

## Synthesis, Structure, and Reactivity of a $\mu$ -Bis(dialkylphosphido)-dilithium $[\text{Li}(\mu\text{-PR}_2)]_2$ $[\text{R} = \text{CH}(\text{SiMe}_3)_2]$ †

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Reaction of lithium shot with  $\text{PClR}_2$  [ $\text{R} = \text{CH}(\text{SiMe}_3)_2$ ] in  $\text{OEt}_2$  at 25 °C affords the title phosphide  $[\text{Li}(\mu\text{-PR}_2)]_2$ , (**1**), which in  $\text{C}_6\text{D}_6$  shows a triplet  $^7\text{Li}$  n.m.r. signal, and reacts as (a) a Lewis acid to afford the monomeric  $\text{Li}(\text{PR}_2)(\text{NMe}_2[\text{CH}_2]_2\text{NMe}_2)$ , (**2**), (which in  $\text{C}_6\text{D}_6$  shows a doublet  $^7\text{Li}$  n.m.r. signal), (b) a  $\bar{\text{P}}\text{R}_2$  transfer agent to yield  $\text{PR}_2\text{X}$  ( $\text{X} = \text{H}$  or  $\text{Me}$ ) with  $\text{XCl}$ , or (c) a reducing agent to furnish  $\bar{\text{P}}\text{R}_2$  with  $\text{Bu}^t\text{Cl}$  or  $\text{SnCl}_2$ ; compound (**1**) has a planar  $\text{Li}_2\text{P}_2$  ring with average Li–P and P–C distances of 2.473(10) and 1.892(7) Å, and mean LiPLi, PLiP, and CPC angles of 72.2(3), 107.8(3), and 102.0(5)°.

Organic lithium compounds  $(\text{LiX})_x$ , in which  $\text{X}^-$  is a monodentate carbon-,<sup>1</sup> nitrogen-,<sup>2</sup> or oxygen-<sup>3</sup> centred ligand, display a wide variety of structures and reactivity. They are of considerable theoretical significance<sup>4</sup> and also of practical value as key  $\text{X}^-$  transfer agents, for example to transition-metal (M) sites to yield compounds of type  $[\text{M}(\text{X})_m\text{L}_n]$ .

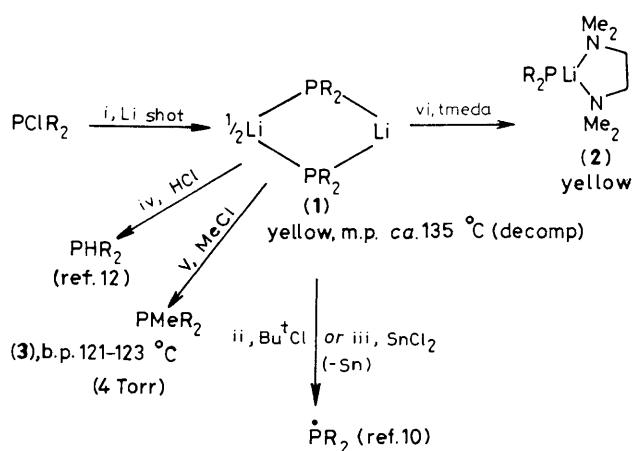
Phosphidolithium compounds  $\text{Li}(\text{PR}_2)_x\text{L}_y$  (L is a neutral ligand) have received little attention. Only two compounds,  $[\text{Li}(\text{P}^t\text{Bu}_2)(\text{thf})_3]_4$  (thf = tetrahydrofuran)<sup>5</sup> and  $[\text{Li}(12\text{-crown-4})_2][\text{PPh}_2]$ ,<sup>6</sup> are fully (X-ray) structurally characterised. Another,  $\text{Li}(\text{PPh}_2)(\text{OEt}_2)_n$ , was assigned a dimeric  $(\mu\text{-PPh}_2)_2$  structure in  $\text{OEt}_2$  at 200 K, on the basis of the 1 : 2 : 1 triplet  $^7\text{Li}$  n.m.r. signal,  $J(^7\text{Li}\text{-}^{31}\text{P})$  45 Hz,<sup>7</sup> and  $\text{LiPPh}_2$  in thf was believed to be a tetramer from  $T_1\text{-}^{13}\text{C}$  n.m.r. data.<sup>8</sup> There is much current activity in transition-metal phosphido com-

plexes, using ligands such as  $\bar{\text{P}}\text{Bu}^t$ ,<sup>5</sup> and  $\bar{\text{P}}\text{R}_2$  [ $\text{R} = \text{CH}(\text{SiMe}_3)_2$ ];<sup>9</sup> the latter has been accessible either through the stable  $\text{P}^{\text{II}}$  compound  $\bar{\text{P}}\text{R}_2$ <sup>10</sup> or its dimer and thence  $\text{NaPR}_2$ .<sup>9</sup>

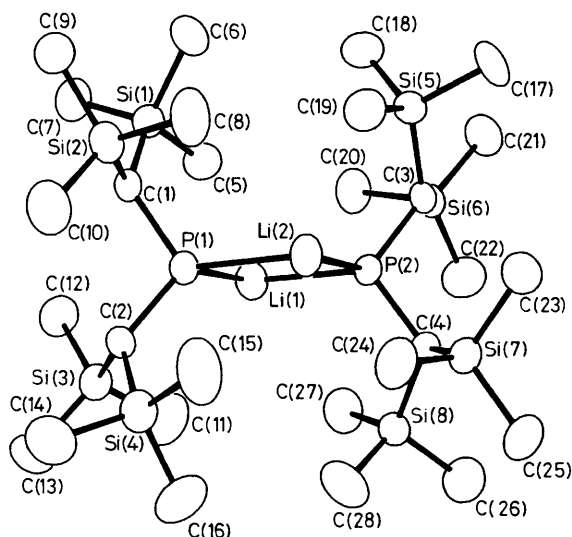
We now report on (a) the synthesis (i in Scheme 1) of the first isolated uncomplexed phosphidolithium,  $[\text{Li}(\mu\text{-PR}_2)]_2$ , (**1**); (b) X-ray data for (**1**), which reveal that it is the first among crystalline  $(\text{LiX})_x$  compounds to have the  $[\text{Li}(\mu\text{-X})_2]$  structure [although for  $\text{X} = \text{N}(\text{SiMe}_3)_2$ , there is a precedent, in the gaseous amide<sup>2</sup>]; (c) the powerful reducing properties of (**1**) (ii and iii, Scheme 1), which are unprecedented in  $(\text{LiX})_x$  chemistry;<sup>1-3</sup> and (d) other reactions of (**1**) in which, by contrast, it behaves as either a  $\bar{\text{P}}\text{R}_2$  transfer agent (iv and v, Scheme 1) or a Lewis acid (vi, Scheme 1).

The  $\text{Li}_2\text{P}_2$  ring in (**1**) is essentially planar, with average Li–P and P–C distances of 2.473(10) and 1.892(7) Å and an average CPC angle of 102.0(5)°. In  $[\text{Li}(12\text{-crown-4})_2][\text{PPh}_2]$ , the mean

† No reprints available.



**Scheme 1.** R = CH(SiMe<sub>3</sub>)<sub>2</sub>; each of i—vi was carried out in OEt<sub>2</sub> at ca. 25 °C. **Characterisation:** (a) <sup>31</sup>P n.m.r. chemical shifts (p.p.m. rel. to 85% H<sub>3</sub>PO<sub>4</sub>): (1) -254 (septet), *J*(<sup>7</sup>Li-<sup>31</sup>P) 80 Hz; (2) -115.5 (q), *J*(<sup>7</sup>Li-<sup>31</sup>P) 122 Hz; (3) -19.4 (br. q); (b) <sup>7</sup>Li n.m.r. chemical shifts (p.p.m. rel. to aq. LiNO<sub>3</sub>): (1) 2.1 (t), *J*(<sup>7</sup>Li-<sup>31</sup>P) 80 Hz; (2) 1.04 (d), *J*(<sup>7</sup>Li-<sup>31</sup>P) 122 Hz; (c) satisfactory microanalytical and spectroscopic [i.r., mass, and <sup>1</sup>H and <sup>13</sup>C n.m.r.] data for compounds (1)—(3); and (d) X-ray diffraction for compound (1) (see Figure 1).

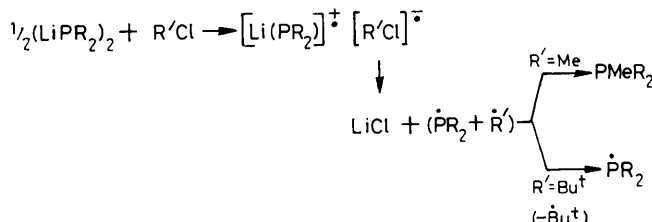


**Figure 1.** The molecular structure and atom numbering scheme for  $\mu$ -bis[bis[tris(trimethylsilyl)methyl]phosphido]dilithium, (1). Some relevant dimensions are: P(1)—C(1) 1.888(7), P(1)—C(2) 1.894(5), P(2)—C(3) 1.898(5), P(2)—C(4) 1.887(7), P(1)—Li(1) 2.481(10), P(1)—Li(2) 2.473(9), P(2)—Li(1) 2.456(9), and P(2)—Li(2) 2.481(10) Å; P(1)—Li(1)—P(2) 108.1(3), P(1)—Li(2)—P(2) 107.5(3), Li(1)—P(1)—Li(2) 72.0(3), and Li(1)—P(2)—Li(2) 72.4(3)°.

P—C bond length is 1.808(4) Å and the mean CPC angle is 105.2(2)°. In [Li<sub>2</sub>(μ<sub>3</sub>-PBu<sup>t</sup>)<sub>2</sub>(μ<sub>2</sub>-PBu<sup>t</sup>)<sub>2</sub>(thf)]<sub>2</sub>, for the doubly bridging phosphorus atoms the mean Li—P distances are 2.488(10) Å and the PLiP angle is 107.7(3)° [cf., 107.8(3)° in (1)].

X-Ray quality crystals of [Li(μ-PR<sub>2</sub>)<sub>2</sub>], (1), were grown from n-C<sub>5</sub>H<sub>12</sub> at -30 °C.

**Crystal data for (1):** C<sub>28</sub>H<sub>76</sub>Li<sub>2</sub>P<sub>2</sub>Si<sub>8</sub>, triclinic, space group P $\bar{1}$ , *a* = 12.907(2), *b* = 13.137(1), *c* = 15.934(6) Å, α = 74.33(2), β = 87.11(2), γ = 62.35(2)°, *U* = 2295.4 Å<sup>3</sup>, *Z* = 2, *D*<sub>c</sub> = 1.03 g cm<sup>-3</sup>.



**Scheme 2**

The structure of (1) (Figure 1) was solved by direct methods and refined to *R* = 0.059, *R'* = 0.075, ‡ using 4131 reflections [*I* > σ(*I*)] measured on a CAD-4 diffractometer with Mo-*K*<sub>α</sub> radiation.

The dichotomy [cf., (ii) and (v) in Scheme 1] in reactivity of [Li(μ-PR<sub>2</sub>)<sub>2</sub>], (1), suggests that the initial step in much of its chemistry is electron-transfer; and the subsequent fate of the radical pair depends primarily on steric effects, as illustrated in Scheme 2. The strong reducing properties of (1) are also indicated by the low first ionisation potential of ca. 7.5 eV [from He I spectroscopy; (1) is a dimer in the vapour, by mass spectrometry], cf., 8.5 eV for [Li(μ-NR'<sub>2</sub>)<sub>2</sub>] (R' = SiMe<sub>3</sub>).<sup>11</sup>

The importance of steric effects is further demonstrated by the observation that while PClR<sub>2</sub> and LiX readily yield PR<sub>2</sub>X if X is not excessively bulky (e.g., X = Me or NMe<sub>2</sub>), there was no reaction (under reflux in n-C<sub>6</sub>H<sub>14</sub> or OEt<sub>2</sub>) for X = NPr<sub>2</sub>, N(SiMe<sub>3</sub>)<sub>2</sub>, or R, or between PClR<sub>2</sub> and Mg(Br)Bu<sup>t</sup>-OEt<sub>2</sub>.

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‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.