

Sodium and potassium derivatives of diphenyl(trimethylsilyl)methane

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Abstract

Base-free sodium and potassium derivatives of $\text{Ph}_2(\text{Me}_3\text{Si})\text{CH}$ have been synthesised from the substituted diphenylmethane and a ‘superbase’ mixture of $n\text{-BuLi}/\text{BuOM}$ ($\text{M} = \text{Na}$ or K) in hexane. Multinuclear NMR studies have demonstrated that the resultant carbanions are highly delocalised in THF- d_8 solution. Crystalline PMDETA (PMDETA = N,N,N',N'',N''' -pentamethyldiethylenetriamine) adducts of both the sodium and potassium diphenylmethyl anions have been isolated from toluene solution and the crystal structure of the sodium derivative has been determined. This exists as a monomeric molecular species with η^3 -coordination of sodium to the carbanion, which is almost planar ($\Sigma_{\text{angles}} = 358.6^\circ$) at the central methyl carbon.

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Keywords: Sodium; Potassium; Diphenylmethyl; Bulky ligands

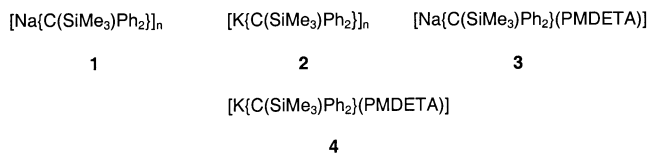
1. Introduction

Bulky heteroatom-substituted methyl ligands have been applied very successfully to the synthesis of many unprecedented low coordinate and low oxidation state organometallic species [1]. As a continuation of our own efforts in this area, we have recently reported syntheses and structural characterisations for a variety of lithiated diphenyl(triorganosilyl)methanes, $\text{Ph}_2(\text{R}_3\text{Si})\text{CH}$ [2]. In common with other silylated methyl derivatives [1a–f], the negative charge of the anion is highly delocalised over the organic framework of the carbanion. The compounds crystallise from ether-containing solutions as unusual solvent-separated ion pairs in which the anions are lithates $[\text{Li}\{\text{C}(\text{SiR}_3)\text{Ph}_2\}_2]^-$ featuring a lithium atom bound to two η^2 -coordinated, diphenylmethyl subunits [2]. Our initial objective was the synthesis of carbanionic ligand transfer reagents that would be suitable for further syntheses of low-coordinate organometallic compounds. Recent years have witnessed an increasing interest in the use of similar

sterically demanding ligand systems for the ‘taming’ of low coordinate organometallics and coordination complexes, due to the ability of such compounds to undergo facile oxidation by small molecule substrates [3]. We were thus optimistic that such bulky deprotonated diphenylmethylys would serve as suitable ligating groups in which an electron deficient metal centre would be stabilised by both the steric demands imparted by the triorganosilyl group and π -aryl interactions with the phenyl substituents. This latter mode of stabilisation is commonly observed in derivatives of the benzyl group, $[\text{CH}_2\text{Ph}]^-$, which can coordinate as an η^1 , η^2 , η^3 , η^5 or even η^7 ligand depending on the degree of unsaturation at the metal centre [4]. Access to derivatives of alkali metals other than lithium is particularly advantageous in cases where lithium halide incorporation into the resultant complex may be likely to occur, for example in the synthesis of trivalent lanthanide derivatives [5]. Sterically demanding benzyl derivatives of the heavier alkali and alkaline earth metals have also received recent attention in their own right as initiators for the anionic polymerisation of styrene [6]. With this in mind we now wish to report syntheses of the base-free sodium and potassium derivatives of $\text{Ph}_2(\text{Me}_3\text{Si})\text{CH}$, **1** and **2**, the respective PMDETA (PMDETA = N,N,N',N'',N''' -pentamethyldiethylenetriamine) adducts, **3** and **4** and the results of an X-diffraction study performed on **3**.

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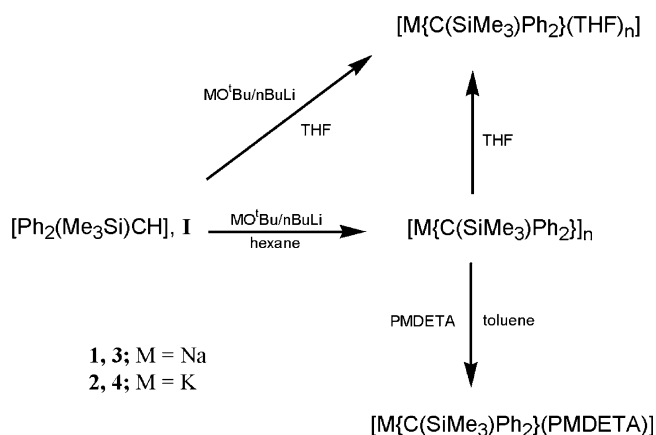
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2. Results and discussion

Initial attempts to form sodium and potassium derivatives of **1** were performed in THF solution by reaction of the substituted methane with a ‘superbase’ mixture formed from stoichiometric quantities of $n\text{BuLi}$ and the appropriate alkali metal *tert*-butoxide (Scheme 1). Although this procedure resulted in gas evolution and deep red–orange solutions consistent with the formation of the highly delocalised carbanion $[\text{Ph}_2(\text{Me}_3\text{Si})\text{C}]^-$ [2,7], removal of solvent produced ill-defined orange tars containing variable amounts (2–3 equivalents) of THF, as gauged from $^1\text{H-NMR}$. Although these materials were readily soluble in benzene and toluene and sparingly soluble in alkanes, repeated attempts to obtain better-defined materials by crystallisation from these solvents were unsuccessful.

More convenient access to the target derivatives was gained by addition of a stoichiometric quantity of $n\text{BuLi}$ to a stirred hexane solution of **1** and sodium or potassium *tert*-butoxide. Under these conditions orange powders precipitated and could be isolated, after further washing with hexane, to give the analytically pure, highly pyrophoric base-free compounds **1** and **2** in effectively stoichiometric yield. The organosodium derivative **1** was sparingly soluble in aromatic solvents but completely insoluble in alkanes. Compound **2** on the other hand was completely insoluble in all available non-coordinating solvents. This behaviour is consistent with a polymeric constitution where polymer propagation occurs through a combination of direct metal-to-carbon σ -interactions and secondary interactions of the extended π -system to the large alkali metal cations.



Scheme 1.

Similar interactions have been observed as an important determining factor in the structures adopted by a number of polarisable aryl-substituted organo derivatives of the heavier alkali metals [8], and have been noted as sufficiently strong to exclude coordinating ethereal solvents during crystallisation [9]. Attempted crystallisation of **1** and **2** from mixed aromatic/ether solutions was however similarly unsuccessful. Both **1** and **2** formed stable solutions in THF- d_8 and were sufficiently soluble for study by multinuclear NMR spectroscopy. This data provided evidence for significant delocalisation of charge over the $[\text{Ph}_2(\text{Me}_3\text{Si})\text{C}]^-$ skeleton. The signals for the central methyl carbon in the $^{13}\text{C-NMR}$ spectra of both **1** (68.0 ppm) and **2** (72.7 ppm) appeared at higher frequency than for the corresponding lithium derivative (63 ppm) [2], while the respective $^{29}\text{Si-NMR}$ shifts (**1**, -16.5 ; **2**, -15.9 ppm) were shifted upfield (vs. δ for Li derivative; -13.6 ppm) consistent with increased nuclear shielding as a result of charge delocalisation via available σ^* orbitals at silicon [10].

Reaction of toluene slurries of **1** and **2** with PMDETA and warming to ca. 50°C resulted in the formation of deep orange solutions from which, after concentration and cooling, the adducts **3** and **4** could be isolated as pyrophoric orange crystals (Scheme 1). Compounds **3** and **4** readily redissolved in hydrocarbon solvents and displayed solution NMR spectra in C_6D_6 consistent with 1:1 adduct formation. The resonances assigned to the central methyl carbon of both **3** and **4** again appear to high frequency (70.1 and 74.0 ppm, respectively) whilst the respective $^1J_{\text{SiC}}$ values associated with these signals (**3**, 81.4 Hz; **4**, 83.9 Hz) are very much larger than that of the precursor methane **1** (46.0 Hz) [2]. These latter values reflect a high degree of *s* character in the Si–C bonds of **3** and **4** and are similar to the $^1J_{\text{SiC}}$ coupling constants observed in lithium derivatives of **1** (ca. 73 Hz) [2] and other highly ionic silyl-substituted methyls such as $[\text{K}\{\text{C}(\text{SiMe}_3)_2\text{Ph}\}]$ (69.9 Hz) [6e] and $[\text{Cs}\{\text{C}(\text{SiMe}_3)_3\}]$ (67 Hz) [11]. The ^1H - and $^{13}\text{C-NMR}$ spectra of **1–4** also display signals ($< \sim 6.5$ and $< \sim 113.5$ ppm, respectively), which are assigned to the *para*-methine resonances of the phenyl groups of the diphenylmethyl anions. Such upfield shifts are characteristic of ionic benzyl derivatives. The observed *para*-methine ^1H shifts of all four compounds are to higher field than that observed in the lithium derivative of **1** (6.50 ppm) [2] and are similar to that reported for $[\text{K}\{\text{C}(\text{SiMe}_3)_2\text{Ph}\}]$ (6.07 ppm) [6e].

The evidence for extensive charge delocalisation in solution was substantiated in the solid state by an X-ray diffraction analysis performed on a single crystal of **3** obtained by slow cooling of a concentrated toluene solution. Although well-formed single crystals of compound **4** could be obtained in a similar manner, these were too small for X-ray data collection. The structure

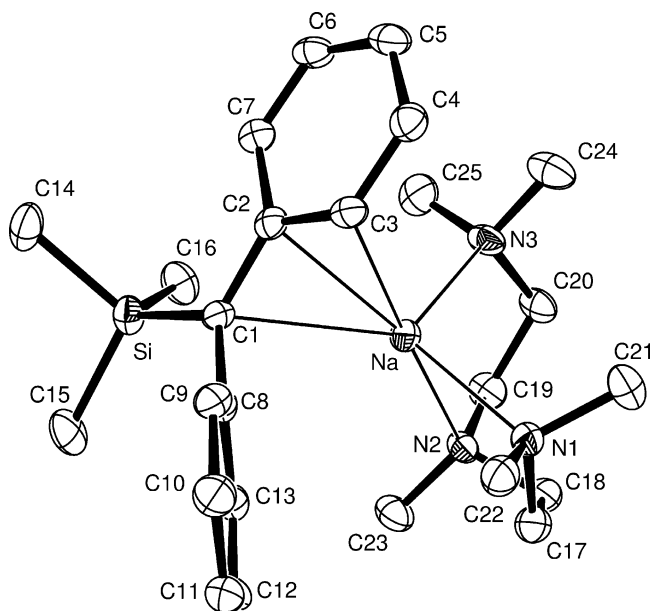


Fig. 1. The molecular structure of **3** in the crystal and the crystallographic numbering scheme used (30% probability ellipsoids). H atoms omitted for clarity.

Table 1
Selected bond lengths (Å) and bond angles (°) for **3**

Bond lengths			
Na–C(1)	2.690(5)	C(3)–C(4)	1.389(6)
Na–C(2)	2.631(5)	C(4)–C(5)	1.398(7)
Na–C(3)	2.784(5)	C(5)–C(6)	1.378(7)
Na–N(1)	2.476(4)	C(6)–C(7)	1.366(7)
Na–N(2)	2.458(4)	C(8)–C(13)	1.409(7)
Na–N(3)	2.490(4)	C(8)–C(9)	1.393(7)
Si–C(1)	1.846(5)	C(9)–C(10)	1.392(7)
C(1)–C(2)	1.454(7)	C(10)–C(11)	1.376(7)
C(1)–C(8)	1.486(7)	C(11)–C(12)	1.375(8)
C(2)–C(3)	1.418(7)	C(12)–C(13)	1.367(7)
C(2)–C(7)	1.437(6)		
Bond angles			
C(1)–Na–C(2)	31.69(14)	C(2)–Na–N(3)	108.92(15)
C(2)–Na–C(3)	30.18(14)	C(3)–Na–N(1)	94.97(15)
C(1)–Na–C(3)	55.35(15)	C(3)–Na–N(2)	171.06(17)
N(1)–Na–N(2)	76.18(15)	C(3)–Na–N(3)	109.78(15)
N(2)–Na–N(3)	75.11(14)	C(2)–C(1)–Is	120.2(4)
N(1)–Na–N(3)	110.69(15)	C(8)–C(1)–Is	118.8(3)
C(1)–Na–N(1)	119.24(15)	C(2)–C(1)–C(8)	119.6(4)
C(1)–Na–N(2)	127.93(15)	C(2)–C(1)–Na	71.9(3)
C(1)–Na–N(3)	128.30(16)	C(8)–C(1)–Na	92.9(3)
C(2)–Na–N(1)	121.16(16)	Si–C(1)–Na	116.6(2)
C(2)–Na–N(2)	156.53(16)		

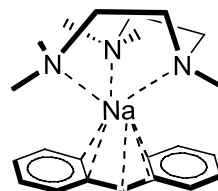
of **3** is shown in Fig. 1, selected metrical parameters are collected in Table 1 and details of the X-ray analysis are collected in Table 2.

Compound **3** exists as monomeric species in the solid state. The sodium ion is bonded in an η^3 -fashion to the organic anion and interacts most strongly with the *ipso*-carbon, [Na–C(2), 2.631(5) Å] of the C(2)–C(7) phenyl

Table 2
Crystal data and structure refinement parameters for compound **3**

3	
Chemical formula	C ₂₅ H ₄₂ N ₃ NaSi
Formula weight	435.70
<i>T</i> (K)	173(2)
Crystal system	Monoclinic
Space group	<i>Cc</i> (no. 9)
Unit cell dimensions	
<i>a</i> (Å)	11.8967(12)
<i>b</i> (Å)	14.7547(13)
<i>c</i> (Å)	15.4226(9)
β (°)	91.477(6)
<i>Z</i>	4
<i>V</i> (Å ³)	2706.4(4)
<i>D</i> _{calc} (Mg m ^{−3})	1.07
μ (mm ^{−1})	0.12
θ Range (°)	3.82–21.95
<i>R</i> ₁ ; <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.054; 0.111
<i>R</i> ₁ ; <i>wR</i> ₂ all data	0.076; 0.123
Measured/independent reflections/ <i>R</i> _{int}	6976/3158/0.087
Reflections with <i>I</i> > 2 σ (<i>I</i>)	2525

ring. The remaining coordination of sodium is provided by longer Na–C contacts to the benzylic C(1) centre [Na–C(1) 2.690(5) Å], the *meta*-carbon of the C(2)–C(7) phenyl ring [Na–C(3) 2.748(5) Å] and the tridentate PMDETA. Although these Na–C bond lengths are typical of those observed in other benzyl sodium derivatives [12], the overall bonding situation contrasts with that of [Na(CHPh₂)(PMDETA)] (**II**) where a symmetrical η^5 -interaction was observed between the sodium atom and the delocalised π -system provided by both phenyl rings and the coplanar central carbon [13]. This bonding situation is most likely induced by the bulky trimethylsilyl substituent of **3**, which effectively prevents the adoption of a completely coplanar configuration at carbon. A similar observation was made in the case of [Li(TMEDA)₂]⁺[C(SiMe₃)Ph₂][−] (TMEDA = *N,N,N',N'*-tetramethylethane-1,2-diamine) which exists as a charge separated species containing a free carbanion [2].



II

The C(1) atom of **3** is only slightly pyramidalised ($\Sigma_{\text{angles}} = 358.6^\circ$) and the planarity of the CSiC₂ core only slightly perturbed through contact to sodium. The silicon atom is displaced by 0.376 Å from the C(1)C(2)C(8)Si least squares plane, while the dihedral

angles of the C(2) and C(8) phenyl rings to this plane are 12.76 and 41.23°, respectively. The dihedral angle of the phenyl group in benzyl anions has been correlated with the extent of π -delocalisation and has been identified as a function of $\cos^2 \theta$ (where θ = dihedral angle between π -planes) [14]. For compound **3** the C(2) and C(8) phenyl twist angles correspond to 95 and 57% overlap between the respective phenyl π -systems and the filled p orbital of the sp^2 hybridised C(1) atom. This results in a shortening of the C(1)–C(2) [1.454(7) Å] and C(1)–C(8) [1.486(7) Å] bonds by ca. 0.07 and ca. 0.04 Å in comparison to the Ph–C bonds of the methane precursor **I**. This C–C contraction is not however as pronounced as that observed in the sodium benzyl derivative [Na{CH₂Ph}(TMEDA)] [1.404(8) Å] [12a], which comprises a single phenyl substituent for delocalisation of the benzylic charge or in the two independent molecules of the sodium diphenylmethyl **II** [range, 1.423(5)–1.446(8) Å] [13]. This latter difference may be attributed to the non-coplanarity of the phenyl rings in **3** as well as the presence of the Me₃Si substituent. The Si–C(1) bond of **3** [1.846(5) Å] is shortened in comparison to that of **I** through further delocalisation of charge which may be ascribed to negative hyperconjugation. Similar contractions observed in several silyl-substituted methyls have previously been discussed in this context [15].

The effects of charge delocalisation in **3** are also transmitted to the individual C–C bonds of the phenyl groups and both rings deviate significantly from regular hexagonal geometry (Fig. 2). The observed variation of bond lengths in both substituents is typical of phenyl rings attached to electropositive metal centres [6,14a]. Both rings are effectively elongated through alternating longer C_{ipso} – C_{ortho} and C_{meta} – C_{para} and shorter C_{ortho} – C_{meta} bonds. The planarity of the rings is preserved by deformations in the C–C–C bond angles, most notably at the C_{ipso} centres that contract for the C(2) and C(8) rings to 113.4(4) and 114.6(3)° respectively. It is also noteworthy that the more coplanar C(2)–C(7) ring, which is also linked directly to Na, is again the most affected

In conclusion, we have elaborated simple synthetic routes to sodium and potassium diphenyl(trimethylsilyl)methyls and have shown that these compounds exist in solution and the solid state as highly charge-delocalised species.

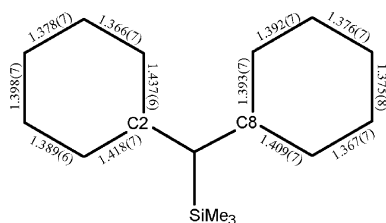


Fig. 2.

We are continuing to study these compounds and are assessing their utility as reagents in the synthesis of other low-coordinate organometallic derivatives.

3. Experimental

3.1. General considerations

All reactions were conducted under an atmosphere of dry Ar and manipulated either on a double manifold vacuum line or in a dinitrogen-filled drybox operating at <1 ppm of O₂. Solvents were purified by distillation from an appropriate drying agent (toluene and THF from potassium, hexane from Na/K alloy). NMR spectra were recorded at 300.13 (¹H), 75.5 (¹³C), 99.4 (²⁹Si), and 132.3 MHz (²³Na) in C₆D₆ unless otherwise stated; intensities of the quaternary and ²⁹Si signals were enhanced by polarisation transfer. Chemical shifts of the ¹H-, ¹³C- and ²⁹Si-NMR spectra are relative to SiMe₄ and ²³Na spectra are referenced to external aqueous NaCl. Compound **I** was synthesised as reported in Ref. [16].

3.2. [Na{C(SiMe₃)Ph₂}]_n (**1**)

A slurry of NaO^tBu (0.80 g, 8.3 mmol) in a solution of **I** (2.00 g, 8.3 mmol) in hexane (20 ml) was treated with an equimolar quantity of ⁿBuLi (3.4 ml of a 2.5 M solution in hexanes) at room temperature (r.t.). The resulting orange suspension was stirred at r.t. for a further 14 h at which point analytically pure **1** was isolated by filtration and washing with hexane (3 × 25 ml) as a pyrophoric orange powder in essentially quantitative yield. ¹H-NMR (THF-*d*₈, δ ppm): 0.05 (s, 9H, SiMe₃), 6.04 (t, 2H, *p*-C₆H₅), 6.65 (m, 4H, *m*-C₆H₅), 6.92 (m, 4H, *o*-C₆H₅). ¹³C{¹H}-NMR (δ ppm): 2.8 (¹J_{CSi} = 49.1 Hz, Me₃Si), 68.0 (CSiPh₂), 112.5 (*p*-C₆H₅), 124.0 (*m*-C₆H₅), 128.3 (*o*-C₆H₅), 153.3 (*i*-C₆H₅). ²⁹Si{¹H}-NMR (δ ppm): –16.5. ²³Na-NMR (δ ppm): –5.4 ($\Delta\nu_{1/2}$ = 500 Hz). Anal. Calc. for C₁₆H₁₉SiNa: C, 73.22; H, 7.31. Found: C, 72.74; H, 6.95%.

3.3. [K{C(SiMe₃)Ph₂}]_n (**2**)

This compound was synthesised by the same general method as employed for **1** using KO^tBu (0.70 g, 6.25 mmol), **I** (1.50 g, 6.25 mmol) and ⁿBuLi (2.5 ml of a 2.5 M solution in hexanes). Compound **2** was isolated as a highly pyrophoric orange powder in essentially quantitative yield. ¹H-NMR (THF-*d*₈, δ ppm): 0.02 (s, 9H, SiMe₃), 5.98 (t, 2H, *p*-C₆H₅), 6.64 (m, 4H, *m*-C₆H₅), 6.79 (d, 4H, *o*-C₆H₅). ¹³C{¹H}-NMR (δ ppm): 2.6 (¹J_{CSi} = 49.1 Hz, Me₃Si), 72.7 (CSiPh₂), 111.5 (*p*-C₆H₅), 123.5 (*m*-C₆H₅), 128.4 (*o*-C₆H₅), 152.9 (*i*-C₆H₅).

$^{29}\text{Si}\{^1\text{H}\}$ -NMR (δ ppm): -15.9 . Anal. Calc. for $\text{C}_{16}\text{H}_{19}\text{SiK}$: C, 68.99; H, 6.89. Found: C, 68.95; H, 6.84%.

3.4. $[\text{Na}\{\text{C}(\text{SiMe}_3)\text{Ph}_2\}(\text{PMDETA})]$ (**3**)

A slurry of **1** (0.50 g, 1.92 mmol) in toluene (15 ml) was treated at r.t. with excess PMDETA (1.00 ml, 4.79 mmol) and warmed (ca. 50 °C) until no more solid would dissolve. At this point the orange solution was filtered hot and allowed to cool slowly to r.t. to produce **3** as orange crystals suitable for single crystal X-ray analysis (0.49 g, 59%). ^1H -NMR (δ ppm): 0.03 (s, 9H, SiMe_3), 1.59–2.06 (br. m, ca. 23H, PMDETA), 6.46 (t, 2H, *p*- C_6H_5), 7.13 (m, 4H, *m*- C_6H_5), 7.30 (m, 4H, *o*- C_6H_5). $^{13}\text{C}\{^1\text{H}\}$ -NMR (δ ppm): 2.3 (Me_3Si), 42.6 (NMe), 46.3 (NMe₂), 54.3 (CH_2N), 55.4 (CH_2N), 70.1 ($^1J_{\text{CSi}} = 81.4$ Hz, CSiPh_2), 113.3 (*p*- C_6H_5), 123.0 (*m*- C_6H_5), 128.6 (*o*- C_6H_5), 152.4 (*i*- C_6H_5). $^{29}\text{Si}\{^1\text{H}\}$ -NMR (δ ppm): -14.9 . ^{23}Na -NMR (δ ppm): -3.4 ($\Delta\nu_{1/2} = 550$ Hz). Anal. Calc. for $\text{C}_{25}\text{H}_{42}\text{N}_3\text{SiNa}$: C, 68.91; H, 9.74; N 9.64. Found: C, 68.60; H, 9.50; N 9.38%.

3.5. $[\text{K}\{\text{C}(\text{SiMe}_3)\text{Ph}_2\}(\text{PMDETA})]$ (**4**)

This compound was synthesised by the same general method as employed for **3** using **2** (0.45 g, 1.62 mmol) and PMDETA (0.80 ml, 3.83 mmol). Slow cooling of a toluene solution to 5 °C yielded **4** as pyrophoric orange needles (0.41 g, 56%). ^1H -NMR (δ ppm): 0.03 (s, 9H, SiMe_3), 1.65, 1.74, 1.80 (PMDETA), 6.45 (t, 2H, *p*- C_6H_5), 7.06 (m, 4H, *m*- C_6H_5), 7.27 (d, 4H, *o*- C_6H_5). $^{13}\text{C}\{^1\text{H}\}$ -NMR (δ ppm): 2.9 (Me_3Si), 41.2 (NMe), 44.9 (NMe₂), 55.3 (CH_2N), 56.9 (CH_2N), 74.0 ($^1J_{\text{CSi}} = 83.9$ Hz, CSiPh_2), 112.3 (*p*- C_6H_5), 123.1 (*m*- C_6H_5), 129.1 (*o*- C_6H_5), 152.4 (*i*- C_6H_5). $^{29}\text{Si}\{^1\text{H}\}$ -NMR (δ ppm): -15.9 . Anal. Calc. for $\text{C}_{25}\text{H}_{42}\text{N}_3\text{SiK}$: C, 66.44; H, 9.39; N 9.30. Found: C, 66.42; H, 9.25; N 9.27%.

3.6. Crystallography

Data for **3** were recorded on a κ -CCD diffractometer by use of Mo-K α radiation ($\lambda = 0.71073$ Å). Further details are given in Table 2. The structure was solved by direct methods (SHELXS-97) [17] and refined by full least-squares on all data (SHELXL-97) [18]. Non-H atoms were anisotropic and H atoms were included in riding mode.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 191810 for compound **3**. 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; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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