. J. D'Souza, S. C. Sinha and E. Keinan, *J. Am. Chem. Soc.*, 2007, **129**, 1246.

12 Oxidation of RLi by O_2 has been reported previously: A. E. H. Wheatley, *Chem. Soc. Rev.*, 2001, **30**, 265; S. R. Boss, R. Haigh, D. J. Linton and A. E. H. Wheatley, *J. Chem. Soc., Dalton Trans.*, 2002, 3129.

13 R. E. Mulvey, *Chem. Commun.*, 2001, 1049.

14 Search of the Cambridge Structural Database using Vista to visualize data. Single P–O bonds are found in the range of 1.27–2.02 Å (mean 1.57 Å). Shortest values are typical of P–O–functionality, *e.g.*, P$^\text{V}$: T. Chivers, M. Krahn, G. Shatte and M. Parvez, *Inorg. Chem.*, 2003, **42**, 3994; P$^\text{III}$: P. C. Andrews, M. Minopoulos and E. G. Roberston, *Eur. J. Inorg. Chem.*, 2006, 2865.

15 For examples of Li_4Cl_4 cubanes see: D. Barr, W. Clegg, R. E. Mulvey and R. Snaith, *J. Chem. Soc., Chem. Commun.*, 1984, 79; E. Iravani and B. Neumuller, *Z. Anorg. Allg. Chem.*, 2006, **632**, 289.

16 R. Snaith and D. S. Wright, Complexes of Inorganic Salts Lithium, in *Chemistry, A Theoretical and Experiment Study*, ed. A.-M. Sapse and P. v. R. Schleyer, John Wiley and Sons, New York, 1994, ch. 8, p. 227.

17 G. M. Sheldrick, *SHELX-97*, University of Göttingen, Germany, 1997.