Crystal Structure of Solvent-free Hexameric $LiP(SiMe_3)_2$: a Ladder with Six Li–P Steps

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The crystal structure of solvent free $LiP(SiMe_3)_2$ shows a hexameric arrangement, with four five-coordinate and two four-coordinate P atoms and four three-coordinate and two two-coordinate Li atoms; the Li–P distances range from 2.38(1) to 2.63(1) Å.

Lithium phosphides $LiPR_2$ are of considerable importance as PR_2^- transfer reagents as well as being of structural and theoretical interest.[1] We have previously reported the crystal structures of two solvated $LiP(SiMe_3)_2$ compounds, the dimeric $Li(thf)_2P(SiMe_3)_2$ **1** and the tetrameric $Li(thf)_{0.5}P(SiMe_3)_2$ **2** (thf = tetrahydrofuran), as well as the spectroscopic properties of monomeric $Li(pmdeta)P(SiMe_3)_2$ (pmdeta = *N,N,N′,N′,N″*-pentamethyltriethylenediamine), and showed how the structures of the $Li/P(SiMe_3)_2$ combination depends on the nature and number of donor molecules.[2]

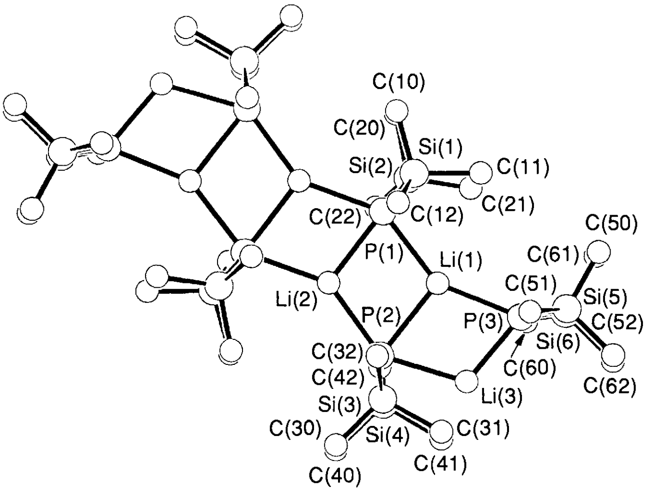

Fig. 1 Hexameric $LiP(SiMe_3)_2$ **3** showing the atom numbering scheme employed. Selected bond lengths and angles are as follows: P(1)–Li(2′) 2.52(1), Li(1)–P(1) 2.52(1), Li(2)–P(1) 2.56(1), Li(2)–P(2) 2.513(9), Li(1)–P(2) 2.63(1), Li(1)–P(3) 2.51(1), Li(3)–P(2) 2.52(1), Li(3)–P(3) 2.38(1), P(1)–Si(1) 2.214(3), P(1)–Si(2) 2.207(4), P(2)–Si(3) 2.212(3), P(2)–Si(4) 2.221(3), P(3)–Si(5) 2.210(3), P(3)–Si(6) 2.210(4) Å, P(2)–Li(3)–P(3) 113.8(4), Li(3)–P(2)–Li(1) 68.0(3), Li(3)–P(2)–Li(2) 141.7(1), Li(1)–P(2)–Li(2) 73.8(3), Si(3)–P(2)–Si(4) 108.6(1), Li(3)–P(3)–Li(1) 72.0(4), Si(5)–P(3)–Si(6) 108.2(1), P(3)–Li(1)–P(2) 106.2(4), P(3)–Li(1)–P(1) 149.3(4), P(2)–Li(1)–P(1) 104.5(4), P(2)–Li(2)–P(1′) 145.1(4), P(2)–Li(2)–P(1) 106.8(4), P(1)–Li(2)–P(1′) 108.1(3), Li(1)–P(1)–Li(2) 74.8(3), Li(1)–P(1)–Li(2′) 146.8(3), Li(2)–P(1)–Li(2′) 71.9(3), Si(1)–P(1)–Si(2) 107.8(1)°.

We now conclude this series of structures of $LiP(SiMe_3)_2$ compounds with the crystal structure of solvent-free $LiP(SiMe_3)_2$ **3**, which was obtained from $HP(SiMe_3)_2$ and $LiBu^n$ in cyclopentane.[3]† Colourless single crystals were grown by cooling a saturated hot toluene solution to ambient temperature.

The structure (Fig. 1)‡ consists of a hexameric arrangement of four five-coordinate and two four-coordinate P atoms, and four three-coordinate and two two-coordinate Li atoms. No interactions between the Li and P atoms of neighbouring hexameric units are observed (shortest Li···P 6.6 Å). Like **1** and **2**, $[LiP(SiMe_3)_2]_6$ **3** lies on a crystallographic inversion centre, the $[LiP]_n$ (n = 2, 4, 6) framework atoms being coplanar (within 0.04 Å in **3**).

Attention has been drawn to the 'laddering principle' in lithium amide[4] and lithium thiolate[5] chemistry, which seems to be also applicable to lithium phosphide chemistry. Thus, the ladder with two Li–P steps in **1** is extended to a four-step ladder in **2**, and finally a six-step ladder in **3**. Clearly, decreasing the number of donor molecules results in increased aggregation.

In **1**, two equal Li–P distances are observed [2.62(2) Å],[2] while in **2** there are four different Li–P distances [2.44(2) to 2.64(2) Å],[2] and eight different ones in **3** [2.38(1) to 2.63(1) Å]. The 'outer' framework of the Li_6P_6 ladder in **3** exhibits equal Li–P distances [2.51(1), 2.52(1) Å], whereas those of the steps of the ladder differ markedly [2.38(1) Li(3)–P(3), 2.63(1) Li(1)–P(2), 2.56(1) Å Li(2)–P(1)]. The Li(3)–P(3) distance of 2.38(1) Å is the shortest observed to date in a lithium phosphide[6] and is probably due to the fact that the Li atom Li(3) is only two-coordinate with a P(2)–Li(3)–P(3) angle of 113.8(4)°, instead of the 180° that is expected but only sometimes observed for two-coordinate Li,[1] and is thus sterically unshielded. The only other structurally characterised solvent-free lithium phosphide is the dimeric $LiP\{CH(SiMe_3)_2\}_2$,[7] in which the sterically demanding $CH(SiMe_3)_2$ ligands prevent both coordination of monodentate donor molecules and oligomerisation. Here, the P–Li–P angles of 107.5(3) and 108.1(3)° are also much smaller than the expected value of 180°. While $[LiP\{CH(SiMe_3)_2\}_2]_2$ can be synthesised in diethyl ether solution,[7] **3** dissolves rapidly in thf with formation of **1**.

Li(1), Li(2) show a distorted trigonal planar geometry [internal bond angles P–Li–P ranging from 104.5(4) to 108.1(3)°, external 145.1(4) and 149.3(4)°], while Li(3) has a much larger internal bond angle of 113.8(4)°. P(1) exhibits a distorted trigonal bipyramidal geometry, while that of the four-coordinate P(3) is distorted tetrahedral. P(2), which is adjacent to the two-coordinate Li(3), has a distorted environment, with two $SiMe_3$ groups [Si(4)–C(41) and Si(3)–C(31)] pointing towards Li(3). The displacement of the $SiMe_3$ groups of P(2) towards Li(3) is clearly due to steric interaction with the $SiMe_3$ groups of P(1), as is shown by molecular models of the hexamer with idealised bond angles. This results in interaction of the hydrogen atoms H(312), H(313), H(412), and H(413) with Li(3) (Li···H 2.32 Å). In lithium alkyls, such as $LiBu^n$ and higher alkyls, Li···H–C bridges are assumed to stabilise the oligomeric structure.[8] A crystallographically characterised example is $2LiBr{\cdot}2C_3H_5Li{\cdot}4OEt_2$, which has a tetrahedral arrangement of four $Li(OEt_2)$ units, with Br^- and $C_3H_5^-$ located above the triangular faces, in which short Li···H distances are observed (2.16, 2.26 Å).[9] Here, as well as in **3**, the Li–H interaction is comparable to that found in $LiBMe_4$.[10]

Cumulative interaction between $SiMe_3$ groups in the hexamer could lead to shielding of Li(3) by the $SiMe_3$ ligands of the neighbouring P atom P(2), which would explain why **3** forms isolated hexameric units rather than infinite polymeric chains.

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† Yield 72%; satisfactory elementary analyses were obtained.

‡ *Crystal data*: **3** $C_{36}H_{108}Li_6P_6Si_{12}$, M_r = 1105.78, triclinic, space group $P\bar{1}$ (No. 2), a = 9.837(6), b = 12.825(10), c = 16.660(12) Å, α = 95.92(6), β = 101.67(5), γ = 112.05(5)°, U = 1870 Å^3, Z = 1, D_c = 0.98 g cm^{-3}, μ = 3.14 cm^{-1}, 5831 independent reflections, $2\theta_{max.}$ = 56°, $F(000)$ = 600, R = 0.081, R_w = 0.072 (Mo-Kα radiation, λ = 0.71069, T = −67 °C). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors Issue No. 1.