

Synthesis, characterization and structures of diphenyldiaminosilanes bearing bulky substituents on nitrogen

Ramaswamy Murugavel^{a,*}, Nallasamy Palanisami^a, Ray J. Butcher^b

^a Department of Chemistry, Indian Institute of Technology-Bombay, Powai, Mumbai 400 076, India

^b Department of Chemistry, Howard University, Washington DC 20059, USA

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Abstract

Aminosilanes bearing bulky substituents on nitrogen centers, [(ArNH)₂SiPh₂] (Ar = 2,6-*i*-Pr₂C₆H₃ (**1**), 2,4,6-Me₃C₆H₂ (**2**), 2,6-Et₂C₆H₃ (**3**)), have been prepared in good yields by the addition of dichlorodiphenylsilane to the corresponding substituted monolithiated aniline. The new compounds have been characterized by elemental analysis and IR, EI mass and NMR (¹H and ²⁹Si) spectroscopic studies. The solid-state structures of **1** and **3** have been determined by single crystal X-ray diffraction studies. The molecules have a C_s symmetry and the two N–H protons are approximately *trans* to each other. The amido nitrogen atoms show significant deviation from trigonal-planar geometry, as a result of which the observed Si–N bonds are marginally longer than those observed in aminosilanes with planar nitrogen atoms.

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1. Introduction

The discovery of metallocene catalysts for alkene polymerization has received considerable attention owing to their role in stereoselective/specific polymerization [1]. While the use of mixed cyclopentadienyl amide and amidine complexes for catalysis has been reported [2], the interest in the synthesis and the application of diimide precursors is emerging only in recent years [3]. Since electron deficient metal centers are required for efficient catalytic systems, the somewhat poorer donation of amide ligands might be expected to offer enhanced activity over the analogous *ansa*-metallocene complexes. In this context, Brookhart and Gibson have recently prepared metal complexes based on chelating bis(imido) ligands, which polymerize olefins with excellent activities [4]. Aminosilanes [(ArNH)₂SiPh₂] could serve as very useful chelating ligands in this regard and may have a marked influence in the activity of the

resulting complex due to the presence of silicon centers adjacent to the ligating nitrogen atoms [5]. Veith and co-workers have synthesized group 13 metal complexes (**A**; Chart 1) based on alkyldiaminosilane ligands [6], and Burger and co-workers have synthesized Group 4 metal complexes based on alkyldiaminoligands (**B**) [7].

Owing to the very weak nature of Si–N bonds in aminosilanes and M–N bonds in their metal complexes, it is desirable to append bulky R groups to the silicon and nitrogen centers and achieve increased kinetic stability of the final metal complexes. Nöth and co-workers have described a series of bulky aryldiamonosilanes [(RNH)(R'NH)SiPh₂] (R or R' = *t*-Bu or *i*-Pr) and studied their molecular structures by X-ray diffraction studies [8]. Subsequently, Kang and co-workers have synthesized complexes based on cycloalkyldiaminosilane ligands (**C**, **D**) [9]. In an effort to further increase the steric bulkiness at the nitrogen center, Power and co-workers have reported the synthesis and X-ray crystal structure of [(2,4,6-Me₃C₆H₂NH)₂SiMe₂]; this compound on treatment with Mn[N(SiMe₃)₂]₂ and Li[N(SiMe₃)₂] yields the manganese amide [Li(Mn{2,4,6-Me₃C₆H₂N}₂SiMe₂)₂N(SiMe₃)₂] [10]. Very recently, Hill and Hitchcock described the utility of

* Corresponding author. Tel.: +91-22-2576-7163; fax: +91-22-2572-3480/2576-7152.

E-mail address: rmv@iitb.ac.in (R. Murugavel).

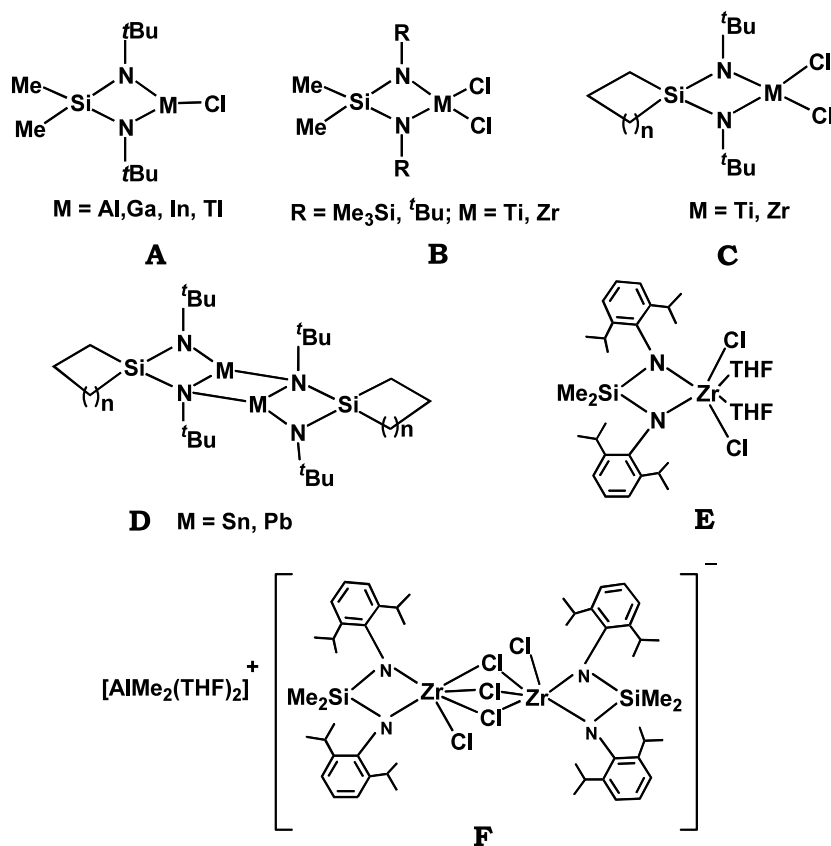


Chart 1.

$[(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{NH})_2\text{SiMe}_2]$ in the synthesis of a stable zirconium amide complex and its reaction with Al_2Me_6 (E, F) [11].

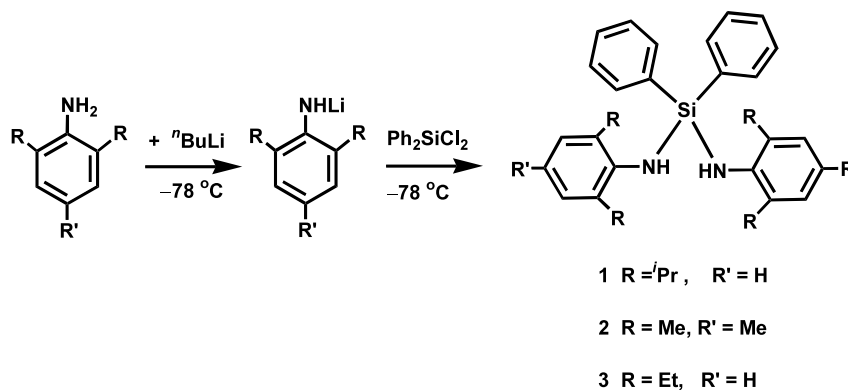
Our interest in this area is to employ bulky substituents both at silicon and nitrogen centers and synthesize new kinetically stabilized diaryldiaminosilanes and explore their utility in preparing early transition metal complexes. Recently we reported on the synthesis and X-ray structure of fully functional sterically hindered dichlorodiaminosilane $[(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{-NH})_2\text{SiCl}_2]$ [12]. Our more recent results in this area, describing the synthesis of three new diphenyldiaminosilanes, spectral characterization, X-ray structure determination of two of these derivatives along with a structural comparison to other diaminosilanes are reported in this paper.

2. Results and discussion

Aminosilanes presented in the following sections have been synthesized using a common two step procedure. The first step is the lithiation of 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 gradual warming of the

reaction mixture to room temperature. The lithium salt so formed was reacted with dichlorodiphenylsilane. The lithium chloride precipitated in these reactions was filtered off to obtain the aminosilane derivatives $[(\text{RNH})_2\text{SiPh}_2]$ ($R = 2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$ (1), $2,4,6\text{-Me}_3\text{C}_6\text{H}_2$ (2), $2,6\text{-Et}_2\text{C}_6\text{H}_3$ (3)) (Scheme 1) as crude products in fairly good yields. Analytically pure compounds have been obtained by recrystallization of the product from light petroleum ether. The compounds are highly soluble in all common organic solvents. Since the compounds are moisture and photosensitive, care was taken to exclude moisture as well as light during all experimental manipulations. However, these compounds can be preserved in pure form for several months under a dry nitrogen atmosphere inside a glove-box.

Products 1–3 have been characterized by elemental analysis, infrared and ^1H - and ^{29}Si -NMR spectroscopy. All products yielded good analytical data. Compounds 1–3 exhibit similar infrared spectral behavior. They show the characteristic N–H stretching vibration around 3370 cm^{-1} . The absorption around 3050 cm^{-1} is due to aromatic C–H stretching vibration. Aliphatic C–H stretching vibrations are observed at around 2900 cm^{-1} . All the compounds show absorption around 1450 cm^{-1} for N–H bending and 900 cm^{-1} for Si–N stretching vibrations. A typical NMR spectrum for 3 has been depicted in Fig. 1.

Scheme 1. Synthesis of aminosilanes [(RNH)₂SiPh₂].

The ²⁹Si-NMR chemical shifts observed for compounds **1–3** fall in the range δ –28 to –30 ppm (Table 1). These values are comparable to related diaminodiphenylsilanes reported by Nöth and co-workers [(PhNH)₂SiPh₂] –30.2; [(*i*PrNH)₂SiPh₂] –27.9; (*t*BuNH)₂SiPh₂] –35.4; (NH^{*i*}Pr)₂ (NH^{*t*}Bu)₂SiPh₂] –31.7 ppm [8], and [(2,6-Me₂C₆H₃NH)₂SiCl₂] (–30.7 ppm) [12].

3. Crystal Structures of [(2,6-*i*Pr₂C₆H₃NH)₂SiPh₂] (**1**) and [(2,6-Et₂C₆H₃NH)₂SiPh₂] (**3**)

Single crystals suitable for single crystal X-ray diffraction studies were grown at 0 °C over a period of few days from a dilute petroleum ether solution. Whereas compound **1** crystallizes in the triclinic centrosymmetric space group *P* $\bar{1}$, compound **3** crystallizes in the orthor-

hombic space group *Pbca*. ORTEP representations of both the molecules (at 50% probability level) are shown in Figs. 2 and 3, respectively. Selected structural parameters are listed in Tables 2 and 3, respectively. A comparison of key structural parameters of **1** and **3** with those of related compounds are given in Table 1.

Unlike in some of the previously reported diaminosilanes (where hydrogen bonding interactions are observed) [8] (Table 1), the molecules of **1** and **3** are isolated in the crystal showing no interaction to the neighboring molecules due to the bulky hydrocarbon envelope. Similarly, it is also interesting to note that molecules **1** and **3** have only a *C_s* symmetry while dialkyl or diaryl diaminosilanes with somewhat less bulkier substituents have a *C₂* symmetry, at least in the solid-state. The observed torsional angles (listed in Table 1) for H–N–Si–N linkages clearly indicate that the hydrogen atoms are not in the N₂Si plane. Further the

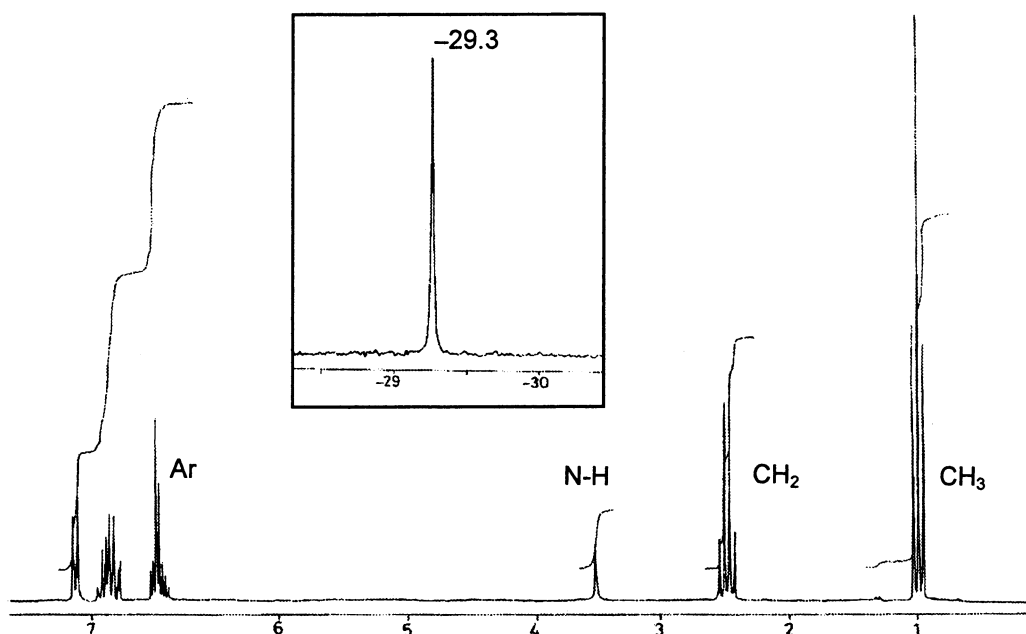
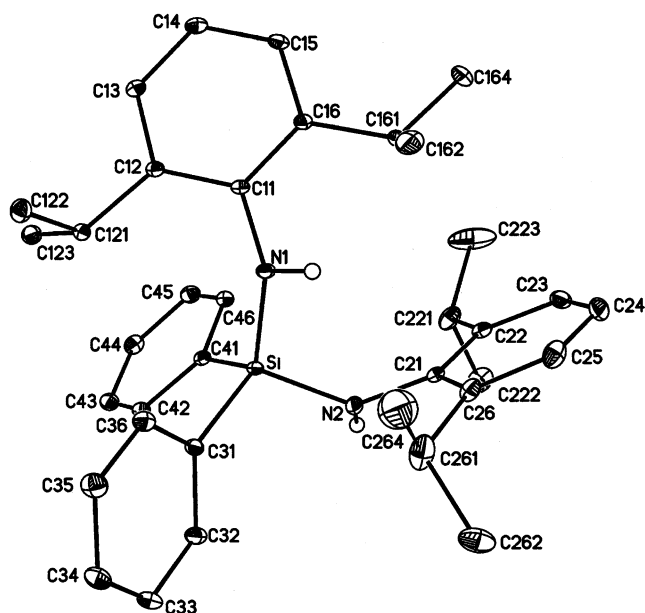
Fig. 1. ¹H-NMR spectrum of [(2,6-Et₂C₆H₃NH)₂SiPh₂] (**3**) in CDCl₃ (400 MHz); ²⁹Si-NMR spectrum (60 MHz).

Table 1

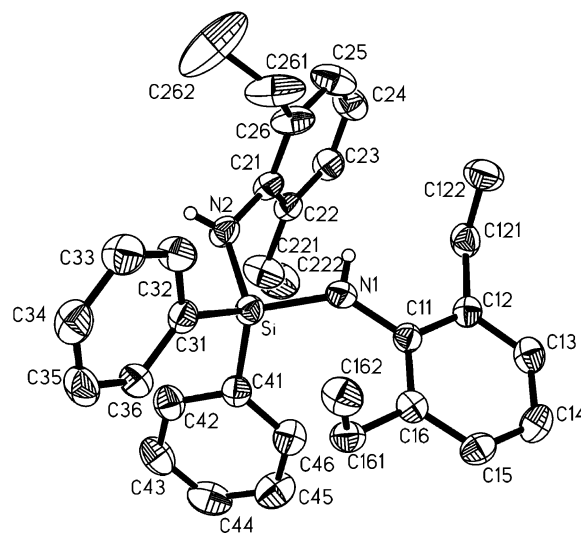
Comparison of ^{29}Si -NMR chemical shifts and selected structural features of **1** and **3** with other aminosilanes bearing bulky substituents

Comp.	$[(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{-NH})_2\text{SiCl}_2]$	$[(2,4,6\text{-Me}_3\text{C}_6\text{H}_2\text{-NH})_2\text{SiMe}_2]$	$[(^i\text{PrNH})_2\text{SiPh}_2]$	$[(^t\text{BuNH})_2\text{SiPh}_2]^a$	$[(^i\text{PrNH})(^t\text{BuNH})\text{SiPh}_2]$	1	3
^{29}Si -NMR (ppm)	−30.7	—	−27.9	−35.4	−31.7	−28.7	−29.2
Mol. symmetry	C_2	C_2	C_s	C_2	C_s	C_s	C_s
Si–N (Å)	1.680	1.730	1.709, 1.700	1.709, 1.711	1.704, 1.710	1.713, 1.718	1.725, 1.730
N–Si–N (°)	110.5	115.6	111.7	113.2, 114.2	113.1	108.2	103.2
H–N–Si (°)	116	106	117, 118	111, 114	119, 113	108, 113	103, 113
H–N–C (°)	115	115	114, 114	112, 111	114, 115	112, 110	112, 114
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
ΣN (°)	360	347.1	358.5, 359.5	355.1, 356.8	359.7, 359.7	353.5, 351.5	355.0, 354.6
H–N–Si–N (°)	38	117	−98, −150	139, 133	136, 125	−32, −136	5, −125
Ref.	[12]	[10]	[8]	[8]	[8]	This work	This work

^a There are two crystallographically independent molecules with C_2 symmetry.Fig. 2. Crystal structure of $[(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{NH})_2\text{SiPh}_2]$ (**1**).

values are indicative of the hydrogen atoms residing above and below the N_2Si plane with a large twist and an approximate 'trans' configuration.

The Si–N distances in **1** (1.715 Å) and **3** (1.727 Å) are longer than those observed for diphenyldialkylaminosilanes reported by Nöth and co-workers (av. 1.705 Å) [8]. This lengthening of Si–N bond distances can be attributed to the significant pyramidalization of nitrogen atoms in **1** ($\Sigma\text{N} = 353.5, 351.5^\circ$) and **3** ($\Sigma\text{N} = 355.0, 354.6^\circ$) compared to the near trigonal-planar geometry around nitrogen atoms in diphenyldialkylaminosilanes listed in Table 1. It is reasonable to assume that the multiple bonding between silicon and nitrogen centers occur via $\text{N}_{\text{LP}} \rightarrow \text{Si}-\text{X} (\sigma^*)$ negative hyperconjugative interactions rather than the conventional $p\pi\text{-}d\pi$ interactions, which have no geometrical constraints [13,14]. The observed torsional angles for $\text{H1N}-\text{N1}-\text{Si}-\text{C31}$

Fig. 3. Crystal structure of $[(2,6\text{-Et}_2\text{C}_6\text{H}_3\text{NH})_2\text{SiPh}_2]$ (**3**).

(88.0°) and $\text{H2N}-\text{N2}-\text{Si}-\text{C31}$ (104.3°) linkages in **1** (and $\text{HN1}-\text{N1}-\text{Si}-\text{C31}$ 107.9° and $\text{HN2}-\text{N2}-\text{Si}-\text{C41}$ 112.6° linkages in **3**) are very close to 90° and hence are ideal for negative hyperconjugative interactions of the nitrogen lone pair with the respective $\text{Si}-\text{C} (\sigma^*)$ orbitals. However, the observed non-planar geometry around the nitrogen atoms reduces the extent of negative hyper-

Table 2

Selected bond lengths (Å) and bond angles (°) of compound **1**

Si–N(1)	1.713(1)	N(1)–C(11)	1.413(2)
Si–N(2)	1.718(1)	N(2)–C(21)	1.424(2)
Si–C(41)	1.855(1)	N(1)–H(1N)	0.84(2)
Si–C(31)	1.861(1)	N(2)–H(2N)	0.90(3)
N(1)–Si–N(2)	108.15(6)	C(11)–N(1)–Si	133.82(9)
N(1)–Si–C(41)	112.34(6)	Si–N(1)–H(1N)	108(1)
N(2)–Si–C(41)	107.17(6)	C(11)–N(1)–H(1N)	112(1)
N(1)–Si–C(31)	109.76(6)	C(21)–N(2)–Si	128.5(1)
N(2)–Si–C(31)	109.68(6)	Si–N(2)–H(2N)	113(2)
C(41)–Si–C(31)	109.67(6)	C(21)–N(2)–H(2N)	110(2)

Table 3
Selected bond lengths (Å) and bond angles (°) of compound 3

Si–N(1)	1.725(3)	Si–C(41)	1.874(4)
Si–N(2)	1.730(3)	Si–C(31)	1.887(4)
N(2)–C(21)	1.435(5)	N(1)–C(11)	1.426(5)
N(2)–H(N2)	0.77(4)	N(1)–H(N1)	0.75(3)
N(1)–Si–N(2)	103.2(2)	N(1)–Si–C(31)	114.5(2)
N(1)–Si–C(41)	112.8(2)	N(2)–Si–C(31)	104.2(2)
N(2)–Si–C(41)	113.3(2)	C(41)–Si–C(31)	108.5(2)
C(11)–N(1)–Si	136.4(3)	C(21)–N(2)–Si	128.0(3)
Si–N(1)–H(N1)	106(2)	C(21)–N(2)–H(N2)	114(3)
C(11)–N(1)–H(N1)	112(2)	Si–N(2)–H(N2)	113(3)

conjugative interaction between the nitrogen lone pair, which now has significant *s*-character, and the Si–C σ^* orbital. As a result, the Si–N bonds observed in **1** and **3** are slightly longer than those observed for other diphenyl(dialkylamino)silanes. Similarly, the observed sum of angles around nitrogen atom in [(2,4,6-Me₃C₆H₂NH)₂SiMe₂] (347.1°), which deviates considerably from the expected value of 360°, clearly explains the longest Si–N bond distance (1.730 Å) among diamino-silanes [10] (Table 1).

4. Conclusion

The diphenyldiaminosilanes of the general formula [(R₂NH)₂SiPh₂] (R = 2,6-*i*-Pr₂C₆H₃ (**1**), 2,4,6-Me₃C₆H₂ (**2**), 2,6-Et₂C₆H₃ (**3**)) have been prepared by the addition of monolithiated amine and dichlorodiphenylsilane. All the compounds were characterized by elemental analysis, IR, EI mass, ¹H-NMR and ²⁹Si-NMR spectroscopy. The molecular structures of [(2,6-*i*-Pr₂C₆H₃NH)₂SiPh₂] (**1**) and [(2,6-Et₂C₆H₃NH)₂SiPh₂] (**3**) have been determined by single X-ray diffraction studies. We are currently exploring the metallation studies of **1–3** 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 would possibly catalyze olefin polymerization reactions under suitable conditions.

5. Experimental

All reactions were carried out under an atmosphere of purified nitrogen 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 (Italy) Model 1106 Elemental Analyzer at IIT-Bombay. The EI-MS data for all compounds were obtained on a Perkin–Elmer GC-MS

system. All other spectral measurements were carried out as described previously [15].

Commercial grade solvents were purified by employing conventional procedures and were distilled prior to their use [16]. Commercially available starting materials such as 2,6-diisopropylaniline (Aldrich), 2,4,6-trimethylaniline (Aldrich), 2,6-diethylaniline (Aldrich), *n*-butyllithium (Aldrich), dichlorodiphenylsilane (Lancaster) were used as received.

5.1. Synthesis of [(2,6-*i*-Pr₂C₆H₃NH)₂SiPh₂] (**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 diphenyldichlorosilane (3.15 ml, 15 mmol) in petroleum ether (20 ml) was added dropwise. The solution was stirred for 8 h and filtered through a frit containing a celite-bed to remove the lithium chloride. The resulting clear filtrate was concentrated to 20 ml. This solution on cooling at –20 °C for 12 h yielded colorless crystals. Yield: 66% (based on Ph₂SiCl₂). Mp; 118–120 °C. Anal. Calc. for C₃₆H₄₆N₂Si: C, 80.5; H, 8.6; N, 5.2. Found; C, 79.6; H, 8.6; N, 5.6. IR (KBr, cm^{–1}); 3374 (s), 3054 (m), 2960 (b), 1446 (vs), 1328 (vs), 1110 (vs), 859 (vs), 702 (vs). ¹H-NMR (300 MHz, CDCl₃) δ (ppm); 0.9 (d, 24H, CH₃, ³*J*_{HH} = 6.6 Hz), 3.2 (sept, 4H, CH), 3.4 (s, 2H, NH), 6.9–7.6 (m, 16H, Ar). ²⁹Si-NMR (60 MHz, CDCl₃) δ (ppm); –28.7. EI-MS (70 eV): *m/z* 535 [M⁺, 3%], 183 [Ph₂Si, 100%].

5.2. Synthesis of [(2,4,6-Me₃C₆H₂NH)₂SiPh₂] (**2**)

A solution of 2,4,6-trimethylaniline (4.12 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 M hexane, 30 mmol) was added dropwise using a dropping funnel. After the addition, the reaction mixture was allowed to reach at room temperature. The lithium anilide formed was again cooled to –78 °C and diphenyldichlorosilane (3.15 ml, 15 mmol) in petroleum ether (20 ml) was added dropwise. The reaction was worked up as described in the case of **1**. Yield: 68% (based on Ph₂SiCl₂). Mp; 76–78 °C. Anal. Calc. for C₃₀H₃₄N₂Si: C, 79.9; H, 7.6; N, 6.2. Found; C, 79.8; H, 7.7; N, 6.9. IR (KBr, cm^{–1}); 3363 (s), 3072 (m), 2930 (s), 1489 (vs), 1435 (vs), 1240 (vs), 913 (vs), 705 (vs). ¹H-NMR (300 MHz, CDCl₃) δ (ppm); 2.1 (s, 12H, CH₃), 2.2 (s, 6H, CH₃), 3.4 (s, 2H, NH), 6.7–7.6 (m, 14H, Ar). ²⁹Si-NMR (60 MHz, CDCl₃) δ (ppm); –30.7. EI-MS (70 eV): *m/z* 452 [M⁺, 3%], 238 [PhSi(NH(2,4,6-Me₃C₆H₂)), 100%].

Table 4
Crystal data and experimental details of **1** and **3**

	1	3
Empirical formula	C ₃₆ H ₄₆ N ₂ Si	C ₃₂ H ₃₈ N ₂ Si
Formula weight	534.84	478.73
Temperature (K)	93(2)	203(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Orthorhombic
Space group	<i>P</i> $\bar{1}$	<i>Pbca</i>
<i>a</i> (Å)	10.516(2)	10.833(2)
<i>b</i> (Å)	10.702(3)	16.014(3)
<i>c</i> (Å)	15.296(4)	31.860(6)
α (°)	73.655(4)	—
β (°)	84.737(4)	—
γ (°)	68.272(5)	—
<i>V</i> (Å ³)	1534.4(6)	5527(2)
<i>Z</i>	2	8
Absorption coefficient (mm ^{−1})	0.103	0.107
Crystal size (mm)	0.08 × 0.40 × 0.72	0.7 × 0.3 × 0.2
Theta range for data collection (°)	2.08–29.28	3.61–22.07
Reflections collected	13 410	3432
Independent reflections	7546 [<i>R</i> _{int} = 0.0274]	3398 [<i>R</i> _{int} = 0.0538]
Data/restraints/parameters	7546/37/439	3398/0/448
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0538 <i>wR</i> ₂ = 0.1370	0.0600 0.1429
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0696 <i>wR</i> ₂ = 0.1479	0.0715 0.1511

5.3. Synthesis of [(2,6-Et₂C₆H₃NH)₂SiPh₂] (**3**)

A solution of 2,6-diethylaniline (4.8 ml, 30 mmol) in diethyl ether/petroleum ether 1:1 (40 ml) was cooled at −78 °C and ^{*n*}BuLi (18.75 ml in 1.6 M hexane, 30 mmol) was added slowly through a dropping funnel. After the addition, the reaction mixture was allowed to reach room temperature. The lithium anilide formed was again cooled to −78 °C and diphenyldichlorosilane (3.15 ml, 15 mmol) in petroleum ether (20 ml) was added dropwise. The reaction was worked up as described in the case of **1**. Yield 72% (based on Ph₂SiCl₂). Mp: 78–80 °C. Anal. Calc. for C₃₂H₃₈N₂Si: C, 80.3; H, 8.0; N, 5.9. Found; C, 79.6; H, 7.9; N, 5.9. IR (KBr, cm^{−1}): 3373 (s), 3078 (m), 2961 (s), 1464 (vs), 1433 (vs), 1280 (s), 1133 (vs), 914 (vs), 710 (vs). ¹H-NMR (400 MHz, CDCl₃) δ: 1.0 (t, 12H, CH₃, ³*J*_{HH} = 6 Hz), 2.3 (quart, 8H, CH₂), 3.5 (s, 2H, NH), 7.3–7.7 (m, 16H, Ar). ²⁹Si-NMR (60 MHz, CDCl₃) δ: −29.2. EI-MS (70 eV): *m/z* 478 [M⁺, 6%], 329 [Ph₂Si(NH(2,6-Et₂C₆H₃)), 100%].

5.4. X-ray structure determination

Single crystals of **1** and **3** for X-ray structure analysis were obtained from petroleum ether. The intensity data for **1** were collected on a Bruker CCD area detector

while the data collection for compound **3** was carried out on a STOE AED2 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 [17]. The final refinement of the structures was carried using full least-squares methods on *F*² using SHELXL-97 [18]. 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 4.

6. Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 205873 and 205874, for complexes **1** and **3**, respectively. Copies of this data may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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