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Preliminary communication

α-Heteroatom-substituted carbanions: the structure of $\{(Me_2NCH_2CH_2NMe_2)Li[(PMe_2)CH(SiMe_3)]\}_2$, an unusual organolithium dimer

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Abstract

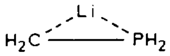
The effect of silyl substitution at the carbanionoid C atoms on structure and bonding of lithium-phosphinomethanides has been investigated by determination of the structure of $\{(Me_2NCH_2CH_2NMe_2)Li[(PMe_2)CH(SiMe_3)]\}_2$, which has a six-membered ring $(P–C–Li)_2$ in twist conformation, and so is markedly different in structure from both the bis-silyl substituted as well as the unsubstituted analogue.

α-Heteroatom substituted carbanions recently have attracted considerable interest both from the theoretical [1] and structural point of view [2]. Calculations show that the carbanions are stabilized to varying extents by heteroatoms of elements of groups 15 to 17 [1]

$[R_2\bar{C}—\bar{P}R_2']^-$

(R = H, $SiMe_3$, PR_2';
R = H, alkyl, aryl)

(I)



(II)

$\{Li[(PMe_2)C(SiMe_3)_nH_{2-n}]\}_2(TMEDA)_x$

(**1**: $n = 0$, $x = 2$;
2: $n = 1$, $x = 2$;
3: $n = 2$, $x = 1$)

This stabilization markedly influences the nucleophilicity of the carbanion. Thus for phosphinomethanides I, a bridged structure II is favoured by the calculations on the lithium derivative, indicating that carbanion and phosphorus lithiophilicity are comparable. In actual systems, the nature of further P and C substituents also has a major influence on the nucleophilicity of phosphinomethanides I: both $SiMe_3$ and PR'_2 groups at the carbanion enhance the reactivity of the P over the C centre towards electrophiles [3]. In an attempt to clarify experimentally the role of increased silyl substitution at phosphinomethanides, we have compared the structures of the closely related lithium phosphinomethanides **1**–**3**.

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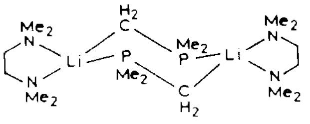
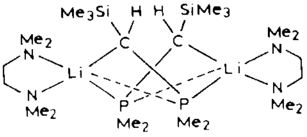
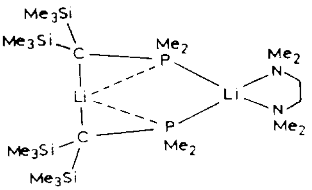


(1)



(2)



(3)

In **1**, a six-membered ring is formed by head to tail dimerisation without unusual deviations from standard bond angles [4]. For **3**, a six-membered ring was again observed, but the two phosphinomethanides were linked together in a head to head fashion. Additional short Li–P contacts (dotted lines in **3**) were observed, although the P atoms are also engaged in bonding to the second Li atom. Because of the bulk of the silyl substituents in **3**, in contrast to **1**, there is not space enough for a TMEDA molecule to complete the coordination sphere of the C-bonded Li atom [5].

We now found that complex **2**, which bears only one SiMe$_3$ substituent at the carbanionoid center, surprisingly has features of both **1** and **3** in that it contains a six-membered ring in twist conformation. Crystalline **2** was obtained by metallation of Me$_2$PCH$_2$SiMe$_3$ [6] in pentane [7] according to eq. 1 and was recrystallized from pentane/THF/TMEDA as colourless crystals.

$$\mathrm{Me_2PCH_2SiMe_3} + {}^{t}\mathrm{BuLi} \xrightarrow{\text{pentane/THF/TMEDA}} \mathbf{2} \qquad (1)$$

The X-ray structure analysis * (Fig. 1) shows the two phosphinomethanide anions to be virtually perpendicular to each other. This results in shorter distances between the P and C atoms across the six-membered ring, respectively, as compared to those in the less crowded **1**. As a consequence, in addition to linking the two phosphinomethanides through Li–C and Li–P interactions, each Li atom also bridges one of the central P–C bonds (P(1)–C(1), P(2)–C(2)) (Fig. 1). The Li–P distances within this bridge decrease on going from **1** (essentially no interaction) to **2** (Li(1)–P(2) 3.042(8), Li(2)–P(1) 3.034(8) Å) to **3** (2.88(1), 2.92(1) Å), whereas the Li–P distances around the six-membered ring perimeter increase in the same order (**1**: 2.593(7)/2.615(6); **2**: 2.680(7)/2.661(8); **3**: 2.716(9)/2.72(1) Å). Thus both different Li–P distances become increasingly similar on going from **1** to **3**.

To adjust to the twist geometry of **2**, most bond angles at P(1)/P(2) and C(1)/C(2) involving lithium deviate noticeably from the tetrahedral standard, although C(1)/C(2) are not in the plane of the substituents (H, Si, P).

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* Crystal structure data: Enraf–Nonius CAD4 diffractometer, Mo-K_α radiation, λ 0.71069 Å, graphite monochromator, T 22°C; triclinic, $P\bar{1}$, a 10.681(1), b 12.378(2), c 15.336(2) Å, α 88.25(1), β 107.83(1), γ 105.98(1)°, V 1852.4 Å^3, $Z = 2$ (dimers), ρ_{calcd} 0.969 g cm^{-3}. 5677 unique reflexions were measured up to $(\sin\vartheta/\lambda)_{max} = 0.572$, 3940 of which with $I > 2\sigma(I)$ were taken as observed. Lp and linear decay corrections were applied. The solution was by direct methods (MULTAN-82). The final residuals were $R(R_w) = 0.057(0.056)$, $w = 1/\sigma^2(F_o)$ for 359 refined parameters (anisotropic, H(1)/H(2) isotropic, SHELX-76). $\Delta\rho_{fin} = +0.38/-0.31$ e Å^{-3}. Tables of atomic coordinates, displacement parameters, and observed and calculated structure factors have been deposited at the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2 under the number CSD 52883.

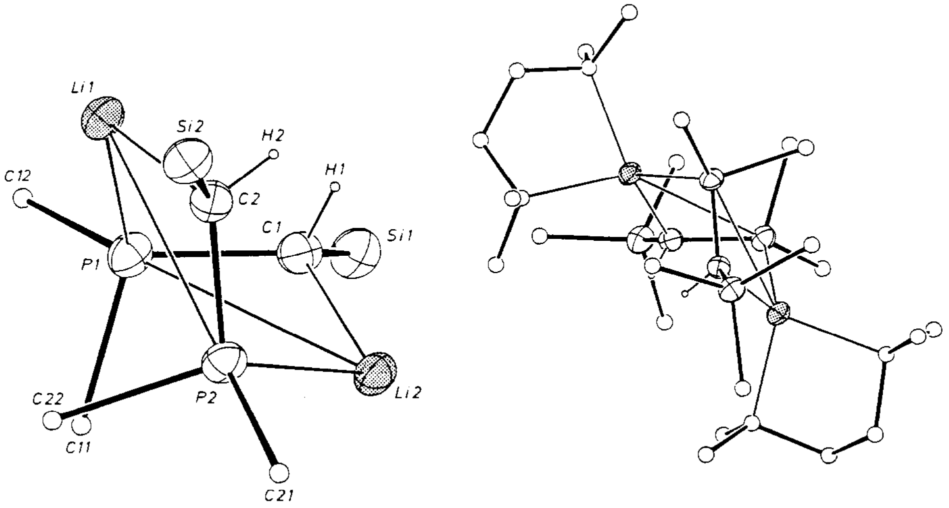

Fig. 1. Molecular structure of **2** (ORTEP; thermal ellipsoids at the 20% probability level). Lefthand side: Li phosphinomethanide core of the molecule (TMEDA molecules and $SiMe_3$ methyl groups omitted for clarity), righthand side: structure of the entire dimer. Important distances (Å) and angles (°): Li(1)–P(1) 2.680(7), Li(2)–P(2) 2.661(8), Li(1)–P(2) 3.042(8), Li(2)–P(1) 3.034(8), Li(1)–C(2) 2.249(9), Li(2)–C(1) 2.26(1), P(1)–C(1) 1.772(5), P(2)–C(2) 1.773(5), C(1)–Si(1) 1.827(5), C(2)–Si(2) 1.824(4); Li(1)–P(1)–C(1) 108.1(2), Li(1)–P(1)–C(11) 122.0(2), Li(1)–P(1)–C(12) 114.5(3), Li(2)–P(2)–C(2) 110.8(2), Li(2)–P(2)–C(21) 114.2(3), Li(2)–P(2)–C(22) 119.4(2), Li(2)–C(2)–P(2) 97.6(3), Li(1)–C(2)–Si(2) 127.5(3), Li(1)–C(2)–H(2) 80(3), Li(2)–C(1)–P(1) 96.9(3), Li(2)–C(1)–Si(1) 128.3(3), Li(2)–C(1)–H(1) 84(3).

The P–C bond bridging by lithium, in dimeric **2** and **3** is reminiscent of the structure of monomeric II indicated by calculations [1], although it should be kept in mind that in II both the C and P lone pairs point to one Li counterion, resulting in a synperiplanar conformation. The increase in bridging on going from **1** to **2** to **3** points to increased electrostatic attraction between P and Li, but steric effects are also evident in **2**. Thus the distances between neighbouring methyl C atoms on the "surface" of the dimer range between 3.5 and 4 Å, which is remarkably close to the usually assumed Van der Waals distance of 4 Å between methyl groups [8]. The ease with which gross structural variations in **1**–**3** are induced by increased silyl substitution at the carbanionoid C atoms provides support for a largely ionic bonding model of organolithium compounds [9], with strongly directional covalent bonding playing only a minor role. It seems that the geometrical position of Li in organolithium compounds may actually serve as an experimental probe for the charge distribution and for the steric requirements within the resulting arrangement.

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