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Reaction of aryl azides with tris(trimethylsilyl)silyllithium: Synthesis of tmeda or thf adducts of [Li{N(Ar)Si(SiMe₃)₃}] and 1,4-trimethylsilyl migration from oxygen to nitrogen

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Abstract

Reaction of ArN₃ (Ar = Ph, *p*-MeC₆H₄, 1-naphthyl) with [Li{Si(SiMe₃)₃}(thf)₃] yielded lithium amides [Li{N(Ar)Si(SiMe₃)₃}L] (L = tmeda or (thf)₂). Similar treatment of *o*-phenylene diazide with 2 equiv. of [Li{Si(SiMe₃)₃}(thf)₃] formed dilithium diamide complex **4**. Reaction between *o*-Me₃SiOC₆H₄N₃ and [Li{Si(SiMe₃)₃}(thf)₃] afforded, via 1,4-trimethylsilyl migration from oxygen to nitrogen, [Li{OC₆H₄{N(SiMe₃)Si(SiMe₃)₃}-2}]₂ (**5**). The structures of complexes **3** and **5** have been determined by single crystal X-ray diffraction techniques.
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Keywords: Tris(trimethylsilyl)silyllithium; Aryl azides; Reaction; Lithium amides; Trimethylsilyl migration

1. Introduction

Reactions of organic azides with nucleophiles have been extensively studied. Organic azides can react with tertiary phosphines to lead to iminophosphoranes [1]. The azides can also react with Grignard reagents and organolithium compounds to give 1,3-disubstituted triazene salts **I** (Scheme 1). The triazene salts can be further converted to an azide (via elimination of R¹M) or a triazene (via hydrolysis) depending on the properties of R¹ [2,3]. These reactions and their application in organic synthesis have been reviewed [2]. By contrast, study on reactions between azides and silyl anions is rare. An example is the reaction between azido-di-*t*-butylchlorosilane and tri-*t*-butylsily1sodium, which gives silaketimine (Eq. (1)) [4]

Scheme 1.

$$t\text{-Bu}_2\text{SiClN}_3 + t\text{-Bu}_3\text{SiNa} \rightarrow t\text{-Bu}_2\text{Si}{=}\text{NSi-}t\text{-Bu}_3 \qquad (1)$$
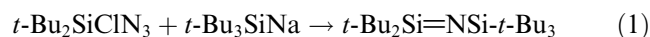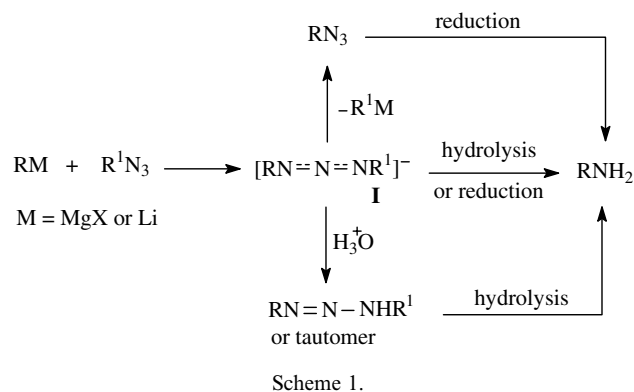
Reactivities of tris(trimethylsilyl)silyl anion have been explored. For example, reactions of tris(trimethylsilyl)silyllithium or potassium with main group or transition metal halides generate the complexes containing metal–silicon bond [5]. Reactions of tris(trimethylsilyl)-
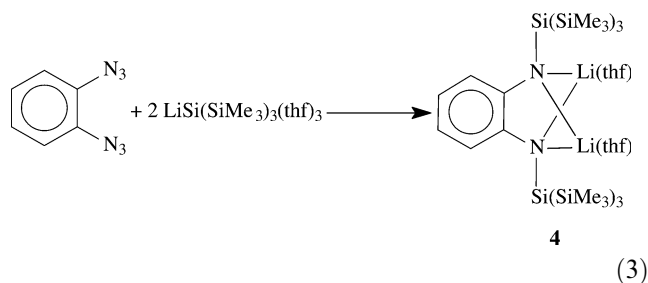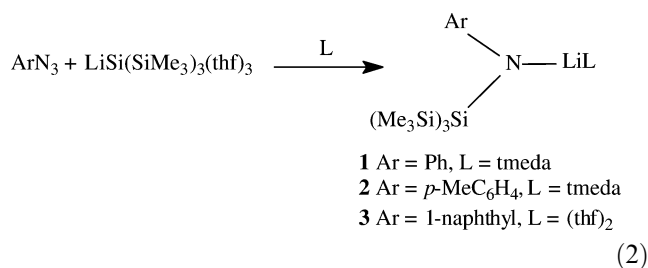
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silyllithium with unsaturated organic compounds such as ketones, nitriles and isonitriles have also been investigated [6]. Herein we report (i) reaction between aryl azides and tris(trimethylsilyl)silyllithium, which affords lithium aryl(tris(trimethylsilyl)silyl)amides, and (ii) a 1,4-trimethylsilyl migration from oxygen to nitrogen during the reaction of o-Me$_3$SiOC$_6$H$_4$N$_3$ with tris-(trimethylsilyl)silyllithium.

2. Results and discussion

Treatment of ArN$_3$ with [Li{Si(SiMe$_3$)$_3$}(thf)$_3$] in the presence of tmeda from about $-80\,^\circ$C to room temperature yielded [Li{N(Ar)Si(SiMe$_3$)$_3$}(tmeda)] (**1**, Ar = Ph; **2**, Ar = p-MeC$_6$H$_4$) in 62% and 64% yields, respectively. Similar reaction in the absence of tmeda in thf afforded thf adduct of lithium amide, [Li{N(Ar)-Si(SiMe$_3$)$_3$}(thf)$_2$] (**3**, Ar = 1-naphthyl) in 56% yield (Eq. (2)). Reaction of o-phenylene diazide with two equivalents of [Li{Si(SiMe$_3$)$_3$}(thf)$_3$] in hexane formed dilithium diamide complex **4** in 67% yield (Eq. (3)).

$$\text{ArN}_3 + \text{LiSi(SiMe}_3)_3(\text{thf})_3 \xrightarrow{\text{L}}$$

1 Ar = Ph, L = tmeda
2 Ar = p-MeC$_6$H$_4$, L = tmeda
**3** Ar = 1-naphthyl, L = (thf)$_2$

(2)

(3)

If the reaction was carried out in diethyl ether or thf, a mixture was obtained. Based on the reaction course of organolithium compounds with azides reported in the literature [2], it is proposed that the reaction of [Si(SiMe$_3$)$_3$]$^-$ with azides also proceeded via a triazenido anion **I** (Scheme 1, R = aryl, R^1=Si(SiMe$_3$)$_3$), followed by release of nitrogen. The elimination of nitrogen from a triazenido anion is rare. An example is that 1-phenyl-3-triphenylsilyltriazenido anion ([PhN$_3$SiPh$_3$]$^-$) prepared from reaction of Ph$_3$SiN$_3$ with PhMgBr decomposes at 100–120 $^\circ$C by elimination of nitrogen to give N-(triphenylsilyl)amide [7]. The bulky amides of lithium are important reagents in both coordination and organic chemistry [8]. The reaction shown above provides a route of preparing sterically hindered amides.
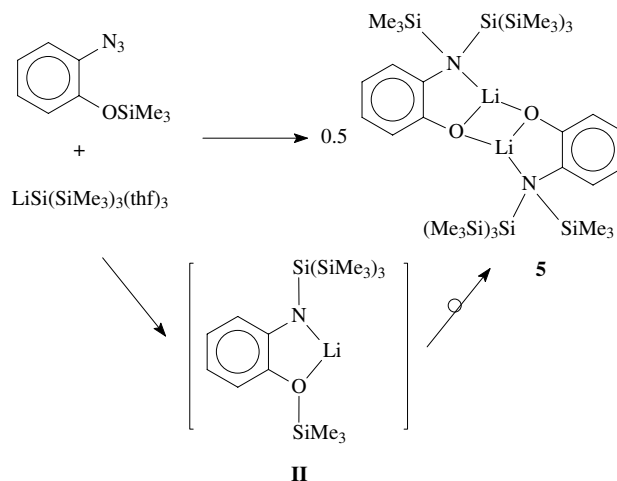
Scheme 2.

Reaction of o-Me$_3$SiOC$_6$H$_4$N$_3$ with [Li{Si(Si-Me$_3$)$_3$}(thf)$_3$] in Et$_2$O or hexane resulted in red brown solution, from which complex **5** was isolated in 30% yield by crystallization from hexane (Scheme 2). No other crystalline species can be obtained. The reaction could proceed through a lithium amide complex **II** and subsequent 1,4-trimethylsilyl migration from oxygen to nitrogen. In order to prove that the conjectural reaction process shown in Scheme 2 is reasonable, we performed the reaction of o-(trimethylsiloxy)-N-(trimethylsilyl)aniline with LiBu^n and [Li{OC$_6$H$_4$N(SiMe$_3$)$_2$-2}] was obtained in high yield (Eq. (4)). The driving force of the rearrangement is probably relative anion stability, although steric factor and bond strength consideration are in opposition. 1,4-Silyl migrations from oxygen to nitrogen are scarce [9]. The reaction provides an example of this kind of rearrangement.

(4)
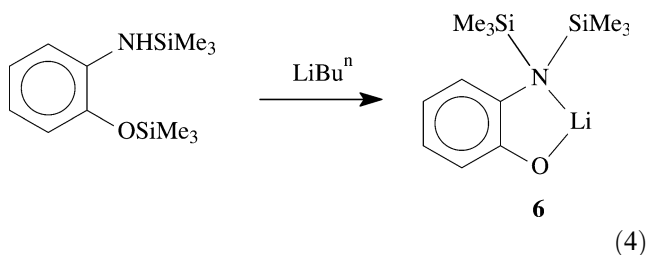
Complexes **1**–**4** are orange (**1**), yellow (**2**, **3**) or yellow–orange (**4**) crystalline solid, while **5** and **6** are colorless crystals. Each of the complexes is very soluble in Et$_2$O and soluble in hexane. The complexes have been characterized by elemental analyses, ^{1}H, ^{13}C (for **1**–**5**) and ^{7}Li (for **5**) NMR spectroscopy. The ^{7}Li NMR spectrum of complex **5** gave single signal at 1.84 ppm (Fig. 1), while its ^{13}C NMR spectrum exhibited 17 phenylene signals and 6 silylmethyl signals (Fig. 2). This shows that complex **5** could be trimeric in solution and each phenylene in the trimer has different chemical environments. It also shows that each lithium atom in
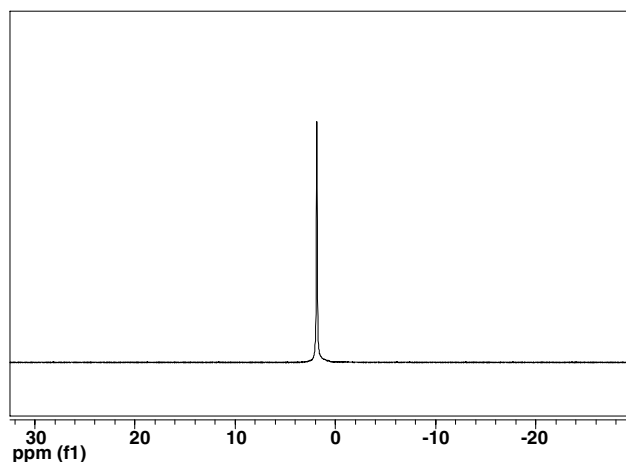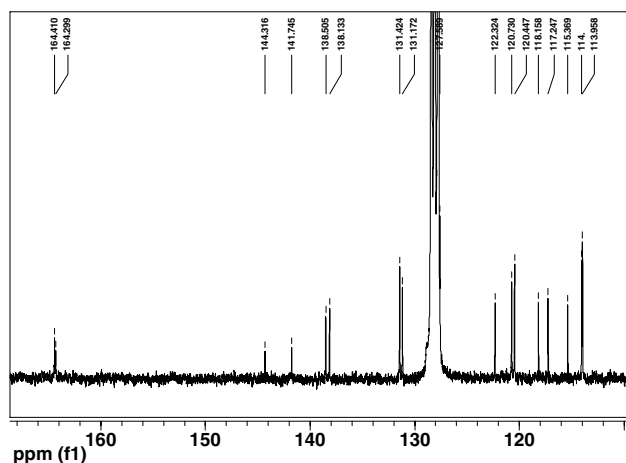
Fig. 1. ^{7}Li NMR spectrum of complex 5.

Fig. 2. ^{13}C NMR spectrum of complex 5 (aromatic ring region).

Fig. 3. Molecular structure and atom labelling for complex 3. 20% thermal ellipsoids are shown; hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Li(1)–N(1) 1.980(11), Li(1)–O(1) 1.884(11), Li(1)–O(2) 1.928(11), Li(1)–C(1) 2.603(12), N(1)–Si(1) 1.720(4); O(1)–Li(1)–O(2) 100.4(5), O(1)–Li(1)–N(1) 116.5(6), O(2)–Li(1)–N(1) 143.1(6), Li(1)–N(1)–C(1) 100.7(5), C(1)–N(1)–Si(1) 122.3(4).

Me$_2$}(OEt$_2$)]$_2$ [11] and 1.943(6) Å in [Li{μ-N(Si-Me$_3$)$_2$}(OEt$_2$)]$_2$ [12]. Complex 5 is a centrosymmetric dimer containing as core a planar LiOLiO ring, with the angles subtended at the oxygen atoms narrower [86.1(4)°] than those at the lithium atoms [93.9(4)°] (Fig. 4). The atoms N(1), Li(1) and O(1) are nearly coplanar with the fused phenyl ring. Each of the nitrogen atoms is four-coordinate, proving that the SiMe$_3$
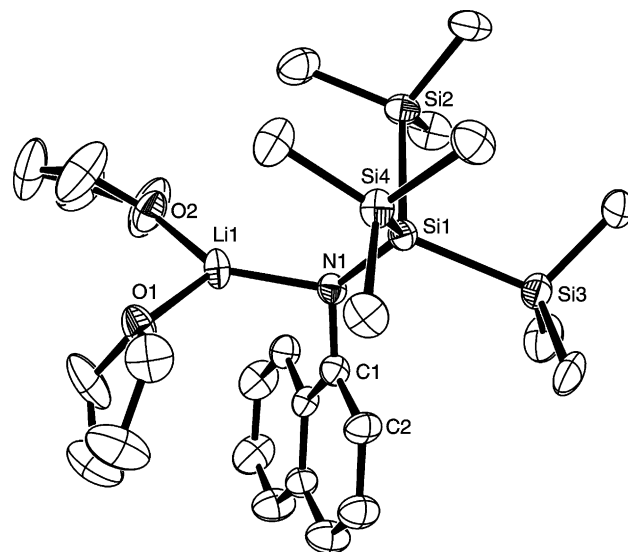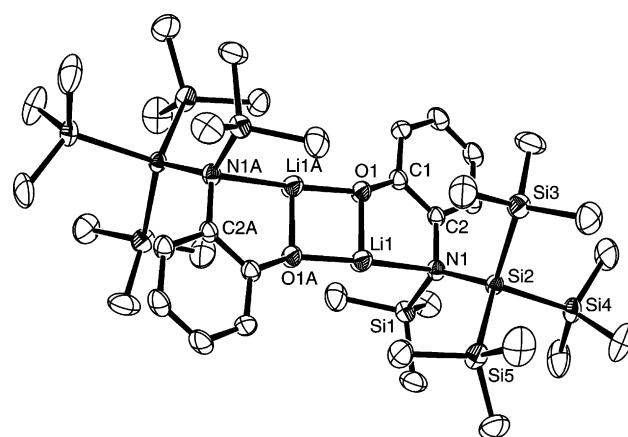

Fig. 4. Molecular structure and atom labelling for complex 5. 30% thermal ellipsoids are shown; hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Li(1)–N(1) 2.332(8), Li(1)–O(1) 1.830(9), Li(1)–O(1A) 1.844(8), Li(1)–Li(1A) 2.508(16), Li(1)–C(1) 2.706(10), Li(1)–Si(1) 3.054(8); O(1)–Li(1)–O(1A) 93.9(4), N(1)–Li(1)–O(1) 84.7(3), N(1)–Li(1)–O(1A) 167.0(5), Li(1)–O(1)–Li(1A) 86.1(4), C(1)–O(1)–Li(1) 117.3(4), C(1)–O(1)–Li(1A) 153.2(4), C(2)–N(1)–Li(1) 97.2(3).

the trimeric structure has the same coordination mode. The ^{1}H NMR spectrum of 6 exhibited single SiMe$_3$ signal, showing that the two SiMe$_3$ groups are equivalent. The NMR spectra of other complexes are unexceptional. The structures of complexes 3 and 5 were also confirmed by single crystal X-ray diffraction techniques.

Crystalline 3 is monomeric (Fig. 3). The lithium atom is three-coordinate and bonded to one amido nitrogen atom and two oxygen atoms of the coordinated thf molecules. The atoms Li(1), N(1), O(1) and O(2) are coplanar, the sum of the angles at the Li atom being 360°. There is also a close contact between Li(1) and C(1), the distance of Li(1)–C(1) being 2.603(12) Å. The Si(1) atom is out of the approximate plane comprising aromatic ring and the nitrogen atom. The torsion angle of Si(1)N(1)C(1)C(2) is 30.5°. The Li(1)–N(1) distance of 1.980(11) Å is usual for a mononuclear lithium amide [10]. Additionally, the Li(1)–O(1) distance of 1.884(11) Å is slightly shorter than that of Li(1)–O(2) [1.928(11) Å], but both are similar to those in related etherates, e.g., 1.883(8) Å in [Li{(μ-NC$_{10}$H$_6$NH-1,8)Si-

group has migrated from O to N during the reaction. The average Li–O distance of 1.837 Å is similar to those in $[LiOC_6H_2(CH_2NMe_2)_2\text{-}2,6\text{-}Me\text{-}4]_3$ [1.828(9)–1.887(9) Å] [13]. The Li–N distance of 2.332(8) Å is also comparable to those in $[LiOC_6H_2(CH_2NMe_2)_2\text{-}2,6\text{-}Me\text{-}4]_3$ [13].

The structure of **4** was also determined by single crystal X-ray diffraction techniques, but the quality of the data is relatively poor. Hence, the data is not reported here. However, from the data the coordination mode of complex **4** can be identified as shown in Eq. (3).

In summary, aryl azides (ArN_3, Ar = Ph, $p\text{-}MeC_6H_4$ or 1-naphthyl) or o-phenylene diazide reacted with [Li-{Si(SiMe_3)_3}(thf)_3] to give lithium amides [Li{N(Ar)Si-(SiMe_3)_3}L] [L = tmeda or (thf)_2] or dilithium diamide [{Li(thf)}_2{1,2-(μ-NSi(SiMe_3)_3)_2}C_6H_4]. Reaction of $o\text{-}Me_3SiOC_6H_4N_3$ with [Li{Si(SiMe_3)_3}(thf)_3] afforded [Li{OC_6H_4{N(SiMe_3)Si(SiMe_3)_3}-2}]_2. This product is believed to form via a 1,4-trimethylsilyl migration from oxygen to nitrogen during the reaction.

3. Experimental

All experiments were performed under nitrogen using standard Schlenk and vacuum line techniques. Solvents (thf, Et_2O and n-hexane) were distilled under nitrogen over sodium-benzophenone and degassed prior to use. C_6D_6 were purchased from Acros Organics and stored over Na/K alloy and degassed prior to use. Tmeda was purchased from Acros Organics, dried with sodium and distilled prior to use. $CDCl_3$, $LiBu^n$ and LiMe were purchased from Acros Organics and used as obtained. $LiSi(SiMe_3)_3(thf)_3$ [14], aryl azides [15], o-phenylene diazide [16] and o-(trimethylsiloxy)-N-(trimethylsilyl)aniline [17] were prepared according to the literature. IR spectra were determined on a Bruker VECTOR-22 spectrometer. NMR spectra were recorded on a Bruker av400 or av300 spectrometer at ambient temperature. The chemical shifts of ^1H and $^{13}C\{^1H\}$ NMR spectra are referenced to internal solvent resonances; the $^7Li\{^1H\}$ NMR spectrum is referenced to external LiCl solution in D_2O (1 M). Elemental analyses were performed by the Analytical Center of University of Science and Technology of China and the Analytical Laboratory of Shanghai Institute of Organic Chemistry. Melting points were uncorrect.

3.1. Reaction of PhN_3 (or $p\text{-}MeC_6H_4N_3$) with $LiSi(SiMe_3)_3(thf)_3$ in the presence of tmeda

PhN_3 (0.29 g, 2.44 mmol) was added to a solution of $LiSi(SiMe_3)_3(thf)_3$ (1.14 g, 2.42 mmol) and tmeda (0.37 ml, 2.45 mmol) in Et_2O (40 ml) at about $-80\ ^\circ$C. The mixture was warmed to room temperature and stirred overnight. Volatiles were removed in vacuo and

the residue was dissolved in hexane and then filtered. The filtrate was concentrated to give orange crystals of complex **1** (0.69 g, 62%), m.p. 92 °C (dec.). Anal. Calc. for $C_{21}H_{48}N_3LiSi_4$: C, 54.61; H, 10.47; N, 9.10. Found: C, 54.07; H, 10.26; N, 8.81%. ^1H NMR (C_6D_6, 300.13 MHz): δ 0.43 (s, 27H, $SiMe_3$), 1.51 (s, 4H, tmeda), 1.69 (s, 12H, tmeda), 6.60 (t, $J = 7.1$ Hz, 1H, Ph), 6.70 (d, $J = 7.7$ Hz, 2H, Ph), 7.19 (t, $J = 7.6$ Hz, 2H, Ph). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.47 MHz): δ 2.14, 45.66, 56.58, 112.12, 122.29, 129.35, 164.36.

Complex **2** was prepared according to the same procedure. Reaction of $p\text{-}MeC_6H_4N_3$ (0.29 g, 2.18 mmol) with a mixture of $LiSi(SiMe_3)_3(thf)_3$ (1.02 g, 2.19 mmol) and tmeda (0.33 ml, 2.19 mmol) in Et_2O (40 ml) afforded pale yellow crystalline complex **2** (0.66 g, 64%), m.p. 168–171 °C. Anal. Calc. for $C_{22}H_{50}N_3LiSi_4$: C, 55.52; H, 10.59; N, 8.83. Found: C, 55.11; H, 10.36; N, 8.48%. ^1H NMR (C_6D_6, 300.13 MHz): δ 0.43 (s, 27H, $SiMe_3$), 1.52 (s, 4H, tmeda), 1.71 (s, 12H, tmeda), 2.31 (s, 3H, Me), 6.64 (d, $J = 8.0$ Hz, 2H, C_6H_4), 6.98 (d, $J = 7.9$ Hz, 2H, C_6H_4). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.47 MHz): δ 2.16, 20.82, 45.62, 56.47, 119.96, 122.09, 129.96, 161.74.

3.2. Reaction of $1\text{-}C_{10}H_7N_3$ with $LiSi(SiMe_3)_3(thf)_3$

1-Naphthyl azide (0.47 g, 2.78 mmol) was added to a solution of $LiSi(SiMe_3)_3(thf)_3$ (1.35 g, 2.87 mmol) in thf (40 ml) at about 80 °C. The color of the solution changed from colorless to blue. The mixture was warmed to room temperature and the color changed to deep red. The solution was stirred at room temperature overnight. Volatiles were removed in vacuo and the residue was dissolved in hexane and then filtered. The filtrate was concentrated to give yellow crystals of complex **3** (0.83 g, 56%), m.p. 98 °C (dec.). Anal. Calc. for $C_{27}H_{50}NO_2LiSi_4$: C, 60.06; H, 9.33; N, 2.59. Found: C, 59.83; H, 9.12; N, 2.24%. ^1H NMR (C_6D_6, 400.13 MHz): δ 0.46 (s, 27H, $SiMe_3$), 1.09–1.14 (m, 8H, thf), 3.10–3.13 (m, 8H, thf), 6.95 (d, $J = 7.9$ Hz, 1H, $C_{10}H_7$), 7.02 (d, $J = 7.5$ Hz, 1H, Ph), 7.09 (t, $J = 7.1$ Hz, 1H, $C_{10}H_7$), 7.23–7.27 (m, 1H, $C_{10}H_7$), 7.41 (t, $J = 7.8$ Hz, 1H, $C_{10}H_7$), 7.71 (d, $J = 8.1$ Hz, 1H, $C_{10}H_7$), 8.45 (d, $J = 8.1$ Hz, 1H, $C_{10}H_7$). $^{13}C\{^1H\}$ NMR (C_6D_6, 100.62 MHz): δ 2.89, 25.65, 68.77, 110.25, 116.18, 122.50, 122.93, 125.28, 128.86, 129.09, 133.30, 137.52, 161.88.

3.3. Reaction of 1,2-diazidobenzene with $LiSi(SiMe_3)_3(thf)_3$

1,2-Diazidobenzene (0.25 g, 1.56 mmol) was added to a solution of $LiSi(SiMe_3)_3(thf)_3$ (1.46 g, 3.10 mmol) in hexane (10 ml) at about 80 °C with stirring. The mixture was allowed to warm to room temperature and stirred overnight. The mixture was filtered and the filtrate was

concentrated to give yellow–orange crystals of complex **4** (0.79 g, 67%), m.p. 102–104 °C. Anal. Calc. for $C_{32}H_{74}N_2O_2Li_2S_8$: C, 50.74; H, 9.85; N, 3.70. Found: C, 49.96; H, 9.80; N, 4.03%. ^1H NMR (C_6D_6, 300.13 MHz): δ 0.38 (s, 54H, $SiMe_3$), 1.19–1.45 (m, 8H, thf), 3.34–3.51 (m, 8H, thf), 6.76–6.80 (m, 2H, C_6H_4), 6.95–6.98 (m, 2H, C_6H_4). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.47 MHz): δ 2.28, 25.48, 68.28, 116.53, 118.52, 149.36.

3.4. Preparation of o-Me₃SiOC₆H₄N₃

Et_3N (0.45 ml, 3.20 mmol) and Me_3SiCl (0.39 ml, 3.05 mmol) were added to a solution of o-$HOC_6H_4N_3$ (0.40 g, 2.96 mmol) in Et_2O (10 ml) at room temperature with stirring. The mixture was stirred overnight and then filtered. The solid was washed with Et_2O (2×10 ml). The filtrate was concentrated in vacuo to give o-$Me_3SiOC_6H_4N_3$ (0.32 g, 52%). ^1H NMR ($CDCl_3$, 300.13 MHz): δ 0.24 (s, 9H, $SiMe_3$), 6.74–6.77 (m, 1H, C_6H_4), 6.82–6.96 (m, 3H, C_6H_4). IR (liquid film): $v(cm^{-1})$ 3070w, 3035w, 2961m, 2902w, 2129vs, 2096vs, 1592s, 1494vs, 1450s, 1412w, 1309vs, 1281vs, 1254vs, 1143w, 1099s, 1038m, 919vs, 847vs, 751vs, 694w, 658w, 646w.

3.5. Reaction of o-Me₃SiOC₆H₄N₃ with LiSi(SiMe₃)₃(thf)₃

o-$Me_3SiOC_6H_4N_3$ (0.24 g, 1.16 mmol) was added to a stirred solution of $LiSi(SiMe_3)_3(thf)_3$ (0.55 g, 1.17 mmol) in Et_2O (10 ml) at about -80 °C. The mixture was warmed to room temperature and stirred overnight. Volatiles were removed in vacuo and the residue was dissolved in hexane. The solution was filtered and the filtrate was concentrated to afford crystalline complex **5** (0.15 g, 30%). The crystalline solid was recrystallized from hexane to give colorless crystals, m.p. 178–182 °C. Calc. for $C_{18}H_{40}NOLiSi_5$: C, 49.83; H, 9.29; N, 3.23. Found: C, 49.08; H, 9.20; N, 2.96%. ^1H NMR (C_6D_6, 300.13 MHz): δ 0.19–0.33 (m, 21H, $SiMe_3$), 0.35 (s, 15H, $SiMe_3$), 6.61–6.68 (m, 1H, C_6H_4), 6.94–6.97 (m, 1H, C_6H_4), 7.05–7.11 (m, 1H, C_6H_4), 7.15–7.20 (m, 1H, C_6H_4). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.47 MHz): δ 0.40, 0.78, 2.51, 2.69, 2.81, 2.84, 113.96, 114.02, 115.37, 117.25, 118.16, 120.45, 120.73, 122.32, 127.59, 131.17, 131.42, 138.13, 138.51, 141.75, 144.32, 164.30, 164.41. $^7Li\{^1H\}$ NMR (C_6D_6, 116.64 MHz): δ 1.84.

3.6. Reaction of o-Me₃SiOC₆H₄NHSiMe₃ with LiBuⁿ

To a cooled (about -80 °C) solution of o-(trimethylsiloxy)-N-(trimethylsilyl) aniline (1.0 g, 3.94 mmol) in Et_2O (20 ml) was added drop-wise $LiBu^n$ (1.6 ml, 4.0 mmol, 2.5 M solution in hexanes) with stirring. The solution was warmed to room temperature and stirred overnight. Solvents were removed and the residue was dissolved in hexane. The solution was filtered and

the filtrate concentrated to give colorless crystals of **6** (0.92 g, 90%). Calc. for $C_{12}H_{22}NOLiSi_2$: C, 55.56; H, 8.55; N, 5.40. Found: C, 55.35; H, 8.40; N, 5.22%. ^1H NMR (C_6D_6, 300.13 MHz): δ 0.31 (s, 18H, $SiMe_3$), 6.68–6.76 (m, 1H, C_6H_4), 6.98–7.05 (m, 2H, C_6H_4), 7.18–7.23 (m, 1H, C_6H_4).

3.7. X-ray crystallography

Crystals were mounted in Lindemann Capillaries under nitrogen. Diffraction data were collected on a Siemens CCD area-detector with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). A semi-empirical absorption correction was applied to the data of **3** and **5**. The structures were solved by direct methods using SHELXS-97 [18] and refined against F^2 by full-matrix least-squares using SHELXL-97 [19]. Crystal data and experimental details of the structure determinations are listed in Table 1.

4. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre CCDC Nos. 255754 and 255755 for compounds **3** and **5**. Copies of this information 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 http://www.ccdc.cam.ac.uk).

Table 1
Details of the X-ray structure determinations of complexes **3** and **5**

	3	**5**
Empirical formula	$C_{27}H_{50}LiNO_2Si_4$	$C_{18}H_{40}LiNOSi_5$
Formula weight	539.98	433.90
Temperature (K)	298(2)	293(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1/n$
a (Å)	9.906(3)	10.067(4)
b (Å)	15.606(5)	16.180(7)
c (Å)	12.029(3)	16.644(6)
β (°)	112.369(5)	90.002(7)
V (Å^3)	1719.5(9)	2711.1(18)
Z	2	4
μ (mm^{-1})	0.194	0.271
Crystal size (mm)	$0.25 \times 0.22 \times 0.18$	$0.18 \times 0.16 \times 0.14$
θ Range for data collection (°)	1.83–26.42	1.22–26.44
Number of reflections collected	10135	15714
Number of independent reflections (R_{int})	5429 (0.0942)	5557 (0.0906)
Number of data/ restraints/parameters	5429/1/316	5557/0/248
Goodness-of-fit on F^2	0.676	1.024
R_1, wR_2 $[I > 2\sigma(I)]^a$	0.0450, 0.0467	0.0599, 0.1163
All data	0.1997, 0.0686	0.1113, 0.1467

^{a} $R_1 = \sum \|F_o| - |F_c\|/ \sum |F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^4)]^{1/2}$.

Acknowledgments

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