

A novel type of phosphide: synthesis and X-ray crystal structure analysis of $(t\text{Bu}_3\text{Si})_3\text{P}_4\text{Li}_3$

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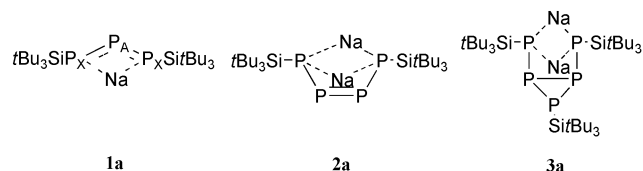
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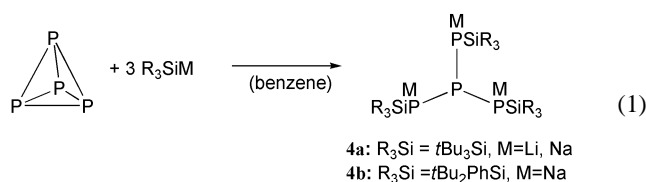
The tetraphosphides $(t\text{Bu}_3\text{Si})_3\text{P}_4\text{M}_3$ ($\text{M} = \text{Li}, \text{Na}$) and $(t\text{Bu}_2\text{PhSi})_3\text{P}_4\text{Na}_3$ have been synthesized in high yield from the reaction of 3 equivalents of the silanides $t\text{Bu}_3\text{SiM}$ ($\text{M} = \text{Li}, \text{Na}$) and $t\text{Bu}_2\text{PhSiNa}$ with P_4 in benzene. $(t\text{Bu}_3\text{Si})_3\text{P}_4\text{M}_3$ ($\text{M} = \text{Li}, \text{Na}$) are transformed into the unsaturated triphosphides $(t\text{Bu}_3\text{Si})_2\text{P}_3\text{M}$ ($\text{M} = \text{Li}, \text{Na}$) and $t\text{Bu}_3\text{SiPM}_2$ in tetrahydrofuran at ambient temperature.

While alkali phosphides P_nM_x of the zintl-type are today a well-established class of main-group element clusters, only a limited number of molecular alkali phosphides $\text{R}_m\text{P}_n\text{M}_x$ have been structurally characterized by X-ray crystallography. In contrast to the nitrogen compounds N_3H_3 and N_4H_4 , the related phosphanes P_3H_3 and P_4H_4 possess cyclic structures without



double bonds.

The molecular structure of the triphosphide $(t\text{Bu}_3\text{Si})_2\text{P}_3\text{Na}$ **1a** shows short P–P bonds and almost planar P_X atoms (P–P distance: 2.10 Å; sum of the angles on P_X : 358.9°).¹ Contrary to **1a** and **2a**, the homologous pentaphosphide **3a** $(t\text{Bu}_3\text{Si})_3\text{P}_5\text{Na}_2$ features a three-membered ring and no double bond.² The sodium tetraphosphide **2a** $(t\text{Bu}_3\text{Si})_2\text{P}_4\text{Na}_2$ has been prepared from the reaction of P_4 with $t\text{Bu}_3\text{SiNa}$ in a molar ratio of 1:2.³



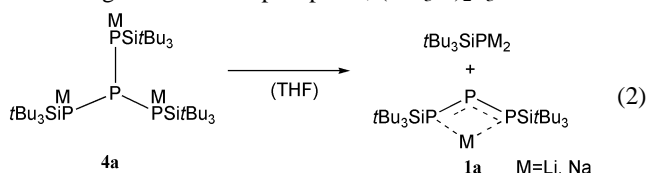
Herein we report on the reaction of P_4 with the silanides $t\text{Bu}_3\text{SiM}$ ($\text{M} = \text{Li}, \text{Na}$) and $t\text{Bu}_2\text{PhSiNa}$ in a 1:3 stoichiometry, which led to the tetraphosphides $(t\text{Bu}_3\text{Si})_3\text{P}_4\text{M}_3$ ($\text{M} = \text{Li}, \text{Na}$) and $(t\text{Bu}_2\text{PhSi})_3\text{P}_4\text{Na}_3$.[†]

According to the ^{31}P NMR spectra of the reaction mixtures, the tetraphosphides are formed in high yield. Solutions of **4a** ($\text{M} = \text{Li}, \text{Na}$) and **4b** in donor solvents like THF or benzene show in ^{31}P NMR spectra a similar signal pattern but the chemical shifts depend strongly on the solvent used. A similar observation had been made in the case of the monophosphides R_3SiPM_2 ($\text{M} = \text{Li}, \text{R}_3\text{Si} = i\text{Pr}_2\text{MesSi}, \text{Me}_2(i\text{PrMe}_2\text{C})\text{Si}, t\text{Bu}_3\text{Si}$; $\text{M} = \text{Na}, \text{R}_3\text{Si} = t\text{Bu}_3\text{Si}$).⁴

The ^{31}P NMR spectra of **4a** ($\text{M} = \text{Li}, \text{Na}$) and **4b** exhibit AX_3 spin systems with large coupling constants (**4a** (Li): $^1J(\text{PP}) = 264.3$ Hz; **4a** (Na): $^1J(\text{PP}) = 267.6$ Hz; **4b**: $^1J(\text{PP}) = 258.9$ Hz). The spectroscopic data for the tetraphosphides **4a** ($\text{M} = \text{Li}, \text{Na}$) and **4b** are consistent with their proposed structures. The most remarkable difference between the phosphide **4a** (Li) on the one

hand and the phosphide **4a** (Na) on the other hand is manifested in an upfield shift of the ^{31}P resonance of P_X in **4a** (Li).

Surprisingly, after tetrahydrofuran solutions of **4a** (Li) had been stored at ambient temperature for one week, the ^{31}P NMR spectrum showed two signals of an AX_2 spin system in the range typical of unsaturated two-coordinated phosphorus atoms and the signal of $t\text{Bu}_3\text{SiPLi}_2$. The chemical shift values for the AX_2 system as well as the large coupling constant ($^1J(\text{PP}) = 442.0$ Hz) are rather similar to the ^{31}P NMR data recorded for the analogous sodium triphosphide, $(t\text{Bu}_3\text{Si})_2\text{P}_3\text{Na}$.¹



By contrast when **4b** had been thermolyzed in tetrahydrofuran, the pentaphosphide $(t\text{Bu}_2\text{PhSi})_3\text{P}_5\text{Na}_2$ was formed rather than $(t\text{Bu}_2\text{PhSi})_2\text{P}_3\text{Na}$. Contrary to the triphosphide $(t\text{Bu}_3\text{Si})_2\text{P}_3\text{M}$ ($\text{M} = \text{Li}, \text{Na}$), the related triphosphide $(t\text{Bu}_2\text{PhSi})_2\text{P}_3\text{Na}$ is unknown up to now.⁵

X-ray quality crystals of **4a** (Li) (trigonal space group $P\bar{3}1c$) and **4a** (Li)· (C_6H_6) (monoclinic space group $P2_1/n$) were grown from benzene at ambient temperature and at 6 °C, respectively. X-ray crystal structure analysis of $(t\text{Bu}_3\text{Si})_3\text{P}_4\text{Li}_3$ has been carried out and the molecular structure of **4a** (Li) is depicted in Figure 1[†] (**4a** (Li)· (C_6H_6) possesses the same core structure). Polyhedral compounds as **4a** (Li) consisting of 14 atoms are very rare. The LiP-cluster **4a** (Li) can be divided into three

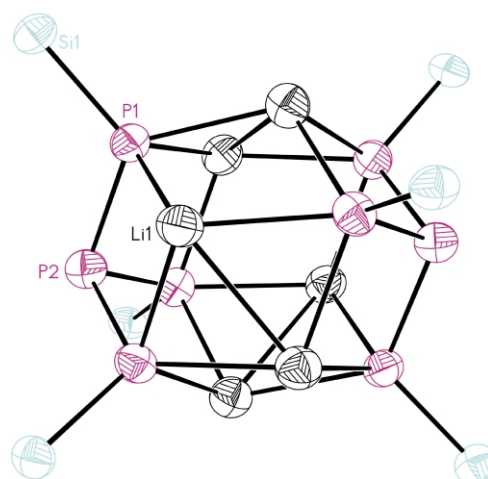


Fig. 1 Thermal ellipsoid plot of **4a** (Li) showing the atom numbering scheme. The displacement ellipsoids are drawn at the 50% probability level. $t\text{Bu}$ groups have been omitted for clarity. Selected bond lengths [Å] and angles [°]: P–Si 2.2700(12) [average], Si–C 1.952(5) [average], P–P–P 101.05(6) [average].

moieties: (i) a trigonal-antiprismatic Li₆ core which is capped by (ii) two (tBu₃Si)₃P₄ moieties.

Structural studies of alkali silylamides have shown that an array of 6 alkali metal ions is preferred.⁶ In lithiated silylamides⁷ six lithium atoms are arranged in a distorted trigonal-antiprismatic fashion like in **4a** (Li). **4a** (Li) features for every Li atom three P–Li contacts (P–Li distance: 2.508(6) Å, average). Apart from these P atoms, the Li atoms are coordinated by three other Li atoms like in the molecular structure of the silylphosphides EtSi[LiP(SiPr₃)₃].^{4a} The central P atom has a pyramidal geometry similar to that in the phosphanes P(PR₂)₃ (PR₂ = P(COPh)₂, P(SiMe₃)Me, PC₄Me₄)⁸ and MeC(CH₂MPPPh₃)₃P⁹ but different to the trigonal planar central P atom in P(PtBu₂)₃.¹⁰ The P–P bonds have an average length of 2.2826(12) Å. This distance is longer than the sum of the atomic radii (sum of the atomic radii: 2.20 Å). The Li···Li contacts in **4a** (Li) (Li···Li distances: 2.824(12) Å, average) are longer than the corresponding bonds in the lithiated silylamides.⁷

Notes and references

† *General Procedures.* All experiments were carried out under dry argon with strict exclusion of air and moisture using standard Schlenk techniques. tBu₃SiLi,¹¹ tBu₃SiNa,¹¹ and tBu₃PhSiNa¹² were prepared according to literature procedures.

Abbreviations: s = singlet; d = doublet; t = triplet; q = quartet; mult = multiplet; br = broad; m = meta; o = ortho; p = para.

Synthesis of (tBu₃Si)₃P₄Li₃ 4a (Li). tBu₃SiLi (0.329 g, 1.60 mmol) in benzene (2.0 mL) was added to freshly sublimed P₄ (0.060 g, 0.484 mmol) at ambient temperature and stirred for 2 h. X-ray quality crystals of **4a** (Li)·(C₆H₆)¹³ were obtained after the reaction mixture had been concentrated to a volume of 1 mL in vacuo and kept at 6 °C for 1 d. Yield: 0.198 g (55%) (spectroscopical yield: 83%). After repeating the reaction under the same conditions solvent-free X-ray quality crystals of **4a** (Li) were obtained from benzene at ambient temperature. Selected data for **4a** (Li): ¹H NMR (C₆D₆, internal TMS): δ 1.34 (br, 81H tBu). ¹³C{¹H}NMR (C₆D₆, internal TMS): δ 25.7 (br, CMe₃), 33.1 (br, CMe₃). ³¹P{¹H}NMR (C₆D₆, external H₃PO₄): δ 1.9 (q, ¹J_{PP} = 264.3 Hz; P_A), –186.1 (d, ¹J_{PP} = 264.3 Hz; P_X), δ 27.2 (dd, ¹J_{SiP} = 51.7 Hz, ²J_{SiP} = 8.0 Hz; br, SiPrBu₃). ⁷Li NMR (C₆D₆, external LiCl): δ 4.22 (br). Anal. Calcd for C₇₂H₁₆₂P₈Li₆Si₆ (1486.03): C, 58.19; H, 10.99. Found: C, 56.39; H, 10.67.

Synthesis of (tBu₃Si)₃P₄Na₃ 4a (Na). After addition of tBu₃SiNa(THF)₂ (0.226 g, 0.616 mmol) in benzene (1.5 mL) to freshly sublimed P₄ (0.024 g, 0.190 mmol), the ³¹P NMR spectrum of the resulting clear solution gave evidence for the formation of (tBu₃Si)₃P₄Na₃. Spectroscopical yield: 61%. Selected data for **4a** (Na): ¹H NMR (C₆D₆, internal TMS): δ 1.35 (br, 81H tBu). ¹³C{¹H}NMR (C₆D₆, internal TMS): δ 25.2 (br; CMe₃), 33.5 (br; CMe₃). ³¹P{¹H}NMR (d₈-toluene, external H₃PO₄): δ –11.3 (q, ¹J_{PP} = 268.7 Hz; P_A), –100.7 (d; ¹J_{PP} = 268.7 Hz; P_X). ³¹P{¹H}NMR (C₆D₆, external H₃PO₄): δ –11.0 (q; ¹J_{PP} = 267.6 Hz; P_A), –100.0 (d, ¹J_{PP} = 267.6 Hz; P_X).

Synthesis of (tBu₂PhSi)₃P₄Na₃ 4b (Na). After addition of tBu₂PhSiNa(THF) (0.268 g, 0.853 mmol) in toluene (1.0 mL) to freshly sublimed P₄ (0.034 g, 0.274 mmol), the ³¹P NMR spectrum of the solution gave evidence for the formation of (tBu₂PhSi)₃P₄Na₃. Spectroscopical yield: 83%. Selected data for **4b** (Na): ¹H NMR (C₆D₆, internal TMS): δ 1.26 (br, 54H; tBu), 7.22 (mult, 9H; o/P–Ph), 7.54 (mult, 6H; m–Ph). ¹³C{¹H}NMR (C₆D₆, internal TMS): δ 22.5 (br, CMe₃), 32.6 (br; CMe₃), 127.7 (mult, m–Ph), 129.0 (mult, P–Ph), 135.5 (mult; o–Ph). ³¹P{¹H}NMR (d₈-toluene, external H₃PO₄): δ –34.4 (q, ¹J_{PP} = 268.7 Hz; P_A), –110.3 (d, ¹J_{PP} = 274.2 Hz; P_X). ³¹P{¹H}NMR (C₆D₆, external H₃PO₄): δ –31.5 (q, ¹J_{PP} = 258.9 Hz; P_A), –108.5 (d, ¹J_{PP} = 258.9 Hz; P_X). ²⁹Si{¹H}NMR (C₆D₆, external TMS): δ –13.4 (br).

Thermolysis of (tBu₃Si)₃P₄Li₃ 4a (Li). After a solution of **4a** (Li) (0.2 mmol) in d₈-THF (0.6 mL) had been stored for one week at ambient temperature in a sealed NMR tube, the resonances of **4a** (Li) were no longer observable in the ³¹P NMR spectrum. New signals appeared instead which can be assigned to the compounds (tBu₃Si)₂P₃Li and tBu₃SiPLi₂⁴ (60 % of P atoms).

(tBu₃Si)₂P₃Li: ¹H NMR (d₈-THF, internal TMS): δ 1.06 (br, 54H; tBu). ¹³C{¹H}NMR (d₈-THF, internal TMS): δ 25.3 (s; CMe₃), δ 33.6 (s; CMe₃). ³¹P{¹H}NMR (d₈-THF, external H₃PO₄): δ 729.8 (t, ¹J_{PP} = 442.0 Hz; P_A), 226.6 (d, ¹J_{PP} = 442.0 Hz; P_X). ²⁹Si{¹H}NMR (d₈-THF, external TMS): δ 16.8 (td, ¹J_{SiP} + ³J_{SiP} = 64.1 Hz, ²J_{SiP} = 10.0 Hz; SiPrBu₃). ⁷Li NMR (d₈-

THF, external LiCl): δ 0.26. tBu₃SiPLi₂: ³¹P{¹H}NMR (d₈-THF, external H₃PO₄): δ –395.7 (br). ⁷Li NMR (d₈-THF, external LiCl): δ 5.0 (br).

Thermolysis of (tBu₃Si)₃P₄Na₃ 4a (Na). After a solution of **4a** (Na) (0.1 mmol) in d₈-THF (0.6 mL) had been stored for one week at ambient temperature in a sealed NMR tube, the resonances of **4a** (Na) were no longer observable in the ³¹P NMR spectrum. New signals appeared instead which can be assigned to the compounds (tBu₃Si)₂P₃Na¹ and tBu₃SiPNa₂⁴ (65% of P atoms).

(tBu₃Si)₂P₃Na: ³¹P{¹H}NMR (d₈-THF, external H₃PO₄): δ 734.0 (t; ¹J_{PP} = 552.7 Hz; P_A), 214.1 (d; ¹J_{PP} = 552.7 Hz; P_X). ²⁹Si{¹H}NMR (d₈-THF, external TMS): δ 18.3 (td; ¹J_{SiP} + ³J_{SiP} = 47.0 Hz, ²J_{SiP} = 7.0 Hz; 2 SiPrBu₃). tBu₃SiPNa₂: ³¹P{¹H}NMR (d₈-THF, external H₃PO₄): δ –404.4.

Thermolysis of (tBu₂PhSi)₃P₄Na₃ 4b (Na). After storing a solution of 0.1 mmol **4b** (Na) in 0.6 mL d₈-THF for one week at ambient temperature the ³¹P NMR spectrum shows the signals of (tBu₂PhSi)₃P₃Na₂⁵ and tBu₂PhSiPNa₂⁵ as main products (48% of P atoms), while the signals of **4b** (Na) disappeared. (tBu₂PhSi)₃P₃Na₂: ¹H NMR (d₈-THF, internal TMS): δ 1.06 (br, 36H tBu), 1.09 (br, 18H tBu), 7.20 (m, o/p–H), 7.51 (m, m–H). ³¹P{¹H}NMR (d₈-THF, external H₃PO₄): δ –89.8 (m), –181.3 (m), –243.1 (m). ²⁹Si{¹H}NMR (d₈-THF, external TMS): δ 24.6 (pseudo-tt, 2 SiPhrBu₂), 8.2 (d, ¹J_{SiP} = 104.2 Hz; SiPhrBu₂). tBu₂PhSiPNa₂: ¹H NMR (C₆D₆, internal TMS): δ 1.01 (s; 18H tBu), 7.18 (m; o/p–H), 7.58 (m, m–H). ³¹P{¹H}NMR (d₈-THF, external H₃PO₄): δ –328.1 (br). ²⁹Si{¹H}NMR (d₈-THF, external TMS): δ 28.4 (d, ¹J_{SiP} = 58.4 Hz; SiPhrBu₂).

‡ *Crystal data for 4a (Li).* C₇₂H₁₆₂Li₆P₈Si₆, trigonal space group P-31c, a = b = 14.2685(10) Å, c = 26.965(2) Å, γ = 120°, V = 4754.3(6) Å³, T = 173(2) K, Z = 2, 14364 reflections measured, 2835 unique (R_{int} = 0.0971) which were used in all calculations. The final wR(F²) was 0.1021 (all data). Crystal data for **4a** (Li)·(C₆H₆) see ref. 13 CCDC reference number: 202252. See <http://www.rsc.org/suppdata/cc/b1/b210984k/> for crystallographic data in cif or electronic format.

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- 13 *Crystal data for 4a (Li)·(C₆H₆).* C₈₁H₁₇₁Li₆P₈Si₆, monoclinic space group P2₁/n, a = 22.146(4) Å, b = 17.600(2) Å, c = 27.087(7) Å, β = 90.046(17)°, V = 10558(4) Å³, T = 173(2) K, Z = 4, 40522 reflections measured, 17323 unique (R_{int} = 0.2602) which were used in all calculations. The crystal was a small not very well diffracting needle. Due to this fact the R_{int} value is relatively high and only a small part of the reflections can be regarded as observed. We decided therefore to repeat the synthesis and to collect the data of a new crystal (**4a**(Li)). The final wR(F²) was 0.0981 (all data). CCDC reference number: 191269.