

A novel, internally-solvated phosphinomethanide; crystal structure of $\text{Li}[\text{C}(\text{SiMe}_3)_2\{\text{P}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2)_2\}]$

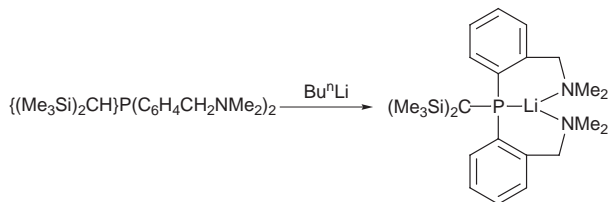
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Metallation of $\text{P}\{\text{CH}(\text{SiMe}_3)_2\}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2)_2$ with Bu^nLi yields a novel lithium phosphinomethanide in which the ligand exhibits an unprecedented tridentate PN_2 coordination mode and in which there are no short contacts between lithium and the planar carbanion centre.

Over the last decade an extensive chemistry has emerged for phosphorus-stabilised carbanionic ligands such as the phosphinomethanides, R_2PCR_2 , and diphosphinomethanides, $(\text{R}_2\text{P})_2\text{CR}$. Interest in these ligands arises from their ability to bind to metal centres in a variety of coordination modes, providing varying degrees of steric hindrance and electron donation. Mono-, di- and tri-phosphinomethanides are known to coordinate as monodentate C-donors,¹ η^2 -CP-donors,² bidentate PP-donors,³ heteroallyl ligands,⁴ and bridging ligands.⁵ We now describe a unique coordination mode for such a ligand in a lithium derivative of an amino-functionalised phosphinomethanide.

Treatment of the tertiary phosphine $\text{P}\{\text{CH}(\text{SiMe}_3)_2\}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2)_2$ **1** with 1 equiv. of Bu^nLi in diethyl ether yields the novel phosphinomethanide $\text{Li}[\text{C}(\text{SiMe}_3)_2\{\text{P}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2)_2\}]$ **2**, isolated in high yield as yellow, air-sensitive plates (Scheme 1).[‡] Whilst metallation of the related ligand $\text{HC}(\text{PMe}_2)(\text{SiMe}_3)_2$ requires heating under reflux with Bu^nLi for three weeks in hexane,¹ metallation of **1** was complete within 12 h at room temperature. It is reasonable to attribute the enhanced susceptibility of **1** towards deprotonation to chelation assistance, *i.e.* the coordination of an amino-group to lithium prior to the deprotonation step.



Scheme 1

The room temperature ^1H NMR spectrum of **2** exhibits two SiMe_3 signals, together with extremely broad resonances due to the benzylic and NMe_2 protons. These latter signals sharpen considerably at 60°C , which suggests a dynamic process, possibly involving changes in chelate ring conformation or dissociation of the NMe_2 -groups, in solution. In contrast, the ^{31}P and ^7Li NMR spectra of **2** consist of a sharp quartet and doublet respectively [$^1J(^{31}\text{P}-^7\text{Li})$ 88.9 Hz], suggesting that a $\text{Li}-\text{P}$ interaction is maintained in solution.

Since the addition of polydentate amines to lithium phosphinomethanides favours the formation of C-bonded species,¹ we were interested to observe the influence of intramolecular coordination of the dimethylamino groups on the structure of **2**. Unexpectedly, an X-ray diffraction study of **2** revealed an unprecedented tridentate PN_2 coordination mode for the phosphinomethanide ligand (Fig. 1).[§] The lithium lies in a trigonal pyramidal environment (sum of angles at $\text{Li} = 326.1^\circ$), coordinated solely by the phosphorus and nitrogen atoms of the

ligand, forming two puckered, six-membered chelate rings, each with a bite angle of *ca.* 98° . The carbanion centre $\text{C}(1)$ is perfectly planar [sum of angles at $\text{C}(1) = 359.4^\circ$] and has no significant intra- or inter-molecular contacts to Li . Few examples of planar, isolated carbanions have been reported and the majority of these contain highly delocalised polyaryl-methanide derivatives.⁶

As is common in phosphinomethanide species, the $\text{P}-\text{C}(1)$ distance in **2** [1.735(3) Å] is substantially shorter than that expected for a $\text{P}-\text{C}$ single bond, suggesting significant $\text{P}-\text{C}$ multiple bond character. Indeed the $\text{P}-\text{C}(1)$ distance in the tertiary phosphine $\{(\text{Me}_3\text{Si})_2\text{CH}\}\text{P}(\text{CH}_2\text{C}_6\text{H}_4-2-\text{NMe}_2)_2$ **3**, which is isomeric with **1**, is 1.865(2) Å.⁷ The $\text{P}-\text{C}(1)$ distance in **2** is considerably longer than both the $\text{P}-\text{CH}_2$ distance of 1.702(2) Å in $[(\text{PhCH}_2)_2\text{NLi}-\text{CH}_2\text{PPh}_3]_n$, a Li complex of a neutral P^{V} ylide,⁸ and the $\text{P}-\text{C}$ bond length range of 1.64(1) to 1.690(5) Å in a series of lithiated phosphine oxide compounds.⁹ Such a difference is to be expected since these latter compounds are P^{V} derivatives with substantial ylidic character. The $\text{Si}-\text{C}(1)$ distances of 1.818(3) and 1.826(3) Å are similar to previously reported $\text{Si}-\text{C}$ distances in other silicon-stabilised carbanions.¹⁰

The $\text{Li}-\text{P}$ distance of 2.427(6) Å is short in comparison to analogous distances in lithium phosphinomethanides where the ligand binds in its more usual coordination modes. For example, the $\text{Li}-\text{P}$ distances in $[\text{Li}\{\text{C}(\text{PMe}_2)(\text{SiMe}_3)_2\}]_2^1$ and $(\text{tmen})\text{-Li}\{\text{C}(\text{PPh}_2)_2(\text{SiMe}_3)\}^3$ are 2.519(4) and 2.530(7) Å, respectively. This may reflect the increased ionic contribution to the $\text{Li}-\text{P}$ interaction associated with the delocalisation of charge from the carbanion centre to phosphorus.

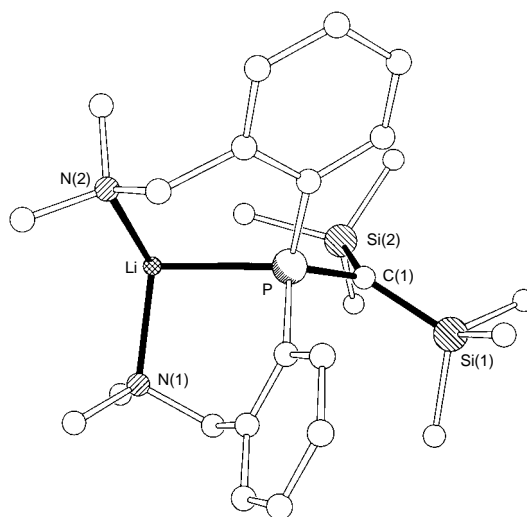


Fig. 1 Molecular structure of **2** (H atoms omitted for clarity). Selected bond lengths (Å) and angles ($^\circ$): $\text{Li}-\text{P}$ 2.427(6), $\text{Li}-\text{N}(1)$ 2.096(6), $\text{Li}-\text{N}(2)$ 2.083(6), $\text{C}(1)-\text{P}$ 1.735(3), $\text{C}(1)-\text{Si}(1)$ 1.818(3), $\text{C}(1)-\text{Si}(2)$ 1.826(3), $\text{P}-\text{Li}-\text{N}(1)$ 98.4(2), $\text{P}-\text{Li}-\text{N}(2)$ 97.4(2), $\text{N}(1)-\text{Li}-\text{N}(2)$ 130.3(3), $\text{Li}-\text{P}-\text{C}(1)$ 126.31(16), $\text{P}-\text{C}(1)-\text{Si}(1)$ 126.26(18), $\text{P}-\text{C}(1)-\text{Si}(2)$ 113.61(17), $\text{Si}(1)-\text{C}(1)-\text{Si}(2)$ 119.49(16).

Investigations into the coordination behaviour of this and related amino-functionalised phosphinomethanides are currently in progress.

Notes and References

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‡ *Characterisation of 2*: ^1H NMR (C_6D_6 , 343K), δ 0.39 (s, SiMe_3), 0.62 (s, SiMe_3), 1.75 (br s, NMe_2), 3.10 (br s, CH_2NMe_2), 6.91–7.16 (m, ArH); ^{31}P NMR (C_6D_6), δ -18.2 [q, $^1J(^{31}\text{P}-^7\text{Li})$ 88.9 Hz]; ^7Li NMR (C_6D_6), δ 1.25 (d).

§ *Crystal data for 2*: $\text{C}_{25}\text{H}_{42}\text{LiN}_2\text{PSi}_2$, $M = 464.7$, triclinic, space group $P\bar{1}$, $a = 9.1358(12)$, $b = 9.3158(13)$, $c = 17.369(2)$ Å, $\alpha = 86.816(3)$, $\beta = 98.275(3)$, $\gamma = 68.972(4)^\circ$, $U = 1378.1(3)$ Å³, $Z = 2$, $D_c = 1.120$ g cm⁻³, $\mu = 0.20$ mm⁻¹ (Mo-K α radiation, $\lambda = 0.71073$ Å), $T = 160$ K, crystal size $0.28 \times 0.18 \times 0.02$ mm. The structure was solved by direct methods and refined on F^2 values of all 4816 unique data (8451 data measured on Bruker AXS SMART diffractometer, $2\theta_{\text{max}} = 50^\circ$, $R_{\text{int}} = 0.0501$) with anisotropic displacement parameters and riding isotropic hydrogen atoms; $wR2 = 0.1161$ for all F^2 values, conventional $R = 0.0539$ for F values of 2925 reflections having $F_o^2 > 2\sigma(F_o^2)$, goodness of fit = 0.985, for all F^2 values and 291 refined parameters. A final difference map was essentially featureless. Programs were standard Bruker AXS SMART, SAINT and SHELXTL together with local programs. CCDC 182/837.

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Received in Basel, Switzerland, 16th February 1998; 8/01342J