

**Synthesis of $[\text{LiPPh}(\text{SiMe}_3)(\text{tmeda})]_2$
(from $\text{Mg}(\text{PPh})_2(\text{tmeda})$ or $\text{Li}(\text{PPh})(\text{tmeda})$)
and the X-ray structure of the *trans*-isomer
($\text{tmeda} = N,N,N',N'$ -tetramethylethylenediamine)**

Evamarie Hey ^{*},

Fachbereich Chemie der Philipps-Universität, Hans-Meerwein-Strasse, 3550 Marburg (F.R.G.)

Colin L. Raston ^{*}, Brian W. Skelton, and Allan H. White

*Department of Physical and Inorganic Chemistry, The University of Western Australia,
Nedlands 6009 (Australia)*

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Abstract

Treatment of either (i) $\text{Mg}(\text{PPh})_2(\text{tmeda})$ with two equivalents of *n*-BuLi then with an excess of Me_3SiCl or (ii) $\text{Li}(\text{PPh})(\text{tmeda})$ with Me_3SiCl followed by *n*-BuLi yields $[\text{LiPPh}(\text{SiMe}_3)(\text{tmeda})]_2$. Below ca. 0 and 5 °C ³¹P and ⁷Li NMR spectroscopy shows that there is coupling of ⁷Li nuclei to two equivalent ³¹P nuclei, and vice versa. This is consistent with the dimeric structure found in the solid for the *trans*-isomer by an X-ray structure determination. The phosphido groups bridge two lithium centres to form Li_2P_2 rings; Li–P (mean) 2.62 Å, Li–N (mean) 2.16 Å, P–Li–P 94.5(6), 92.0(6)°, Li–P–Li 85.5(5), 88.0(5)°.

Transition metal phosphido complexes have recently become the subject of extensive synthetic and structural studies. Perhaps the most important method for their preparation is that involving the use of lithium phosphides as phosphido group transfer reagents. More recently, the lithium phosphides themselves have received increasing attention since they often exhibit novel structural features and interesting chemical properties. Since 1983, the structures of fourteen phosphidolithium compounds [1–9] (some structural parameters are summarised in Table 1) and of some bis(phosphido)dilithium compounds [10,11] have been reported. In contrast, the synthetic potential of magnesium phosphides, $[\text{Mg}(\text{PR}_2)_2]$, has been barely explored, and little is known about their structures [12].

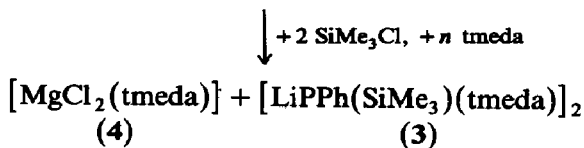
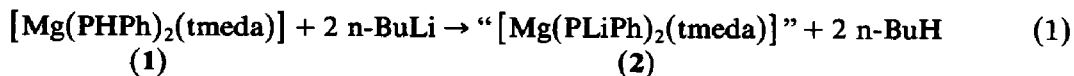
^{*} Present address: Division of Science and Technology, Griffith University, Nathan 4111, Australia.

Table 1

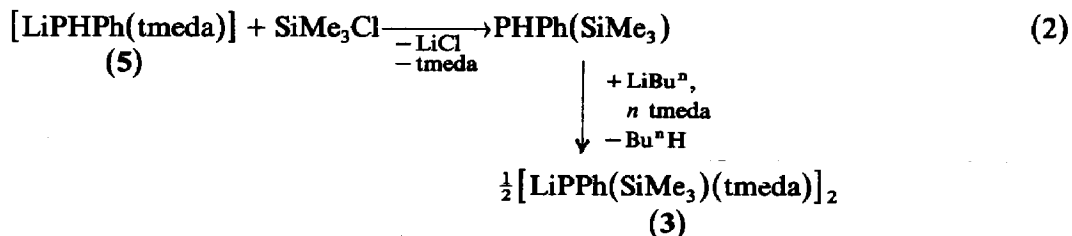
Selected bond distances (Å) and angles (°) in lithium phosphides [R = SiMe₃, Cy = cyclohexyl, pmdeta = *N,N,N',N'',N'''*-pentamethyldiethylenetriamine, THF = tetrahydrofuran, Mes = 2,4,6-Me₃C₆H₂, DME = 1,2-dimethoxyethane]

Compound	Li-P	Li-O,N	Li-P-Li	P-Li-P	Ref.
[LiPR ₂ (THF) _{0.5}] ₄	2.44(2)–2.64(2)	1.89(3)	72.9(8), 73.1(8), 77.6(8), 145.9(9)	104.0(7), 105.4(9), 106.9(9), 149(1)	1
[LiPR ₂ (THF) ₂] ₂	2.62(2)	1.92(2), 2.03(3)	80.0(7)	100.0(8)	1
[LiPBU ₂ ^t (THF) _{0.5}] ₄	2.476(10)–2.669(9)	1.923(10)	–	–	2
[Li(12-crown-4)][PPh ₂]	–	2.308(7)– 2.487(6)	–	–	3
[LiP{CH(SiMe ₃) ₂] ₂] ₂	2.456(9)–2.481(10)	–	72.0(3), 72.4(3)	107.5(3), 108.1(3)	4
[LiPPh ₂ (OEt ₂) _n]	2.483(10)–2.496(10)	1.925(10), 1.966(1)	126.0(3), 136.9(4)	129.6(4), 139.6(4)	5
[LiPPh ₂ (THF) ₂] _n	2.629(22),2.634(21)	1.937(22), 1.988(22)	135.0(5)	123.1(8)	5
[LiPCy ₂ (THF)] _n	2.455(9),2.543(9)	1.936(8)	119.7(2)	145.6(3)	5
[LiPPh ₂ (pmdeta)]	2.567(6)	2.091(6)– 2.150(6)	–	–	6
[LiPPh ₂ (tmeda)] ₂	2.57(2)–2.62(2)	2.11(2)– 2.20(2)	86.4(5), 90.1(6)	89.2(5), 94.1(6)	6
[LiPPh(SiMe ₃)(tmeda)] ₂	2.60(2)–2.63(1)	2.12(2)– 2.19(2)	89.9(9), 88.0(5)	92.0(6), 94.5(6)	this work
[LiPMes ₂ (OEt ₂) ₂]	2.483(1),2.479(11)	1.926(11), 1.924(11)	81.7(4), 80.9(4)	98.2(4), 99.2(4)	7
[LiPHMes(THF) ₃]	2.533(9)	1.961(15), 1.950(9), 1.940(10)	–	–	7
[LiPHMes(THF) ₂] _n	2.641(6),2.655(16)	1.979(6), 1.971(6)	129.9(2)	122.3(2)	9
[LiPH ₂ (DME)] _n	2.550(8),2.597(8)	2.063(7) 2.036(7)	176.9(1)	117.0(2)	8

We recently reported the synthesis and X-ray structure of [Mg(PHPh)₂(tmeda)] (1) [13] (tmeda = *N,N,N',N'*-tetramethylethylenediamine), and have since undertaken an investigation of its chemistry. Since PH₂Ph can be doubly deprotonated to yield Li₂PPh [14] we expected that 1 would also undergo proton abstraction by bases. The magnesium phosphide 1 was treated with two equivalents of *n*-BuLi in the presence of tmeda, and the reaction mixture was subsequently quenched with Me₃SiCl (eq. 1).



Work up gave $[\text{MgCl}_2(\text{tmeda})]$ (4) (identified by IR spectroscopy) and $[\text{LiPPh}(\text{SiMe}_3)(\text{tmeda})]_2$, which has been characterised by multinuclear NMR, IR spectroscopy and X-ray crystallography. The compound $[\text{Mg}(\text{LiPPh})_2(\text{tmeda})]$ (2), which was not isolated, is a possible intermediate in the reaction. For this the observed products, 3 and 4, would be the result of MgP bond cleavage rather than LiP bond cleavage. Compound 3 can also be obtained in high yield by treating $[\text{LiPPh}(\text{tmeda})]$ (5) [15] with Me_3SiCl , followed by *n*-BuLi (eq. 2).

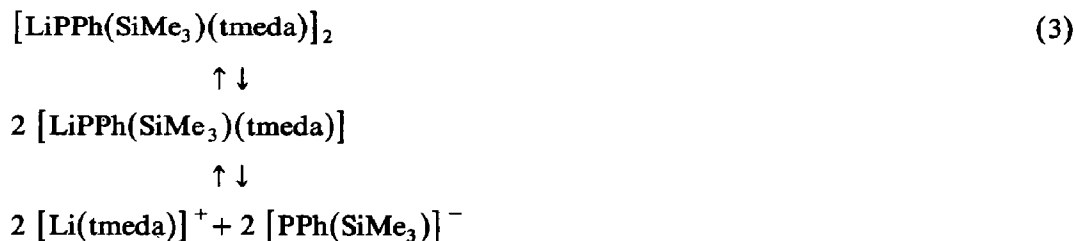


^7Li and ^{31}P spectroscopic studies

Variable temperature ^7Li and ^{31}P NMR spectra for 3 were recorded in C_7D_8 . At room temperature the ^{31}P spectrum (Table 2) consisted of a singlet, which upon cooling split into a binomial septet (Fig. 1, $J(^{31}\text{P}-^7\text{Li})$ 40 Hz), indicating coupling to two equivalent ^7Li nuclei (I 3/2, rel. abundance 92.6%).

The ^7Li NMR spectrum (Table 2) also exhibited a single resonance at ambient temperature. At lower temperature, the singlet split into a binomial triplet (Fig. 2, $J(^{31}\text{P}-^7\text{Li})$ 40 Hz), showing that the ^7Li nuclei couple to two equivalent ^{31}P nuclei. The ^{31}P spectra indicated a coalescence temperature of 0°C , and the ^7Li NMR spectra one of $+5^\circ\text{C}$. In each case the accuracy of measurement was limited by the broadness of the signals at coalescence (^{31}P , line width ca. 150 Hz at 0°C ; ^7Li , line width 29 Hz at 5°C).

The ^{31}P and ^7Li data are consistent with a dimeric structure for 3 in solution at low temperature. The absence of $^{31}\text{P}-^7\text{Li}$ coupling at ambient temperature could be explained if the dimer were in equilibrium with two monomeric units, which could dissociate into separated ion pairs (eq. 3).



However, in the non-coordinating solvent toluene, such a process would be expected to be highly unfavourable, since it gives rise to a highly unsaturated two-coordinate lithium cation.

For several other lithium phosphides the observance or non-observance of Li-P coupling has been found to be strongly dependent upon temperature and solvent [16]. Thus, for example, the ^7Li and ^{31}P NMR spectra of LiPPh_2 consist of singlets at room temperature in the solvents Et_2O or THF. At 200 K coupling is observed in Et_2O solution but not in THF [16]. The absence of coupling in the latter case has

Table 2

Chemical shifts and coupling constants in the ^{31}P and ^7Li NMR spectra of $[\text{LiPPh}(\text{SiMe}_3)(\text{tmeda})]_2$ (3) in the temperature range 240 to 298 K

	T (K)	δ (ppm)
$^{31}\text{P}\{^1\text{H}\}^a$	298	-142.3, s
	243–270	-145.0, septet, $^1J(^{31}\text{P}-^7\text{Li})$ 40 Hz coalescence temperature -1°C
$^7\text{Li}\{^1\text{H}\}^b$	298	1.43, s
	268–277	1.48, triplet, $^1J(^{31}\text{P}-^7\text{Li})$ 40 Hz coalescence temperature $+5^\circ\text{C}$

^a In C_7D_8 , ref. ext. 85% H_3PO_4 . ^b In C_7D_8 , ref. ext. 1 M $\text{LiBr}/\text{H}_2\text{O}$ in C_7D_8 .

Table 3

Non-hydrogen atom coordinates

Atom	Molecule A			Molecule B		
	x	y	z	x	y	z
Li	0.4511(6)	0.561(1)	0.952(1)	0.0385(7)	-0.0948(17)	-0.097(2)
<i>Ligand</i>						
P	0.4280(1)	0.2754(2)	0.8416(2)	0.0869(1)	0.1904(2)	0.1479(2)
Si	0.3858(1)	0.0730(3)	0.6019(3)	0.1704(1)	0.3305(3)	0.3709(3)
C(11)	0.3931(6)	-0.0926(10)	0.5820(11)	0.1864(5)	0.5247(10)	0.5206(9)
C(12)	0.4394(5)	0.1614(11)	0.4984(10)	0.1436(5)	0.1952(11)	0.4541(10)
C(13)	0.2952(5)	-0.0224(11)	0.4948(10)	0.2533(4)	0.3807(12)	0.3465(10)
C(1)	0.3771(4)	0.1868(8)	0.9421(7)	0.1142(4)	0.3153(8)	0.0584(7)
C(2)	0.3263(4)	0.0177(9)	0.8804(8)	0.1734(4)	0.4767(9)	0.1294(8)
C(3)	0.2935(4)	-0.0360(10)	0.9698(10)	0.1902(4)	0.5586(10)	0.0483(10)
C(4)	0.3084(5)	0.0718(12)	1.1200(10)	0.1484(5)	0.4827(10)	-0.0993(9)
C(5)	0.3572(4)	0.2392(11)	1.1854(9)	0.0897(5)	0.3242(10)	-0.1708(8)
C(6)	0.3911(4)	0.2938(9)	1.0951(8)	0.0722(4)	0.2414(10)	-0.0920(8)
<i>tmeda</i>						
N(1)	0.4427(3)	0.6472(7)	0.7989(6)	0.0557(3)	-0.2639(7)	-0.0891(7)
C(11)	0.5005(4)	0.8195(9)	0.8678(9)	-0.0072(5)	-0.4286(10)	-0.1653(11)
C(12)	0.4371(5)	0.5506(10)	0.6448(9)	0.0905(5)	-0.2111(12)	0.0697(11)
C(1)	0.3789(4)	0.6289(11)	0.7977(10)	0.1023(5)	-0.2524(11)	-0.1724(11)
C(2)	0.3711(5)	0.6757(11)	0.9485(11)	0.0820(5)	-0.2511(11)	-0.3161(11)
N(2)	0.3732(3)	0.5789(7)	1.0104(7)	0.0825(3)	-0.1053(7)	-0.2742(7)
C(21)	0.3069(4)	0.4128(10)	0.9322(10)	0.0437(5)	-0.1339(12)	-0.4165(10)
C(22)	0.3849(5)	0.6624(12)	1.1754(10)	0.1515(4)	0.0425(11)	-0.2115(11)

Table 4

Lithium atom environments

	Molecule A	Molecule B
<i>Distance (Å)</i>		
Li–P	2.62(2)	2.63(1)
Li–P'	2.61(1)	2.60(2)
Li–N(1)	2.19(2)	2.16(2)
Li–N(2)	2.12(2)	2.16(2)
Li...Li	3.55(3)	3.63(3)
<i>Angles (degrees)</i>		
P–Li–P'	94.5(6)	92.0(6)
P–Li–N(1)	120.9(5)	123.0(7)
P–Li–N(2)	117.6(5)	120.1(6)
P'–Li–N(1)	117.7(5)	115.1(6)
P'–Li–N(2)	122.6(5)	122.9(7)
N(1)–Li–N(2)	86.4(8)	86.9(8)

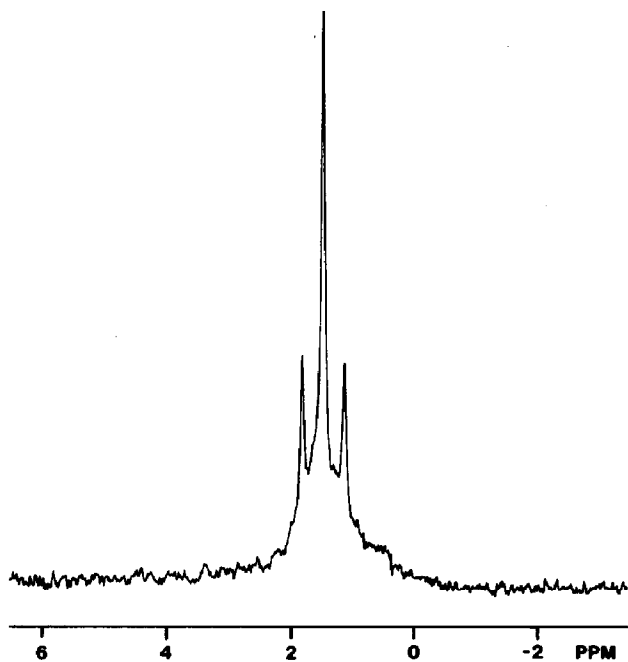


Fig. 1. ${}^7\text{Li}\{{}^1\text{H}\}$ NMR spectrum of $[\text{LiPPh}(\text{SiMe}_3)(\text{tmeda})]_2$ (**3**) at 268 K.

been explained in terms of a rapid intermolecular exchange of lithium units, which occurs without formation of separated ion pairs. It seems likely that such a process takes place for compound **3** at room temperature, leading to a loss of Li–P coupling.

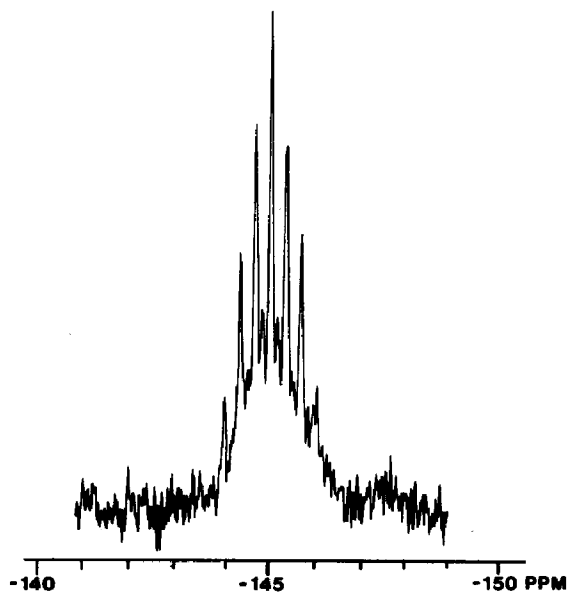
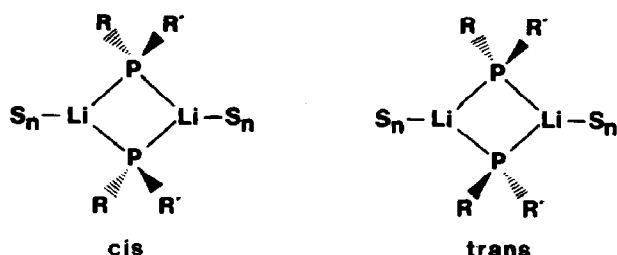


Fig. 2. The ${}^{31}\text{P}\{{}^1\text{H}\}$ NMR spectrum of $[\text{LiPPh}(\text{SiMe}_3)(\text{tmeda})]_2$ (**3**) at 258 K.

Dimeric lithium phosphides of the general formula $[\text{LiPRR}'(\text{S})_n]$ ($\text{S} = \text{solvent}$) can exist as two different geometrical isomers:



For those unsymmetrically substituted lithium phosphides, LiPRR' , for which low temperature NMR data are available, only one septet in the ^{31}P NMR and one triplet in the ^7Li NMR spectrum were observed [16], as is the case for **3**. This leads to the conclusion that either the energy barrier to conversion of the isomers is low or that the formation of one isomer is favoured, perhaps for steric reasons. Furthermore, the X-ray diffraction study of **3** showed that in the solid state only the *trans*-isomer is present (vide infra).

Crystallographic studies

Compound **3** crystallizes as the *trans*-isomer in the space group $P\bar{1}$; two independent half molecules comprise the asymmetric unit, the other halves being generated by inversion centres, Fig. 3. Bond distances and angles in the Li_2P_2 cores are not significantly different to those in $[\text{LiPPh}_2(\text{tmeda})]_2$ [6], Table 1, which is the only other authenticated structure of a lithium phosphido/bidentate tertiary amine. Tetrahedral coordination about the metal centres is achieved by bridging of the phosphido groups to two lithium centres; tetrahedral coordination without such bridging occurs for $\text{Li}-\text{PPh}_2$ bound to the tridentate tertiary amine *pmdeta* ($= N,N,N',N'',N''$ -pentamethyldiethylenetriamine) [6], with marginal shortening of the $\text{Li}-\text{P}$ distance. A lower degree of solvation with the retention of bridging phosphido groups results in more pronounced shortening of the $\text{Li}-\text{P}$ distances, e.g. in $[\text{LiP}\{\text{CH}(\text{SiMe}_3)_2\}_2]_2$ [4].

Difference in the geometries of the two pseudosymmetrically disposed molecules of **3** are trivial; there is no asymmetry in the $\text{Li}-\text{P}-\text{Li}$ linkages. Within the phosphido ligands the aromatic ring, the phosphorus, and silicon atoms, and a methyl carbon atom, directed away from the phenyl group, are co-planar. This minimizes buttressing between the methyl substituents on silicon and the phenyl group; in the diphenyl analogue the phenyl groups are twisted relative to the C_2P plane, as in PPh_3 , because of otherwise unfavourable non-bonding interactions. The $\text{C}-\text{P}-\text{Si}$ angles, $106.5(2)$ and $107.3(2)^\circ$, molecules **A** and **B**, are similar to the corresponding angles in $[\text{LiP}(\text{SiMe}_3)_2(\text{THF})_2]_2$, $104.7(2)$ [1], and $[\text{LiPPh}_2(\text{tmeda})]_2$, 104.9° [6], as are the $\text{Si}-\text{P}$ distances, $2.191(4)$ and $2.200(5)$ Å, and $\text{C}-\text{P}$ distances, $1.826(9)$ and $1.844(10)$ Å, molecules **A** and **B** ($\text{Si}-\text{P}$ $2.196(5)$, $2.194(6)$ Å in $[\text{LiP}(\text{SiMe}_3)_2(\text{THF})_2]_2$ [1]; $\text{C}-\text{P}$ 1.85 Å in $[\text{LiPPh}_2(\text{tmeda})]_2$ [6]). Overall, within the precision of the structure determinations, there is no apparent geometrical effect on replacing one or two of the hydrocarbonyl groups in PPh_2^- with silyl groups while maintaining two co-ligands associated with each metal centre.

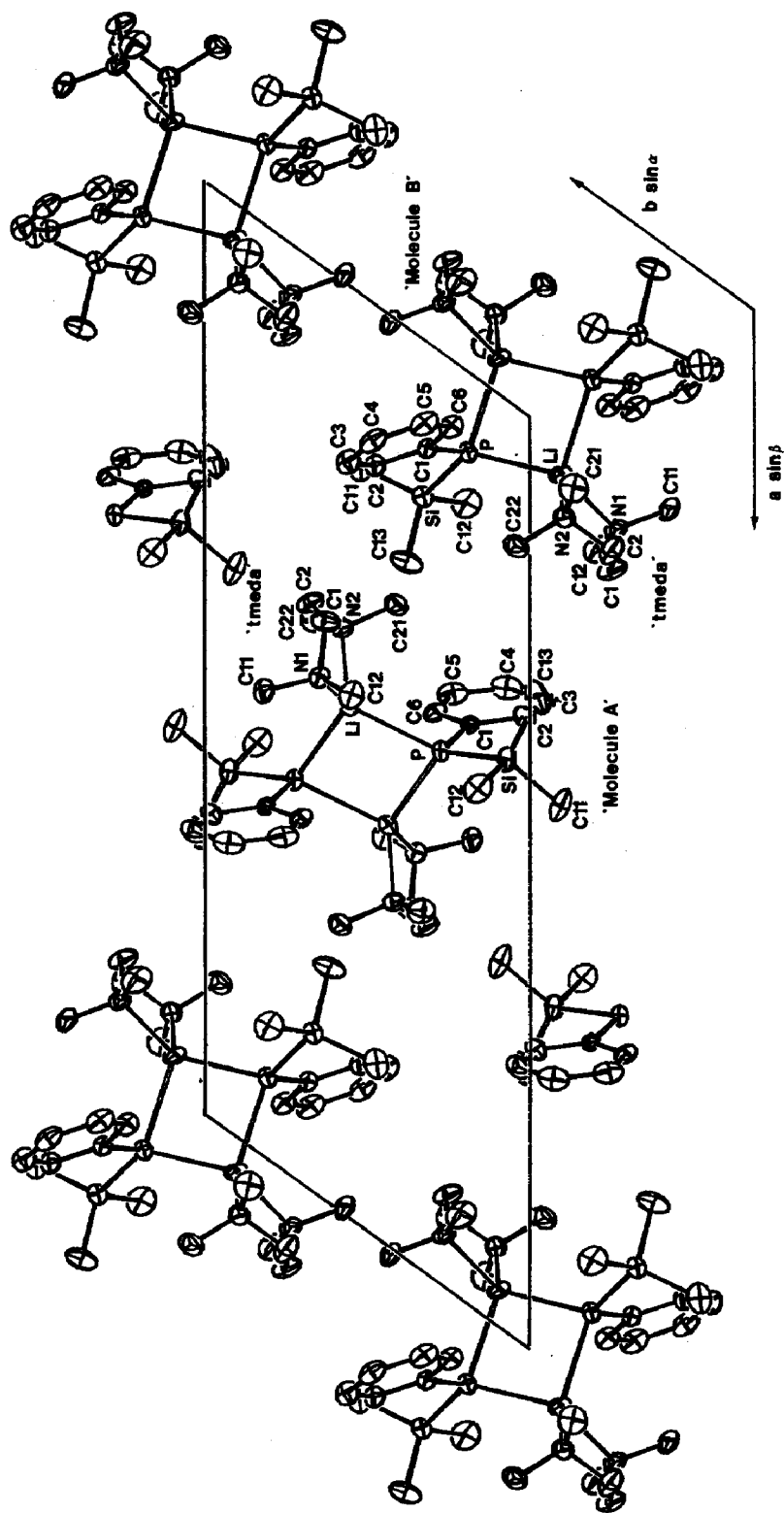


Fig. 3. The packing of the molecules of $[\text{LiPPH}(\text{SiMe}_3)(\text{tmeda})]_2$ (3) in the unit cell, viewed down the c -axis.

Experimental

All the compounds were handled under argon by standard Schlenk techniques. $[\text{Mg}(\text{PPh})_2(\text{tmeda})]$ (**1**) [14] and $[\text{LiPPh}(\text{tmeda})]$ [15] were prepared by published procedures. Me_3SiCl , tmeda, and n-BuLi were commercially available samples. Solvents were rigorously dried, distilled under argon, and degassed prior to use. NMR spectra were recorded on a Bruker AC 300 instrument (^1H , 300 MHz; ^{13}C , 75.5 MHz; ^{31}P , 121.5 MHz). ^7Li spectra were recorded at 116.7 MHz (AC 300) relative to external aqueous LiBr with C_7D_8 as lock. Infrared spectra were recorded on a Perkin-Elmer 577 spectrometer. The melting point was determined in a sealed capillary and is uncorrected. Analytical data were obtained by Analytische Laboratorien, Engelskirchen, Germany.

Synthesis of $[\text{LiPPh}(\text{SiMe}_3)(\text{tmeda})]_2$ (**3**)

(a) From $[\text{Mg}(\text{PPh})_2(\text{tmeda})]$ (**1**). A solution of n-BuLi in hexane (1.4 ml, 1.6 mol l^{-1} , 2.89 mmol) was slowly added to a stirred solution of **1** (0.35 g, 1.44 mmol) and tmeda (3 ml) in toluene (15 ml). The orange mixture was stirred at room temperature, and after 15 min, Me_3SiCl (0.34 g, 3.15 mmol) was added. The orange colour was immediately discharged. After a further 20 min stirring the volatiles were removed in vacuo and the pale-yellow residue extracted into toluene (15 ml)/hexane (5 ml). The extract was filtered then cooled to -30°C to give $[\text{MgCl}_2(\text{tmeda})]$ (0.4 g), which was filtered off (infrared spectrum (nujol, CsI): 4000–600 cm^{-1} absorptions of tmeda, 585s, 489s, 460s, 440s, 382s, 300vs,br cm^{-1} , no signal in the ^{31}P NMR spectrum, ^1H NMR shows only tmeda). Concentration of the filtrate and cooling to -30°C gave the title compound **3** as white crystals (0.4 g, 45%).

(b) From $[\text{LiPPh}(\text{tmeda})]$ (**5**). Me_3SiCl (0.26 g, 2.39 mmol) was added to a stirred solution of **5** (0.55 g, 2.37 mmol) and tmeda (1 ml) in THF (15 ml). The colourless solution was stirred for 15 min at room temperature then a solution of n-BuLi in hexane (1.6 ml, 1.6 mol l^{-1} , 2.56 mmol) was added. In an exothermic reaction an orange solution was formed, and this was stirred at room temperature for 15 min. After removal of the volatiles in vacuum, the pale yellow residue was extracted into toluene (15 ml). The extract was filtered and reduced to approximately half its volume then pentane (5 ml) was added. Cooling to -30°C afforded **3** as pale yellow microcrystals (0.59 g, 82%), m.p. 131–133 $^\circ\text{C}$. Found: C, 57.40, H, 9.51, N, 8.67. $\text{C}_{15}\text{H}_{30}\text{N}_2\text{LiPSi}$ (304.43 g), calc.: C, 59.18, H, 9.93, N, 9.20%. Infrared spectrum (Nujol, CsI, T = absorption of tmeda, Ph = absorption of phenyl ligand): 3048mw (Ph), 2798s (T), 2780m,sh (T), 1571s (Ph), 1560w,sh (Ph), 1445m,sh (SiMe_3 , T), 1438w,sh, 1357m (T), 1290s (T), 1268m (T), 1250ms (SiMe_3), 1240s, 1188m (Ph), 1160w (T), 1132m (T), 1095w,sh,br (T), 1074m, 1035ms (T), 1026s (Ph, T), 992ms, 951s, 882w (T), 840–820vs,br (SiMe_3 , T, Ph), 793m, 750w,sh (SiMe_3), 735vs, 700s (Ph), 680m (SiMe_3), 628s (SiMe_3), 478m [$\nu_{\text{as}}(\text{LiN}_2)$, B_{3u}], 448mw [$\nu_{\text{as}}(\text{Li}_2\text{P}_2)$, B_{3u}], 348w [$\nu_{\text{s}}(\text{LiN}_2)$, B_{2u}], 322m [$\nu_{\text{s}}(\text{Li}_2\text{P}_2)$, B_{2u}], 280w,br (SiMe_3), 250w (SiMe_3) cm^{-1} .

^1H NMR (C_7D_8 , $\delta(\text{ppm})$): -0.01d (0.7H, $^3J(^{31}\text{P}-^1\text{H})$ 4.7 Hz), 0.17d (1.1H, $^3J(^{31}\text{P}-^1\text{H})$ 4.9 Hz), 0.55s (7.8H, SiCH_3), 1.81s (4H, $\text{N}-\text{CH}_2-\text{CH}_2-\text{N}$), 1.89s (12H, $\text{N}-\text{CH}_3$), 6.71tt (1H, *p*-H, $^3J(^1\text{H}-^1\text{H})$ 7.2 Hz, $^4J(^1\text{H}-^1\text{H})$ ca. 1 Hz), $6.88-6.95\text{m}$ (*m*-H), 7.62dd (2H, *o*-H, $^3J(^1\text{H}-^1\text{H})$ 7.3 Hz). ^{13}C NMR (C_7D_8 , $\delta(\text{ppm})$): 3.91 ($\text{Si}-\text{CH}_3$), 46.16 ($\text{N}-\text{CH}_2-\text{CH}_2-\text{N}$), 57.85 ($\text{N}-\text{CH}_3$), 120.08 (*p*-C), 127.60 (*m*-C), 132.76 (*P*-C).

Structure determination

A very large crystal, ca. 1 mm³, encapsulated in some decomposition product in a capillary and presenting considerable difficulty in centring and alignment, was used for the structure determination. A unique data set was measured to a 2θ limit of 50° at 295 K using P2₁ four-circle diffractometer in conventional $2\theta/\theta$ scan mode (monochromatic Mo-K α radiation source, λ 0.71069 Å). A total of 6537 independent reflections were obtained, 2770 with $I \geq 3\sigma(I)$ being considered 'observed' and used in the large block least squares refinement, without absorption correction, after solution of the structures by direct methods. Anisotropic thermal parameters were refined for the non-hydrogen atoms; (x , y , z , U_{iso})_H were constrained at estimated values. Residuals at convergence 0.071, 0.066 are conventional R , R' on $|F|$; statistical weights used were derived from $\sigma^2(I) = \sigma^2(I_{\text{diff}}) + 0.00017 \sigma^4(I_{\text{diff}})$. Neutral atom complex scattering factors were used [17]; computation used the XTAL program system [18] implemented by Hall on a Perkin-Elmer 3241 computer. Results are given in the Tables and Fig. 3; the latter shows the non-hydrogen atom numbering.

Crystal data (3). C₃₀H₆₀Li₂N₄P₂Si₂, $M = 608.8$, triclinic, space group $P\bar{1}$ (C_i^1 , No. 2), a 24.46(4), b 11.16(2), c 10.17(1) Å, α 114.14(10), β 94.46(10), γ 120.91(9)°, U 2018(5) Å³. D_c ($Z = 2$) 1.00 g cm⁻³, $F(000) = 664$, $\mu(\text{Mo})$ 1.8 cm⁻¹.

Acknowledgements

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