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Synthesis and spectral characterization of diorganodiaminosilanes [(ArNH)$_2$SiPhMe] (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$; 2,4,6-Me$_3$C$_6$H$_2$) and lithium silylamide [(2,6-Et$_2$C$_6$H$_3$NLi)(2,6-Et$_2$C$_6$H$_3$NH)SiPh$_2$]

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Abstract

Aminosilanes bearing bulky substituents on nitrogen centers, [(ArNH)$_2$SiPhMe] (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$ (**1**), 2,4,6-Me$_3$C$_6$H$_2$ (**2**)) and half-sandwich lithium silylamide [(2,6-Et$_2$C$_6$H$_3$NLi)(2,6-Et$_2$C$_6$H$_3$NH)SiPh$_2$] (**3**) have been prepared and characterized by elemental analysis, IR, EI mass and NMR (^{1}H and ^{29}Si) spectroscopic studies. The solid state structures of **2** and **3** have been determined by single crystal X-ray diffraction studies. The molecule **2** has a C_1 symmetry due to the steric crowding, and the two N–H protons are approximately *trans* to each other. The amido nitrogen atoms in **2** show significant deviation from trigonal-planar geometry, and as a result, the observed Si–N bonds are marginally longer than those observed in aminosilanes with planar nitrogen atoms. The molecule **3** exists as discrete dimer with an inversion center. The Li ion in **3** forms intramolecular π-complex with the neighboring aryl (2,6-Et$_2$C$_6$H$_3$) group, to form a half-sandwich lithium silylamide.

Keywords: Aminosilanes; Half-sandwich lithium; NMR spectroscopy; X-ray diffraction

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1. Introduction

The structural chemistry of lithiated aminosilanes has been of considerable interest due to their abundant use as precursors in the preparation of transition and main group metal amido complexes [1]. The single crystal X-ray diffraction studies have shown interesting structural features for lithium compounds, which depend upon the nature of the solvent and reaction conditions. There are few examples of crystal structures of lithium amides based on arylaminosilane in the literature. Burger and co-workers have reported the crystal structure of a lithium salt based on arylaminosilane [(^{t}BuN(Li))$_3$SiPh]$_2$ (**A**; Chart 1) [2]. Power et al. have subsequently reported the synthesis and X-ray crystal structure of [(2,4,6-Me$_3$C$_6$H$_2$NLi)$_2$SiMe$_2$]$_2$ (**B**) with increased steric bulkiness at nitrogen [3]. Recently, Hill and Hitchcock reported synthesis and solid state structure of [(2,6-^{i}Pr$_2$C$_6$H$_3$NLi)$_2$SiMe$_2$]$_2$ (**C**) [4].

Our interest in this area is to employ bulky substituents both at silicon and nitrogen centers and synthesize new kinetically stabilized aryldiaminosilanes and explore their utility in preparing metal complexes [5]. We have recently reported in this journal on the synthesis and characterization of sterically hindered diaryldiaminosilanes [(RNH)$_2$-SiPh$_2$] (R = 2,6-^{i}Pr$_2$C$_6$H$_3$, 2,4,6-Me$_3$C$_6$H$_2$, 2,6-Et$_2$C$_6$H$_3$) [5b], among which the molecular structures of [(2,6-^{i}Pr$_2$C$_6$H$_3$NH)$_2$SiPh$_2$)] and [(2,6-Et$_2$C$_6$H$_3$NH)$_2$SiPh$_2$)] have been determined by single crystal X-ray diffraction studies. The amido nitrogens of both compounds exhibit considerable deviation from the expected trigonal-planar geometry. The observed dihedral angles and the orientation of lone pair in the compound point to the role of $N_{\mathrm{l.p}} \rightarrow \mathrm{Si–X}\ \sigma^*$ negative hyperconjugative interactions in Si–N multiple bonding.

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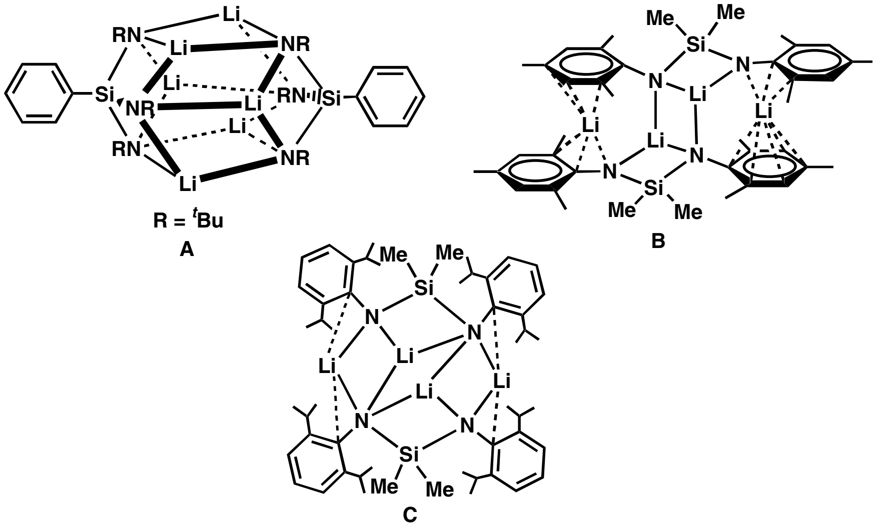


Chart 1.

In the literature, there is no reported example of monolithium complex of arylsubstituted diaminosilane. Herein we wish to describe the synthesis of two new methylphenyldiaminosilanes and the monolithium derivative of an aryl substituted diaminosilane, their spectral characterization, and X-ray structure determination.

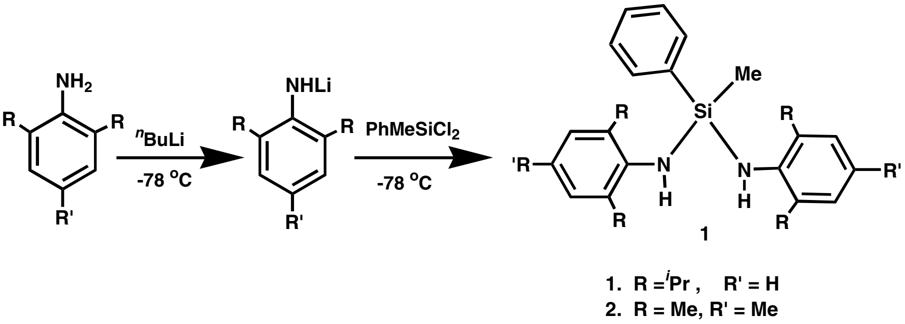
2. Result and discussion

2.1. Synthesis

The new aminosilanes have been synthesized using a common two step procedure. The first step is the lithiation of the substituted aniline, which is carried out strictly at −78 °C to avoid abstraction of both the protons of the primary aniline to form the dilithium salt. The completion of this reaction was achieved by slow warming of the reaction mixture to room temperature. The lithium salt so formed was reacted with dichloromethylphenylsilane. The lithium chloride precipitated was removed by filtration to obtain the aminosilane derivatives [(RNH)$_2$SiPhMe] (R = 2,6-^{i}Pr$_2$C$_6$H$_3$ (**1**) and 2,4,6-Me$_3$C$_6$H$_2$ (**2**)) (Scheme 1) as crude products in fairly good yields. Analytically pure compounds have been obtained for **1** and **2** by recrystallization of the product from light petroleum ether. The compounds are highly soluble in most of the common organic solvents. Since the compounds are moisture and light sensitive, care was taken to exclude moisture as well as light during all experimental manipulations. However, these compounds can be stored in pure form for several months under dry nitrogen atmosphere inside a glove-box.

Products **1** and **2** have been characterized by elemental analysis, and infrared and ^{1}H and ^{29}Si NMR spectroscopy. Compounds **1** and **2** exhibit a similar infrared spectral pattern. They show the characteristic N–H stretching vibration at around 3370 cm^{-1}. The absorption observed at around 3050 cm^{-1} is due to the aromatic C–H stretching vibration. Aliphatic C–H stretching vibrations are observed at around 2900 cm^{-1}. All the compounds show absorption at around 1450 cm^{-1} for N–H bending vibration and around 900 cm^{-1} for Si–N stretching mode.

The ^{1}H NMR spectra of **1** and **2** show a singlet at around 0.4 ppm due to –SiMe group. Compound **1** shows a doublet at 1.0 ppm ($^3J_{H-H}$ = 6.6 Hz), which corresponds to the protons of the CH$_3$ groups of the isopropyl substituents. As expected, the methine proton of isopropyl group shows a septet. Compound **2** shows two singlets (1:2) for the protons of the two different types of methyl groups of



Scheme 1. Synthesis of aminosilanes [(RNH)$_2$SiPhMe] (**1**–**2**).

the mesityl substituent. The singlet observed at 2.8 ppm is assignable for the N–H protons. The aromatic protons appear as multiplets in the region 6.8–7.8 ppm.

The ^{29}Si NMR chemical shifts observed for compounds **1** and **2** fall in the range δ −17 to −19 ppm. These values are considerably downfield shifted compared to the related diaminodiphenylsilanes ([$(PhNH)_2SiPh_2$] −30.2, [$(^iPrNH)_2SiPh_2$] −27.9 [6], [$(^tBuNH)_2SiPh_2$] − 35.4, [$(NH^iPr)_2(NH^tBu)_2SiPh_2$] −31.7, [$(2,6\text{-}^iPr_2C_6H_3NH)_2SiPh_2$] −28.7, [$(2,6\text{-}Et_2C_6H_3NH)_2SiPh_2$] −29.2, [$(2,4,6\text{-}Me_3C_6H_2NH)_2SiPh_2$] −30.7) and the diaminodichlorosilane [$(2,6\text{-}Me_2C_6H_3NH)_2SiCl_2$] − 30.7 ppm [5,6].

2.2. Crystal structure of [$(2,4,6\text{-}Me_3C_6H_3NH)_2SiPhMe$] (2)

Colorless single crystals of X-ray quality for [$(2,4,6\text{-}Me_3C_6H_2NH)_2SiPhMe$] (**2**) were obtained after 12 h from petroleum ether at 0 °C. The compound crystallizes in triclinic space group $P\bar{1}$. A perspective view of the molecule is shown in Fig. 1 and the selected structural parameters are listed in Table 1.

Unlike in some of the previously reported diaminosilanes (where hydrogen bonding interactions are observed) (Table 2), the molecules of **2** are isolated in the crystal, showing no interaction to the neighbors presumably due to the bulky hydrocarbon envelope. The observed torsional angles for H–N–Si–N linkages in **2** clearly indicate that the hydrogen atoms are not in the N_2Si plane, but residing above and below the N_2Si plane with a large twist.

Table 1
Selected bond lengths (Å) and bond angles (°) of [$(2,4,6\text{-}Me_3C_6H_3NH)_2SiPhMe$] (**2**)

Si(1)–N(2)	1.718(2)	N(1)–H(1A)	0.86(3)
Si(1)–N(1)	1.736(2)	N(2)–H(2A)	0.74(3)
Si(1)–C(7)	1.862(2)	N(1)–C(11)	1.411(2)
Si(1)–C(1)	1.872(2)	N(2)–C(21)	1.429(2)
N(2)–Si(1)–N(1)	117.74(8)	C(11)–N(1)–Si(1)	133.48(13)
N(2)–Si(1)–C(7)	106.52(9)	C(11)–N(1)–H(1A)	109.9(2)
N(1)–Si(1)–C(7)	103.79(10)	Si(1)–N(1)–H(1A)	114.5(18)
N(2)–Si(1)–C(1)	108.48(8)	C(21)–N(2)–Si(1)	127.10(13)
N(1)–Si(1)–C(1)	107.42(8)	C(21)–N(2)–H(2A)	113.6(18)
C(7)–Si(1)–C(1)	113.00(10)	Si(1)–N(2)–H(2A)	117.5(18)

The Si–N distance in **2** (av. 1.727 Å) is marginally longer than those observed for diphenyldialkylaminosilanes reported by Nöth et al. (av. 1.705 Å) [6]. This lengthening of Si–N bond distances can be attributed to the significant pyramidalization of nitrogen atoms in **2** compared to the near trigonal-planar geometry around nitrogen atoms in diphenyldialkylaminosilanes listed in Table 2. It is now generally believed that the multiple bonding between silicon and nitrogen centers occur via $N_{l.p} \rightarrow Si\text{–}X\ \sigma^*$ negative hyperconjugative interactions rather than the pπ–dπ interactions, which have no geometrical constraints [7]. However, the observed non-planar geometry around the nitrogen atoms (i.e. slightly pyramidalized nitrogen centers) reduces the extent of negative hyperconjugative interaction between the nitrogen lone pair, which now has significant s-character (sp^3 to sp^2), and a Si–C σ^* orbital. Similarly, the sum of angles around nitrogen in [$(2,4,6\text{-}Me_3C_6H_2NH)_2SiMe_2$] (347.1°) clearly explains the longest Si–N distance (1.730 Å) among diaminosilanes (Table 2) [3].

2.3. Synthesis and spectral studies of [$(2,6\text{-}Et_2C_6H_3NH)(2,6\text{-}Et_2C_6H_3NLi)SiPh_2$] (3)

Addition of ^{n}BuLi to a solution of [$(2,6\text{-}Et_2C_6H_3NH)SiPh_2$] in a 1:1 or 1:2 stoichiometry in toluene at room temperature generates dimeric half-sandwich lithium silylamide **3** (Scheme 2). Even when an excess of ^{n}BuLi was used in this reaction, only the monolithiated product was obtained. Unlike, previously reported lithium amides {[$(2,6\text{-}^iPr_2C_6H_3NLi)_2SiMe_2$]$_2$ (**A**) [4], [$(2,4,6\text{-}Me_3C_6H_2NLi)_2SiMe_2$]$_2$ (**B**) [3], {[$^tBuN(Li)_3$]SiPh}$_2$ (**C**) [2]} (Chart 1) in the literature, compound **3** is the monolithiated product probably due to the bulky substitution both at silicon and nitrogen atoms.

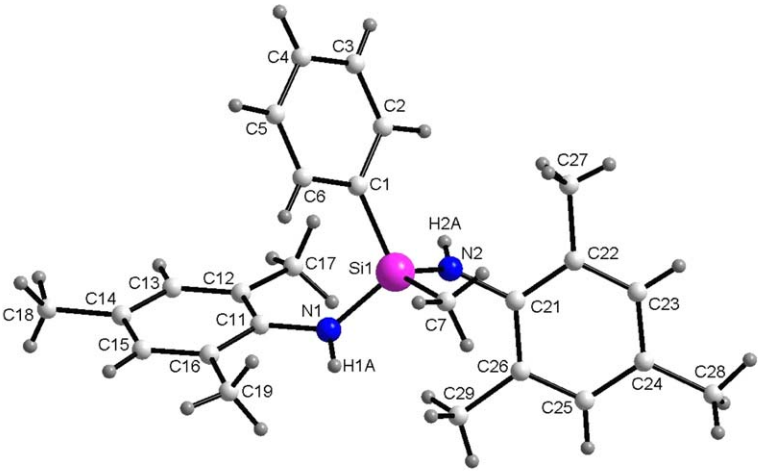


Fig. 1. Crystal structure of [$(2,4,6\text{-}Me_3C_6H_3NH)_2SiPhMe$] (**2**).

Table 2
Comparison of structural features of **2** with a few aminosilanes bearing bulky substituents

Comp.	[(2,6-$Me_2C_6H_3NH)_2$-$SiCl_2$]	[(2,4,6-$Me_3C_6H_2NH)_2$-$SiMe_2$]	[(^{i}PrNH)$_2$-$SiPh_2$]	[(^{t}BuNH)$_2$-$SiPh_2$]^a	[(^{i}PrNH)(^{t}BuNH)-$SiPh_2$]	[(2,6-$^i Pr_2C_6H_3NH)_2SiPh_2$]	[(2,6-$Et_2C_6H_3NH_2SiPh_2$]	[2,4,6-$Me_3C_6H_2$-$NH)_2$SiPhMe]
^{29}Si NMR (ppm)	−30.7	–	−27.9	−35.4	−31.7	−28.7	−29.2	−18.0
Molecular symmetry	C_2	C_2	C_s	C_2	C_s	C_s	C_s	C_1
Si–N (Å)	1.680	1.730	1.709, 1711	1.709, 1711	1.704, 1.710	1.713, 1.718	1.725, 1.730	1.736, 1.717
N–Si–N (°)	110.5	115.6	111.7	113.2, 114.2	113.9	108.2	103.2	117.7
H–N–Si (°)	116	106	117, 118	111, 114	119, 113	108, 113	103, 113	117.6, 114.5
H–N–C (°)	115	115	114, 114	112, 111	114, 115	112, 110	112, 114	113.6, 110.0
C–N–Si (°)	129	128.0	128.1, 126.9	132.1, 131.7	126.7, 132.3	133.8, 128.5	128.0, 136.4	133.5, 127.1
$\sum$N (°)	360	347.1	358.5, 359.5	355.1, 356.8	359.7, 359.7	353.5, 351.5	355.0, 354.6	357.9, 358.2
H–N–Si–N (°)	38	117	−98, −150	139, 133	136, 125	−32, −136	5, −125	103.1, 97.6
Reference	[5a]	[6]	[6]	[6]	[6]	[5b]	[5b]	This work

[a] There are two crystallographically independent molecules with C_2 symmetry.

A sharp absorption observed at 3355 cm^{-1} in the spectrum of **3** indicates the presence of N–H group in the molecule. In the ^{1}H NMR spectrum, expected resonances due to aryl and ethyl protons are observed. Additionally, a singlet for N–H proton is detected at δ 3.4 ppm. The ratio of the intensities of the ^{1}H NMR peaks indicate that only one N–H group of the starting material has undergone lithiation.

*2.4. Single crystal X-ray structure of [(2,6-$Et_2C_6H_3NH$)(2,6-$Et_2C_6H_3NLi$)$SiPh_2$] (**3**)*

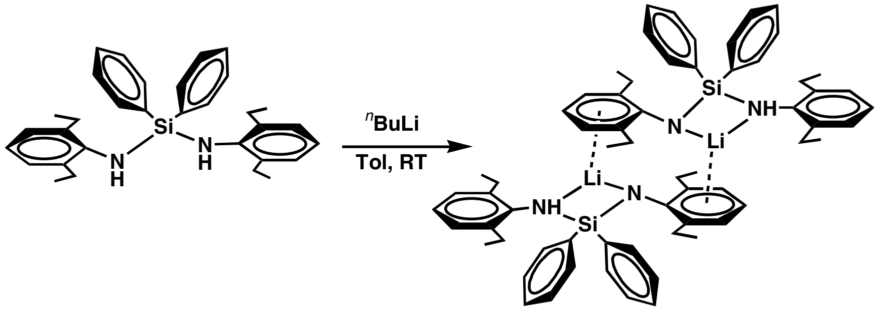
The X-ray diffraction quality crystals were grown from a concentrated solution of **3** in toluene. A perspective view of the molecular structure of **3** is shown in Fig. 2 and the selected structural parameters are listed in Table 3. The compound crystallizes in the triclinic space group $P\bar{1}$. The molecule exists as a discrete dimer with an inversion center. Owing to the lithiation at N(2), the Si(1)–N(2) bond is considerably shorter (1.525(3) Å) than that of the unlithiated nitrogen (1.818(3) Å) (Fig. 3).

Unlike many N–Li compounds known in literature, Li ions in **3** are not complexed by solvent molecules or other donors [1]. The dimer is composed of two Li–N(1)–Si–N(2) four membered rings. The primary coordination sites of the lithium atoms are the amido nitrogen centers. The Li–N distances, 1.981(6) and 2.058(7) Å, are comparable to those found in other ionic lithium amides {[(2,6-$^i Pr_2$-$C_6H_3NLi)_2SiMe_2]_2$ (**A**) av. Li–N 2.05(8) Å [4], [(2,4,6-$Me_3C_6H_2NLi)_2SiMe_2]_2$ (**B**) av. Li–N 1.996(5) Å [3], and {[^{t}BuN(Li)$_3$]SiPh}$_2^2$ (**C**) av. Li–N 2.04(9) Å [2]}. Interestingly, the lithium ions are bonded to three nitrogens in **A** and **C**, while there is only one Li–N interaction in **B**. In addition to the coordination by two nitrogen centers on one side, the lithium ions form an η^6–π-complex on the other side by interacting with the aromatic cloud of the 2,6-diethyl phenyl group coming from the adjacent –NAr group (Fig. 3). The C–Li distances, which vary over a small range (2.146(7)–2.560(7) Å), are comparable to those observed for **B** [3].

The average Li–C bond distance (2.472(2)) Å is marginally longer than those found the [(2,6-$^i Pr_2C_6H_3NLi)_2$-$SiMe_2]_2$ (2.327(8) Å), [(2,4,6-$Me_3C_6H_2NLi)_2SiMe_2]_2$ (2.392(6) Å) but shorter than those found for {[^{t}BuN(Li)$_3$]-SiPh}$_2$ (2.52(5) Å [2–4]. Similarly, the Li–C distance in [Li(indenofluorenyl)] (2.40 Å) [8], which features lithium ion sandwiched between two η^6–π systems suggests that the aromatic ring is strongly attracted by lithium ion in **3**. A comparison of key structural parameters of **3** with those of related compounds is presented in Table 4.

3. Conclusion

The successful synthesis and isolation of phenylmethyldiaminosilanes [$(RNH)_2$SiPhMe] and the half-sandwich monolithium silylamide [(2,6-$Et_2C_6H_3NLi$)(2,6-$Et_2C_6H_3$-NH)$SiPh_2$] have opened up further scope for studies on



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Scheme 2. Synthesis of lithium silylamide [(2,6-$Et_2C_6H_3NLi$)(2,6-$Et_2C_6H_3NH$)$SiPh_2$] (**3**).

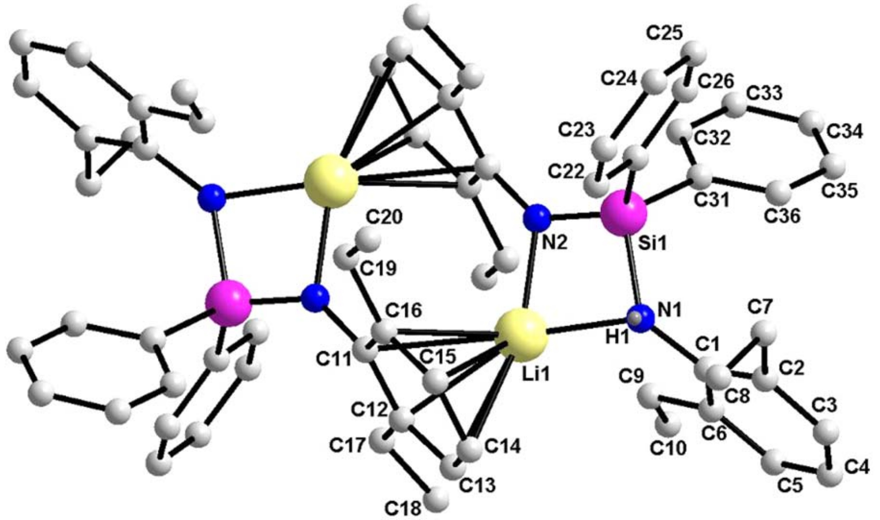

Fig. 2. Molecular structure of [(2,6-$Et_2C_6H_3NLi$)(2,6-$Et_2C_6H_3NH$)$SiPh_2$] (**3**) (all the hydrogen atoms are omitted for clarity).

transition metal–silylamides. We are currently exploring the metallation studies of **1** and **2** with alkali metal ions as well as the utility of these new sterically crowded diaminosilanes as ligands in the preparation of new early transition metal amide complexes (e.g. Ti, Zr and V) which are proven olefin polymerization catalysts under suitable conditions [9]. In particular the Li-amide **3** could prove a useful starting material for the preparation of transition metal–silylamide complexes in view of the simultaneous presence of SiN–H and SiN–Li linkages, which could selectively be reacted with metal alkyls and halides, respectively. We are currently exploring these possibilities.

Table 3
Selected bond lengths (Å) and bond angles (°) of [(2,6-$Et_2C_6H_3NLi$)(2,6-$Et_2C_6H_3NH$)$SiPh_2$] (**3**)

Si(1)–N(2)	1.525(3)	Li(1)–C(12)#1	2.488(7)
Si(1)–N(1)	1.818(3)	Li(1)–C(16)#1	2.550(7)
N(1)–Li(1)	2.058(7)	C(11)–Li(1)#1	2.560(7)
N(2)–Li(1)	1.981(6)	Li(1)–C(13)#1	2.430(7)
Li(1)–C(14)#1	2.416(7)	Li(1)–C(15)#1	2.467(7)
N(2)–Si(1)–N(1)	101.49(14)	N(1)–Si(1)–Li(1)	52.04(16)
N(2)–Si(1)–C(21)	116.69(16)	Si(1)–N(1)–Li(1)	83.8(2)
N(1)–Si(1)–C(21)	100.73(16)	C(1)–N(1)–Si(1)	126.6(2)
N(2)–Si(1)–C(31)	111.52(17)	Si(1)–N(2)–Li(1)	94.6(2)
N(1)–Si(1)–C(31)	113.80(14)	C(11)–N(2)–Si(1)	135.2(2)
N(2)–Si(1)–Li(1)	49.55(17)	N(2)–Li(1)–N(1)	79.9(2)

Symmetry transformations used to generate equivalent atoms: #1 $1 - x$, $-y$, $1 - z$.

4. Experimental

All reactions were carried out under an atmosphere of purified dinitrogen using standard Schlenk line techniques. Manipulations of all compounds were carried out in a M-Braun glove box. Elemental analyses were performed on a Carlo Erba Model 1106 Elemental Analyzer. The EI-MS data for all compounds were obtained on a Perkin–Elmer GC–MS system. Electro spray mass ionization mass spectrum was recorded on Micromass Waters-4185 GC in CH_2Cl_2. Infrared spectra were recorded on a Perkin–Elmer spectrometer as KBr diluted discs. The ^1H NMR spectra were recorded on a Varian 300 S and Varian 400 S spectrometers using Me_4Si as external standard.

Commercial grade solvents were purified by employing conventional procedures and were distilled prior to their

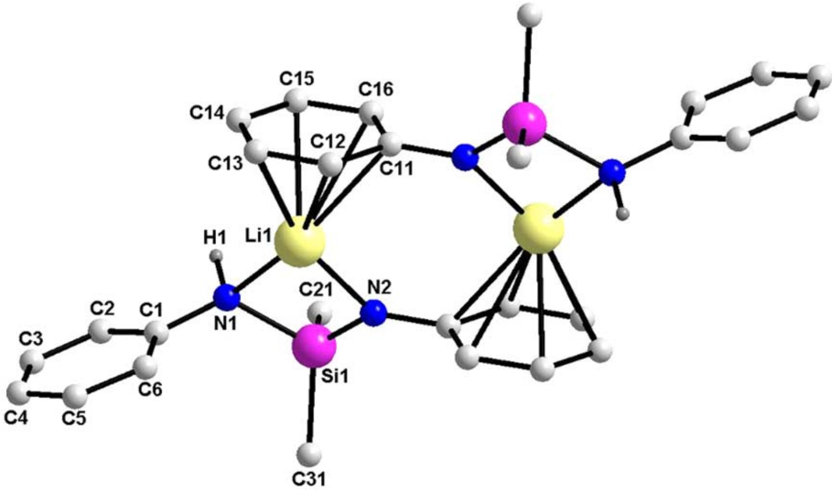

Fig. 3. View of half-sandwich lithium in [(2,6-$Et_2C_6H_3NLi$)(2,6-$Et_2C_6H_3NH$)$SiPh_2$] (**3**) (all the hydrogen atoms are omitted for clarity).

Table 4
Comparison of structural features of **3** with a few lithium amides bearing bulky substituents

Comp.	[(2,6-$Et_2C_6H_3NLi$) (2,6$Et_2C_6H_3NH$)$SiPh_2$] (**3**)	[(2,6-$^iPr_2C_6H_3NLi)_2$-$SiMe_2]_2$ (**A**)	[(2,4,6-$Me_3C_6H_2$ $NLi)_2$-$SiMe_2]_2$ (**B**)	{[$^tBuN(Li)_3$] $SiPh\}_2$ (**C**)
^{29}Si NMR (ppm)	−46.9, −50.9	−15.9	–	–
Si–N (Å)	1.525(3), 1.818(3)	1.710(3), 1.716(3), 1.730(3), 1.735(3)	1.717(4), 1.707(3)	1.755(1), 1.751(1), 1.752(1)
N–Li (Å) (av.)	2.021(5)	2.05(8)	1.996(5)	2.04(9)
Li–C (Å) (av.)	2.485(2)	2.327(8)	2.392(6)	2.52(5)
N–Si–N (°)	101.49(1)	103.5(7)	102.5(2)	104.0(8), 103.3(7), 105.2(8)
C–N–Si (°)	126.6(2), 135.2(2)	118.7(3)	112.4(2)	132.9(1)
N–Li–N (°)	79.9(2)	63.0(4), 88.9(6), 111.6(5), 144.9(7)	76.2(3), 103.8(3), 83.2(3), 125.3(5)	68.6(1), 108.6(2), 87.6(2), 108.8(2)
Nature of the compound	Dimer	Dimer	Dimer	Dimer
Reference	This work	[4]	[3]	[2]

use [10]. Commercially available starting materials such as 2,6-diisopropylaniline (Aldrich), 2,4,6-trimethylaniline (Aldrich), 2,6-diethylaniline (Aldrich), *n*-butyllithium (Aldrich), dichlorodiphenylsilane and dichlorophenylmethylsilane (Lancaster) were used as received.

*4.1. Synthesis of [(2,6-$^iPr_2C_6H_3NH)_2SiPhMe$] (**1**)*

A solution of 2,6-diisopropylaniline (5.8 mL, 30 mmol) in diethyl ether/petroleum ether 1:1 (40 mL) was cooled to −78 °C and ^{n}BuLi (18.75 mL in 1.6 mL hexane solution, 30 mmol) was added dropwise using a dropping funnel. After the addition, the mixture was allowed to reach room temperature. The lithium anilide formed was again cooled to −78 °C and phenylmethyldichlorosilane (2.4 mL, 15 mmol) in petroleum ether (20 mL) was added dropwise. The solution was stirred for 8 h and filtered through a frit containing celite-bed to remove the lithium chloride. The resulting clear filtrate was concentrated to 20 mL. This solution on cooling to −20 °C for 12 h yielded colorless crystals of **1**. Yield: 68%. Mp: 91–93 °C. Anal. Calc. for $C_{31}H_{44}N_2Si$: C, 78.8; H, 9.4; N, 5.9. Found: C, 78.8; H, 9.2; N, 6.5%. IR (KBr, cm^{-1}); 3364 (s), 3061(m), 3054(m), 2954(s), 2865(w), 1558(s), 1445(vs), 1384(s), 1227(vs), 1117(vs), 1092(vs), 917(vs), 892(vs), 746(vs). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm); 0.4 (s, 3H, SiMe) 1.0 (dd, 24H, CH_3, $^3J_{HH} = 6.6$ Hz), 3.2 (sept, 4H, CH), 2.8 (s, 2H, NH), 6.8–7.8 (m, 11H, Ar). ^{29}Si NMR (60 MHz, $CDCl_3$) δ (ppm); −18.9. LC–MS (ESI, CH_2Cl_2) 473 [M^+, 5%], 279 [(2,6-$^iPr_2C_6H_3N$)PhSi, 100%].

*4.2. Synthesis of [(2,4,6-$Me_3C_6H_2NH)_2SiPhMe$] (**2**)*

Compound **2** was prepared in a similar manner to **1**. Yield: 65%. Mp: 110–111 °C. Anal. Calc. for $C_{25}H_{32}N_2Si$: C, 77.3; H, 8.3; N, 7.2. Found: C, 73.2; H, 8.1; N, 7.5%. IR (KBr, cm^{-1}); 3368(s), 3068(m), 3011(w), 2968(w), 2918(s), 2854(w), 1488(vs), 1423(s), 1384(s), 1306(s), 1252(vs), 1231(s), 1159(s), 1113(s), 934(s), 910(vs), 860(s), 796(s), 721(vs), 699(s). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm); 0.4 (s, 3H, SiMe), 2.1 (s, 12H, CH_3), 2.2 (s, 6H, CH_3), 2.8 (s, 2H, NH), 6.7–7.7 (m, 9H, Ar). ^{29}Si NMR (60 MHz, $CDCl_3$) δ (ppm); −18.0. EI-MS (70 eV): *m*/*z*: 388 [M^+, 25%], 253 [(2,4,6-$Me_3C_6H_2NH$)PhMeSi, 100%].

*4.3. Synthesis of [(2,6-$Et_2C_6H_3NLi$)(2,6-$Et_2C_6H_3NH$)$SiPh_2$]$_2$ (**3**)*

A solution of ^{n}BuLi (3.8 mL of a 1.6-M solution in hexane) was added dropwise to a stirred solution of [(2,6-$Et_2C_6H_3NH)_2SiPh_2$] (1.44 g, 3 mmol) in toluene (30 mL) at room temperature, producing an exothermic reaction and a colorless precipitate. The reaction mixture was heated under reflux for 1 h. Slow cooling of the mixture yielded **3** as a colorless crystals which suitable for single crystal X-ray diffraction studies. Mp: 195–210 °C (decomposed). Anal. Calc. for $C_{32}H_{37}N_2SiLi$: C, 79.2; H, 7.6; N, 5.8. Found: C, 77.8; H, 7.6; N, 6.3%. IR (Nujol, cm^{-1}); 3355(s), 3072(m), 2854(b), 1584(s), 1466(vs), 1374(s), 1275(m), 1196(s), 873(vs), 702(vs). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm); 0.9 (dt, 6H, CH_3, $^3J_{HH} = 7.4$ Hz), 1.0 (t, 6H, CH_3, $^3J_{HH} = 7.4$ Hz), 2.4 (q, 2H, CH_2, $^3J_{HH} = 9.4$ Hz), 2.6 (q, 6H, CH_2, $^3J_{HH} = 7.4$ Hz), 3.5 (s, 1H, NH), 6.8–7.8 (m, 16H, Ar). ^{29}Si NMR (60 MHz, $CDCl_3$) δ (ppm); −46.9 and −50.9 ppm.

4.4. X-ray structure determination

Single crystals of **2** and **3** for X-ray structure analysis were obtained from petroleum ether. A suitable crystal of each compound was used for the diffraction studies on a STOE AED-2 diffractometer. The cell parameters were derived from well-centered reflections chosen over a wide 2θ range. The structure solution was achieved by direct methods as implemented in SHELXS-97 [11]. The final refinement of the structures was carried using full least-squares methods on F^2 using SHELXL-97 [12]. The positions of hydrogen atoms attached to nitrogen atoms were identified from the successive difference Fourier maps and were included in further calculations and refinement. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms isotropically. Other details pertaining to data collection, structure solution, and refinement are given in Table 5.

Table 5
Crystal data and structure refinement for **2** and **3**

	2	**3**
Empirical formula	$C_{25}H_{32}N_2Si$	$C_{32}H_{37}LiN_2Si$
Formula weight	388.63	484.67
Temperature (K)	150(2)	133(2)
Diffractometer	STOE AED2	STOE AED2
Wavelength (Å)	0.71073 Å	0.71073
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	7.7914(16)	10.0123(11)
b (Å)	10.757(2)	10.0017(16)
c (Å)	13.828(3)	14.046(2)
α (°)	94.60(3)	103.284(10)
β (°)	92.47(3)	99.45(3)
γ (°)	100.07(3)	105.781(8)
V (Å^3)	1135.5(4)	1278.2(3)
Z	2	2
D_{calc} (Mg/m^3)	1.137	1.259
Absorption coefficient (mm^{-1})	0.116	0.116
F(000)	420	520
Crystal size (mm^3)	1.50 × 0.70 × 0.30	0.40 × 0.30 × 0.20
θ Range (°)	3.56–25.07	3.57–24.12
Data/restraints/parameters	3999/0/381	3491/0/473
Goodness-of-fit on F^2	1.038	1.073
R_1 [$I > 2\sigma(I)$]	0.0538	0.0606
R_2 (all data)	0.0568	0.0794

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.03.039.

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