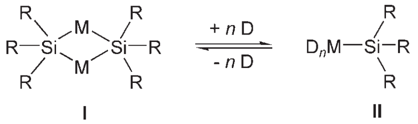
Silanide Clusters

DOI: 10.1002/anie.200703575

The Multidentate Ligand $(\mathrm{MeOMe_2Si})_3\mathrm{Si}^-$: Unusual Coordination Modes in Alkali Metal Silanides[**]

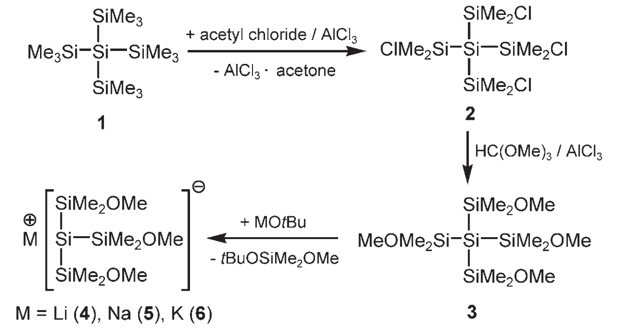
Clemens Krempner, Malcolm H. Chisholm, and Judith Gallucci*

Alkali metal silanides, $\mathrm{R_3SiM}$ ($\mathrm{R} =$ alkyl, aryl, silyl)[1] are important reagents in the synthesis of compounds with silicon–silicon bonds, such as disilenes,[2] disilynes,[3] silicon clusters,[4] and oligosilane dendrimers.[5] In the solid state, the majority of these silanides form either solvated monomers, such as $[\mathrm{R_3SiM(donor)}_n]$ ($\mathrm{M} =$ Li, Na, K, Rb, Cs; donor $=$ THF, TMEDA (N,N,N′,N′-tetramethylethylenediamine), DME (1,2-dimethoxyethane), $\mathrm{C_6H_6}$, [18]crown-6, [15]crown-5, [12]crown-4) or unsolvated dimers, such as $[\{\mathrm{R_3Si(\mu\text{-}M)}\}_2]$ (Scheme 1).[1f] Herein we report that lithium, sodium, and potassium derivatives of the new ligand $\mathrm{Si(SiMe_2OMe)_3}$ (trimethoxyhypersilanide) have very different structures, crystallizing as a result of strong coordinative interactions of the methoxy groups to the metal centers as clusters (K) or polymeric chains (Li, Na).[6] NMR spectroscopic investigations show that even in THF solutions, in which these aggregates dissociate into monomers, intramolecular oxygen-to-metal coordination is maintained.



Scheme 1. Structural types of alkali metal silanides (D = donor).

The synthetic route to the metal trimethoxyhypersilanides **4**–**6** is given in Scheme 2. Reaction of $\mathrm{(Me_3Si)_4Si}$ (**1**) with $\mathrm{AlCl_3}$ and acetyl chloride furnishes $\mathrm{(ClMe_2Si)_4Si}$ (**2**) in 90–95% yield.[7] Compound **2** was converted into tetrakis(methoxydimethylsilyl)silane, $\mathrm{(MeOMe_2Si)_4Si}$, (**3**) in about 90% yield by reaction with $\mathrm{HC(OMe)_3}$ in the presence of catalytic amounts of $\mathrm{AlCl_3}$. Finally, the lithium, sodium, and potassium trimethoxyhypersilanides **4**–**6** were obtained upon treatment of MO*t*Bu (M = Li, Na, K, respectively) with **3** in THF at room temperature. These reactions proceed smoothly to give **6** within about two hours, and **4** and **5** in about 10–12 hours, and were essentially quantitative according to NMR spectroscopic measurements. In contrast, the reaction of $\mathrm{(Me_3Si)_4Si}$ with NaO*t*Bu or LiO*t*Bu does not give the related hypersilanides $\mathrm{(Me_3Si)_3SiLi}$ and $\mathrm{(Me_3Si)_3SiNa}$ under similar conditions; no reaction occurred even after three days at room temperature.[8] Evidently, the methoxy groups of **3** significantly increase the electrophilicity of the silicon atoms of the $\mathrm{SiMe_2OMe}$ groups and consequently facilitate selective Si–Si bond cleavage by nucleophilic attack of the *tert*-butoxide anion.



Scheme 2. Synthesis of the alkali metal trimethoxyhypersilanides **4**–**6**.

The colorless trimethoxyhypersilanides **4**–**6** are surprisingly thermally stable. Upon increasing the temperature to 55 °C in $[\mathrm{D_8}]$THF, no structurally irreversible changes, such as protonation, elimination of methoxide, skeletal rearrangements to metal siloxides, or condensation reactions to polysilanes, occurred. In the solid state, **4**–**6** began to decompose only above 200 °C, with formation of reddish-brown liquids. The solubility of **4** and **5** in organic solvents differs significantly from that of **6**. The latter readily dissolves in THF and hydrocarbons such as benzene, toluene, and *n*-hexane, whereas the lithium and sodium derivatives are almost insoluble in benzene and *n*-hexane.

The solid-state structures of **4**–**6** were determined by X-ray crystallography,[9] and the results are shown in Figure 1–3 along with selected average bond lengths and angles in Table 1. Lithium silanide **4** (Figure 1) is formally composed of zwitterionic bicyclooctane units, $\mathrm{(Si(SiO)_3Li)}$, which are associated in a head-to-tail fashion to give a linear infinite chain. The four-coordinate lithium ion binds tripodally to the three methoxy groups, and bridges each of the $\{\mathrm{Si(SiO)_3Li}\}$ units with the negatively charged central silicon. The Si4–Li distance (276.3 pm) in **4** is significantly longer than in the closely related hypersilanides $[\mathrm{(Me_3Si)_3SiLi(dme)_{1.5}}]$ (263 pm),[10] $[\mathrm{(Me_3Si)_3SiLi(thf)_3}]$ (264 pm),[11] $[\mathrm{(Me_3Si)_3Si(\mu\text{-}Li)}]_2$ (267 pm),[12] and $[\mathrm{(Me_3Si)Si(\mu\text{-}Li(thf))}]_2$ (271 pm).[13] The Si-Si-Si angles are reduced from an ideal tetrahedral value of 109.5° as in $\mathrm{Si(SiMe_3)_4}$ to an average value of 98° in **4**. These findings show that ionic interactions are predominant

---

[*] Dr. C. Krempner, Prof. Dr. M. H. Chisholm, Dr. J. Gallucci
Department of Chemistry
Ohio State University
100 West 18th Avenue, Columbus, Ohio (USA)
Fax: (+49) 381-498-6382
E-mail: clemens.krempner@uni-rostock.de

[**] We gratefully acknowledge the support of our work by the DFG.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

© 2008 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

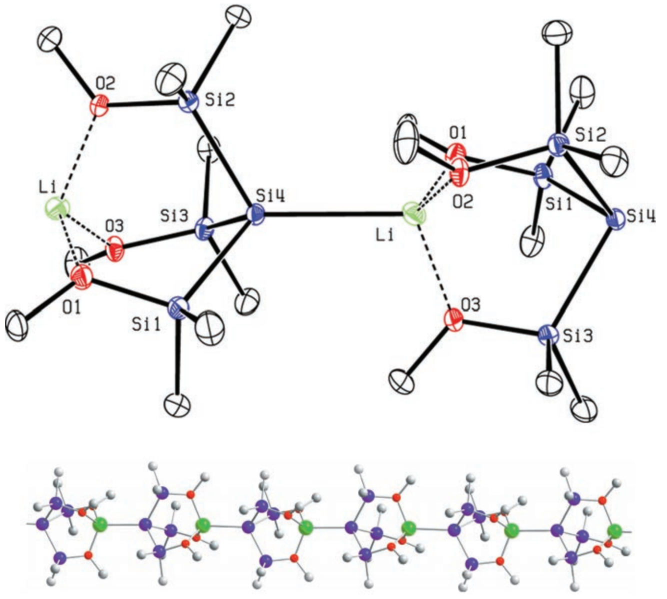


Figure 1. Solid-state structure of **4**. Thermal ellipsoids are set at 30% probability (hydrogen atoms omitted for clarity).

Table 1: Selected average bond lengths [pm] and angles [°] of compounds **4**–**6**.

Comp.	M-O	M-Si	Si-Si	Si-O	O-M-O	Si-Si-O	Si-O-M
4 (M = Li)	197	276	232	170	107	110	116
5 (M = Na)	242	302	232	168	93	113	124
6 (M = K)	272	356	232	169	100	104	117

between lithium and silicon, although significant lithium–oxygen interactions (Li–O average distance 197 pm), may also account for the relatively small Si-Si-Si angles.[14]

Sodium derivative **5** forms an infinite chain with a zigzag conformation (Figure 2). The most striking difference to **4**, however, is the head-to-head orientation of two trimethoxyhypersilanide subunits, so that the Na1 and Na2 ions are each coordinated to six methoxy donors to give spirocyclic bicyclooctane units, $\{Si(SiO)_3Na(OSi)_3Si\}$.[15] These units are bridged by the ion Na3 with an angle Si1-Na3-Si5 of 132.49(7)°. In addition, two disordered THF molecules are weakly bonded to each of the bridging sodium ions.[16] Such a coordination of two dianions to a bridging sodium ion has only been observed in a few diorgano sodium compounds.[17]

In contrast to the aforementioned structures, the potassium silanide **6** features a distorted heterocubane structure, $\{Si_4K_4\}$ (Figure 3). All of the methoxy donors of the four trimethoxyhypersilanide subunits each coordinate to one of three neighboring potassium ions, which stabilizes the cubane structure. The potassium ions have a distorted octahedral coordination environment with relatively short potassium–oxygen bonds (average 272 pm). Consequently, the silicon–potassium bonds (average ca. 356 pm) are significantly longer than in the closely related dimeric and monomeric hypersilanides $[\{(Me_3Si)_3Si(\mu\text{-}K)\}_2]$ (337–342 pm),[12] $[(Me_3Si)_3SiK(C_6H_6)_3]$ (332–335 pm),[12] $[(Me_3Si)_3SiK(tmeda)_2]$ (339 pm),[18] and $[(Me_3Si)_3SiK([18]crown\text{-}6)]$ (345 pm).[19]

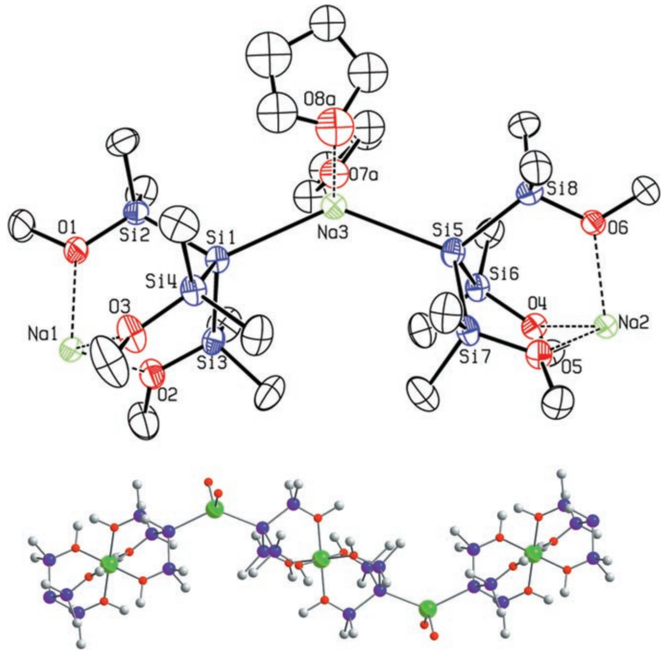


Figure 2. Solid-state structure of **5**. Thermal ellipsoids are set at 30% probability (hydrogen atoms and alternative positions of the two disordered THF molecules are omitted for clarity).

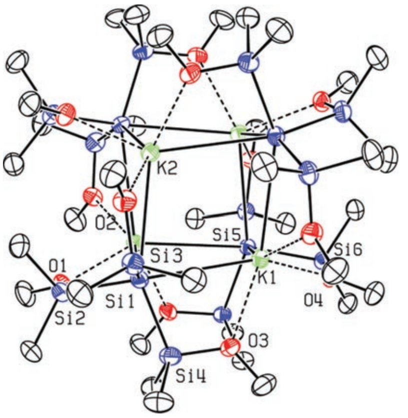


Figure 3. Solid-state structure of **6**. The thermal ellipsoids correspond to 30% probability; hydrogen atoms omitted for clarity).

Similar structural behavior has been observed in the tridentate 3-sila-β-diketiminates, $[Me_3SiSi\{C(R){=}NSiMe_3\}_2M]$, in which the metal ion is coordinated to the internal N-donors to give either monomeric (Li) or dimeric (Na) zwitterionic cyclohexane structures; the latter, has significant intramolecular Si···Na (318 pm) contacts. The potassium derivative forms a dimer consisting of a central $\{Si_2K_2\}$ core.[20]

Surprisingly, the strong donor THF only weakly coordinates to the sodium ion in **5**, and lithium silanide **4** does not contain any THF in the solid state, although single crystals of both compounds were grown from THF. This situation clearly shows the excellent donor properties and the ambivalent nature of the trimethoxyhypersilanide ligand, which is capable of coordinating to the metal in a monodentate fashion by the anionic silicon atom and a tridentate mode by the methoxy groups. To clarify whether these coordination modes also persist in solution, ^{7}Li, ^{23}Na, ^{39}K, and ^{29}Si NMR and ^{7}Li–^{1}H HOESY NMR spectroscopic studies were performed in [D$_8$]THF as solvent.

For the typical donor solvent THF, the formation of solvent-separated ion pairs (SSIPs) is expected to dominate over contact ion pairs (CIPs) in ionic compounds such as metal silanides. Consequently, this would lead to very similar NMR chemical shifts for the metal nuclei irrespective of the substitution pattern of the central silanide moiety, as the chemical environment and consequently the NMR chemical shift of the metal ion is mainly determined by the coordinated THF. However, a comparison of the NMR shifts of **4**–**6** with those of the parent hypersilanides [(Me$_3$Si)$_3$SiM] (M = Li (**8**), Na (**9**), K (**10**)) reveals some remarkable differences (Table 2). In the ^{39}K NMR spectrum of **6**, the potassium signal is shifted significantly upfield ($\Delta\delta = 10.5$ ppm) compared to that of the closely related potassium hypersilanide **10**. Similar upfield shifts are observed for the sodium ($\Delta\delta = 15.4$ ppm) and the lithium ($\Delta\delta = 1$ ppm) silanides. Upon addition of the chelating agent TMEDA to THF solutions of the hypersilanides **8** and **9**, the signals of the lithium and sodium nuclei are shifted markedly downfield, which is consistent with a replacement of THF in the solvation shell of the metal ion by TMEDA. The chemical shift of the corresponding signals of the lithium and sodium derivatives **4** and **5**, however, do not change significantly even in the presence of 20 equivalents of TMEDA (see Supporting Information), suggesting strong binding between metal and ligand.

Table 2: ^{29}Si, ^{7}Li, ^{23}Na, and ^{39}K NMR chemical shifts [ppm] of compounds **3**–**10**.[a]

	δ M	δ ^{29}*Si*	δ ^{29}Si	Si-Si-Si[f]
$(\mathrm{MeOMe_2Si})_4\mathit{Si}$ (**3**)	–	−140.6	23.9	–
$[(\mathrm{MeOMe_2Si})_3\mathit{Si}\mathrm{Li}]$ (**4**)	−0.6[c]	−217.2	44.3	98°
$[(\mathrm{MeOMe_2Si})_3\mathit{Si}\mathrm{Na}]$ (**5**)	−0.9[d]	−199.4[b]	42.9[b]	103°
$[(\mathrm{MeOMe_2Si})_3\mathit{Si}\mathrm{K}]$ (**6**)	4.7[e]	−199.5	37.0	101°
$(\mathrm{Me_3Si})_4\mathit{Si}$ (**7**)	–	−135.5	−9.8	110°[g]
$[(\mathrm{Me_3Si})_3\mathit{Si}\mathrm{Li(thf)_3}]$ (**8**)	0.4[c]	−190.7	−5.1	102°[g]
$[(\mathrm{Me_3Si})_3\mathit{Si}\mathrm{Na(thf)}_n]$ (**9**)	14.5[d]	−187.1	−5.2	103°[h]
$[(\mathrm{Me_3Si})_3\mathit{Si}\mathrm{K(thf)}_n]$ (**10**)	15.2[e]	−194.0	−5.1	102°[h]

[a] Measured in [D$_8$]THF at 300 K unless otherwise stated. [b] Measured at 328 K. [c] ^{7}Li NMR. [d] ^{23}Na NMR. [e] ^{39}K NMR. [f] Average Si-Si-Si angles obtained from the X-ray data, [g] taken from Ref. [11]. [h] The average Si-Si-Si angles of [{(Me$_3$Si)$_3$Si(μ-Na)}$_2$] and [{(Me$_3$Si)$_3$Si(μ-K)}$_2$] were taken from Ref. [12], as no X-ray data are available for the THF adducts **9** and **10**.

In the ^{29}Si NMR spectra, the signals of the central anionic silicon atom of **5**, **6**, **8**, **9**, and **10** are found within a small chemical shift range ($\delta = -187$ to -200 ppm), which reflects the almost identical geometry around the central silicon atom, with only a few degrees of variation found in the average Si-Si-Si angles (101–103°). In lithium trimethoxyhypersilanide **4**, however, this angle is somewhat smaller (98°) and the corresponding ^{29}Si signal at $\delta = -217.2$ ppm is not in the expected range for silicon anions in metal silanides. In addition, the signals of the SiMe$_2$OMe groups of **4**–**6** are shifted significantly downfield relative to the parent (MeOMe$_2$Si)$_4$Si (**3**), which is similar to what was seen in complexation reactions of lithium salts by cyclic siloxanes.[21]

Based on these differences in chemical shifts, it can be assumed that the internal methoxy groups of **4**–**6** also coordinate to the metal ions in solution. Strong coordination is particularly evident for the lithium derivative **4**, as confirmed by ^{7}Li–^{1}H HOESY NMR spectroscopic measurements, which reveal strong interactions between the lithium and the methoxy protons and a very weak correlation with the SiMe$_2$ protons (Figure 4). These correlations are consistent with short lithium–oxygen contacts and indicate a tridentate coordination of the lithium ion by the trimethoxyhypersilanide ligand in solution, which is similar to that found for the solid-state structure of **4**.

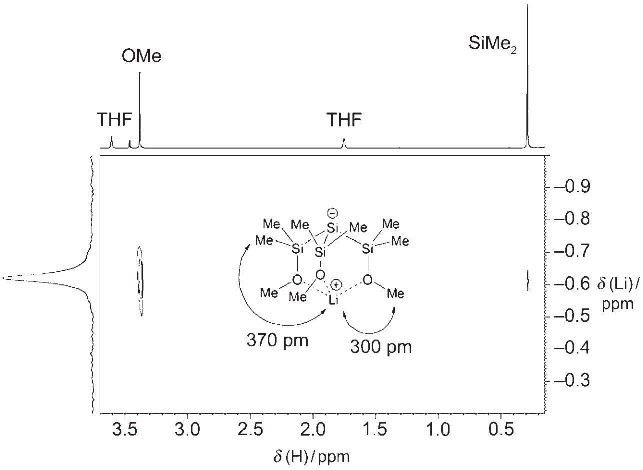


Figure 4. Two-dimensional ^{1}H–^{7}Li HOESY NMR spectrum of **4** acquired in [D$_8$]THF at 300 K.

The sodium silanide **5** has only one signal in the ^{23}Na NMR spectrum instead of two expected from the solid-state structure, which might be an indication of the presence of monomers in solution and only one sodium ion being coordinated. To determine the degree of aggregation of **4**–**6** in solution, we measured their diffusion coefficients by means of ^{1}H-DOSY NMR spectroscopy and using (MeOMe$_2$Si)$_4$Si (**3**) and (Me$_3$Si)$_4$Si (**7**) as reference compounds.[22] From these data (Table 3) we calculated the related hydrodynamic radii by applying a modified Stokes–Einstein equation.[23,24] For comparison, the radii of the monomer subunits, [(MeOMe$_2$Si)$_3$SiM], were estimated from the X-ray data. The hydrodynamic radii of **4**–**6**, in the order $r_h(\mathbf{6}) > r_h(\mathbf{5}) > r_h(\mathbf{4})$, are slightly larger than those derived from the X-ray data of **4**–**6** and of the reference compounds **3** and **7**. This implies that monomers are mainly present in [D$_8$]THF solutions. The observed deviations from the radii of the monomer subunits estimated from the X-ray data of **4**–**6** can be ascribed to coordinative interactions with THF solvent molecules. Assuming a volume of approximately 71 Å^3 for a single coordinated [D$_8$]THF molecule, the data correspond well to compounds having the general formula [(MeO-

Table 3: Diffusion coefficients D [$10^{-10} \times m^2 s^{-1}$][a] and hydrodynamic radii r_h [Å] of compounds **3**–**7**.

	Solvent	T [K]	D [$m^2 s^{-1}$]	r_h	r[b]
$(Me_3Si)_4Si$ (**7**)	[D_8]THF	300	13.0	4.31	4.47
$(MeOMe_2Si)_4Si$ (**3**)	[D_8]THF	300	12.3	4.48	4.65
$[(MeOMe_2Si)_3SiLi]$ (**4**)	[D_8]THF	300	12.1	4.54	4.19
$[(MeOMe_2Si)_3SiNa]$ (**5**)	[D_8]THF	300	11.4	4.74	4.18
$[(MeOMe_2Si)_3SiK]$ (**6**)	[D_8]THF	300	10.9	4.89	4.47
	C_6D_6	302	6.79	5.94	5.64[c]

[a] $c = 10$ mM. [b] The volumes of **7** and of the monomer subunits of **4**–**6**, $\{(MeOMe_2Si)_3SiM\}$, were estimated from their solid-state structures by using the software package Chem3D Ultra. The structure of **3** was optimized using Chem3D Ultra and the volume was calculated. From the obtained volumes the radii were calculated by assuming spherical shapes of the molecules. [c] A dimeric subunit of **6** was used to calculate the volume.

$Me_2Si)_3SiM([D_8]thf)_n]$ with $n = 1$ for Li and $n = 2$ for Na and K. In the nonpolar solvent [D_6]benzene, potassium derivative **6** forms mainly dimers, as evident from the significantly smaller diffusion coefficient.

In summary, it is evident that the metal ions in compounds **4**–**6** are in close proximity to the anionic silanide ligands as a consequence of intramolecular M–O interactions. There is experimental evidence, particularly for the lithium and sodium derivatives **4** and **5**, that the zwitterionic bicyclooctane structure, which was found in the solid state, also persists in solution. Whether or not this structural motif can be proposed for the potassium derivative **6** remains unclear. Owing to the larger radius of the potassium ion, an intramolecular coordination of only one of the methoxy donors is more likely.

Received: August 7, 2007
Published online: November 16, 2007

Keywords: lithium · potassium · silanides · sodium · X-ray crystallography

[1] For reviews see: a) P. D. Lickiss, C. Smith, *Coord. Chem. Rev.* **1995**, *145*, 75; b) K. Tamao, A. Kawachi, *Adv. Organomet. Chem.* **1995**, *38*, 1; c) N. Wiberg, *Coord. Chem. Rev.* **1997**, *163*, 217; d) J. Belzner, U. Dehnert in *The Chemistry of Organic Silicon Compounds*, *Vol. 2* (Eds.: Z. Rappoport, Y. Apeloig), Wiley, Chichester, **1998**, p. 779; e) A. Sekiguchi, V. Y. Lee, M. Nanjo, *Coord. Chem. Rev.* **2000**, *210*, 11; f) H.-W. Lerner, *Coord. Chem. Rev.* **2005**, *249*, 781; g) C. Marschner, *Organometallics* **2006**, *25*, 2110.

[2] a) H. Kobayashi, T. Iwamoto, M. Kira, *J. Am. Chem. Soc.* **2005**, *127*, 15376; b) M. Weidenbruch, S. Wilms, W. Saak, G. Henkel, *Angew. Chem.* **1997**, *109*, 2612; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2503.

[3] a) A. Sekiguchi, R. Kinjo, M. Ichinohe, *Science* **2004**, *305*, 1755; b) N. Wiberg, S. K. Vasisht, G. Fischer, P. Mayer, *Z. Anorg. Allg. Chem.* **2004**, *630*, 1823.

[4] a) N. Wiberg, C. M. M. Finger, K. Polborn, *Angew. Chem.* **1993**, *105*, 1140; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1054; b) J. Fischer, J. Baumgartner, C. Marschner, *Science* **2005**, *310*, 825; c) G. Fischer, V. Huch, P. Mayer, S. K. Vasisht, M. Veith, N. Wiberg, *Angew. Chem.* **2005**, *117*, 8096; *Angew. Chem. Int. Ed.* **2005**, *44*, 7884; d) D. Scheschkewitz, *Angew. Chem.* **2005**, *117*, 3014; *Angew. Chem. Int. Ed.* **2005**, *44*, 2954.

[5] a) J. B. Lambert, J. L. Pflug, C. L. Stern, *Angew. Chem.* **1995**, *107*, 106; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 98; b) A. Sekiguchi, M. Nanjo, C. Kabuto, H. Sakurai, *J. Am. Chem. Soc.* **1995**, *117*, 4195; c) C. Krempner, M. Köckerling, C. Mamat, *Chem. Commun.* **2006**, 720.

[6] The only structurally characterized metal silanides having alkoxy groups attached are $[MeO(Me_3Si)_2Si][K[18]crown\text{-}6]$ and $[\{MeO(Me_3Si)_2Si(Me_3Si)_2SiK\}_2]$: P. R. Likhar, M. Zirngast, J. Baumgartner, C. Marschner, *Chem. Commun.* **2004**, 1764.

[7] U. Herzog, N. Schulze, K. Trommer, G. Roewer, *J. Organomet. Chem.* **1997**, *547*, 133.

[8] For the synthesis of $[(Me_3Si)_3SiK(thf)_3]$ from $(Me_3Si)_4Si$ and KO*t*Bu see: C. Marschner, *Eur. J. Inorg. Chem.* **1998**, 221.

[9] Details regarding the X-ray structure refinement of **4**–**6** are available in the Supporting Information. CCDC-655080 (**4**), CCDC-655081 (**5**), and CCDC-655082 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[10] G. Becker, H.-M. Hartmann, A. Muench, H. Z. Riffel, *Z. Anorg. Allg. Chem.* **1985**, *530*, 29.

[11] A. Heine, R. Herbst-Irmer, G. M. Sheldrick, D. Stalke, *Inorg. Chem.* **1993**, *32*, 2694.

[12] K. Klinkhammer, *Chem. Eur. J.* **1997**, *3*, 1418.

[13] M. Nanjo, E. Nanjo, K. Mochida, *Eur. J. Inorg. Chem.* **2004**, 2961.

[14] The carbon analogue of **4**, $[\{LiC(SiMe_2OMe)_3\}_2]$, forms a cage dimer in which both lithium atoms are also four-coordinate: N. H. Buttrus, C. Eaborn, S. H. Gupta, P. B. Hitchcock, J. D. Smith, A. C. Sullivan, *J. Chem. Soc. Chem. Commun.* **1986**, 1043.

[15] A similar spirocyclic bicyclooctane structure, involving a tin anion and a six-coordinate lithium cation, was found in $[Li(thf)_4][\{(C_4H_3O)_3Sn\}_2Li]$: M. Veith, C. Ruloff, V. Huch, F. Tollner, *Angew. Chem.* **1988**, *100*, 1418; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1381.

[16] Upon drying single crystals of **5** under high vacuum, THF is completely removed, as shown by ^1H NMR spectroscopy.

[17] a) R. E. Dinnebier, S. Neander, U. Behrens, F. Olbrich, *Organometallics* **1999**, *18*, 2915; b) S. S. Al-Juaid, C. Eaborn, P. B. Hitchcock, K. Izod, M. Mallien, J. D. Smith, *Angew. Chem.* **1994**, *106*, 1336; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1268; c) F. Antolini, P. B. Hitchcock, M. F. Lappert, P. Merle, *Chem. Commun.* **2000**, 1301.

[18] W. Teng, K. Ruhland-Senge, *Chem. Eur. J.* **2005**, *11*, 2462.

[19] D. M. Jenkins, W. Teng, U. Englich, D. Stone, K. Ruhland-Senge, *Organometallics* **2001**, *20*, 4600.

[20] a) P. B. Hitchcock, M. F. Lappert, M. Layh, *Chem. Commun.* **1998**, 2179; b) J. D. Farwell, M. A. Fernandes, P. B. Hitchcock, M. F. Lappert, M. Layh, B. Omondi, *Dalton Trans.* **2003**, 1719.

[21] The ^{29}Si NMR signal of $[Li(Me_2SiO)_6][Al\{OC(CF_3)_2Ph\}_4]$ ($\delta = -9.2$ ppm) was shifted significantly downfield towards that found for the neutral compound $(Me_2SiO)_6$ ($\delta = -22.7$ ppm), as a consequence of coordination of the lithium ion: A. Decken, J. Passmore, X. Wang, *Angew. Chem.* **2006**, *118*, 2839; *Angew. Chem. Int. Ed.* **2006**, *45*, 2773.

[22] For recent reviews on NMR diffusion methods see: a) Y. Cohen, L. Avram, L. Frish, *Angew. Chem.* **2005**, *117*, 524; *Angew. Chem. Int. Ed.* **2005**, *44*, 520; b) P. S. Pregosin, *Prog. Nucl. Magn. Reson. Spectrosc.* **2006**, *49*, 261.

[23] A. Gierer, K. Wirtz, *Z. Naturforsch. A* **1953**, *8*, 522.

[24] H.-C. Chen, S.-H. Chen, *J. Phys. Chem.* **1984**, *88*, 5118.

© 2008 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim