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Synthesis and Structures of [(Trimethylsilyl)methyl]sodium and -potassium with Bi- and Tridentate N-Donor Ligands

William Clegg,[a] Ben Conway,[b] Alan R. Kennedy,[b] Jan Klett,*[b] Robert E. Mulvey,[b] and Luca Russo[a]

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[(Trimethylsilyl)methyl]sodium [$NaCH_2SiMe_3$] (**1**) was prepared by a metathesis reaction of [(trimethylsilyl)methyl]lithium [$LiCH_2SiMe_3$] with sodium *tert*-butoxide in *n*-hexane. Polydentate donors such as *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) and *N*,*N*,*N*′,*N*′′,*N*′′-pentamethyldiethylenetriamine (PMDETA) form *n*-hexane-soluble complexes of **1** and the potassium congener [KCH_2SiMe_3] (**2**). The crystal structures of the polymers [(TMEDA)$NaCH_2SiMe_3$] (**1a**) and [(PMDETA)KCH_2SiMe_3] (**2a**) were determined as infinite helical chains exhibiting 3_1 or 3_2 screw-axis symmetry. Compound **2b** was obtained as the donor-deficient heterocubane pseudotetramer [$(TMEDA)_3(KCH_2SiMe_3)_4$], with intermolecular interactions of the TMEDA-uncoordinated potassium atom with a peripheral methyl group of a neighbouring tetramer to form infinite chains. The relatively easy accessibility and stability should make these (trimethylsilyl)methyl compounds of sodium and potassium valuable starting points for further exploration of the chemistry of these common-utility heavier alkali metals.

Introduction

Compared to the widely used organometallic compounds of lithium[1] and magnesium,[2] the alkyl compounds of the heavier alkali metals (Na–Cs) are much less frequently employed in organometallic and organic chemistry. Efforts have been made to develop the organometallic chemistry of sodium and potassium,[3] and many examples are reported of their successful use in synthesis.[4] However, the preparation and characterisation of these highly polar (more so than lithium or magnesium) compounds is complicated by several possible side reactions, including most notably metalation of the organic solvent,[5] β-elimination[6] or self-metalation.[7] Their preparations could be achieved in aliphatic hydrocarbons through halogen/metal exchange[8] (direct synthesis), reaction of alkylmercury compounds with alkali metals (transmetalation)[9] or reaction of alkyllithium compounds with alkali metal *tert*-butoxides (metal/metal exchange).[10] Because of their low stability and low solubility in hydrocarbons, few alkylsodium and -potassium compounds have been structurally characterised. Only the polymeric structures of compounds of simple alkyl groups, such as methyl- and ethylsodium as well as methylpotassium could be identified by powder diffraction.[11] More structural information is known for alkylsodium and -potassium compounds with more stabilising modified/functionalised alkyl groups (see Table 1), such as benzyl,[12] diphenylmethyl,[12,13] triphenylmethyl,[14] bis(trimethylsilyl)methyl,[15,16] tris(trimethylsilyl)methyl,[17,18] and phenylbis(trimethylsilyl)methyl.[19] Structural motifs which can be found in this group of compounds range from solvated monomers,[14] solvated dimers,[13] separated ion pairs,[17] solvated tetramers,[12,16b] chains,[15,18a,19] and solvated chains.[16a,16b,18b]

Table 1. Structural types of selected alkylsodium and -potassium compounds.

Alkylmetal compound	Type of structure	Ref.
(PMDETA)$KCPh_3$	solvated monomer	[14]
(thf)[$KCHPh_2$]$_2$	solvated dimer	[13]
$Na(TMEDA)_2(thf)\{Na[C(SiMe_3)_3]_2\}$	separated ion pair	[17]
[(TMEDA)$NaCHPh_2$]$_4$	solvated tetramer (ring)	[12]
$(PMDETA)_2[KCH(SiMe_3)_2]_4$	solvated tetramer	[16b]
$[NaCH(SiMe_3)_2]_\infty$	chain	[15]
$[KC(SiMe_3)_3]_\infty$	chain	[18a]
$[KC(SiMe_3)_2Ph]_\infty$	chain	[19]
$[(PMDETA)NaCH_2Ph]_\infty$	solvated chain	[12]
$[(thf)KCH(SiMe_3)_2]_\infty$	solvated chain	[16a]
$[(MeO\mathit{t}Bu)KCH(SiMe_3)_2]_\infty$	solvated chain	[16b]
$[(TMEDA)KC(SiMe_3)_3]_\infty$	solvated chain	[18b]

Inspection of these results immediately draws attention to the large proportion of these compounds containing silyl-substituted methyl groups. These groups improve stability because of the absence of a β-hydrogen atom, but also through their bulkiness and electronic stabilisation. Surprisingly, considerably less is known about the alkali metal

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[a] School of Chemistry, Newcastle University,
Newcastle upon Tyne, NE1 7RU, U.K
[b] WestCHEM, Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, G1 1XL, U.K
Fax: +44-141-548 4787
E-mail: jan.klett@strath.ac.uk

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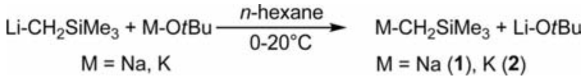
compounds of the smallest and simplest member of this family of silyl-substituted methyl groups, namely the (trimethylsilyl)methyl (CH_2SiMe_3) or monosyl group.[20] Again, the most examined (trimethylsilyl)methyl compound to date is the lithium congener, [(trimethylsilyl)methyl]lithium $[Me_3SiCH_2Li]_n$, which is known to form a hexamer (n = 6) in the solid state,[21] whereas both *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) and the (–)-sparteine adducts form dimers (n = 2), and the higher-denticity ligand *N*,*N*,*N*′,*N*′′,*N*′′-pentamethyldiethylenetriamine (PMDETA) forms a monomer (n = 1).[22] [(Trimethylsilyl)methyl]potassium has been used in *C*-metallation reactions of cyclohexene,[23] toluene,[24] and tetrahydrofuran,[25] and in an *N*-metallation reaction of a secondary amine to form potassium 2,2,6,6-tetramethylpiperidide[26] in situ,[27] which has recently been employed as a convenient precursor in synergic mixed-metal chemistry.[28] The primary aim of the present work is to fully characterise the [(trimethylsilyl)methyl] compounds of sodium and potassium as a prelude to developing them further in synthetic applications.

Results and Discussion

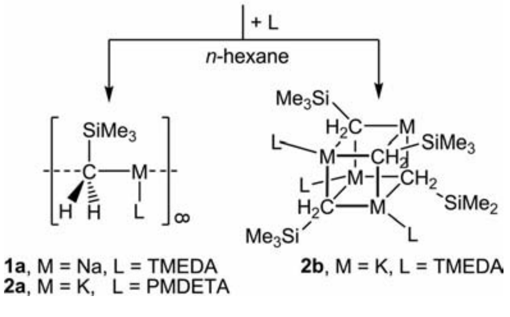
[(Trimethylsilyl)methyl]sodium $[NaCH_2SiMe_3]$ (**1**) can be prepared in a similar way to that previously reported for [(trimethylsilyl)methyl]potassium $[KCH_2SiMe_3]$ (**2**).[27a,27b] Thus avoiding the use of bis[(trimethylsilyl)methyl]mercury[29] with an alkali metal in a transmetalation,[24] a method which proved to be unsuccessful in the case of sodium, the commercially available [(trimethylsilyl)methyl]lithium was treated with sodium *tert*-butoxide in *n*-hexane (Scheme 1), taking advantage of the energetically preferred formation of lithium *tert*-butoxide and the precipitation of insoluble [(trimethylsilyl)methyl]sodium. The reaction is easily carried out in *n*-hexane between 0 °C and room temperature, and the resulting insoluble [(trimethylsilyl)methyl]alkali metal compounds **1** or **2** can be conveniently isolated through filtration as off-white pyrophoric powders, which show no sign of decomposition even after months while stored under an inert gas.



Scheme 1.

Although compounds **1** and **2** showed high reactivity towards THF[25] and benzene and only low solubility in the latter solvent, both compounds could still be identified by NMR spectroscopy in the corresponding deuterated solvents. All the samples showed significant protolysis (by formation of $SiMe_4$), and only traces of *tert*-butoxide or lithium could be detected in both samples. In deuterated benzene the ^1H NMR spectrum shows a singlet for the trimethylsilyl group at δ = 0.15 ppm and another singlet for the CH_2 group at δ = –2.44 ppm for **1**, with the corresponding signals for **2** appearing at δ = 0.18 and –2.60 ppm, respectively. In $[D_8]$THF the corresponding signals can be observed at δ = –0.19 and –2.20 ppm for **1** and at δ = –0.20 and –2.22 ppm for **2**. No meaningful ^{13}C NMR spectra could be obtained, due to the fast protolysis of the solvents used.

Treatment of *n*-hexane suspensions of **1** with equimolar amounts of TMEDA or PMDETA, or **2** with a 3 to 5 mol-equiv. excess, produces clear solutions, which rapidly decompose at room temperature with the formation of brown precipitates.[30] This decomposition can be avoided when the resulting yellowish solutions are immediately stored at –70 °C for several days. In this way it was possible to obtain TMEDA- or PMDETA-containing crystalline samples of [(trimethylsilyl)methyl]sodium and -potassium (Scheme 2). The yellowish crystals of the PMDETA solvate of [(trimethylsilyl)methyl]sodium melted and decomposed below 0 °C, but the TMEDA solvate of [(trimethylsilyl)methyl]sodium $[(TMEDA)NaCH_2SiMe_3]$ (**1a**) and of [(trimethylsilyl)methyl]potassium $[(TMEDA)_3(KCH_2SiMe_3)_4]$ (**2b**) and the PMDETA solvate of [(trimethylsilyl)methyl]potassium $[(PMDETA)KCH_2SiMe_3]$ (**2a**) could be isolated intact from solution and subsequently characterised by X-ray crystallography and NMR spectroscopy. Due to the even more aggressive behaviour of **1a**, **2a** and **2b** towards deuterated benzene and THF compared to that of **1** and **2**, only deuterated cyclohexane produced useful NMR spectra without showing advanced solvolysis. The ^1H NMR spectrum of compound **1a** shows signals for the trimethylsilyl group at δ = –2.27 ppm and for the CH_2 group at –0.10 ppm, while the TMEDA Me and CH_2 groups appear at δ = 2.23 and 2.30 ppm, respectively. The corresponding signals of these groups in the ^{13}C NMR spectrum are located at δ = –7.5, 5.8, 46.6 and 58.2 ppm. The ^1H NMR spectra for **2a** and **2b** show very similar chemical shifts for the CH_2 groups (δ = –2.29 and –2.40 ppm) and the trimethylsilyl groups (δ = –0.13 and –0.10 ppm), and the signals for PMDETA or TMEDA are situated in the range δ = 2.18–2.38 or 2.17–2.29 ppm, respectively. In the ^{13}C NMR spectra the signal of the CH_2 groups **2a/2b** can be found at δ = 1.3/4.1 ppm, for the trimethylsilyl group at δ = 6.5/5.9 ppm, the PMDETA of **2a** shows signals at δ = 43.1, 46.1, 57.2 and 58.6 ppm, whereas the TMEDA signals of **2b** can be observed at δ = 46.2 and 58.7 ppm. Whereas crystalline **1a** and **2a** are stable under an inert gas at room temperature for several days, crystals of **2b** quickly melt and turn dark as a sign of rapid decomposition.



Scheme 2.

Turning to the X-ray crystallographic results, compound **1a** crystallises in the trigonal space group $P3_1$ (or $P3_2$, these being indistinguishable in the absence of significant anomalous scattering effects), with three crystallographically independent helical polymer chains, each exhibiting 3_1 screw-axis symmetry along the *c* axis (Figure 1). The sodium atoms are coordinated by two nitrogen atoms of TMEDA at distances ranging from 2.52 to 2.57 Å and CH$_2$ groups of two different trimethylsilylmethyl groups with alternating shorter and longer Na–C bonds. The shorter Na–C bonds with lengths between 2.523(9) and 2.530(8) Å represent the orientation of lone pairs of the methanide anions in accordance with the positions of the two hydrogen atoms, whereas the longer Na–C bonds have lengths between 2.581(8) and 2.643(9) Å implying a greater electrostatic contribution to the interaction. These differences in bond lengths compared to the corresponding symmetric Na–C bonding in the unsolvated polymer [NaCH(SiMe$_3$)$_2$]$_\infty$ [2.555(10) Å],[15] can be explained by the pyramidal configuration of the CH$_2$(SiMe$_3$) group and the additional coordination by TMEDA.

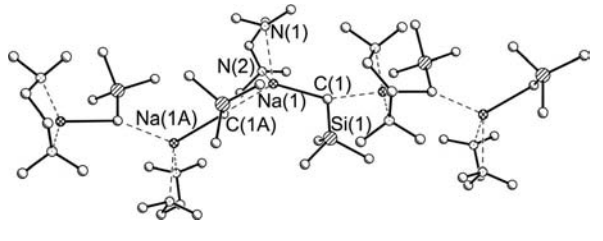


Figure 1. Pentameric section of one of three crystallographically independent polymeric chains of **1a**. Hydrogen atoms are omitted for clarity. Symmetry operator A: $-y + 1$, $x - y + 1$, $z + 1/3$. Dotted lines represent longer (electrostatic) Na–C interactions as well as Na–N dative interactions.

Two nitrogen atoms of the chelating TMEDA molecule form a bite angle at the corresponding sodium atoms between 71.7(3) and 73.7(3)°, whereas the anionic carbon centres of the more bulky (trimethylsilyl)methyl groups make wider obtuse angles between 123.1(2) and 125.7(2)°. The Na(1)–C(1)–Si(1) and Na(11)–C(11)–Si(11) or Na(21)–C(21)–Si(21) angles are found in the range 104.6(4)–107.5(4)° and are closer to the ideal tetrahedral angle of 109.5° than the corresponding Na(1A)–C(1)–Si(1) (and equivalent) angles with an average of 100.7°, confirming the existence of a more covalent bond for Na(1)–C(1) and a more ionic bond between Na(1A) and C(1) to the next monomer unit on the opposite side. The Na(21)–C(21) bond shows an opposite orientation along the crystallographic *c* axis compared to the Na(1)–C(1) and Na(11)–C(11) bonds in the corresponding polymeric chains, i.e. one helical polymer runs in the opposite direction to the other two. Compound **2a** adopts a closely related structure (Figure 2), which crystallises in the enantiomorphic trigonal space groups $P3_1$ and $P3_2$ (twinned) but with only one helical polymeric chain per unit cell along the crystallographic *c* axis. The chain is formed by potassium atoms coordinated by the three nitrogen atoms of PMDETA [K(1)–N(2) 2.9250(18), K(1)–N(3) 2.9265(16), K(1)–N(4) 2.9512(16) Å] and two carbon atoms of two (trimethylsilyl)methyl CH$_2$ groups; again alternating potassium–carbon distances [K(1)–C(1) 2.9151(19), K(1)–C(1A) 3.0358(19) Å] as well as the corresponding K–C–Si bond angles [K(1)–C(1)–Si(1) 109.86(9), K(1)–C(1A)–Si(1A) 98.67(8)°] indicate a more covalent character of the K(1)–C(1) bond compared to a more ionic K(1)–C(1A) interaction.

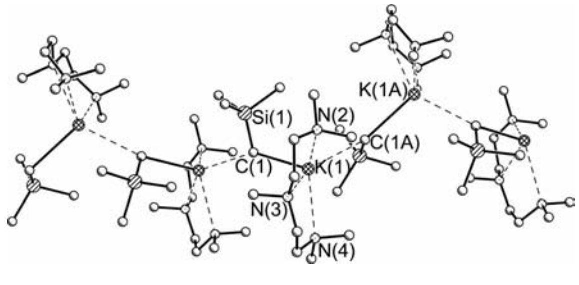


Figure 2. Pentameric section of chain polymer **2a**. Hydrogen atoms are omitted for clarity. Symmetry operator A: $-x + y + 1$, $-x + 1$, $z + 1/3$ (for space group $P3_2$). Dotted lines represent longer (electrostatic) K–C interactions as well as K–N dative interactions.

Due to the longer potassium–nitrogen distances in **2a** compared to those in **1a**, the nitrogen atoms of the PMDETA molecule take part in even more acute N–K–N angles [N(2)–K(1)–N(3) 61.09(5), N(3)–K(1)–N(4) 60.48(5)°] than those in the corresponding Na/TMEDA compound **1a**. Along the chain the two (trimethylsilyl)methyl CH$_2$ groups subtend an angle of 110.28(3)° at the potassium atom, whereas the corresponding carbon atom and the two potassium ions form a bond angle of 150.47(7)°.

Whereas the TMEDA-solvated potassium compound of the bis(trimethylsilyl)methyl group[16b] [(PMDETA)$_2${KCH(SiMe$_3$)$_2$}$_4$] forms an "open tetramer"[31] (with a central K$_2$C$_2$ core, which is extended by two bridging alkyl groups and two terminal PMDETA-coordinated potassium atoms), the corresponding (trimethylsilyl)methyl compound **2b**, which crystallises in the triclinic space group $P\bar{1}$, forms an asymmetric tetranuclear unit with only three of the four potassium atoms chelated by two TMEDA nitrogen atoms each. The donor-deficient molecule **2b** is best described as a tetrahedron based on four potassium atoms, with each of the four triangular faces capped by the methanide carbon atoms of four (trimethylsilyl)methyl groups, completing a distorted K$_4$C$_4$ heterocubane (Figure 3). This motif is not unusual for alkyllithium compounds, but to the best of our knowledge is so far unknown for alkylsodium or -potassium congeners.[32] Its K–CH$_2$ distances span the range 2.922(3)–3.247(3) Å (see Table 2). The distance of the carbon atom to the middle (centroid) of the corresponding K$_3$ triangle lies between 1.897 and 2.038 Å. The trimethylsilyl group and the two hydrogen atoms occupy a staggered position relative to the corresponding three potassium atoms. Three (trimethylsilyl)methyl groups [including the methanide carbon atoms C(1), C(2), and C(3)] are directed away from the plane formed by the TMEDA-coordinated potassium atoms K(1), K(2) and K(3). The free electron pairs of the (trimethylsilyl)methyl groups are directed towards the midpoints X_n of the K(3)···K(4) and K(2)···K(4) lines, this description being supported by the corresponding Si(1)–C(1)–X_1, Si(2)–C(2)–X_2 and Si(3)–C(3)–X_2 angles with a close to tetrahedral range from 105.5 to 112.5°. Also, the corresponding K(3)···K(4) and K(2)···K(4) internuclear separations show the shortest K···K distances of 3.8397(8) and 3.7596(8) Å, respectively. The peripheral methyl groups [C(13), C(22) and C(33)] of the (trimethylsilyl)methyl groups also engage in short interactions with K(4) at distances of 3.304, 3.494 and 3.456 Å. The fourth (trimethylsilyl)methyl group [including C(4)], which caps the K(1)–K(2)–K(3) plane, shows interactions with the potassium atom K(4) of the next molecule, forming chains along the crystallographic *a* axis (Figure 4).

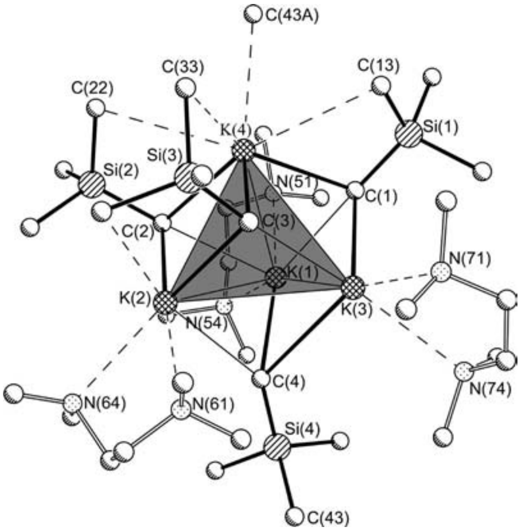


Figure 3. Tetrameric section of polymeric **2b**. Hydrogen atoms are omitted for clarity. Symmetry operator A: *x* – 1, *y*, *z*. The distorted K_4 tetrahedron is shaded. Short K–C interactions are emphasised by full lines.

Table 2. Selected bond lengths [Å] of compound **2b**.

	K(1)	K(2)	K(3)	K(4)
C(1)	2.993(3)	–	3.056(3)	2.972(3)
C(2)	3.076(3)	3.029(3)	–	2.932(3)
C(3)	–	2.958(3)	3.098(3)	2.922(3)
C(4)	2.985(3)	3.129(3)	3.247(3)	–
K(1)	–	4.3565(8)	3.9214(7)	4.0258(8)
K(2)	4.3565(8)	–	3.9977(8)	3.7596(8)
K(3)	3.9214(7)	3.9977(8)	–	3.8397(8)
K(4)	4.0258(8)	3.7596(8)	3.8397(8)	–
N(51)/N(61)/N(71)	2.952(2)	3.053(3)	3.026(4)	–
N(54)/N(64)/N(74)	2.939(2)	2.893(2)	2.946(2)	–

Though unusual for alkyl compounds of the heavier alkali metals sodium and potassium, many examples of potassium heterocubanes are known for more complex heteroatom anionic systems, including alkoxides,[33] silanolates,[34] enolates,[35] hydroxylamides,[36] phosphoraneiminates[37] and silanides.[38]

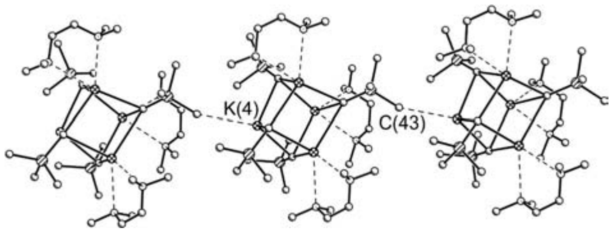


Figure 4. Trimeric section of infinite chains of tetranuclear units of **2b** along the crystallographic *a* axis. Hydrogen atoms are omitted for clarity. Symmetry operator A: *x* – 1, *y*, *z*. Short K–C and K–N interactions are represented by dotted lines.

Recently, Stalke et al.[39] and Mitzel et al.[40] could identify very similar structural motifs in solvated alkyllithium compounds. The example from the former group shows a tetramer of [(trimethylsilyl)methyl]lithium asymmetrically coordinated by two diethyl ether molecules $[(LiCH_2SiMe_3)_4(Et_2O)_2]$, whereas the latter group's example consists of tetramers of methyllithium coordinated by three monodentate molecules of 1,3,5-trimethyl-1,3,5-triazacyclohexane (TMTAC), and the uncoordinated lithium atom interacts with a methyl group of the neighbouring tetramer to form linear chains of tetramers $[\{(LiMe)_4(TMTCA)_3\}_\infty]$, similar to the structure of **2b**. Also very recently we reported the structure of unsolvated [(trimethylsilyl)methyl]sodium (**1**) consisting of tetrameric subunits, which form polymeric chains by using two of the four (trimethylsilyl)methyl groups for additional agostic-type interactions.[41]

Conclusions

We have described a convenient and efficient synthesis for solvent-free [(trimethylsilyl)methyl]sodium (**1**), which could be characterised by solution NMR spectroscopy. Similar to the congeneric potassium compound it has a high potential to be used in the formation of sodium alkylmetallates or sodium amides. In addition treatment of [(trimethylsilyl)methyl]sodium (**1**) and -potassium (**2**) with TMEDA or PMDETA led to highly reactive solvated derivatives, which could be isolated as extremely air- and moisture-sensitive crystalline materials. Despite their good solubility in *n*-hexane, the molecular structures of the TMEDA-solvated [(trimethylsilyl)methyl]sodium (**1a**) and the PMDETA-solvated [(trimethylsilyl)methyl]potassium (**2a**) were found to be polymeric chains formed by repeating metal–alkyl–metal interactions. In contrast, the TMEDA complex of [(trimethylsilyl)methyl]potassium (**2b**) shows a solvent-deficient pseudotetrameric structure with a novel heterocubane K_4C_4 arrangement. The relatively easy accessibility and stability should make these (trimethylsilyl)methyl compounds of sodium and potassium valuable starting points for further exploration of the chemistry of these common-utility heavier alkali metals.

Experimental Section

General Methods: *n*-Hexane was distilled from sodium/benzophenone, TMEDA and PMDETA were distilled from CaH_2. All synthetic work was carried out under argon by using standard Schlenk and glove-box techniques. KCH_2SiMe_3 was prepared according to literature procedures.[27a,27b] ^1H NMR spectra were recorded with a Bruker AV 400 MHz spectrometer; data for X-ray crystal structure determination were obtained with Oxford Diffraction Xcalibur Gemini A Ultra diffractometers by using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Selected crystallographic data for compounds **1a**, **2a** and **2b** are given in Table 3. Disorder was resolved satisfactorily for the TMEDA ligands in **2b**. **2a** was found to be twinned both merohedrally (emulating the higher-symmetry trigonal Laue class) and by inversion (both enantiomorphic space groups present in an approx. 2:1 ratio). H atoms were positioned geometrically and treated as riding atoms in each case. CCDC-793015 (**1a**), -793016 (**2a**) and -793017 (**2b**) contain the supplementary crystallographic data for this publication. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Microanalyses were carried out, but due to instability, oxidation/hydrolysis, desolvation and possibly carbide formation[42] no satisfactory elemental analysis could be obtained.

[$NaCH_2SiMe_3$] (1): NaO*t*Bu (0.96 g, 10.0 mmol) was dissolved in *n*-hexane (50 mL) in a Schlenk tube and placed in an ice bath. A solution of $LiCH_2SiMe_3$ in pentane (1 M; 10 mL, 10.0 mmol) was added, and the reaction mixture was stirred at room temperature overnight to form an off-white suspension. The solid was filtered, washed with hexane (20 mL), and dried in vacuo to afford a white solid (0.95 g, 86.4% yield). ^1H NMR (400.13 MHz, 298 K, [D_6]benzene): δ = –2.44 (s, 2 H, CH_2), 0.15 [s, 9 H, $Si(CH_3)_3$] ppm. ^1H NMR (400.13 MHz, 298 K, [D_8]THF): δ = –2.20 (s, 2 H, CH_2), –0.19 [s, 9 H, $Si(CH_3)_3$] ppm.

[(TMEDA)$NaCH_2SiMe_3$] (1a): $NaCH_2SiMe_3$ (**1**, 0.22 g, 2.0 mmol) was suspended in *n*-hexane (20 mL). To this suspension TMEDA (0.3 mL, 2.0 mmol) was added to yield a clear yellow solution. Storage of the solution at 0 °C for 2 d afforded colourless crystals (0.15 g, 65.2% yield). Alternatively, some solvent can be removed in vacuo and the precipitated solid dissolved by warming the solution to yield a crop of crystals after cooling. ^1H NMR (400.13 MHz, 298 K, [D_6]benzene): δ = –1.80 (s, 2 H, CH_2), 0.44 [s, 9 H, $Si(CH_3)_3$], 1.86 (s, 4 H, CH_2-TMEDA), 1.90 (s, 12 H, CH_3-TMEDA) ppm. ^1H NMR (400.13 MHz, 298 K, [D_{12}]cyclohexane): δ = –2.27 (s, 2 H, CH_2), –0.10 [s, 9 H, $Si(CH_3)_3$], 2.23 (s, 12 H, CH_3-TMEDA), 2.30 (s, 4 H, CH_2-TMEDA) ppm. ^{13}C NMR (100.62 MHz, 298 K, [D_{12}]cyclohexane): δ = –7.5 (CH_2), 5.8 [$Si(CH_3)_3$], 46.6 (CH_3-TMEDA), 58.2 (CH_2-TMEDA) ppm.

[(PMDETA)KCH_2SiMe_3] (2a): KCH_2SiMe_3 (**2**, 0.24 g, 2.0 mmol) was suspended in *n*-hexane (10 mL). To this suspension PMDETA (1.26 mL, 6.0 mmol) was added to yield a clear yellow solution. Storage of the solution at –70 °C for 2 d afforded colourless crystals (0.32 g, 53.5% yield). ^1H NMR (400.13 MHz, 298 K, [D_{12}]cyclohexane): δ = –2.29 (s, 2 H, CH_2), –0.13 [s, 9 H, $Si(CH_3)_3$], 2.18 (s, 15 H, CH_3-PMDETA), 2.32 (s, 4 H, CH_2-PMDETA), 2.38 (s, 4 H, CH_2-PMDETA) ppm. ^{13}C NMR (100.62 MHz, 298 K, [D_{12}]cyclohexane): δ = 1.3 (CH_2), 6.5 [$Si(CH_3)_3$], 43.1 (CH_3-PMDETA), 46.1 (CH_3-PMDETA), 57.2 (CH_2-PMDETA), 58.6 (CH_2-PMDETA) ppm.

[$(TMEDA)_3(KCH_2SiMe_3)_4$] (2b): KCH_2SiMe_3 (**2**, 0.12 g, 1.0 mmol) was suspended in *n*-hexane (10 mL). To this suspension TMEDA (0.75 mL, 5.0 mmol) was added to yield a clear yellow solution. Immediate removal of some solvent in vacuo and storage of the solution at –70 °C for 2 d afforded large colourless prisms (0.12 g, 56.2% yield). ^1H NMR (400.13 MHz, 298 K, [D_{12}]cyclohexane): δ = –2.40 (s, 8 H, CH_2), –0.10 [s, 36 H, $Si(CH_3)_3$], 2.17 (s, 36 H, CH_3-TMEDA), 2.29 (s, 12 H, CH_2-TMEDA) ppm. ^{13}C NMR (100.62 MHz, 298 K, [D_{12}]cyclohexane): δ = 4.1 (CH_2), 5.9 [$Si(CH_3)_3$], 46.2 (CH_3-TMEDA), 58.7 (CH_2-TMEDA) ppm.

Supporting Information (see footnote on the first page of this article): Detailed synthetic information as well as NMR spectroscopic data.

Table 3. Selected crystallographic data for compounds **1a**, **2a** and **2b**.[a]

Compound	**1a**	**2a**	**2b**
Formula	$C_{10}H_{27}N_2NaSi$	$C_{13}H_{34}KN_3Si$	$C_{34}H_{92}K_4N_6Si_4$
M_r [g mol^{-1}]	226.42	299.62	853.90
Crystal system	trigonal	trigonal	triclinic
Space group	$P3_1$	$P3_2$	$P\bar{1}$
a [Å]	17.4307(8)	10.7730(1)	11.2401(3)
b [Å]	17.4307(8)	10.7730(1)	11.3805(3)
c [Å]	13.6159(8)	14.6261(3)	22.4476(4)
α [°]	90	90	85.459(2)
β [°]	90	90	80.045(2)
γ [°]	120	120	79.359(2)
V [Å^3]	3582.7(3)	1470.05(4)	2776.27
Z	9	3	2
$\rho_{calcd.}$ [g cm^{-3}]	0.944	1.015	1.021
μ(Mo-K_α) [mm^{-1}]	0.150	0.324	0.433
T [K]	150	123	123
Measured reflections	6090	8954	51394
Independent reflections	2943	4955	13352
Observed reflections[b]	2002	4285	9192
Refined parameters	400	183	482
$R1$[c] ($R1$ all data)	0.0677 (0.1633)	0.0308 (0.0495)	0.0550 (0.1269)
$w2$[d] ($wR2$ all data)	0.0983 (0.1693)	0.0388 (0.0509)	0.0924 (0.1386)
Max/min electron density [e Å^{-3}]	0.23/–0.22	0.23/–0.20	1.10/–1.24

[a] All data were collected by using Mo-K_α radiation (λ = 0.71073 Å). [b] Observation criterion: $I > 2\sigma(I)$. [c] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [d] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

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