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Syntheses and structures of an unsolvated tetrakisimidophosphate $\{Li_3[P(NBu^t)_3(NSiMe_3)]\}_2$ and the face-sharing double-cubane $\{Li_2(THF)[P(O)(NBu^t)_2(NHBu^t)]\}_2$

Andrea Armstrong, Tristram Chivers,* Mark Krahn, Masood Parvez and Gabriele Schatte
Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4.
E-mail: chivers@ucalgary.ca; Fax: (403) 289-9488; Tel: (403) 220-5741

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The treatment of $Me_3SiN{=}P(NHBu^t)_3$ with three equivalents of $LiBu^n$ in toluene produces $\{Li_3[P(NBu^t)_3(NSiMe_3)]\}_2$ comprised of a Li_6N_6 cyclic ladder capped on the two hexagonal faces by μ_3-$PNSiMe_3$ groups; the corresponding reaction of $O{=}P(NHBu^t)_3$ yields the face-sharing double-cubane $\{Li_2(THF)P(O)(NBu^t)_2(NHBu^t)\}_2$ with a central Li_2O_2 ring.

Polyimido anions of the main group elements are of current interest in view of the novel cluster structures formed by their alkali metal derivatives and the versatile ligand properties of the anions themselves.[1] In addition, the chalcogen-containing systems $\{Li_2[E(NBu^t)_3]\}_2$ (E = S, Se) form highly coloured, persistent radicals upon oxidation.[2,3] Phosphorus-centred anions have attracted considerable attention.[4] Known isoelectronic analogues of common oxo-anions include $[P(NR)_3]^-$ (metaphosphates),[5] $[P(NR)_4]^{3-}$ (orthophosphates),[6] and $[HP(NR)_3]^{2-}$ (phosphites).[7] The only example of a tetrakisimidophosphate was isolated in low yield as the solvent-separated ion pair $[Li(THF)_4]^+[(THF)_2Li(\mu\text{-}NR)_2P(\mu\text{-}NR)_2Li(THF)_2]^-$ (R = naph) by the curious redox reaction between P_2I_4 and Li_2Nnaph (generated *in situ*) in THF/NEt_3.[6]

In connection with our interest in the structural consequences of the replacement of one (or more) of the imido groups in the anions of these clusters by an oxo ligand,[8] we wished to compare homoleptic $[P(NR)_4]^{3-}$ systems with the isoelectronic, heteroleptic anions $[OP(NR)_3]^{3-}$. To this end we have developed a rational synthesis of tetrakisimidophosphates from the iminophosphoranes $Me_3SiN{=}P(NHR)_3$ (**1a**, R = Bu^t, **1b**, R = Cy). We report, here, the synthesis and X-ray structures of $\{Li_3[P(NBu^t)_3(NSiMe_3)]\}_2$, **2**, the first *unsolvated* trilithium tetrakisimidophosphate and the face-sharing double-cubane $\{Li_2(THF)[P(O)(NBu^t)_2(NHBu^t)]\}_2$, **3**.

The trisamidoimidophosphoranes **1a** and **1b** are readily obtained by reaction of $Cl_3P{=}NSiMe_3$[9] with three equivalents of LiNHR. For example, **1a** is obtained in *ca.* 50% yield as an air-stable crystalline solid by this route. The reaction of **1a** with three equivalents of $LiBu^n$ in toluene at 23 °C effected trilithiation to give **2** in *ca.* 70% yield.†

An X-ray analysis of **2** revealed a centrosymmetric dimer with threefold symmetry (Fig. 1).‡ The structure is comprised of a Li_6N_6 cyclic ladder (hexagonal prism) with the two $PNSiMe_3$ groups capping the hexagonal faces in a $\mu_3(N,N',N'')$ fashion. This structural pattern is also found for $\{Li_6[Sb(NBu^t)_3]_2\}$[10] and $\{Li_3(THF)[Si(NPr^i)_3(NHPr^i)]\}$.[11] A notable feature of the structure of **2** is the perfect linearity of the *exo*-cluster PNSi arrangement. An almost linear configuration [174(2)°] has been observed for the exocyclic P=N–$SiMe_3$ linkages in the rhenium complex $(Me_3SiN)_2P(\mu\text{-}NSiMe_3)_2[\mu_3\text{-}Re(CO)_3]P(NSiMe_3)[N(SiMe_3)]_2$ in which a four-coordinate phosphorus center is surrounded by four $NSiMe_3$ groups.[12] The P=N and Si–N bond lengths of 1.550(2) and 1.659(2) Å, respectively, in **2** are typical for imidophosphoranes, *e.g.* $[Py_2P(NSiMe_3)(NHSiMe_3)]$.[13] However, the bond angle ∠PNSi is 146.89(11)° in the latter complex. Consequently, the structure of **1a** was also determined for comparison with that of **2**.‡ The value of ∠PNSi in **1a** is also 180.0°, prompting the suggestion that the linearity of the PNSi units in **1a** and **2** is determined by the steric influence of the three *tert*-butyl groups (Fig. 2). This rationale is corroborated by the observation that ∠PNSi = 131.7(2)° in the less sterically crowded **1b**.[14] The P–N bond lengths within the cluster core of **2** are *ca.* 0.03 Å longer than those in **1a**, reflecting the formal negative charge on nitrogen in **2**.

The reaction of $OP(NHBu^t)_3$ with an excess of $LiBu^n$ in THF at 23 °C produced the dilithium derivative $\{Li_2(THF)[P(O)(NBu^t)_2(NHBu^t)]\}_2$ (**3**) in 65% yield as an air- and moisture-sensitive white solid.† The ^1H NMR spectrum of **3** in d_8-THF showed two sets of NBu^t resonances at δ 1.35 and 1.20 with relative intensities 1 : 2, in addition to an NH resonance at δ 1.68, suggesting that only partial lithiation had occurred. The X-ray analysis of **2** confirmed this conclusion (Fig. 3). The structure consists of a centrosymmetric dimer in which two

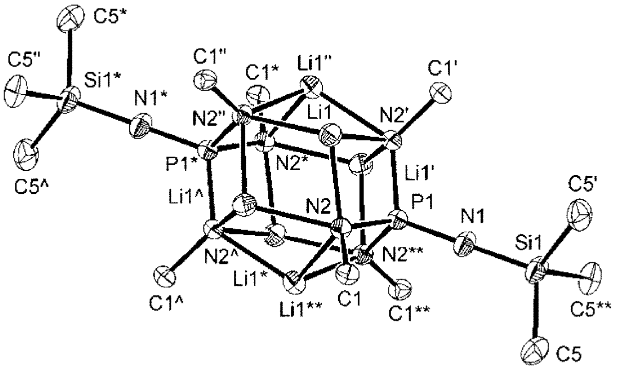

Fig. 1 Structure of **2**. For clarity only the α-carbon atoms of Bu^t groups are shown. Selected bond distances [Å] and bond angles [°]: P(1)–N(1) 1.5502(18), P(1)–N(2) 1.6980(10), Si(1)–N(1), 1.6586(18); P(1)–N(1)–Si(1) 180.0, N(1)–P(1)–N(2) 116.07(4), N(2)–P(1)–N(2) 102.14(4). Symmetry transformations used to generate equivalent atoms: * $-x, -y, -z$; ** $-y, x - y, z$; ′ $-x + y, -x, z$; ″ $y, -x + y, z$; ^ $x - y, x, -z$.

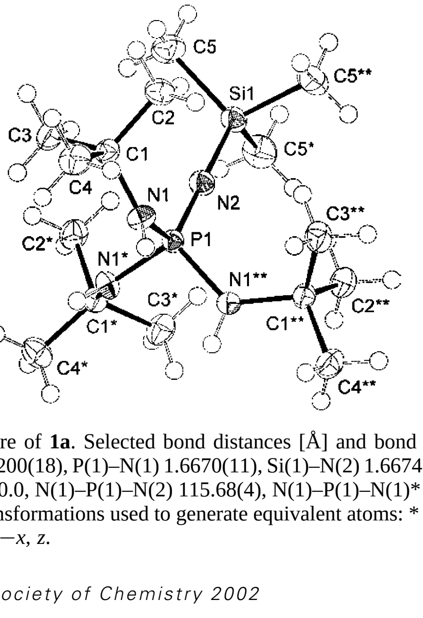

Fig. 2 Structure of **1a**. Selected bond distances [Å] and bond angles [°]: P(1)–N(2) 1.5200(18), P(1)–N(1) 1.6670(11), Si(1)–N(2) 1.6674(18); P(1)–N(2)–Si(1) 180.0, N(1)–P(1)–N(2) 115.68(4), N(1)–P(1)–N(1)* 102.61(5). Symmetry transformations used to generate equivalent atoms: * $-y, x - y, z$; ** $-x + y, -x, z$.

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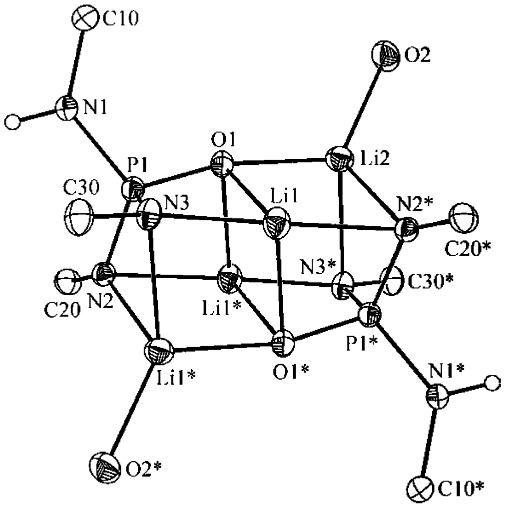

Fig. 3 Structure of **3**. For clarity only the α-carbon atoms of Bu^t groups and oxygen atoms of THF molecules are shown. Selected bond distances [Å] and bond angles [°]: P(1)–O(1) 1.5504(16), P(1)–N(1) 1.677(2), P(1)–N(2), 1.619(2), P(1)–N(3) 1.613(2), Li–O (range) 1.936(4)–2.134(4), Li–N (range) 1.925(4)–2.270(5). Symmetry transformations used to generate equivalent atoms: $*-x, -y, -z + 1$.

$[P(O)(NBu^t)_2(NHBu^t)]^{2-}$ dianions (isoelectronic with $[HPO_4]^{2-}$) are linked by four Li^+ cations. The terminal $N(H)Bu^t$ groups attached to each phosphorus atom appear to be favorably oriented for deprotonation. However, attempts to metallate **3** with excess $LiBu^n$ or KCH_2Ph in boiling THF were unsuccessful. The amido-trisimidosilicate $\{Li_3(THF)[Si(NPr^i)_3(NHPr^i)]\}$ exhibits a similar reluctance to undergo further metallation.[11] The formation of **3** also provides an interesting contrast with the reaction of $SP(NHBu^t)_3$ with two (or more) equivalents of $LiBu^n$, which results in P=S bond cleavage to give the trisimidometaphosphate $[(THF)LiP(NBu^t)_3]_2$.[15]

In summary, a rational synthesis of tetrakisimidophosphates has been developed that will facilitate investigations of the coordination chemistry of these multidentate trianions. In view of the versatile ligand properties of the isoelectronic $[PO_4]^{3-}$ trianion and the variety of coordination complexes formed by polyimido anions of antimony,[16] sulfur[17] and tellurium,[1a,18] this chemistry is likely to be extensive. In addition, solutions of **2** become deep blue upon exposure to oxygen, *cf.* the formation of radicals upon oxidation of the chalcogen-centred polyimido anions in $\{Li_2[E(NBu^t)_3]\}_2$ (E = S, Se).[2,3] EPR investigations of these phosphorus-containing radicals are in progress.

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Notes and references

† *Synthesis* of **1a**: $Cl_3PNSiMe_3$[9] (1.56 g, 6.96 mmol) was added slowly to a stirred slurry of $LiNHBu^t$ (1.65 g, 20.9 mmol) in Et_2O (25 mL) at 23 °C. After 4 h, the mixture was filtered to give a clear yellow solution. The solvent was removed *in vacuo* and the resulting residue was recrystallized from *n*-pentane (7 mL) at −35 °C to give **1a** as a pale yellow powder (1.12 g, 3.35 mmol, 48%). X-Ray quality crystals were obtained from a *n*-pentane solution at −18 °C. ^1H NMR ($CDCl_3$, 23 °C): δ 1.95 (d, $^2J(^1H-^{31}P)$ = 6.0 Hz, NH, 3H), 1.24 (s, Bu^t, 27H), −0.01 (s, $SiMe_3$, 9H). ^{13}C NMR ($CDCl_3$, 23 °C): δ 50.26 [$C(CH_3)_3$], 31.72 [$C(CH_3)_3$], 3.79 ($SiMe_3$). ^{31}P NMR ($CDCl_3$, 23 °C): δ −13.6.

Synthesis of **2**: a solution of $LiBu^n$ in hexanes (2.5 M, 4.05 mL, 10.1 mmol) was added to a solution of $(Bu^tNH)_3PNSiMe_3$ (1.12 g, 3.35 mmol) in toluene (20 mL) at 23 °C. After 4 h the solution was decanted, and the last traces of solvent were removed *in vacuo*. The residue was washed with *n*-pentane (10 mL) to give **2** as a fine white powder (0.81 g, 2.28 mmol, 68%). X-Ray quality crystals were obtained from a solution of the crude product in *n*-hexane at 23 °C. ^1H NMR (d_8-THF): δ 1.26 (s, Bu^t, 27H), −0.03 (s, $SiMe_3$, 9H). ^{13}C NMR (d_8-THF, 23 °C): δ 50.81 [$C(CH_3)_3$], 36.33 [$C(CH_3)_3$], 5.92 ($SiMe_3$). ^{31}P NMR (solid state): δ 6.7.

Synthesis of **3**: a solution of $LiBu^n$ in hexanes (2.5 M, 4.55 mL, 11.38 mmol) was added to a solution of $OP(NHBu^t)_3$[19] (1.00 g, 3.79 mmol) in THF (30 mL) at 23 °C. After 18 h the solvent was removed under vacuum and the product was washed with pentane (2 × 5 mL) to give a white powder. Recrystallization from THF/hexane at 23 °C gave X-ray quality crystals of **3** (0.854 g, 1.22 mmol, 65%). ^1H NMR (d_8-THF, 23°C): δ 3.58 (m, $[O(CH_2)_2(CH_2)_2]$), 1.74 (*m*, $[O(CH_2)_2(CH_2)_2]$), 1.68 (s, 1H, NH), 1.35 (s, 9H, Bu^t), 1.20 (s, 18H, Bu^t). $^{31}P\{^1H\}$NMR (d_8-THF, 173 K): δ 17.7 (s); (solid state): δ 18.0 (s). ^7Li NMR (C_6D_6, 23 °C): δ −2.38 (s). IR/cm^{-1}: 3388 [ν(N–H)]. EIMS (*m/z*, %): 248, 79 [$(M - Li_2O)^+$].

‡_ *Crystal data* for **1a**: $C_{15}H_{39}N_4PSi$, M = 334.56, trigonal, space group $R3$, $a = b$ = 14.7950(4), c = 16.3978(4) Å, $\alpha = \beta = 90$, γ = 120°, V = 3108.46(14) Å^3, Z = 6, D_c = 1.072 g cm^{-3}, μ(Mo-Kα) = 1.9 cm^{-1}, T = 173 K. Crystal dimensions 0.25 × 0.25 × 0.20 mm. Data collection, structural solution and refinement were as described for **2**. R_1 = 0.045 [$I > 2\sigma(I)$] and wR_2 = 0.108 (all data).

_*Crystal data* for **2**: $C_{15}H_{36}Li_3N_4PSi$, M = 352.36, trigonal, space group $R3$, $a = b$ = 14.8927(4), c = 16.0178(6) Å, $\alpha = \beta = 90$, γ = 120°, V = 3076.6(2) Å^3, Z = 6, D_c = 1.141 g cm^{-3}, μ(Mo-Kα) = 1.95 cm^{-1}. Crystal dimensions 0.25 × 0.20 × 0.15 mm. Data were collected at 173 K on a Nonius Kappa CCD diffractometer and corrected for absorption. The structure was solved by direct methods (SIR 92), expanded using Fourier techniques (DIRDIF 94) and refined anisotropically using SHELX97-2. The final agreement factors were R_1 = 0.038 [$I > 2\sigma(I)$] and wR_2 = 0.122 (all data).

_*Crystal data* for **3**: $C_{32}H_{72}Li_4N_6O_4P_2$, M = 694.66, triclinic, space group $P1$, a = 10.3775(15), b = 10.5873(16), c = 11.5111(17) Å, α = 103.906(2), β = 92.088(2), γ = 119.424(2)°, V = 1051.3(3) Å^3, Z = 1, D_c = 1.097 g cm^{-3}, μ(Mo-Kα) = 1.42 cm^{-1}. Data were collected at 193 K on a Bruker AXS P4/RA/SMART 1000 CCD diffractometer on a crystal (0.43 × 0.40 × 0.17 mm) coated with Paratone oil. The structure was solved by direct methods (SHELXS-97) and the non-hydrogen atoms were refined anisotropically using data that were corrected for absorption (SHELXL97-2). The final agreement factors were R_1 = 0.0552 [$I > 2\sigma(I)$], wR_2 = 0.1534 (all data).

CCDC reference numbers 190648, 190649 and 190650. See http://www.rsc.org/suppdata/cc/b2/b207197e/ for crystallographic data in CIF or other electronic format.

1 (*a*) For recent reviews, see: T. Chivers and J. K. Brask, *Angew. Chem., Int. Ed.*, 2001, **40**, 3960; (*b*) G. M. Aspinall, M. C. Copsey, A. P. Leedham and C. A. Russell, *Coord. Chem. Rev.*, 2002, **227**, 217.

2 (*a*) R. Fleischer, S. Freitag, F. Pauer and D. Stalke, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 204; (*b*) R. Fleischer, S. Freitag and D. Stalke, *J. Chem. Soc., Dalton Trans.*, 1998, 193.

3 (*a*) T. Chivers, M. Parvez and G. Schatte, *Inorg. Chem.*, 1996, **35**, 4094; (*b*) J. K. Brask, T. Chivers, B. McGarvey, G. Schatte, R. Sung and R. T. Boeré, *Inorg. Chem.*, 1998, **37**, 4633.

4 A. Steiner, S. Zacchini and P. I. Richards, *Coord. Chem. Rev.*, 2002, **227**, 193.

5 E. Niecke, M. Frost, M. Nieger, V. von der Gönna, A. Ruban and W. W. Schoeller, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2111.

6 P. R. Raithby, C. A. Russell, A. Steiner and D. S. Wright, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 649.

7 L. T. Burke, E. H-Freire, R. Holland, J. C. Jeffery, A. P. Leedham, C. A. Russell, A. Steiner and A. Zagorski, *Chem. Commun.*, 2000, 1769.

8 J. K. Brask, T. Chivers, M. Parvez and G. Schatte, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1986.

9 B. Wang, E. Rivard and I. Manners, *Inorg. Chem.*, 2002, **41**, 1690.

10 M. A. Beswick, N. Choi, C. N. Harmer, A. D. Hopkins, M. McPartlin, M. A. Paver, P. R. Raithby, A. Steiner, M. Tombul and D. S. Wright, *Inorg. Chem.*, 1998, **37**, 2177.

11 J. K. Brask, T. Chivers and M. Parvez, *Inorg. Chem.*, 2000, **39**, 2505.

12 O. J. Scherer, J. Kerth and M. L. Ziegler, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 503.

13 S. Wingerter, M. Pfeiffer, A. Murso, C. Lustig, T. Stey, V. Chandrasekhar and D. Stalke, *J. Am. Chem. Soc.*, 2001, **123**, 1381.

14 A. Armstrong, T. Chivers and M. Parvez, unpublished results.

15 T. Chivers, M. Krahn, M. Parvez and G. Schatte, *Chem. Commun.*, 2001, 1922.

16 M. A. Beswick and D. S. Wright, *Coord. Chem. Rev.*, 1998, **176**, 373.

17 R. Fleischer and D. Stalke, *Coord. Chem. Rev.*, 1998, **176**, 431.

18 T. Chivers, *Can. J. Chem.*, 2001, **79**, 1841.

19 R. R. Holmes and J. A. Forstner, *Inorg. Chem.*, 1963, **2**, 380.