Insertion of $LiPEt_2$ into Poly(dimethylsiloxane) to give $[LiOSiMe_2PEt_2]_6$

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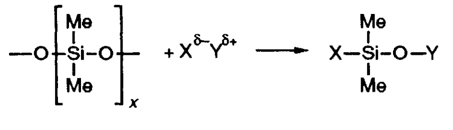
The hexameric structure of the product of the reaction of lithium diethylphosphide with poly(dimethylsiloxane) (silicone stopcock grease) has been determined by X-ray crystallography; it forms a distorted hexagonal prism with the vertices occupied alternately by lithium and oxygen atoms.

Small polar molecules are known chemically to degrade polydimethylsiloxanes (PDMS) and oligomeric dimethylsiloxanes (ODMS) by attacking at the Si–O bond.[1] The insertion product derived from the attack of PDMS–ODMS by a highly polarized complex might be expected to follow in the form of eqn (1). A major manufacturer of PDMS has even suggested the use of PDMS as a means of deactivating potentially hazardous solutions of alkyllithium reagents.[2]

We have been studying the structural aspects and reactivity patterns of main group lithium complexes $LiER_2$ (E = P or As) which are, in some cases, similar to their carbon counterparts (LiR).[3] Herein we report the reaction of $LiPEt_2$ with PDMS to give the unusual hexameric $[LiOSiMe_2PEt_2]_6$ **1**. This compound is of interest for its novel structural features as well as representing the first well characterized example of a product from the reaction of a lithium dialkylphosphide with an alkyl siloxide. One may view this compound as the product from the insertion of $LiPEt_2$ into the Si–O bonds of PDMS.



$$-O\left[\begin{array}{c}Me\\ |\\ Si{-}O\\ |\\ Me\end{array}\right]_x + X^{\delta-}Y^{\delta+} \longrightarrow X{-}\overset{\displaystyle Me}{\underset{\displaystyle Me}{Si}}{-}O{-}Y \qquad (1)$$

Compound **1** was originally isolated from a solution of $LiPEt_2$ in diethyl ether which had been stored at −20 °C for several months. The identity of the compound was confirmed by an X-ray crystallographic study and the synthesis repeated under controlled conditions using Dow Corning silicone stopcock grease as the source of PDMS. The reaction is evidently quite slow and takes several months at −20 °C for crystals of **1** to appear. The yields of **1** are also variable from 0 to 20% based on $LiPEt_2$.† A ^{31}P NMR spectrum of the reaction mixture shows a singlet at δ −81 indicating the formation of a new species distinct from $LiPEt_2$. Spectroscopic data are in support of the solid-state structure. Thus, in the ^1H NMR spectrum, the silylmethyl groups appear as a doublet at δ 0.51 ($^2J_{PH}$ 1.8 Hz). The ethyl groups attached to the phosphorus atom appear as a doublet of triplets δ 1.21 (CH_3, J_{HH} 7.5 Hz, $^2J_{PH}$ 14.7 Hz) and a multiplet at δ 1.64 (CH_2).

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† **1**, m.p. 173–175 °C; NMR: ^1H (300 MHz; C_6D_6, 26 °C), δ 0.51 (d, $^2J_{PH}$ 1.8 Hz, $SiMe_2$), 1.21 (dt, J_{HH} 7.5, $^2J_{PH}$ 14.1 Hz, $P[CH_2CH_3]_2$), 1.64 (m, $P[CH_2CH_3]_2$); $^{31}P\{^1H\}$ (121.5 MHz; C_6D_6; rel. aq. H_3PO_4), δ −81 (s).

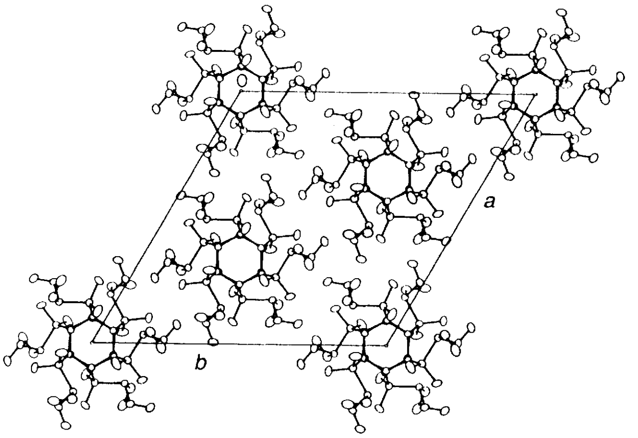

Fig. 1 Cell packing diagram of **1** showing the aggregate structure adopted in the solid state

An X-ray crystallographic analysis shows that an aggregate structure of six $LiOSiMe_2PEt_2$ units exists in the solid state.‡ A view of the cell packing is shown in Fig. 1 with the central $[LiOSi]_6$ core shown in Fig. 2.

The $[LiOSi]_6$ core of the molecule forms a distorted hexagonal prism which may also be viewed as a cyclic ladder structure. The vertices of the prism are occupied by alternating Li and O atoms with the associated phosphino silyl ligands arranged in axial positions bonded to μ_3-O atoms.

Aggregate structures have been documented before for other alkali metal alkoxides.[4] The related hexamer $[LiOCMe_2Ph]_6$, recently reported by Chisholm, also contains a hexagonal prismatic core constructed of three-coordinate Li and four-coordinate O atoms.[5] Comparison of the central bonding cores of **1** and $LiOCMe_2Ph$ shows nearly identical bond lengths for both complexes, Li–O_{av} = 1.93 Å for **1** *vs.* 1.91 Å for $[LiOCMe_2Ph]_6$. Similar ranges in O–Li–O angles are also found {97.1(4)–123.9(4) for **1** *vs.* 97.75(12)–126.277(12)° for $[LiOCMe_2Ph]_6$}.

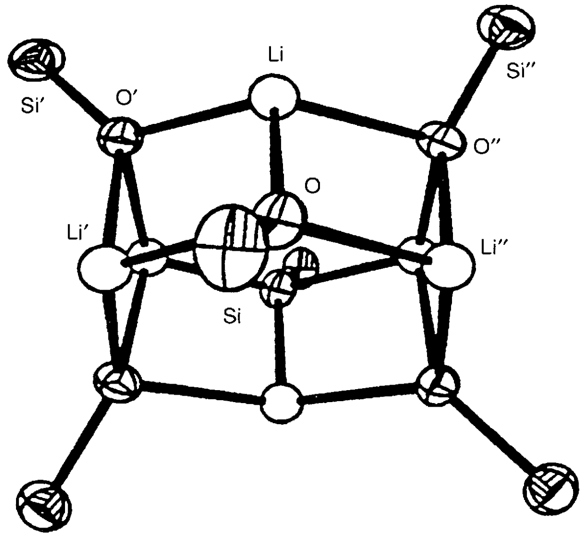

Fig. 2 ORTEP view of the central bonding core of **1**

Although the phosphorus substituents of the siloxide moiety of **1** are bent towards neighbouring lithium atoms, the Li–P distance of 2.760(5) Å would seem to disfavour any significant bonding interaction in the solid state.

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‡ *Crystal data* for **1**, $C_6H_{16}OPLi$: rhombohedral, space group $R\bar{3}$, a = 22.176(1), b = 22.176(1), c = 11.4524(4) Å, V = 5632.0(8) Å^3, Z = 3, D_c = 1.065 g cm^{-3}, μ(Cu-Kα) = 11.26 cm^{-1}, λ(Cu-Kα) = 1.5413 Å. A total of 1209 unique observed reflections [$F > 6\sigma(F)$] (1452 measured) were collected on an Enraf-Nonius CAD-4F diffractometer at 23 ± 1 °C. Data were collected over the range $2 < 2\theta < 110°$ using the ω–2θ scan mode. The data were corrected for Lorentz, polarization, decay and absorption. The structure was solved by direct methods (Multan). All non-hydrogen and non-lithium atoms were refined anisotropically. Lithium atoms were located and refined isotropically. Hydrogen atoms were refined with fixed isotropic parameters. Final R = 0.0456, R_w = 0.0514. Highest peak in the final difference Fourier was 0.18 e Å^{-3} and located near P. 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.

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