Synthesis and structure of [(Bu^{t}N)P(μ-NBu^t)$_2$P(PCy)Li$_2$·thf]$_2$; an unusual cage compound containing an amido/phosphido functionalised [(Bu^{t}N)P(μ-NBu^t)$_2$P(PCy)]$^{2-}$ dianion (Cy = C$_6$H$_{11}$)

Alan Bashall,^{a} Benjamin R. Elvidge,^{b} Michael A. Beswick,*^{b} Sara J. Kidd,^{b} Mary McPartlin^a 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

The reaction of [(Bu^{t}NH)P(μ-NBu^t)$_2$PCl] (1) with CyPHLi and Bu^{n}Li in toluene gives [(Bu^{t}N)P(μ-NBu^t)$_2$P(PCy)-Li$_2$·thf]$_2$ (2), an unusual aggregate containing the first example of a phosphine-functionalised cyclodiphosphazane anion [(Bu^{t}N)P(μ-NBu^t)$_2$P(PCy)]$^{2-}$.

In recent years there has been increasing interest in the synthesis and coordination chemistry of anionic ligand systems based on imido group 15 molecular frameworks.[1] The most extensively studied have been complexes containing [E$_2$(NR)$_4$]$^{2-}$ anions, (E = P,[2] As,[3] Sb,[4] Bi[5]), capable of coordinating a variety of metal centres using a combination of their μ-N and terminal N donor functionality.[6] Although imido frameworks of this type are comparatively robust, we found recently that the analogous phosphide systems of the heavier group 15 elements decompose at low temperatures to give cyclic [(RP)$_n$E]$^-$ anions (n = 3, 4; E = As–Bi) and Zintl compounds.[7] Indeed, the only group 15 phosphide which has been stable enough to isolate (< 30 °C) and structurally characterise so far is the [Sb(PCy)$_3$]$^{3-}$ trianion, present in the cage complex [{Sb(PCy)$_3$}$_2$Li$_6$·6Me$_2$NH].[8] Motivated by the scarcity of stable phosphide ligands of this type, we have turned our attention to those based on phosphorus frameworks which are likely to be more stable. We report here the first example of a phosphine-functionalised cyclodiphosphazane anion present in the unusual cage complex [(Bu^{t}N)P(μ-NBu^t)$_2$P(PCy)Li$_2$·thf]$_2$ (1).

Complex 1 was prepared by the reaction of [(Bu^{t}NH)P(μ-NBu^t)$_2$PCl] (1 equiv.) with CyPHLi (1 equiv.) followed by reaction with Bu^{n}Li (2 equiv.),† the formation of the dianion resulting from a combination of addition of CyPH$^-$ to the framework of [(Bu^{t}NH)P(μ-NBu^t)$_2$PCl] and deprotonation with Bu^{n-} (Scheme 1).

Low-temperature X-ray crystallography‡ reveals that 1 is composed of centrosymmetric dimers, which are constructed from the association of two [(Bu^{t}N)P(μ-NBu^t)$_2$P(PCy)Li$_2$·thf] cubane units through a central P$_2$Li$_2$ ring (Fig. 1). In addition there is a thf molecule within the lattice. The unusual manner of the association of the cubane units of 1 can be compared to related group 15 complexes containing [E$_2$(NR)$_4$]$^{2-}$ anions. Complete solvation of the Li$^+$ cations in [{E$_2$(NBu^t)$_4$}Li$_2$·2thf] (E = P,[2a] Bi[5]) results in discrete cubane structures, whereas in [{E$_2$(NBu^t)$_4$}Li$_2$]$_2$ (E = P,[2b] As,[3] Sb[4]) the absence of Lewis base solvation results in aggregation into 'interlocked-cubane' cages. The arrangement in 1 can be regarded as representing an

intermediate situation in which solvation of only one of the Li$^+$ cations within the cubane constituents leaves 'side-on' aggregation as the most viable method of increasing the coordination number of the unsolvated Li centre.

The presence of the CyP substituent has little effect on the P–N framework of the [(Bu^{t}N)P(μ-NBu^t)$_2$P(PCy)]$^{2-}$ dianions of 1, the geometry of the [(Bu^{t}N)P(μ-NBu^t)$_2$P] fragment and bond lengths involved being very similar to those found in complexes containing the related [(Bu^{t}N)P(μ-NBu^t)$_2$P(NBu^t)]$^{2-}$ dianion.[2] In particular, the endocyclic P–N bonds (mean 1.78 Å) and endocyclic P–N–P and N–P–N angles (mean 96.9 and 83.1°, respectively) present in the planar P$_2$N$_2$ rings of 1 are similar to those found in the bis-thf solvate [{P$_2$(NBu^t)$_4$}Li$_2$·2thf].[2a] This similarity suggests that the relatively short exocyclic P–P(Cy) bond in the [(Bu^{t}N)P(μ-NBu^t)$_2$P(PCy)]$^{2-}$ dianions of 1 [P(2)–P(3) 2.171(3) Å; cf. single P–P ca. 2.21 Å and double P=P bond ca. 2.1 Å[9]] is largely the result of electrostatic factors (i.e., stemming from the bonding of P(2) to two electronegative N
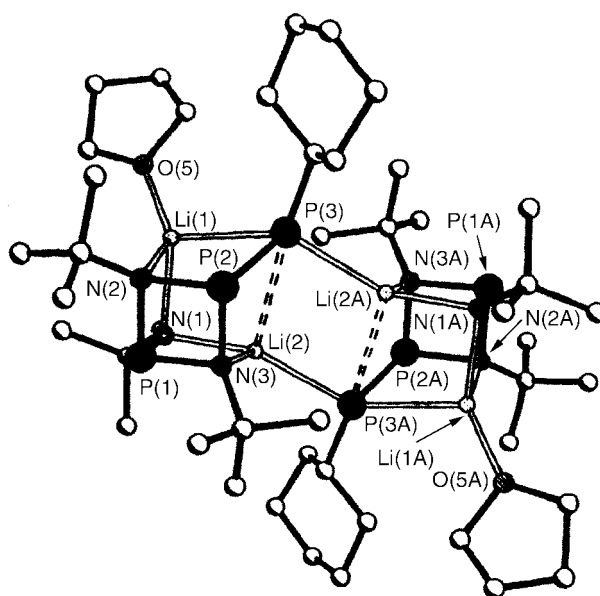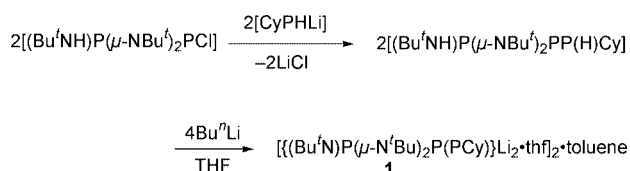

Fig. 1 Structure of dimeric molecules of 1. H-atoms and the lattice-bound thf molecules have been omitted for clarity. Key bond lengths (Å) and angles (°); P(1)–N(1) 1.651(5), P(1)–N(2) 1.787(5), P(1)–N(3) 1.792(5), P(2)–N(2) 1.773(6), P(2)–N(3) 1.772(5), P(2)–P(3) 2.171(3), N(1)–Li(1) 2.09(1), Li(1)–O(5) 1.94(1), N(1)–Li(2) 1.98(1), N(2)–Li(1) 2.11(1), N(3)–Li(2) 2.11(1), P(3)–Li(1) 2.62(1), P(3)–Li(2) 2.88(1), P(3)–Li(2A) 2.57(1), N(1)–P(1)–N(2) 101.0(3), N(1)–P(1)–N(3) 97.9(3), N(2)–P(1)–N(3) 82.6(2), P(1)–N(2)–P(2) 97.0(3), P(1)–N(3)–P(2) 96.8(2), N(2)–P(2)–P(3) 104.1(2), N(3)–P(2)–P(3) 98.6(2), N(2)–P(2)–N(3) 83.6(2), Li(1)–N(1)–Li(2) 92.6(5), Li(1)–P(3)–Li(2) 64.4(4), N(1)–Li(1)–P(3) 102.4(5), N(1)–Li(2)–P(3) 97.1(5), Li(2)–P(3)–Li(2A) 67.6(4), P(3)–Li(2)–P(3A) 112.4(4), Li(1)–P(3)–Li(2A) 125.2(4).

2[(Bu^{t}NH)P(μ-NBu^t)$_2$PCl] $\xrightarrow[-2\text{LiCl}]{2[\text{CyPHLi}]}$ 2[(Bu^{t}NH)P(μ-NBu^t)$_2$PP(H)Cy]

$\xrightarrow[\text{THF}]{4\text{Bu}^n\text{Li}}$ [{(Bu^{t}N)P(μ-N^{t}Bu)$_2$P(PCy)}Li$_2$·thf]$_2$·toluene
1

Scheme 1

centres, rather than indicating the presence of any partial multiple bonding).

The coordination of the bifunctional [(Bu^{t}N)P(μ-NBu^t)$_2$P(PCy)]$^{2-}$ ligand to the Li$^+$ cations in **1** inherently results in major distortion of the [(Bu^{t}N)P(μ-NBu^t)$_2$P(PCy)Li$_2$] cubane framework. The NLi$_2$P ring unit in **1** is butterfly-shaped primarily as a consequence of the relative shortness of the terminal P–N(Bu^t) bond [P(1)–N(1) 1.651(5) Å] of the ligand compared to the terminal P–P(Cy) bond. In addition, this distortion is exacerbated further by the relative shortness of the Li–N bonds [range 1.98(1)–2.11(1) Å[10]] compared to the P–Li bonds [P(3)–Li(1) 2.62(1), P(3)–Li(2) 2.88(1) Å]. Finally, it is interesting to note that the P(3)–Li(2) interaction is well outside the range found in lithium phosphide complexes (*ca.* 2.6[11]) and significantly longer than the P–Li bonds linking the cubane units [P(3A)–Li(2) 2.57(1) Å]. This observation may indicate that aggregation of the monosolvated cubane units of **1** *via* P–Li bonding, rather than the attainment of a discrete cubane structure by thf-solvation of both cations, is a consequence of the inability of the exocyclic P donor centre to coordinate both of the Li$^+$ cations effectively within a discrete cubane arrangement.

In summary, the first example of a phosphine-functionalised cyclodiphosphazane anion, [(Bu^{t}N)P(μ-NBu^t)$_2$P(PCy)]$^{2-}$, has been prepared, structural studies showing that the Li salt [(Bu^{t}N)P(μ-NBu^t)$_2$P(PCy)Li$_2$·thf]$_2$ has a unique arrangement in the solid state. In view of this structural pattern and of the very different geometric demands of this anion compared to related amides, further studies of the coordination chemistry of this and other phosphides should be of interest.

Notes and references

† *Synthesis of* **1**: the novel precursor [(Bu^{t}NH)P(μ-NBu^t)$_2$PCl] was prepared by the reaction of PCl$_3$ with Bu^{t}NH$_2$ (2 : 8 equiv.) in toluene. It was characterised by elemental analysis (C,H,N) and ^{1}H and ^{31}P NMR spectroscopy, and X-ray crystallography.[12] A suspension of CyPHLi (6.43 mmol) in hexane (20 ml) was added to a solution of [(Bu^{t}NH)P(μ-NBu^t)$_2$PCl] (2.0 g, 6.43 mmol) in toluene (5 ml)/hexane (20 ml) at room temperature. The white solid produced (LiCl) was removed by filtration and the orange filtrate reduced to *ca.* 5 ml under vacuum. To this was added Bu^{n}Li (8.6 ml, 1.50 mol dm^{-3} in hexanes, 12.9 mmol). A yellow precipitate was produced which was dissolved by the dropwise addition of thf (*ca.* 5 ml) to the suspension at reflux. Storage of the solution at 5 °C (48 h) gave small colourless cubes of **1**. Yield 1.33 g (40%). Decomp. to red solid *ca.* 180 °C. ^{1}H NMR ([^{2}H$_8$]thf, +25 °C, 400.129 MHz), 3.50 (m, *ca.* 6H, thf), 1.70 (m, *ca.* 6H, thf), *ca.* 2.1–1.0 (overlapping m, 11H, Cy), 1.13 (s, 27H, Bu^t). ^{31}P NMR ([^{2}H$_8$]thf, +25 °C, 161.975 Hz, rel. to 80% H$_3$PO$_4$/D$_2$O), 187.9 (d, $J_{P–P}$ = 376 Hz, CyPP), 167.6 (s, PNBu^t), −10.2 (d, $J_{P–P}$ = 376 Hz, CyP). Correct analysis (C, H, N) were obtained for **1**.

‡ *Crystal data for* **1**: C$_{50}$H$_{104}$Li$_4$N$_6$O$_3$P$_6$, M = 1022.92, monoclinic, space group $P2_1/n$, Z = 2, a = 10.679(2), b = 21.224(8), c = 13.847(3) Å, β = 95.46(2)°, V = 3124.0(15) Å^3, μ(Mo–Kα) = 0.211 mm^{-1}, T = 223(2) K. Data were collected on a Siemens *P*4 four circle diffractometer and corrected for absorption using Ψ scans. Of a total of 4884 reflections collected, 3836 were independent (R_{int} = 0.075). The structure was solved by direct methods and refined by full-matrix least squares on F^2.[13] Final $R1$ = 0.077 [$I > 2\sigma(I)$] and $wR2$ = 0.242 (all data). Three peaks of electron density were interpreted as a molecule of thf disordered across an inversion centre in such a way that the carbon atoms in the two components overlap. CCDC 182/1696. See http://www.rsc.org/suppdata/cc/b0/b0034681/ for crystallographic files in .cif format.

1 M. A. Beswick and D. S. Wright, *Coord. Chem. Rev.*, 1998, **176**, 373; M. A. Beswick, M. E. G. Mosquera and D. S. Wright, *J. Chem. Soc., Dalton Trans.*, 1998, 2437, and references cited therein.
2 (*a*) I. Schranz, L. Stahl and R. J. Staples, *Inorg. Chem.*, 1998, **37**, 1493; (*b*) J. K. Brask, T. Chivers, M. L. Krahn and M. Parvez, *Inorg. Chem.*, 1999, **38**, 290.
3 M. A. Beswick, E. A. Harron, A. D. Hopkins, P. R. Raithby and D. S. Wright, *J. Chem. Soc., Dalton Trans.*, 1999, 107.
4 R. A. Alton, D. Barr, A. J. Edwards, M. A. Paver, P. R. Raithby, M.-A. Rennie, C. A. Russell and D. S. Wright, *J. Chem. Soc., Chem. Commun.*, 1994, 1481.
5 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.
6 (*a*) D. Barr, A. J. Edwards, S. Pullen, M. A. Paver, M.-A. Rennie, P. R. Raithby and D. S. Wright, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1875; (*b*) M. A. Beswick, C. A. Harmer, M. A. Paver, P. R. Raithby, A. Steiner and D. S. Wright, *Inorg. Chem.*, 1997, **36**, 1740; (*c*) L. Grocholl, V. Huch, L. Stahl, R. Staples, P. Steinhart and A. Johnson, *Inorg. Chem.*, 1997, **36**, 4451; (*d*) L. Grocholl, I. Schranz, L. Stahl and R. J. Staples, *Inorg. Chem.*, 1998, **37**, 2496; (*e*) D. F. Moser, I. Schranz, M. C. Gerrety, L. Stahl and R. J. Staples, *J. Chem. Soc. Dalton Trans.*, 1999, 751; (*f*) A. Bashall, M. A. Beswick, E. A. Harron, A. D. Hopkins, S. J. Kidd, M. McPartlin, P. R. Raithby, A. Steiner and D. S. Wright, *Chem. Commun.*, 1999, 1145.
7 (*a*) M. A. Beswick, N. Choi, C. N. Harmer, A. D. Hopkins, M. McPartlin and D. S. Wright, *Science*, 1998, **281**, 1500; (*b*) M. A. Beswick, N. Choi, A. D. Hopkins, M. E. G. Mosquera, M. McPartlin, P. R. Raithby, A. Rothenberger, D. Stalke, A. E. H. Wheatley and D. S. Wright, *Chem. Commun.*, 1998, 2485; (*c*) M. A. Beswick, N. Choi, A. D. Hopkins, M. E. G. Mosquera, M. McPartlin, P. R. Raithby, A. E. H. Wheatley and D. S. Wright, *J. Chem. Soc., Dalton Trans.*, 2000, 479.
8 M. A. Beswick, J. M. Goodman, C. N. Harmer, A. D. Hopkins, M. A. Paver, P. R. Raithby, A. E. H. Wheatley and D. S. Wright, *Chem. Commun.*, 1997, 1879.
9 R. A. Jones, M. H. Seeberger and B. R. Whittlesey, *J. Am. Chem. Soc.*, 1985, **107**, 6424, and references cited therein.
10 These Li–N bonds are typical of amido lithium compounds, see: (*a*) K. Gregory; P. v. R. Schleyer and R. Snaith, *Adv. Inorg. Chem.*, 1991, **37**, 47; (*b*) R. E. Mulvey, *Chem. Rev.*, 1991, **20**, 167.
11 M. A. Beswick and D. S. Wright, *Comprehensive Organometallic Chemistry; Alkali Metals*, ed. E. W. Abel, F. G. Stone and G. Wilkinson, vol. ed. C. E. Housecroft, 1994, ch. 1, p. 1 and references cited therein.
12 The structure of [(Bu^{t}NH)P(μ-NBu^t)$_2$PCl] has a similar *cis* arrangement to that of [{(Me$_3$Si)$_2$N}P(μ-NBu^t)(μ-NMes)PCl]. See: G. David, E. Nieke, M. Nieger, V. von der Gönna and W. W. Schoeller, *Chem. Ber.*, 1993, **126**, 1513. The synthesis and structure of [(Bu^{t}NH)P(μ-NBu^t)$_2$PCl] will form part of a later full paper.
13 SHELXTL PC version 5.03, Siemens Analytical Instruments, Madison, WI, 1994.