Cooperative cation and anion coordination by a bifunctional imidophosphorane ligand framework; syntheses and structures of [LiCl{Bu^{t}NHP)μ-NBu^t)$_2$PNH(2-py)}$_3$] and [{Bu^{t}NP(μ-NBu^t)$_2$PN(2-py)}Li$_2$·{Li(Bu^{t}N)$_2$P}]†

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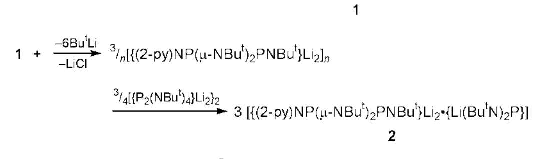
The neutral ligand [Bu^{t}NHP(μ-NBu^t)$_2$PNH(2-py)] and its dilithiate [{Bu^{t}NP(μ-NBu^t)$_2$PN(2-py)}Li$_2$] exhibit a parallel ability to coordinate cations and anions, as revealed in the structures of the tris-solvate [LiCl{Bu^{t}NHP(μ-NBu^t)$_2$PNH(2-py)}$_3$] 1 and the unusual co-complex [{Bu^{t}NP(μ-NBu^t)$_2$PN(2-py)}Li$_2$·{Li(Bu^{t}N)$_2$P}] 2.

In recent years the coordination chemistry of new ligand systems based on Group 15 element/nitrogen frameworks has been the focus of an increasing number of investigations.[1] The most intensively studied species of this class are [E$_2$(NR)$_4$]$^{2-}$ dianions, which have been prepared for all the Group 15 elements (E = P–Bi).[2–5] For the heavier congeners (As–Bi) the dianion frameworks are readily established by condensation reactions of the dimers [Me$_2$NE(μ-NR)]$_2$ with primary amido lithium complexes ([RNHLi]$_n$).[3–5] However, the phosphorus analogues are obtained by metallation of the pre-formed acids [RNHP(μ-NR)]$_2$ with organolithium reagents.[2] The structures of the resulting lithium cages are based on [{E$_2$(NR)$_4$}Li$_2$] cubane units, generally being of the type [{E$_2$(NR)$_4$}Li$_2$·2thf]^{2a,5} or [{E$_2$(NR)$_4$} Li$_2$]$_2$[2b,3,4] (depending on the presence or absence of thf solvation). We recently showed that the precursor [Bu^{t}NHP(μ-NBu^t)$_2$PCl] is useful in the synthesis of non-symmetrical dianions, the reaction of the former with [CyPHLi] (Cy = cyclohexyl)/Bu^{n}Li giving the bifunctional (hard/soft) dianion [Bu^{t}NP(μ-NBu^t)$_2$PPCy]$^{2-}$.[6]

Both NMR spectroscopic and analytical investigations revealed that the reaction of (2-py)NHLi with [Bu^{t}NHP(μ-NBU^t)PCl][6] does not yield the free ligand [Bu^{t}NHP(μ-NBu^t)PNH(2-py)] (py = pyridyl), rather the product is the lithium chloride complex [LiCl{Bu^{t}NHP(μ-NBu^t)PNH(2-py)}$_3$] (Scheme 1) (ESI†). Addition of Bu^{n}Li to a solution of **1** [prepared *in situ* from the 1:1 reaction of [Bu^{t}NHP(μ-NBu^t)PCl] with (2-py)NHLi] (1.6 equiv., respectively)] leads to precipitation of LiCl and the formation of [{BuNP(μ-NBu^t)$_2$PN(2-py)}Li$_2$·{Li(Bu^{t}N)$_2$P}] **2** (in 19% yield) (ESI†). A ^{31}P NMR study of the reaction mixture before and after the addition of Bu^{n}Li reveals that the production of **2** stems from the formation of [Bu^{t}NHP(μ-NBu^t)]$_2$ as a significant byproduct in the synthesis of **1**. ^{31}P NMR studies also show that only the dilithiate [{Bu^{t}NP(μ-NBu^t)$_2$PN(2-py)}Li$_2$]$_n$ is produced by lithiation of *pure* **1**. However, addition of [{P$_2$(NBu^t)$_4$}$_2$Li$_2$]$_2$ (the product of lithiation of [Bu^{t}NHP(μ-NBu^t)]$_2$[2b]) to a solution of [{Bu^{t}NP(μ-NBu^t)$_2$PN(2-py)}Li$_2$]$_n$ in the correct stoichiometric ratio gives **2**.‡ The formation of **2** can therefore be explained in both cases by symmetrical cleavage of the P$_2$N$_2$ ring units of [{P$_2$(NBu^t)$_4$}$_2$Li$_2$]$_2$ (Scheme 1). Of particular interest is the highly deshielded nature of the P centre of the [(Bu^{t}N)$_2$P]$^-$ anion in **2**, whose resonance is found at δ 395.3 (+25 °C). This value is considerably greater than observed for other [(RP)$_2$N]$^-$ anions (*ca.* δ 340–360).[2b,7] suggesting an even greater degree of charge separation within the anion backbone in **2** [*i.e.* N$^-$–P$^+$–N$^-$ rather than (N$\doteq$P$\doteq$N)$^-$]. The extent of this charge separation is probably related to the unusual coordination mode of the [(Bu^{t}N)$_2$P]$^-$ anion observed in the later structural characterisation of the complex (involving two N–Li bonds to each of the N centres of the anion, rather than only one as in all other previously characterised lithiates[2b,7]).

Confirmation of the structure proposed on the basis of spectroscopic and analytical studies is provided by a low-temperature X-ray crystallographic study of **1**.‡ This reveals that **1** is monomeric in the solid state, being composed of a lithium chloride unit which is coordinated by three neutral [Bu^{t}NHP(μ-NBu^t)PNH(2-py)] ligands (the molecules having exact C_{3v} symmetry about the Li–Cl bond axis) (Fig. 1). Although other tris-pyridine complexes of LiCl have been structurally characterised,[8] the 'cooperative' mode of coordination of the LiCl unit in **1** (by a combination of (pyridyl)N–Li bonding and H-bonding to the Cl$^-$ anion within the hydrophilic ligand cavity) is, to our knowledge, unprecedented for such an inorganic ligand system. This behaviour has closer parallels



Scheme 1

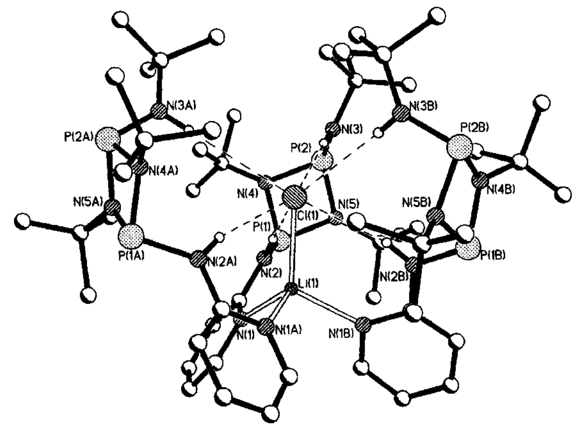


Fig. 1 Structure of the tris-solvate **1**: H-atoms (except those attached to N) have been omitted for clarity. Key bond lengths (Å) and angles (°); Li(1)–Cl(1) 2.325(9), N(1)–Li(1) 2.093(5), P(1)–N(2) 1.710(3), P(1)–N(4) 1.703(3), P(1)–N(5) 1.705(3), P(2)–N(3) 1.642(3), P(2)–N(4) 1.728(3), P(2)–N(5) 1.733(3), Cl(1)···H(2N) 2.65; [N(2)–H(2N)···Cl(1) 165.2], Cl(1)···H(3N) 3.18 [N(3)–H(3N)···Cl(1) 176.7], *exo*-N–P(1,2)–μ-N range 103.03(4)–104.9(2), N(4)–P(1)–N(5) 81.4(1), N(4)–P(2)–N(5) 80.0(1), P(1)–N(4)–P(2) 98.5(2), P(1)–N(5)–P(2) 98.2(2).

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† Electronic supplementary information (ESI) available: syntheses of **1** and **2**. See http://www.rsc.org/suppdata/cc/b0/b010093p/

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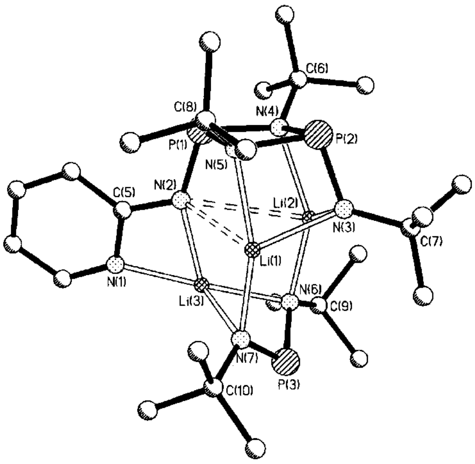

Fig. 2 Structure of the co-complex **2**; H-atoms have been omitted for clarity. Key bond lengths (Å) and angles (°); *dianion*: P(1)–N(2) 1.670(3), P(1)–N(4) 1.754(2), P(1)–N(5) 1.756(3), P(2)–N(3) 1.646(3), P(2)–N(4) 1.790(2), P(2)–N(5) 1.787(3); exo-N–P(1,2)–μ-N range 99.5(1)–101.2(1), N(4)–P(1)–N(5) 83.2(2), N(4)–P(2)–N(5) 81.3(1), P(1)–N(4)–P(2) 97.3(1), P(1)–N(5)–P(2) 97.4(1); *monoanion*: P(3)–N(6) 1.613(3), P(3)–N(7) 1.606(3); N(6)–P(3)–N(7) 102.0(1); Li–N *framework*: N(1)–Li(3) 2.002(6), N(2)–Li(3) 2.040(6), N(2)···Li(1) 2.523(7), N(2)···Li(2) 2.823(7), N(3)–Li(1) 2.085(6), N(3)–Li(2) 2.022(6), N(4)–Li(2) 2.152(6), N(5)–Li(1) 2.164(6), N(6)–Li(2) 2.087(6), N(7)–Li(1) 2.080(6), N(6)–Li(3) 2.087(6), N(7)–Li(3) 2.109(6).

with organic ligand frameworks such as the mode of coordination of HSO_4^- and $H_2PO_4^-$ ions by the tripodal naphthylurea receptor $N\{CH_2CH_2NHC(=O)NHC_{10}H_7\}_3$.[9] Judging by the lengths of the N–H···Cl interactions involved, the H-bonds with the NH(2-py) groups [Cl(1)···H(2N) 2.647(3) Å] are far more significant than those to the Bu^{t}NH groups [Cl(1)···H(3N) 3.177(3) Å]. This conclusion is confirmed by the variable-temperature ^{1}H NMR spectrum of the complex, in which the (2-py)NH proton resonance shifts from δ 6.40 at 20 °C to δ 5.60 at 40 °C with disruption of the N–H···Cl H-bonds. In comparison, the resonance for the Bu^{t}NH protons remains almost static (at δ 3.30).

The structure of **2**‡ consists of a co-complex of the anticipated pseudo-cubane [{Bu^{t}NP(μ-NBu^t)$_2$N(2-py)}Li$_2$] with a [(Bu^{t}N)$_2$P]Li monomer (Fig. 2). Alkali metal complexes containing $[(RN)_2P]^-$ anions have only been observed previously where sterically demanding organic substituents are present, which prevent dimerisation into $[P_2(NR)_4]^{2-}$ dianions (such as 2,4,6-Bu$^t_3$C$_6$H$_2$ or 1-adamantyl).[2b,7,10] Significantly, the steric demands of the Bu^t group alone are insufficient to prevent dimerisation in [{P$_2$(NBu^t)$_4$}Li]$_2$[2b] or its thf solvate [{P$_2$(NBu^t)$_4$}Li$_2$·2thf].[2a] Clearly, the disruption of this dimerisation and the 'trapping' of the [(Bu^{t}N)$_2$P]$^-$ anion in **2** stem from the ability of the supporting [{Bu^{t}NP(μ-NBu^t)$_2$PN(2-py)}Li$_2$] pseudo-cubane to coordinate cooperatively the cation and anion of the [(Bu^{t}N)$_2$P]Li monomer (behaviour which parallels that of the neutral [Bu^{t}NHP(μ-NBu^t)PNH(2-py)] ligand in **1**, *i.e.* the Li$^+$ cations now playing a similar role to the H atoms in anion coordination). A similar ability to form co-complexes of this type has also been observed for the Group 15 complex [{Sb(NCy)$_3$}$_2$Li$_6$][11] and the Group 16 complex [S(NBu^t)$_3$Li$_2$].[12]

Examination of the Li–N bond lengths found in the core of **2** reveals that chelation of Li(3) by the N(2-py) group plays a decisive role in stabilising the [(Bu^{t}N)$_2$P]Li monomer. In fact, bonding of the imido N centre of the N(2-py) group to the two Li$^+$ cations within the [{BuNP(μ-NBu^t)$_2$PN(2-py)}Li$_2$] fragment [N(2)–Li(1) 2.523(7), N(2)–Li(2) 2.823(7) Å] is almost completely sacrificed to allow effective coordination of Li(3) by the N(2-py) group [N(1)–Li(3) 2.003(6), N(2)–Li(3) 2.040(6) Å]. Thus, Li(1) and Li(2) only interact significantly with the terminal and μ-NBu^t groups of the [Bu^{t}NP(μ-NBu^t)$_2$PN(2-py)]$^{2-}$ dianion [N(3)–Li(1,2) mean 2.05, N(4,5)–Li(1,2) mean 2.16 Å], and these Li$^+$ cations are therefore primed (spacially and electronically) for coordination by the two N centres of the [(Bu^{t}N)$_2$P]$^-$ anion [Li(1,2)–N(7,6) 2.08 Å]. Although the P∸N bond lengths within the [(Bu^{t}N)$_2$P]$^-$ anion [P(3)–N(6) 1.613(3), P(3)–N(7) 1.606(3) Å] are similar to those found in [(RN)$_2$P]Li complexes containing bulky substituents (*ca.* 1.58–1.60 Å),[2b,7] unlike the latter the PN$_2$Li ring in **2** is non-planar as a result of the interaction of the N atoms of the anion with Li(1) and Li(2). This is a unique coordination mode for any [(RN)$_2$P]$^-$ anion.[2b,7,10,13]

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Notes and references

‡ *Crystal data*: for **1**; $C_{51}H_{99}ClLiN_{15}P_6$, M = 1150.66, rhombohedral, space group $R3$, Z = 6, $a = b$ = 22.563(2), c = 23.8030(10) Å, V = 10493.4(14) Å^3, μ(Mo-Kα) = 0.223 mm^{-1}, T = 230(2) K. Data were collected on a Nonius KappaCCD diffractometer. Of a total of 12953 reflections collected, 4938 were independent (R_{int} = 0.071). The structure was solved by direct methods and refined by full-matrix least squares on F^2. Final $R1$ = 0.066 [$I > 2\sigma(I)$] and $wr2$ = 0.232 (all data).[14] The H atoms attached to N(2) and N(3) were placed geometrically and allowed to ride during subsequent refinement. All of the Bu^t groups exhibit rotational disorder. This was modelled with 50% occupancy in each of the sites.

For **2**; $C_{25}H_{49}Li_3N_7P_3$, M = 561.44, monoclinic, space group $P2_1/n$, Z = 4, a = 17.1197(5), b = 10.5016(4), c = 18.8343(4) Å, β = 98.535(2)°, V = 3348.61(18) Å^3, μ(Mo-Kα) = 0.202 mm^{-1}, T = 180(2) K. Data were collected on a Nonius KappaCCD diffractometer. Of a total of 24258 reflections collected, 7577 were independent (R_{int} = 0.067). The structure was solved by direct methods and refined by full-matrix least squares on F^2. Final $R1$ = 0.0723 [$I > 2\sigma(I)$] and $wR2$ = 0.207 (all data).[14] The Bu^t groups attached to N(6) and N(7) exhibit disorder about the C–N bonds rotational axis. This was modelled with 50% occupancy in two sites. CCDC 155955 and 155956. See http://www.rsc.org/suppdata/cc/b0/b010093p/ for crystallographic data in .cif or other electronic format.

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