

## Synthesis and structures of the 2-(dimethylsila)pyrimidine derivatives

$[\text{Si}(\text{Me})_2\text{NC}(\text{Ar})\text{C}(\text{H})\text{C}(\text{Ar})\text{NX}]_n$  (Ar = Ph,  $\text{C}_6\text{H}_4\text{Bu}^t\text{-4}$ ; X = H,  $\text{SiMe}_3$ ,  $\text{Li}(\text{hmpa})_2$ ,  $\text{K}(\text{thf})_3$ ;  $n = 1, 2$ )

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### ABSTRACT

Five crystalline 2-(dimethylsila)pyrimidine derivatives  $[\text{Si}(\text{Me})_2\text{NC}(\text{Ar})\text{C}(\text{H})\text{C}(\text{Ar})\text{NX}]_n$  (**Z**) have been prepared in excellent **1–4** or satisfactory **5** yield and characterised. The source of each was ultimately  $\text{Li}[\text{CH}(\text{SiMe}_2\text{R})(\text{SiMe}_2\text{OMe})]$  [R = Me (**B**) or OMe (**I**)]. Compound **1** (**Z** with Ar = Ph, X =  $\text{SiMe}_3$ ,  $n = 1$ ) was obtained from **Z** [with Ar = Ph, X =  $\text{Li}(\text{OEt}_2)$ ,  $n = 4$ ; previously isolated from **B** [P.B. Hitchcock, M.F. Lappert, X.-H. Wei, J. Organomet. Chem. 689 (2004) 1342]] and  $\text{Me}_3\text{SiCl}$ . The potassium salt **2** [**Z** with Ar =  $\text{C}_6\text{H}_4\text{-Bu}^t\text{-4}$ ; X =  $\text{K}(\text{thf})_3$ ,  $n = 2$ ] was made from  $\text{K}[\text{CH}(\text{SiMe}_3)(\text{SiMe}_2\text{OMe})]$  (**C**) (via **B**) and  $4\text{-Bu}^t\text{C}_6\text{H}_4\text{CN}$ . Treatment of **2** with 1,2-dibromoethane afforded **3** (**Z** with Ar =  $4\text{-Bu}^t\text{C}_6\text{H}_4$ ; X = H,  $n = 1$ ); which when reacted with successively *n*-butyllithium and  $\text{Me}_3\text{SiCl}$  produced **4** (**Z** with Ar =  $4\text{-Bu}^t\text{C}_6\text{H}_4$ , X =  $\text{SiMe}_3$ ,  $n = 1$ ). Compound **5** [**Z** with Ar =  $4\text{-Bu}^t\text{C}_6\text{H}_4$ , X =  $\text{Li}(\text{hmpa})_2$ ,  $n = 1$ ] resulted from **I** with  $4\text{-Bu}^t\text{C}_6\text{H}_4\text{CN}$  and then  $\text{OP}(\text{NMe}_2)_3$  ( $\equiv$  hmpa). Plausible reaction pathways from the appropriate alkali metal alkyl **C** or **I** to **2** or **5**, respectively, are suggested; these involve regioselective 1,3-migrations of  $\text{SiMe}_2\text{OMe}$  from C  $\rightarrow$  N and electrocyclic loss of  $\text{Me}_3\text{SiOMe}$  or  $\text{SiMe}_2(\text{OMe})_2$ , respectively. The X-ray structures of crystalline **1**, **2** and **5** are presented.

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## 1. Introduction

We have previously reported on reactions of selected trimethylsilylmethylolithium compounds with various nitriles free from  $\alpha$ -hydrogen giving rise *inter alia* to lithium  $\beta$ -diketimines. Some reactions relevant to the present study, in which  $\text{Li}[\text{CH}(\text{SiMe}_3)_2]$  and PhCN were the precursors, are shown in Scheme 1 [1,2]. This demonstrates (i) the formation of the derived lithium  $\beta$ -diketiminate by a process implicating successive 1,3-trimethylsilyl migrations from C  $\rightarrow$  N [1], (ii) a ligand transfer reaction yielding the potassium  $\beta$ -diketiminate [2], and (iii) the protodesilylation of the latter giving rise to the macrocyclic potassium salt **A** [2].

An extension of this chemistry featured the ligands  $[\text{CH}(\text{SiMe}_3)(\text{SiMe}_{3-n}(\text{OMe})_n)]^-$  ( $n = 1, 2$ ),  $[\text{CH}(\text{SiMe}_2(\text{OMe}))_2]^-$  and  $[\text{CH}(\text{SiMe}_3)(\text{SiMe}_2\text{Ph})]^-$  including the alkali metal methoxysilylmethyls  $[\text{Li}\{\text{CH}(\text{SiMe}_3)(\text{SiMe}_2\text{OMe})\}]_8$  (**B**) and  $\text{K}[\text{CH}(\text{SiMe}_3)(\text{SiMe}_2\text{OMe})]$  (**C**) [3]. The synthesis and structures of four crystalline lithium  $\beta$ -diketimines derived from reactions of **B** with two equivalents of benzonitrile, or successive equivalents of  $\text{Bu}^t\text{CN}$  and PhCN, have been reported [4]. Relevant to the present study was the

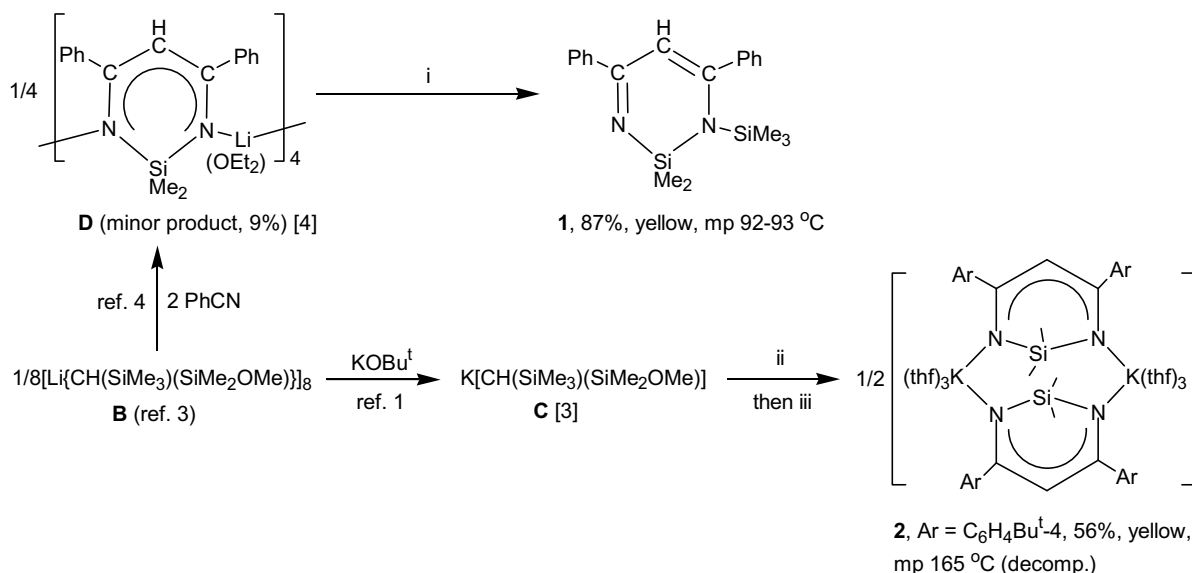
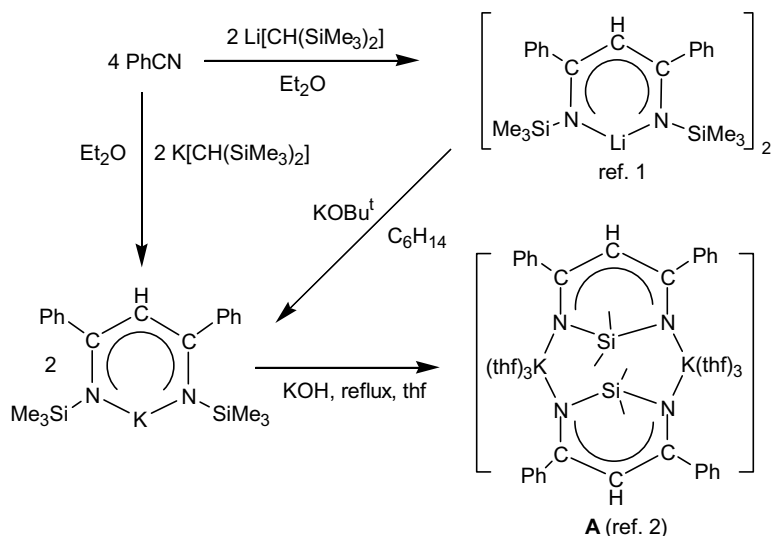
isolation (albeit as a very minor product) of the crystalline reduced *N*-lithiosilapyrimidine **D** (Scheme 2) from **B** and PhCN; the major products were the 1-azaallyllithium compound  $[\text{Li}\{\text{N}(\text{SiMe}_2\text{OMe})\text{C}(\text{Ph})\text{CH}(\text{SiMe}_3)\}]_3$  (showing regioselective  $\text{SiMe}_2\text{OMe}$ , rather than  $\text{SiMe}_3$ , 1,3-C  $\rightarrow$  N migration) and also  $[\text{Li}(\text{OEt}_2)\{\text{NSi}(\text{Me})_2\text{C}(\text{SiMe}_3)\text{C}(\text{Ph})\text{N}\}]_2$  (structurally related to **D** of Scheme 2) [4]. The tetracyclic structure of crystalline **D** had previously been established crystallographically, although the data were of poor quality [4].

## 2. Results and discussion

### 2.1. Synthesis of compounds **1** and **2** derived from $[\text{Li}\{\text{CH}(\text{SiMe}_3)(\text{SiMe}_2\text{OMe})\}]_8$ (**B**)

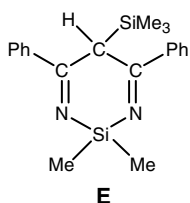
Reactions leading to the crystalline yellow compounds **1** and **2** are summarised in Scheme 2. Thus, the reduced *N*-trimethylsilyl-*N,N*-dimethyl-2-silapyrimidine **1** was isolated from **D** and trimethyl(chloro)silane. The dimeric reduced *N*-tris(thf)potassium-*N,N*-dimethyl-2-silapyrimidine **2** was obtained from the potassium alkyl **C** and 4-*tert*-butylbenzonitrile. The cited yields (excellent for **1**, good for **2**) refer to isolated crystalline complexes, and were not optimised.

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The structures of **1** and **2** were established by good (**1**) but only modest (**2**) quality X-ray data. For **2**, this is in part attributed to the rather loosely bound  $\text{thf}$  ligands. For this reason, crystalline **2** was thermally freed from  $\text{thf}$ , prior to its characterisation by microanalysis (the low carbon value is considered to have been caused by incomplete combustion of **2** due to the formation of carbon silicide), NMR spectroscopy and EI-mass spectrometry.

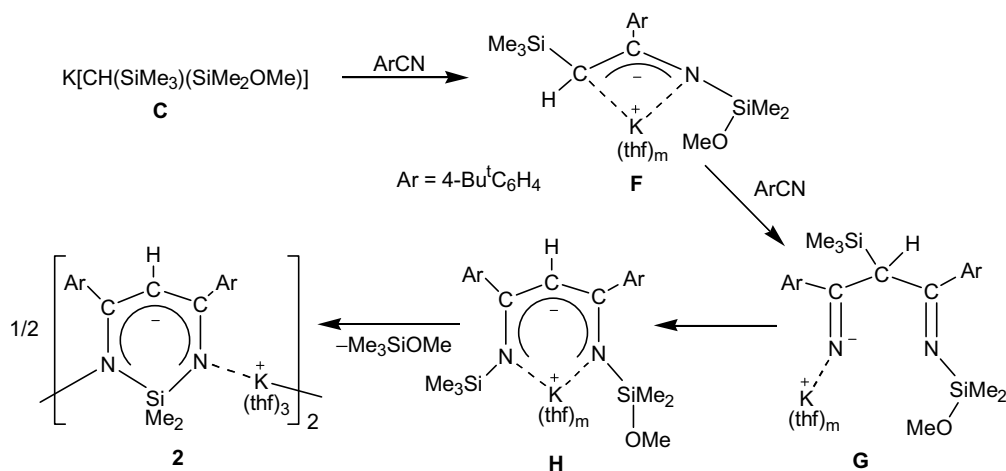
Compound **1** is an isomer of **E**. The latter had been obtained in good yield from  $[\text{Y}\{\text{CH}(\text{SiMe}_3)(\text{SiMe}_2\text{OME})\}_3]$  and six equivalents of benzonitrile by heating in toluene, with  $\text{Y}(\text{OME})_3$  as co-product, demonstrating regioselective 1,3-migration of  $\text{SiMe}_2\text{OME}$  (rather than  $\text{SiMe}_3$ ) from  $\text{C} \rightarrow \text{N}$  [5].



The formation of **2** from **C** is attributed to the reaction sequence shown in Scheme 3. The first step, involving equivalent portions of **C** and  $4\text{-Bu}^t\text{C}_6\text{H}_4\text{CN}$ , is believed to be a similar regioselective process leading to the 1-azaallypotassium compound **F**. In support, we cite the reaction of equivalent portions of **B** and  $\text{PhCN}$  which afforded the crystalline complex  $[\text{Li}\{\text{N}(\text{SiMe}_2\text{OME})\text{C}(\text{Ph})\text{CH}(\text{SiMe}_3)\}_3]$  [6]. Nucleophilic attack of **F** on a second equivalent of the nitrile, with an  $\text{SiMe}_3$  1,3-shift from  $\text{C} \rightarrow \text{N}$ , is suggested to have given a further intermediate **H** (possibly via **G**), which ultimately underwent an  $\text{Me}_3\text{SiOME}$  fragmentation in yielding **2**.

## 2.2. The X-ray structure of the crystalline compounds **1** and **2**

The molecular structure of the crystalline compound **1** is shown in Fig. 1 and selected geometrical parameters are listed in Table 1. The atoms  $\text{N1C1C2C3}$  of the reduced 2-silapyrimidine ring are coplanar; the  $\text{Si}$  and  $\text{N2}$  atoms are on opposite sides (by  $0.52$  and  $-0.27\text{ \AA}$ , respectively) of this plane, as are the *ipso*-carbon atoms  $\text{C4}$  and  $\text{C10}$  (by  $-0.44$  and  $0.13\text{ \AA}$ , respectively) of the phenyl rings attached to  $\text{C1}$  and  $\text{C3}$ , respectively. Each of the atoms  $\text{C1}$ ,  $\text{C3}$  and



Scheme 3.

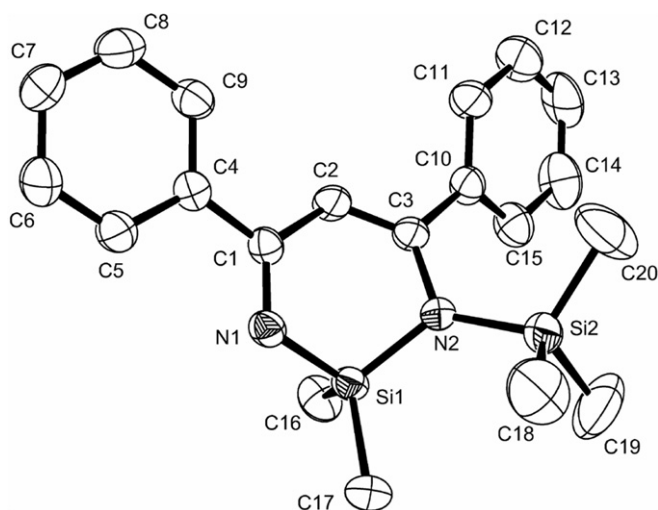


Fig. 1. ORTEP representation of the molecular structure of **1** (50% ellipsoids; H atoms omitted).

N2 (and presumably also C2) is in a distorted trigonal planar environment. Each of the endocyclic bond angles subtended at N1, C1, C2 and C3 is closely similar,  $123.2 \pm 0.7^\circ$ . Compound **1** is an isomer of **E** [5], the two compounds being related by a notional 1,3-C N trimethylsilylropy; some comparative structural data for **E** are included in Table 1.

The molecular structure of the crystalline, centrosymmetric, tetracyclic potassium compound **2** is shown in Fig. 2. Selected geo-

metrical parameters are listed in Table 2, together with those for the homologous compound **A** [3]. There is an outer twelve-membered macrocycle  $\overline{\text{KN2C1C2C3N1K'N2'C1'C2'C3'N1'}}$ . Its core is an almost planar (K and K' are 0.08 Å out of the N1N2N1'N2' plane) hexacycle. The atoms N1 and N2 are also part of a boat-shaped ring in which the atoms Si and C2 are 0.44 and 0.12 Å, respectively, out of the C1N2N1C3 plane; as are the *ispo*-carbon atoms C4 and C14 (attached to C1 and C3, respectively) by  $-0.15$  and  $-0.19$  Å, respectively. The dihedral angle between the C5C4C9 and the N2C1C2 planes is  $24^\circ$ , and that between the C15C14C19 and the N1C3C2 planes is  $23^\circ$ . Each of the atoms C1, C3, N1 and N2 is in a three-coordinate environment: distorted trigonal planar and pyramidal arrangements are found at the carbon and nitrogen atoms, respectively. The potassium atoms are at the centre of a severely distorted trigonal bipyramid.

### 2.3. Synthesis of the crystalline 2-(dimethylsilyl)pyrimidine derivatives **3**, **4** and **5**

The preparation of compounds **3** and **4** is outlined in Scheme 4. Thus, treatment of the potassium salt **2** with more than two equivalents of 1,2-dibromoethane afforded compound **3**, presumably with elimination of 2KBr and C<sub>2</sub>H<sub>4</sub>. Compound **3** with successively *n*-butyllithium and chloro(trimethyl)silane gave **4**. The crystalline compounds **3** and **4** were each obtained in excellent yield.

The related crystalline lithium salt **5** was isolated in modest yield from Li[CH(SiMe<sub>2</sub>OMe)<sub>2</sub>] (**I**) [3] with two equivalents of 4-Bu<sup>t</sup>C<sub>6</sub>H<sub>4</sub>CN and then hmpa [hmpa = OP(NMe<sub>2</sub>)<sub>3</sub>], Eq. (1).

Table 1  
Selected bond lengths (Å) and angles (°) for **1** and **E** [5]

Bond lengths	<b>1</b>	<b>E</b> [5]	Bond angles	<b>1</b>	<b>E</b> [5]
Si1–N1	1.7342(16)	1.7367(18)	N1–Si1–N2	104.94(7)	107.44(9)
Si1–N2	1.7593(16)	1.7429(18)	S1–N1–C1	116.27(12)	121.02(14)
N1–C1	1.289(2)	1.281(3)	S1–N2–C3	109.00(12)	120.20(15)
N2–C3	1.409(2)	1.280(3)	N1–C1–C2	122.49(16)	124.72(18)
C1–C2	1.469(2)	1.516(3)	N2–C3–C2	122.48(15)	125.39(19)
C2–C3	1.359(3)	1.521(3)	C1–C2–C3	123.93(16)	115.71(17)
N2–Si2	1.7688(16)	–	Si1–N2–Si2	126.96(9)	–
C1–C4	1.494(2)	–	N1–C3–C10	119.94(15)	–
C3–C10	1.495(2)	–	N2–C3–C10	118.44(15)	–

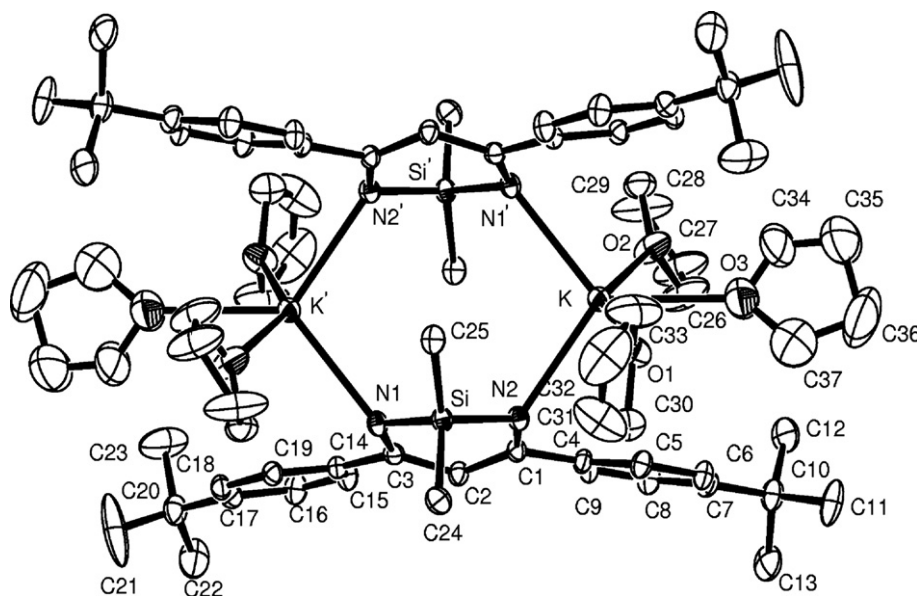
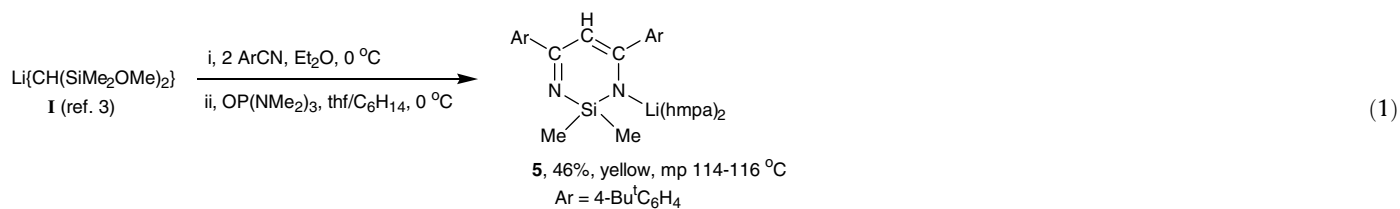
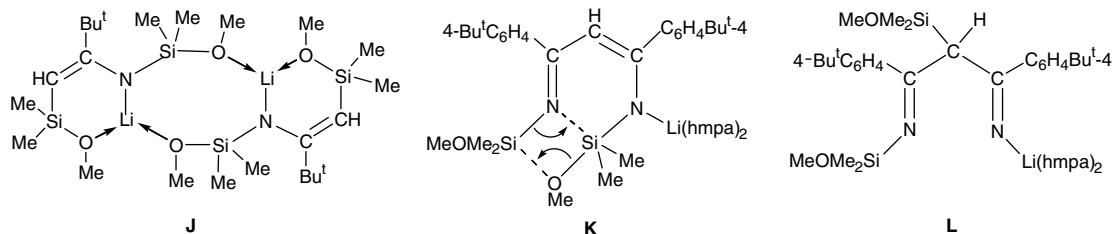


Fig. 2. ORTEP representation of the molecular structure of **2** (20% ellipsoids; H atoms omitted). Symmetry transformation to equivalent atoms:  $-x + 1, -y + 1, -z + 1$ .

The only previously related reaction of **1** was with Bu<sup>t</sup>CN producing the lithium azaallyl **J** [6]. Hence it is presumed that the first intermediate from equivalent portions of **1** and the nitrile is the 1-azaallyllithium compound Li[N(SiMe<sub>2</sub>OMe)C(C<sub>6</sub>H<sub>4</sub>Bu<sup>t</sup>-4)CH(SiMe<sub>2</sub>OMe)], which with a second equivalent of the nitrile and hmpa gives **K** (possibly via **L**). The final step in the formation of **5** is attributed to the electrocyclic elimination of SiMe<sub>2</sub>(OMe)<sub>2</sub> as depicted in **K**.

atom (attached to N1) and the C4 and C14 atoms (attached to C1 and C3, respectively) are  $-0.97, -0.15$  and  $-0.31$  Å, respectively, out of that plane. The aryl rings attached to C1 and C3 are twisted from this plane; thus, the dihedral angles between (i) the C5C4C9 and N1C1C2 planes and (ii) the C15C14C19 and N2C3C2 planes are  $36^\circ$  (i) and  $6^\circ$  (ii). The lithium atom is in a distorted trigonal planar environment and the angles subtended at the attached O1 and O2 atoms are  $163.4(3)$  and  $149.9(3)^\circ$ , respectively.



The compounds **3**, **4** and **5** were characterised by satisfactory C/H/N microanalysis, and NMR solution spectra and in the case of **5** by single crystal X-ray diffraction.

#### 2.4. The X-ray structure of the crystalline lithium compound **5**

The molecular structure of the crystalline lithium compound **5** is illustrated in Fig. 3 and selected geometric data are provided in Table 3. Its core is an envelope-shaped reduced 2-silapyrimidine ring in which the Si atom is 0.41 Å out of the essentially planar (C2 deviates by 0.02 Å from this plane) N1C1C2C3N2 array, while the Li

### 3. Experimental

#### 3.1. General details

Experiments were performed under an atmosphere of argon, or in a vacuum, using Schlenk apparatus and vacuum line techniques. The solvents used were reagent grade or better and were freshly distilled under dry nitrogen gas and freeze/thaw degassed prior to use. The drying agents used were sodium benzophenone (Et<sub>2</sub>O, thf), sodium-potassium alloy (C<sub>5</sub>H<sub>12</sub>, C<sub>6</sub>H<sub>14</sub>). Solvents were stored over a potassium mirror (C<sub>5</sub>H<sub>12</sub>, C<sub>6</sub>H<sub>14</sub>) or molecular sieves

**Table 2**  
Selected bond lengths (Å) and angles (°) for **2** and **A** [3]

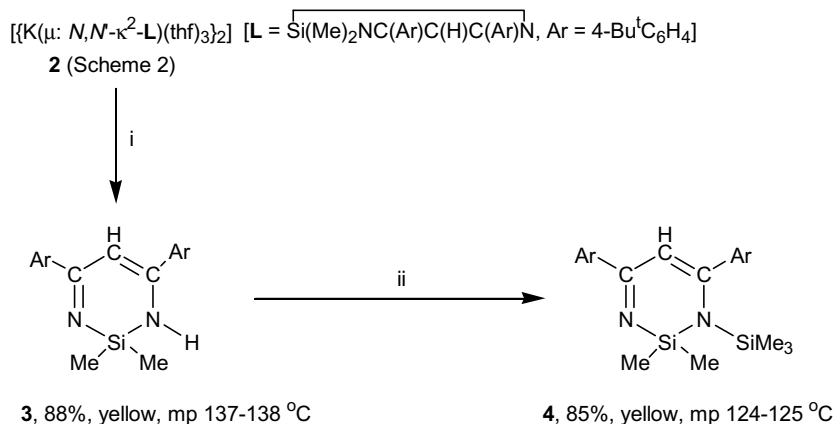
Bond lengths	<b>2</b>		<b>A</b> [3]		Bond angles	<b>2</b>		<b>A</b> [3]	
K–N1'	2.794(4)	2.829(6)	N1–K'–N2'	105.61(12)	108.6(2)	108.6(2)	108.6(3)	108.6(3)	
K–N2	2.782(4)	2.828(4)	N2'–Si'–N1'	108.6(2)	108.6(2)	108.6(2)	108.6(3)	108.6(3)	
N1'–Si1'	1.732(4)	1.733(6)	K–N2–C1	115.5(3)	114.2(4)	114.2(4)	114.2(4)	114.2(4)	
Si1'–N2'	1.735(4)	1.725(6)	Si'–N1'–K	117.0(2)	114.6(2)	114.6(2)	114.6(2)	114.6(2)	
N1–C3	1.308(6)	1.314(8)	K–N2–Si	119.4(2)	117.4(2)	117.4(2)	117.4(2)	117.4(2)	
N2–C1	1.318(6)	1.326(9)	Si–N2–C1	114.2(3)	115.2(5)	115.2(5)	115.2(5)	115.2(5)	
C1–C2	1.418(7)	1.414(10)	N2–C1–C2	126.1(4)	125.7(6)	125.7(6)	125.7(6)	125.7(6)	
C3–C2	1.412(7)	1.398(9)	C1–C2–C3	121.6(4)	121.9(6)	121.9(6)	121.9(6)	121.9(6)	
C1–C4	1.514(7)	1.514(9)	C3–N1–Si	114.7(3)	114.8(5)	114.8(5)	114.8(5)	114.8(5)	
C3–C14	1.528(7)	1.519(10)							

4 Å [Et<sub>2</sub>O, thf, C<sub>6</sub>D<sub>6</sub>, C<sub>5</sub>D<sub>5</sub>N, CDCl<sub>3</sub>, (CD<sub>3</sub>)<sub>2</sub>SO]. The NMR spectra were recorded at 298 K using a Bruker DPX 300 (at 300.1 MHz for <sup>1</sup>H, 75.5 MHz for <sup>13</sup>C and 116.6 MHz for <sup>7</sup>Li) or AMX 500 (at 99.4 MHz for <sup>29</sup>Si) instrument, and were referenced externally (<sup>7</sup>Li, using LiCl; <sup>29</sup>Si using SiMe<sub>4</sub>) or internally (<sup>1</sup>H, <sup>13</sup>C) to the residual solvent resonances. Electron impact mass spectra were ta-

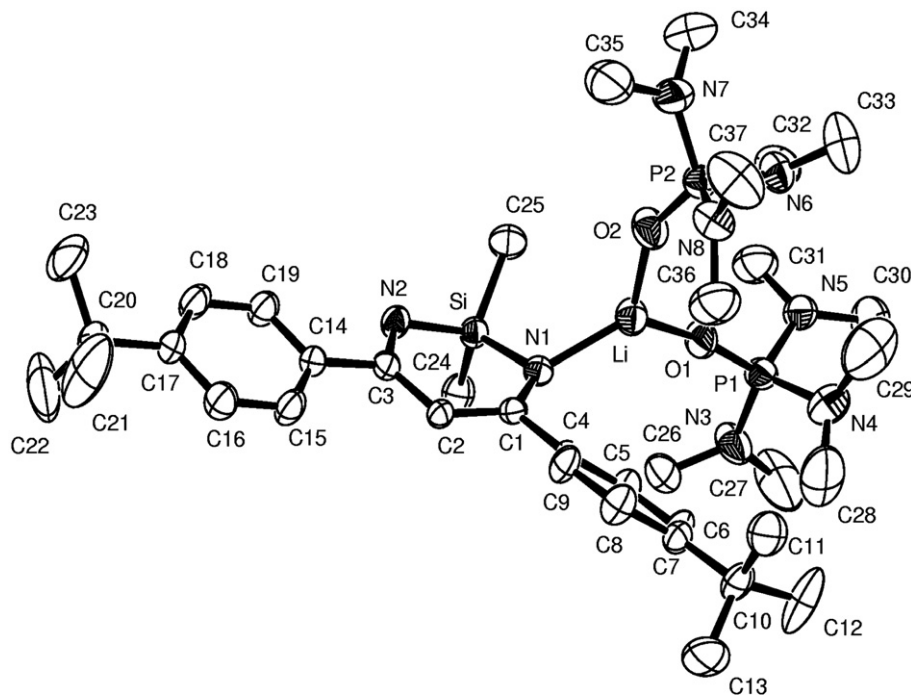
ken from solid samples using a Kratos MS 80 RF instrument. Elemental analyses were determined by Medac Ltd, Brunel University. The compounds Li[CH(SiMe<sub>3</sub>)(SiMe<sub>2</sub>OMe)] (**B**) [3], Li[CH(SiMe<sub>2</sub>OMe)<sub>2</sub>] (**I**) [3], K[CH(SiMe<sub>3</sub>)(SiMe<sub>2</sub>OMe)] (**C**) [3], and [Li{NC(Ph)C(H)C(Ph)NSi(Me)<sub>2</sub>}(OEt<sub>2</sub>)<sub>4</sub>] (**D**) [4] were prepared by published procedures. The compounds 4-Bu<sup>t</sup>C<sub>6</sub>H<sub>4</sub>CN, 1,2-Br<sub>2</sub>C<sub>2</sub>H<sub>4</sub>, Si(Cl)Me<sub>3</sub>, (Me<sub>2</sub>N)<sub>3</sub>PO (hmpa), and LiBu<sup>n</sup> in hexane were commercially available samples.

### 3.2. 1,1-Dimethyl-3,5-diphenyl-6-trimethylsilyl-2,6-diaza-1-silahexa-2,4-diene (**1**)

Chloro(trimethyl)silane (0.12 cm<sup>3</sup>, 0.92 mmol) was added to a stirred suspension of the diethyl ether-free lithium β-diketiminatodimethylsilane **D** (0.16 g, 0.56 mmol, based on monomer) in a mixture of thf (5 cm<sup>3</sup>) and hexane (25 cm<sup>3</sup>) at 0 °C. The mixture was set aside for 12 h at ca. 20 °C, then filtered. The filtrate was



**Scheme 4.** Reagents and conditions: (i) 2[CH<sub>2</sub>Br]<sub>2</sub>, thf/C<sub>6</sub>H<sub>14</sub>, 0 °C; (ii) LiBu<sup>n</sup>, C<sub>6</sub>H<sub>14</sub>, –30 °C and then Me<sub>3</sub>SiCl.



**Fig. 3.** ORTEP representation of the molecular structure of **5** (20% ellipsoids; H atoms omitted).

**Table 3**  
Selected bond lengths (Å) and angles (°) for **5**

Bond lengths				Bond angles							
Si–N1	1.735(3)	C1–C2	1.408(5)	N1–Li	1.986(7)	N1–Si–N2	108.59(15)	C1–C2–C3	122.3(3)	N1–C1–C4	116.4(3)
Si–N2	1.721(3)	C2–C3	1.424(5)	Li–O1	1.856(7)	Si–N1–C1	115.4(3)	Si–N1–Li	112.3(3)	N2–C3–C14	116.2(3)
N1–C1	1.334(5)	C1–C4	1.499(5)	Li–O2	1.879(7)	Si–N2–C3	116.7(3)	Li–N1–C1	127.5(3)	C2–C1–C4	117.8(3)
N2–C3	1.312(5)	C3–C14	1.522(5)	O1–P1	1.476(3)	N1–C1–C2	125.8(3)	N1–Li–O1	123.8(9)	C2–C3–C14	118.3(3)
				O1–P2	1.478(3)	N2–C3–C2	125.5(3)	N1–Li–O2	121.8(4)		

concentrated (to ca. 10 cm<sup>3</sup>) and stored at –25 °C for 2 d, whereafter pale yellow crystals of compound **1** (0.17 g, 87%) (Anal. Calc. for C<sub>20</sub>H<sub>24</sub>N<sub>2</sub>Si<sub>2</sub>: C, 68.6; H, 7.43; N, 8.00. Found: C, 68.3; H, 7.39; N, 8.02%), m.p. 92–93 °C, were obtained. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ –0.12 (s, 9 H, SiMe<sub>3</sub>), 0.55 (s, 6 H, SiMe<sub>2</sub>), 6.51 (s, 1 H, CH), 7.06 (m, 3 H, Ph), 7.09 (m, 3 H, Ph), 7.18 (m, 2 H, Ph), 8.24 ppm (m, 2 H, Ph); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 0.21, 3.13, 110.6, 128.6, 141.0, 143.4, 158.3, 171.7 ppm; <sup>29</sup>Si NMR (CDCl<sub>3</sub>): δ –1.11 (SiMe<sub>2</sub>), 7.74 ppm (SiMe<sub>3</sub>). MS (*m/z*% and assignment): 350 (90, [M]<sup>+</sup>), 335 (22, [M–Me]<sup>+</sup>), 232 (72%), 130 (100%), 73 (70, [SiMe<sub>3</sub>]<sup>+</sup>).

### 3.3. The potassium salt $[[K(\text{:N,N}'\text{-}\kappa^2\text{-L})(\text{thf})_3]_2] (\mathbf{2})$ [L = Si(Me)<sub>2</sub>NC(C<sub>6</sub>H<sub>4</sub>Bu<sup>t</sup>-4)C(H)C(C<sub>6</sub>H<sub>4</sub>Bu<sup>t</sup>-4)N]

4-*tert*-Butylbenzotrile (0.42 cm<sup>3</sup>, 2.64 mmol) was added by syringe to a solution of the potassium alkyl **C** (0.28 g, 1.31 mmol) in diethyl ether (20 cm<sup>3</sup>), which immediately become orange. The reaction mixture was stirred for 18 h at ambient temperature. The supernatant liquor was removed by decantation. The bright yellow residual solid was dissolved in thf (10 cm<sup>3</sup>) and stored at –15 °C for 48 h, whereafter yellow crystals of compound **2** (0.47 g, 56%), m.p. 145 °C (decomp.), were obtained. The sample for analysis was heated to remove thf (Anal. Calc. for C<sub>25</sub>H<sub>23</sub>KN<sub>2</sub>Si: C, 70.0; H, 7.76; N, 6.53. Found: C, 66.6; H, 7.43; N, 6.62%) (the value for C was very low, attributed to formation of carbon silicide). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>/C<sub>5</sub>D<sub>5</sub>N): δ 0.52 (s, 6 H, SiMe<sub>2</sub>), 1.26 (s, 18 H, CMe<sub>3</sub>), 6.75 (s, 1 H, CH), 7.20 (d, 4 H, C<sub>6</sub>H<sub>4</sub>), 7.43 ppm (d, 4 H, C<sub>6</sub>H<sub>4</sub>); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>/C<sub>5</sub>D<sub>5</sub>N): δ 2.99, 31.2, 94.4, 124.8, 127.1, 127.6, 144.3, 172.4 ppm; <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>/C<sub>5</sub>D<sub>5</sub>N): δ 5.69 ppm.

### 3.4. 1,1-Dimethyl-3,5-di(4'-*tert*-butylphenyl)-2,6-diaza-1-silahexa-2,4-diene (**3**)

1,2-Dibromoethane (0.053 cm<sup>3</sup>, 0.63 mmol) was added by syringe to a solution of the potassium salt **2** (0.32 g, 0.25 mmol) in a mixture of thf (10 cm<sup>3</sup>) and hexane (45 cm<sup>3</sup>) at 0 °C. The reaction mixture was stirred for 18 h at ambient temperature, then filtered.

The filtrate was concentrated to ca. 15 cm<sup>3</sup> and stored at –25 °C for 24 h, whereafter pale yellow crystals of compound **3** (0.17 g, 88%) (Anal. Calc. for C<sub>25</sub>H<sub>34</sub>N<sub>2</sub>Si: C, 76.9; H, 8.72; N, 7.18. Found: C, 76.1; H, 8.69; N, 7.15%), m.p. 137–138 °C, were obtained. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 0.41 (s, 6 H, SiMe<sub>2</sub>), 1.12 (s, 18 H, CMe<sub>3</sub>), 3.91 (s, 1 H, NH), 6.34 (s, 1 H, CH), 7.24–7.36 (m, 6 H, C<sub>6</sub>H<sub>4</sub>), 8.31 ppm (d, 2 H, C<sub>6</sub>H<sub>4</sub>); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): δ 31.3, 34.6, 92.5, 125.8, 126.1, 140.3, 150.8, 164.2 ppm; <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>): δ 6.35 ppm. MS (*m/z*% and assignment): 390 (100%, [M]<sup>+</sup>), 333 (70%, [M–Bu<sup>t</sup>]<sup>+</sup>), 216 (86%), 180 (48%), 57 (28%, [Bu<sup>t</sup>]<sup>+</sup>).

### 3.5. 1,1-Dimethyl-3,5-di(4'-*tert*-butylphenyl)-2,6-diaza-4-trimethylsilyl-1-silahexa-2,4-diene (**4**)

*n*-Butyllithium (0.26 cm<sup>3</sup> of a 1.6 mol dm<sup>–3</sup> solution in hexane, 0.41 mmol) was added dropwise to a cooled and stirred solution of the compound **3** (0.16 g, 0.41 mmol) in diethyl ether (60 cm<sup>3</sup>) at –30 °C. The mixture was brought to ambient temperature and stirred for 4 h; then re-cooled to –78 °C before adding chloro(trimethyl)silane (0.05 cm<sup>3</sup>, 0.41 mmol) by syringe. The mixture was brought to ambient temperature and set aside with stirring for 12 h. The volatiles were removed *in vacuo* and the residue was extracted into hexane (30 cm<sup>3</sup>). The extract was concentrated to ca. 15 cm<sup>3</sup> and stored at –25 °C for 24 h, yielding pale yellow crystals of compound **4** (0.16 g, 85%) (Anal. Calc. for C<sub>28</sub>H<sub>42</sub>N<sub>2</sub>Si<sub>2</sub>: C, 72.7; H, 9.09; N, 6.06. Found: C, 71.4; H, 8.97; N, 6.12%), m.p. 124–125 °C. <sup>1</sup>H NMR [(CD<sub>3</sub>)<sub>2</sub>SO]: δ 1.19 (s, 18 H, CMe<sub>3</sub>), 5.78 (s, 2 H, NH), 6.84 (s, 1 H, CH), 7.36 (d, 4 H, C<sub>6</sub>H<sub>4</sub>), 8.28 ppm (d, 4 H, C<sub>6</sub>H<sub>4</sub>); <sup>13</sup>C NMR [(CD<sub>3</sub>)<sub>2</sub>SO]: δ 31.3, 41.2, 92.4, 125.7, 126.1, 139.4, 151.7, 166.4 ppm.

### 3.6. *N*-Bis(hmpa)lithium[2,2-dimethyl-3-aza-4,6-di(4'-*tert*-butylphenyl)-2-sila-3,5-dienyl]amide (**5**)

4-*tert*-Butylbenzotrile (0.26 cm<sup>3</sup>, 1.64 mmol) was added by syringe to a stirred solution of bis[dimethyl(methoxy)silyl]methyllithium (**I**) in diethyl ether (25 cm<sup>3</sup>) at 0 °C. Stirring of the mixture

**Table 4**  
Crystal data and structure refinement for **1**, **2** and **5**

Compound	<b>1</b>	<b>2</b>	<b>5</b>
Formula	C <sub>20</sub> H <sub>26</sub> N <sub>2</sub> Si <sub>2</sub>	C <sub>14</sub> H <sub>14</sub> K <sub>2</sub> N <sub>4</sub> O <sub>6</sub> Si <sub>2</sub> ·3(C <sub>4</sub> H <sub>8</sub> O)	C <sub>37</sub> H <sub>69</sub> LiN <sub>6</sub> O <sub>2</sub> P <sub>2</sub> Si
<i>M</i>	350.61	1506.38	754.97
Temperature (K)	223(2)	173(2)	223(2)
Crystal system	Orthorhombic	Triclinic	Triclinic
Space group	<i>Pna</i> 2 <sub>1</sub> (No. 33)	<i>P</i> 1 (No. 2)	<i>P</i> 1 (No. 2)
<i>a</i> (Å)	11.8450(2)	11.0985(4)	11.2203(5)
<i>b</i> (Å)	19.9636(3)	13.5475(6)	13.2485(7)
<i>c</i> (Å)	8.4915(1)	16.3214(7)	15.5275(8)
α (°)	90	87.381(2)	96.010(2)
β (°)	90	73.110(2)	102.637(3)
γ (°)	90	79.508(2)	97.405(4)
<i>U</i> (Å <sup>3</sup> )	2055.27(5)	2308.9(2)	2212.3(2)
<i>Z</i>	4	1	2
Absorption coefficient (mm <sup>–1</sup> )	0.18	0.18	0.17
Unique reflections [ <i>R</i> <sub>int</sub> ]	4801, 0.053	6205, 0.084	7207, 0.062
Reflections with <i>I</i> > 2σ( <i>I</i> )	4236	4758	4832
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )] <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub>	0.040, 0.097	0.115, 0.337	0.073, 0.158
<i>R</i> indices (all data) <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub>	0.050, 0.102	0.142, 0.367	0.120, 0.185

was continued for 24 h at ambient temperature; a yellow precipitate had formed. Volatiles were removed *in vacuo* and the residue was washed twice with pentane, then extracted into diethyl ether (25 cm<sup>3</sup>). The extract was concentrated to *ca.* 10 cm<sup>3</sup> and stored for a few days at –27 °C, yielding yellow microcrystals. Crystallisation from hmpa (0.5 cm<sup>3</sup>)/thf (5 cm<sup>3</sup>)/hexane (15 cm<sup>3</sup>) at 0 °C afforded yellow crystals of **5** (0.28 g, 46%) (Anal. Calc. for C<sub>37</sub>H<sub>69</sub>LiN<sub>8</sub>O<sub>2</sub>P<sub>2</sub>Si: C, 58.9; H, 9.21; N, 14.83. Found: C, 58.7; H, 8.97; N, 14.47%), m.p. 114–116 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>/C<sub>5</sub>D<sub>5</sub>N): δ 0.69 (s, 6 H, SiMe<sub>2</sub>), 1.21 (s, 18 H, CMe<sub>3</sub>); 2.26, 2.29 [s, 18 + 18 H, OP(NMe<sub>2</sub>)<sub>3</sub>], 6.63 (s, 1 H, CH), 7.31 (d, 4 H, C<sub>6</sub>H<sub>4</sub>), 8.23 ppm (d, 4 H, C<sub>6</sub>H<sub>4</sub>); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>/C<sub>5</sub>D<sub>5</sub>N): δ 5.04, 31.5, 34.4, 36.5, 94.2, 124.8, 127.1, 145.6, 171.5 ppm; <sup>7</sup>Li (C<sub>6</sub>D<sub>6</sub>/C<sub>5</sub>D<sub>5</sub>N): δ –0.84 ppm.

### 3.7. X-ray crystallographic studies

Diffraction data were collected on a Nonius Kappa CCD diffractometer (program package WINGX) using monochromated Mo K $\alpha$  radiation,  $\lambda$  0.71073 Å at 173(2) K. Crystals were coated with oil and then directly mounted on the diffractometer under a stream of cold nitrogen gas. In **2** there were two very poorly defined solvate molecules: one disordered in a general position and one disordered about an inversion centre. For both, atoms were included as isotropic C atoms with H atoms omitted. The diffraction from the crystal of **2** was weak and did not extend to high angle; the high *R* factors are a reflection of these problems; however, the complex is clearly defined.

Absorption corrections were not applied. Refinement was carried out using SHELXL-97 [7]. Further details are in Table 4.

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### Appendix A. Supplementary material

CCDC 691609, 691610 and 691611 contains the supplementary crystallographic data for **1**, **2** and **5**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.07.019.

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