

# Heavy Alkali Metal Tris(trimethylsilyl)silanides: A Synthetic and Structural Study

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Treatment of lithium tris(trimethylsilyl)silanide,  $\text{Li}(\text{THF})_3\text{Si}(\text{SiMe}_3)_3$ , with heavier alkali metal *tert*-butoxides yielded the alkali metal silanides  $\text{MSi}(\text{SiMe}_3)_3$  ( $\text{M} = \text{K}, \text{Rb}, \text{or Cs}$ ) in a simple, high-yielding, one-step procedure. Separation of the two solid reaction products was achieved by addition of crown ether, which also determines the formation of contact or separated ion pairs in the solid state. Here we report the synthesis and structural characterization of the contact ion  $\text{K}(18\text{-crown-6})\text{Si}(\text{SiMe}_3)_3$ , **2**, in addition to the separated  $[\text{K}(12\text{-crown-4})_2][\text{Si}(\text{SiMe}_3)_3]$ , **1**,  $[\text{Rb}(15\text{-crown-5})_2][\text{Si}(\text{SiMe}_3)_3]$ , **3**, and  $[\text{Cs}(18\text{-crown-6})_2][\text{Si}(\text{SiMe}_3)_3]$ , **5**.  $[\text{Rb}(18\text{-crown-6})_2][\text{Si}(\text{SiMe}_3)_3][\text{Rb}(18\text{-crown-6})\text{Si}(\text{SiMe}_3)_3]_2$ , **4**, is a rare example where both contact and separated ions are observed in the solid state. The investigation of synthetic routes toward the target compounds also examined the previously published metalation of  $\text{Si}(\text{SiMe}_3)_4$  with potassium *tert*-butoxide. This route proved to be temperamental: depending on reaction conditions and solvent systems, either adducts between product and unreacted starting material, namely,  $[\{\text{K}(\text{THF})\text{Si}(\text{SiMe}_3)_3\}\{\text{KO}^t\text{Bu}\}_3]$ , **6**, or the target compound  $\text{KSi}(\text{SiMe}_3)_3$  was isolated. All compounds were characterized by X-ray crystallography and NMR spectroscopy.

## Introduction

$\text{Li}(\text{THF})_3\text{Si}(\text{SiMe}_3)_3$  ( $\text{Si}(\text{SiMe}_3)_3^- =$  hypersilanide), initially reported by Gilman and Smith,<sup>1</sup> has been recognized as a reagent for the preparation of numerous transition and main group silanides.<sup>2</sup> The role of  $\text{Si}(\text{SiMe}_3)_3^-$  as a versatile ligand is based on the ease of preparation, the high solubility of products even in hydrocarbon solvents, and large steric demand, providing critical kinetic stabilization of the resulting metal complexes.

Well-characterized examples of heavier alkali metal hypersilanides are limited to a series of  $[\text{MSi}(\text{SiMe}_3)_3]_2$  derivatives ( $\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$ ), obtained by treatment of zinc, cadmium, or mercury silanides with the corresponding alkali metals.<sup>3</sup> Among those, the heavy, more reactive metals, specifically in combination with the heaviest group 12 element, mercury, provide the best synthetic results. Crystallization of the alkali

metal silanides from aromatic solvents provided a series of dimeric derivatives,  $[\text{MSi}(\text{SiMe}_3)_3]_2$  ( $\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$ ). A rare example of an ether-solvated product is  $[\text{CsSi}(\text{SiMe}_3)_3]_2\text{THF}$ , with the ether bridging the two cesium centers. All compounds in this series display cation–anion contacts.<sup>3</sup>

An alternative entry into heavy alkali metal silanide chemistry was reported with a series of  $\text{MSi}(\text{Bu})_3$  derivatives ( $\text{M} = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$ ;  $\text{Si}(\text{Bu})_3^- =$  supersilanide), involving treatment of silylhalides with the appropriate alkali metals.<sup>4</sup> This sequence is not without problems, since the formation of side products including  $(\text{Bu})_3\text{SiH}$  and  $(\text{Bu})_3\text{SiSi}(\text{Bu})_3$  is frequently observed. Moreover, the heavier alkali metal derivatives are strong bases capable of deprotonating compounds such as tetrahydrofuran or benzene under formation of  $\text{Si}(\text{Bu})_3\text{H}$ .

A recent report by Marschner outlines the treatment of  $\text{Si}(\text{SiMe}_3)_4$  with  $\text{KO}^t\text{Bu}$  in THF or DME (dimethoxyethane) to obtain  $\text{KSi}(\text{SiMe}_3)_3$  under subsequent formation of trimethylsilyl *tert*-butyl ether.<sup>5</sup> Work performed in our laboratory and reported here indicates limitations associated with this approach. In addition to undesired redox chemistry, adducts of unreacted starting material and product are identified.

Since we were interested in utilizing heavy alkali metal silanides in synthetic applications, a system with

(1) (a) Gilman, H.; Smith, C. L. *J. Organomet. Chem.* **1968**, *14*, 91. (b) Gutekunst, G.; Brook, A. G. *J. Organomet. Chem.* **1982**, *225*, 1.

(2) See for example: (a) Henkel, S.; Klinkhammer, K. W.; Schwarz, W. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 681. (b) Heine, A.; Stalke, D. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 121. (c) Arnold, J.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *Inorg. Chem.* **1987**, *26*, 2106. (d) Meyer, J.; Willnecker, J.; Schubert, U. *Chem. Ber.* **1989**, *122*, 223. (e) Piana, H.; Wagner, H.; Schubert, U. *Chem. Ber.* **1991**, *124*, 63. (f) Arif, A. M.; Cowley, A. H.; Elkins, T. M. *J. Organomet. Chem.* **1987**, *325*, C11. (g) Arif, A. M.; Cowley, A. H.; Elkins, T. M.; Jones, R. A. *J. Chem. Soc., Chem. Commun.* **1986**, 1776. (h) Freeman, W. P.; Tilley, D. T.; Arnold, F. P.; Rheingold, A. L.; Gantzel, P. K. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1887. (i) Farwell, J. D.; Lappert, M. F.; Marschner, C.; Strissel, C.; Tilley, D. T. *J. Organomet. Chem.* **2000**, *603*, 185.

(3) Klinkhammer, K. W. *Chem. Eur. J.* **1997**, *3*, 1418.

(4) Wiberg, N.; Amelunxen, K.; Lerner, H.-W.; Schuster, H.; Nöth, H.; Krossing, I.; Schmidt-Amelunxen, M.; Seifert, T. *J. Organomet. Chem.* **1997**, *542*, 1.

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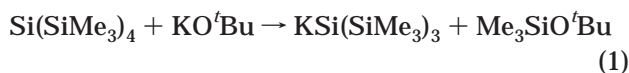
good solubility properties and steric demand providing significant kinetic stabilization was needed. Additional requirements included the ready availability of the ligands without contact to toxic reagents and products (e.g., mercury and its compounds). However, the most extensively documented synthetic access toward the alkali metal hypersilanides requires the use of mercury silanides and subsequent formation of elemental mercury. An alternative route to potassium hypersilanides focusing on the previously published metalation of Si(SiMe<sub>3</sub>)<sub>4</sub> with KO<sup>t</sup>Bu proved to be temperamental. Consequently, we decided to examine an alternative synthetic strategy toward potassium, rubidium, and cesium hypersilanides.

We here report a facile, one-pot approach to heavy alkali hypersilanides involving the reaction of lithium tris(trimethylsilyl)silanide with alkali metal *tert*-butoxide. Crown ether coordination of the alkali metal target molecules affords a series of compounds in which the type of crown ether induces the formation of either contact or separated ion pairs in the solid state. Crystallographic studies identified the contact pair K(18-crown-6)Si(SiMe<sub>3</sub>)<sub>3</sub>, **2**, and the donor separated ions [K(12-crown-4)<sub>2</sub>][Si(SiMe<sub>3</sub>)<sub>3</sub>], **1**, [Rb(15-crown-5)<sub>2</sub>][Si(SiMe<sub>3</sub>)<sub>3</sub>], **3**, and [Cs(18-crown-6)<sub>2</sub>][Si(SiMe<sub>3</sub>)<sub>3</sub>], **5**. Compound **4**, [Rb(18-crown-6)<sub>2</sub>][Si(SiMe<sub>3</sub>)<sub>3</sub>][Rb(18-crown-6)-Si(SiMe<sub>3</sub>)<sub>3</sub>]<sub>2</sub>, is an unusual example displaying both separated and contact ions in the solid state. Importantly, compounds **1**, **3**, **4**, and **5** provide the first structural proof for isolated silanide anions. <sup>29</sup>Si NMR studies indicate that solvation and consequent formation of separated silanide anions is prevalent.

The exploration of an alternative entry into alkali metal silanides focused on the treatment of Si(SiMe<sub>3</sub>)<sub>4</sub> with potassium *tert*-butoxide. This chemistry reproducibly afforded the cluster species [{K(THF)Si(SiMe<sub>3</sub>)<sub>3</sub>}-{KO<sup>t</sup>Bu}<sub>3</sub>], **6**, an adduct between the target compound and unreacted starting material, if the reaction was conducted in THF.

## Results and Discussion

**Synthetic Chemistry.** Marschner reports the formation of KSi(SiMe<sub>3</sub>)<sub>3</sub> by treatment of Si(SiMe<sub>3</sub>)<sub>4</sub> with KO<sup>t</sup>Bu under formation of silyl ether (eq 1).<sup>5</sup>

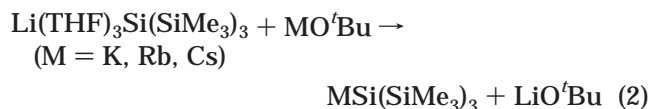


The easy availability of starting materials indicates this route to be ideal for the preparation of potassium silanides.<sup>5</sup> Marschner discusses two possible solvent choices, THF and DME, outlining that both afford clean reaction products, but THF requires longer reaction times. Utilizing this scheme to prepare potassium tris(trimethylsilyl)silanide, and opting to use THF, the reproducible formation of a black powder, typically after 1–2 h of reaction time, was observed. After removal of this precipitate by filtration, a clear, orange-colored solution was obtained. NMR analysis of the solid product from the supernatant indicates mixtures containing KSi(SiMe<sub>3</sub>)<sub>3</sub>, KO<sup>t</sup>Bu, and a small amount of Si(SiMe<sub>3</sub>)<sub>4</sub>.

The adjustment of reaction conditions, including lower temperature, shorter reaction time, and slightly altered stoichiometric ratios, did not prevent the formation of the black powder, and the product mixture mentioned above was obtained. The formation of the Si(SiMe<sub>3</sub>)<sub>4</sub> may be interpreted twofold: (1) as unreacted starting material or (2) the product of SiMe<sub>3</sub> migration, indicating redox chemistry under formation of elemental silicon, presumably the black powder. In addition to Si(SiMe<sub>3</sub>)<sub>4</sub>, NMR analysis indicates the presence of KSi(SiMe<sub>3</sub>)<sub>3</sub> and KO<sup>t</sup>Bu varying between the ratios 1:3 and 1:1, depending on reaction times. Specifically, a cluster species involving one K(THF)Si(SiMe<sub>3</sub>)<sub>3</sub> unit and three KO<sup>t</sup>Bu molecules, [{K(THF)Si(SiMe<sub>3</sub>)<sub>3</sub>}{KO<sup>t</sup>Bu}<sub>3</sub>], **6**, was identified by NMR spectroscopic and crystallographic analysis. The formation of this mixture is not observed if the reaction is conducted in DME; however, the formation of the black powder under subsequent formation of Si(SiMe<sub>3</sub>)<sub>4</sub> persists. Compound **6** as an adduct between a potassium silanide and potassium *tert*-butoxides is the first example of a mixed cluster of this type. However, alkoxide-alkyl clusters have been isolated and structurally characterized.<sup>6</sup>

Reduction or decomposition of alkali or alkaline earth metal group 14 derivatives has been observed previously, but more prominently for the heavier group 14 analogues. Often, reduction coincides with migration, as observed for the decomposition of M(SnPh<sub>3</sub>)<sub>2</sub> (M = Ca, Sr), resulting in M(Sn(SnPh<sub>3</sub>)<sub>3</sub>)<sub>2</sub>, Sn(SnPh<sub>3</sub>)<sub>4</sub>, SnPh<sub>4</sub>, and elemental Sn.<sup>7</sup> Other examples include the decomposition of Li(PMDTA)PbPh<sub>3</sub> (PMDTA = *N,N,N',N',N'*-pentamethyldiethylenetriamine), where the formation of a black powder, presumably elemental Pb, was observed.<sup>8</sup> However, no further details are given about other products formed in this process.

The temperamental nature of the metalation reaction prompted the investigation of metal exchange reactions as possible entry into heavy alkali metal hypersilanides. The reaction focused on the treatment of lithium silanides with alkali metal *tert*-butoxides (eq 2) due to the easy availability of the starting materials.



This sequence proceeds smoothly, as indicated by NMR spectroscopic studies, but the separation of the two solid reaction products by common methods (crystallization, sublimation, extraction) does not allow the facile isolation of pure silanides. To achieve separation, various crown ethers were added to the respective reaction mixtures, allowing for effective separation in a single, simple extraction step. Remarkably, any sized crown ether may be added to achieve separation, since the crown sequesters only the alkali metals in the silanides, while the alkoxides remain donor-free (NMR spectral evidence).

(6) See for example: (a) Thomas, R.; Huang, H. *J. Am. Chem. Soc.* **1999**, *121*, 11239. (b) DeLong, G. T.; Hoffmann, D.; Nguyen, H. D.; Thomas, R. D. *J. Am. Chem. Soc.* **1997**, *119*, 11998. (c) Harder, S.; Streitwieser, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1066.

(7) English, U.; Ruhlandt-Senge, K.; Uhlig, F. *J. Organomet. Chem.* **2000**, *613*, 139.

(8) Armstrong, D. R.; Davidson, M. G.; Moncrieff, D.; Stalke, D.; Wright, D. S. *J. Chem. Soc., Chem. Commun.* **1992**, 1413

**Table 1. Correlation of  $^{29}\text{Si}$  NMR Shifts and Geometry at the Central Silicon Atoms for Selected Alkali Metal Hypersilanides**

| compound   | $\delta$ ( $^{29}\text{Si}$ ) Si( <i>S</i> Me <sub>3</sub> ) <sub>3</sub> | $\delta$ ( $^{29}\text{Si}$ ) <i>S</i> (SiMe <sub>3</sub> ) <sub>3</sub> | angle sum at <i>S</i> (SiMe <sub>3</sub> ) <sub>3</sub> | ref      |
|--|---|--|---|----------|
| [NaSi(SiMe <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub> <sup>*</sup>   | -6.0  | -179.8   | 307.5<br>309.9  | 3        |
| [KSi(SiMe <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub>   | -5.8  | -185.7   | 306.9   | 3        |
| [K(12-crown-4) <sub>2</sub> ][Si(SiMe <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub>   | -4.2  | -196.0   | 308.1   | <i>a</i> |
| K(18-crown-6)Si(SiMe <sub>3</sub> ) <sub>3</sub>   | -4.0  | -191.1   | 305.9   | <i>a</i> |
| [K(THF)Si(SiMe <sub>3</sub> ) <sub>3</sub> ][KO <sup>t</sup> Bu] <sub>3</sub>  | -4.9  | -194.5   | 307.3, 308.0  | <i>a</i> |
| [RbSi(SiMe <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub>  | -5.6  | -184.4   | 307.2   | 3        |
| [Rb(15-crown-5) <sub>2</sub> ][Si(SiMe <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub>  | -4.0  | NA <sup>b</sup>  | 301.2   | <i>a</i> |
| [Rb(18-crown-6)Si(SiMe <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub> ·[Rb(18-crown-6) <sub>2</sub> ][Si(SiMe <sub>3</sub> ) <sub>3</sub> ] <sup>b</sup> | -4.1  | -188.9   | 307.4, 309.6 <sup>c</sup><br>298.1 <sup>d</sup>         | <i>a</i> |
| [Cs(18-crown-6) <sub>2</sub> ][Si(SiMe <sub>3</sub> ) <sub>3</sub> ]   | -3.8  | -187.8   | 300.2, 296.9  | <i>a</i> |
| [CsSi(SiMe <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub> <sup>**</sup>  | -5.3  | -179.4   | 306.9, 303.6, 302.7                                     | 3        |

<sup>a</sup>This work. <sup>b</sup>Not available due to solubility problems. <sup>c</sup>Contact and separated ion in one crystal. <sup>d</sup>Separated ion. <sup>e</sup>Contact pair. <sup>\*</sup>Representing two different solvates. <sup>\*\*</sup>Representing three different solvates.

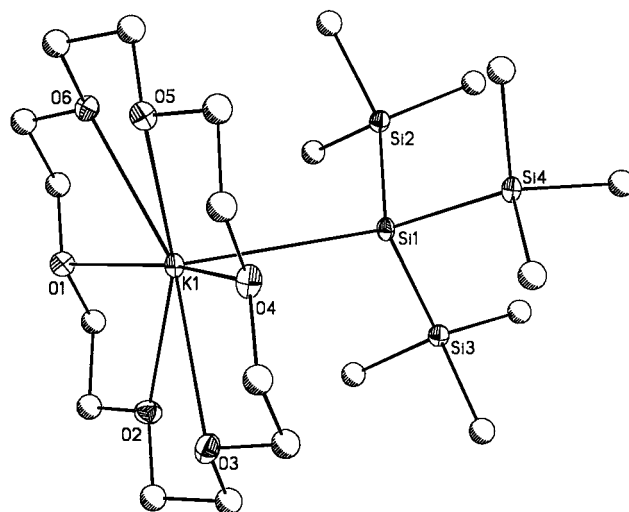
Metal exchange chemistry has been used previously for the preparation of organoalkali metal derivatives, as indicated in eq 3.<sup>9</sup>



Difficulties typically encountered in this chemistry focus on the separation of the two solid reaction products. In some instances, alkali metal sources other than the *tert*-butoxides were required to affect sufficiently different solubility enabling effective separation.<sup>9</sup>

The target compounds are highly sensitive to oxygen and moisture, but can be kept under strict inert gas conditions and exclusion of light without decomposition. Significantly, the contact species **2** displays lower sensitivity toward oxygen and moisture, as opposed to the donor-separated species. A significant increase in reactivity is observed upon descending the group of alkali metals, making the separated cesium species **5** extremely reactive. Consequently, very careful handling techniques were required for synthesis and characterization.

**Spectroscopic Studies.** All compounds were analyzed using <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectroscopy. <sup>29</sup>Si NMR spectroscopic values for compounds **1–6** and closely related alkali metal hypersilanides are provided in Table 1. A comparison of chemical shifts indicates that the clear distinction between contact and separated ions observed in the solid state does not persist in solution. This trend is effectively demonstrated by <sup>29</sup>Si NMR data for **4**, where solid state data indicate both separated and contact pairs. In solution, only one set of signals is observed, indicating that only the separated species prevail in the aromatic solvents used in the NMR experiments. Arene-based solvents coordinate effectively to the alkali metal center,<sup>10</sup> thus facilitating the formation of separated ions in solution. Arene coordination in alkali metal silanides has also been documented with the crystallographically characterized K(C<sub>6</sub>D<sub>6</sub>)<sub>3</sub>Si(SiMe<sub>3</sub>)<sub>3</sub>.<sup>3</sup> The small range of <sup>29</sup>Si NMR shifts



**Figure 1.** Molecular structure of **2**. Non-carbon atoms are depicted with 30% occupancy; hydrogen atoms have been omitted for clarity.

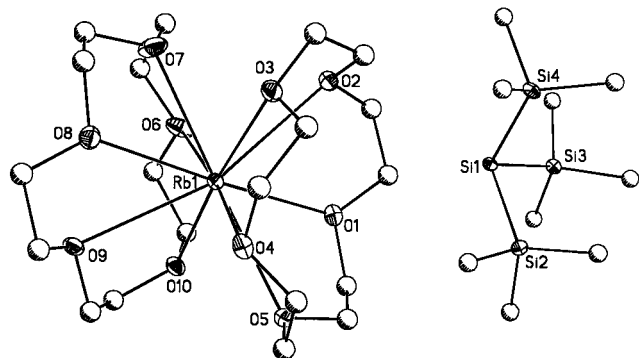
also reflects the essentially identical geometry of the silanides (see Table 1) with only a few degrees of variation in the Si–Si–Si angles and no discernible trend, indicating a closely related metal–ligand charge distribution in the contact or charge-separated species. The weak metal–silicon bonds in the contact pairs can be easily broken in favor of solvation.

**Structural Chemistry. Structure Descriptions.** **[K(12-crown-4)<sub>2</sub>][Si(SiMe<sub>3</sub>)<sub>3</sub>], 1.** Compound **1** displays separated cations and anions, more than 5 Å apart from each other. The potassium cation is surrounded by two 12-crown-4 macrocycles, resulting in a coordination number of eight, with K–O bond lengths ranging from 2.713(6) to 2.794(5) Å. The silanide anion displays a central silicon atom connected to three SiMe<sub>3</sub> groups with Si–Si bond lengths between 2.329(10) and 2.332(10) Å. The angle sum at the central silicon atom is 308.1°.

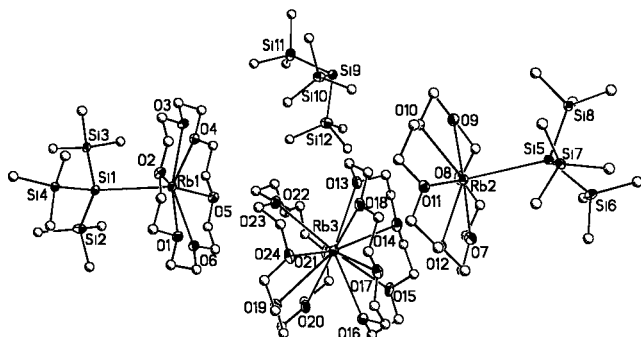
**K(18-crown-6)Si(SiMe<sub>3</sub>)<sub>3</sub>, 2.** Compound **2**, depicted in Figure 1, displays a central potassium atom connected to one silanide anion, and one 18-crown-6 donor, resulting in a coordination number of seven at potassium. Potassium–oxygen distances are observed between 2.787(2) and 2.926(2) Å. The potassium–silicon distance is 3.447(8) Å. The Si–Si distances in the Si(SiMe<sub>3</sub>)<sub>3</sub> anion range from 2.346(9) to 2.350(9) Å. The angle sum at the central silicon atom is 305.9°.

(9) (a) Boesveld, W. M.; Hitchcock, P. B.; Lappert, M. F.; Liu, D.-S.; Tian, S. *Organometallics* **2000**, *19*, 4030. (b) A recent review article describes this method as the most widely used for the preparation of organometallic compounds of the heavier alkali metals: Smith, D. J. *Adv. Organomet. Chem.* **1999**, *43*, 267.

(10) (a) Lehn, J.-M. *Angew. Chem.* **1988**, *100*, 91. (b) Cram, D. J. *Angew. Chem.* **1988**, *100*, 1041. (c) Pederson, C. J. *Angew. Chem.* **1988**, *100*, 1053.



**Figure 2.** Molecular structure of **3**. Non-carbon atoms are depicted with 30% occupancy; hydrogen atoms have been omitted for clarity.

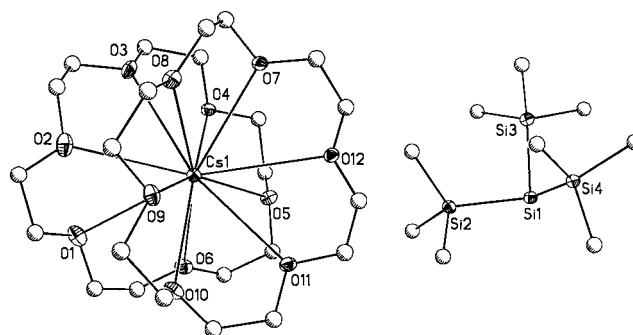


**Figure 3.** Molecular structure of **4**. Non-carbon atoms are depicted with 30% occupancy; hydrogen atoms have been omitted for clarity.

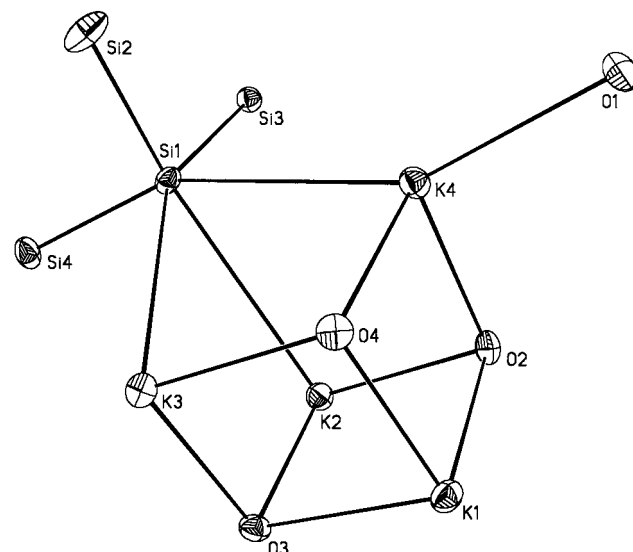
**[Rb(15-crown-5)<sub>2</sub>][Si(SiMe<sub>3</sub>)<sub>3</sub>], 3.** Compound **3**, shown in Figure 2, displays separated cations and anions (>5 Å). The rubidium cation is surrounded by two 15-crown-5 macrocycles, resulting in a coordination number of 10. The rubidium–oxygen distances range from 2.905(4) to 3.014(4) Å. Si–Si distances in the silanide anion are on average 2.34 Å, and the angle sum at the central silicon is 301.2°.

**[Rb(18-crown-6)<sub>2</sub>][Si(SiMe<sub>3</sub>)<sub>3</sub>][Rb(18-crown-6)Si(SiMe<sub>3</sub>)<sub>3</sub>]<sub>2</sub>, 4.** Compound **4**, shown in Figure 3, displays two different ion association modes in one crystal: separated species, where the rubidium is saturated by two 18-crown-6 ligands, and no cation–anion interactions are apparent; and contact ions, with rubidium–silicon interactions. The separated species display rubidium cations surrounded by two 18-crown-6 molecules, resulting in a coordination number of 12 and rubidium–oxygen distances between 3.119(2) and 3.431(2) Å. The silanide anion, more than 5 Å away from the cation, displays a central silicon atom connected to three SiMe<sub>3</sub> groups with Si–Si distances of 2.315(1), 2.328(1), and 2.338(1) Å, and an angle sum of 298.1°. Two contact ions are contained in the asymmetric unit. Their rubidium centers are connected to one 18-crown-6 macrocycle and one Si(SiMe<sub>3</sub>)<sub>3</sub> anion, resulting in a coordination number of 7, and Rb–O distances between 2.826(2) and 2.984(2) Å. The rubidium–silicon distances are 3.436(8) and 3.452(7) Å. Si–Si distances in the silanide anions are observed between 2.317(1) and 2.336(1) Å. The angle sums at the central silicon atoms are observed at 307.4° and 309.6°.

**[Cs(18-crown-6)<sub>2</sub>][Si(SiMe<sub>3</sub>)<sub>3</sub>], 5.** Compound **5**, shown in Figure 4, contains two independent molecules



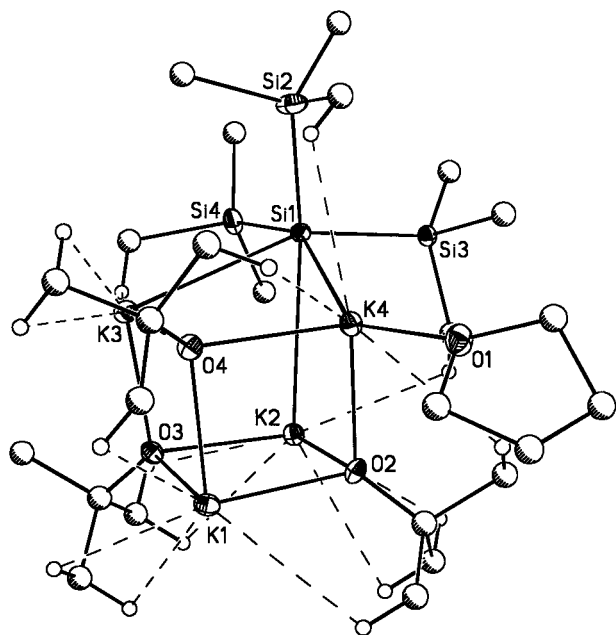
**Figure 4.** Molecular structure of **5**. Non-carbon atoms are depicted with 30% occupancy; hydrogen atoms have been omitted for clarity. Only one of two independent molecules is shown.



**Figure 5.** Framework structure of **6**. All atoms are shown with 30% occupancy. Only one of the two independent molecules is shown.

in each asymmetric unit, of which only one is pictured. The compound consists of separated cations and anions. The cation is surrounded by two 18-crown-6 macrocycles, resulting in a coordination number of 12, and cesium–oxygen distances between 3.141(2) and 3.560(2) Å. The silanide anions, formally separated from the cation by more than 5 Å, display Si–Si distances in the range 2.333(9)–2.340(9) Å. The angle sums at the central silicon atoms are observed at 296.9° and 300.2°.

**[[K(THF)Si(SiMe<sub>3</sub>)<sub>3</sub>]{KO<sup>t</sup>Bu}<sub>3</sub>]<sub>3</sub>, 6.** Compound **6** crystallizes with two independent molecules in each asymmetric unit. The compound represents a cluster, with four potassium centers occupying four diagonally located centers of a cube and three oxygen and one silicon center located on the remaining four corners. The cluster may formally be described as an aggregate between the THF-solvated target molecule K(THF)Si(SiMe<sub>3</sub>)<sub>3</sub> and three unsolvated KO<sup>t</sup>Bu groups. Figure 5 shows the skeleton structure of the cluster (only one of the two independent molecules is shown). It can be clearly seen that the cube is asymmetric, with significantly longer K–Si (between 3.487(10) and 3.571(10) Å) than K–O (*tert*-Bu) bond lengths (2.593 Å av). The distortion in the cluster also becomes apparent by considering the angles of the corner atoms. The O–K–O



**Figure 6.** Molecular structure of **6**. Non-carbon atoms (except hydrogen) are depicted with 30% occupancy; hydrogen atoms, except those displaying metal–hydrogen contacts, have been omitted for clarity. Only one of the two independent molecules is shown.

(*tert*-Bu) angles are close to 90°, whereas the O–K–Si angles are close to 95°. One of the potassium centers bears a THF donor with K–O (THF) interactions of 2.715 Å av. The potassium centers also display weak interaction with hydrogen atoms off the *tert*-butoxide and SiMe<sub>3</sub> groups (>2.88 Å). Figure 6 presents one of the two independent molecules showing secondary interactions. The silanide anion displays Si–Si distances of 2.338 Å (av) and an angle sum at Si of 307.3° and 308.0°.

**Structural Aspects.** The coordination of crown ethers to alkali metals as a structure-determining factor has been well documented.<sup>11</sup> In the solid state, the crown ether coordination in compounds **1**–**5** results in the formation of either contact or separated ion pairs. The potassium cation with the size matching 18-crown-6 affords a contact pair, K(18-crown-6)Si(SiMe<sub>3</sub>)<sub>3</sub>, **2**, while 2 equiv of 12-crown-4 induces the formation of the separated sandwich complex [K(12-crown-4)<sub>2</sub>][Si(SiMe<sub>3</sub>)<sub>3</sub>], **1**. Complexation by crown ethers that are too small for the heavier alkali metals gives rise to separated species, as also observed in [Rb(15-crown-5)<sub>2</sub>][Si(SiMe<sub>3</sub>)<sub>3</sub>], **3**, and [Cs(18-crown-6)<sub>2</sub>][Si(SiMe<sub>3</sub>)<sub>3</sub>], **5**. The combination of rubidium and 18-crown-6 results in the formation of compound **4**, displaying two contact pairs, Rb(18-crown-6)Si(SiMe<sub>3</sub>)<sub>3</sub>, and the separated [Rb(18-crown-6)<sub>2</sub>][Si(SiMe<sub>3</sub>)<sub>3</sub>]. The reaction yielding compound **4** was initially performed by adding only 1 equiv of crown ether per metal center. Remarkably, compound **4** was isolated as the sole product in high purity, but reduced yield. After identifying **4**, the synthesis was repeated with the correct crown:ligand stoichiometry, resulting in almost quantitative formation of **4**. The existence of both contact and separated species in one crystal, even with

improper reagent stoichiometry, supports the argument that both species must be energetically similar. Only few compounds displaying simultaneously contact and separated ions in the solid state have been reported. An example includes a tetraphenylbutadiene disodium derivative published by Bock et al.<sup>12</sup>

No discernible trend with regards to the geometry of the silanides can be deduced from structural data (Table 1). Klinkhammer discusses a slight angle compression in the dimeric [MSi(SiMe<sub>3</sub>)<sub>3</sub>]<sub>2</sub> derivatives upon descending the alkali metal group.<sup>3</sup> He interprets this trend with increased metal–ligand charge transfer in the heavier alkali metal derivatives, coinciding with a weakened metal–ligand bond. The extreme case of this trend, the separation of cation and anion, should result in the largest degree of angle compression. Indeed, angle sums for the separated species are observed at 301.2° for **3**, 298.1° for the separated anion in **4**, and 300.2° and 296.9° for **5**, consistent with complete transfer of electron density from the metal to the ligand. While this trend seems to affect most separated species, not all compounds show this trend: the separated **1** exhibits an angle sum at the central Si of 308.1°, a value higher than for some contact pairs (Si–Si–Si for **2** is 305.9°). Considering the small range of Si–Si–Si angles, the geometry at the central silicon atom seems to be largely independent of ion association, indicating a significant charge transfer, which then is responsible for the easy formation of separated silanide anions in solution. This interpretation is also consistent with <sup>29</sup>Si NMR data.

A significant or complete charge transfer from metal to ligand in either the contact or the separated species results in increased *s*-character at the lone pair at silicon and consequently higher *p*-character in the Si–Si bond within the ligand, coinciding with a compressed geometry at the central silicon. Narrow ligand angles have also been observed in a series of alkali metal derivatives linked to heavy group 14 ligands. Increasing pyramidity of the group 14 ligand atom on descending the group is demonstrated by Li(THF)<sub>3</sub>SiPh<sub>3</sub> (C–Si–C 101.3° (av)),<sup>13</sup> Li(PMDTA)SnPh<sub>3</sub> (C–Sn–C 96.1° (av)),<sup>14</sup> and a C–Pb–C angle of 94.3° (av) in Li(PMDTA)PbPh<sub>3</sub>.<sup>7</sup> The values presented in this paper are in good agreement with previously published silanides.

It is instructive to compare the metal–ligand bond lengths in **2** and **4**. The potassium–silicon distance in the seven-coordinate **2** is 3.447(8) Å, whereas the two contact pairs in **4** display metal–ligand bond lengths of 3.436(8) and 3.452(7) Å. It is an initially puzzling result that the larger rubidium cation exhibits metal–ligand bond lengths almost analogous with the smaller potassium ion, indicating that arguments on the basis of ionic radius cannot be employed. The comparison of **2** and **4** with related compounds indicates that the K–Si bond length in **2** is slightly longer than in related species (see Table 2), whereas the metal–silicon distance in the contact pairs of **4** is shorter than that of other hyper-silanides. On the basis of these data, it seems plausible that the lengthening of the potassium–silicon distance

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**Table 2. Selected Bond Distances (Å) and Angles (deg) for Heavy Alkali Metal Silanides**

| compound  | M–Si (Å)                        | M–donor (Å)              | Si–Si–Si/C–Si–C (deg) | Si–Si/Si–C (Å)       | ref |
|---|---------------------------------|--------------------------|-----------------------|----------------------|-----|
| [Na(THF) <sub>2</sub> Si( <sup>t</sup> Bu) <sub>3</sub> ] <sub>2</sub>                                | 2.919(1)                        | 2.32 <sup>a</sup>        | 106.9 <sup>a</sup>    | 1.994 <sup>a</sup>   | 4   |
| Na(PMDTA)Si( <sup>t</sup> Bu) <sub>3</sub>  | 2.967(2)                        | 2.51 <sup>a</sup>        | 106.6 <sup>a</sup>    | 1.993 <sup>a</sup>   | 4   |
| [NaSi(SiMe <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub>   | 2.94–3.03 <sup>a</sup>          | N/A                      | 103.3 <sup>a</sup>    | 2.340 <sup>a</sup>   | 3   |
| [NaSi(SiMe <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub> ·C <sub>6</sub> H <sub>6</sub>                  | 3.00–3.05                       | N/A                      | 102.5 <sup>a</sup>    | 2.344 <sup>a</sup>   | 3   |
| [NaSi( <sup>t</sup> Bu) <sub>3</sub> ] <sub>2</sub>   | 3.073(4)                        | N/A                      | 107.3 <sup>a</sup>    | 1.978 <sup>a</sup>   | 4   |
|   | 3.060(4)                        |                          |                       |                      |     |
| [KSi(SiMe <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub>  | 3.37–3.42 <sup>a</sup>          | N/A                      | 102.3 <sup>a</sup>    | 2.338 <sup>a</sup>   | 3   |
| K(C <sub>6</sub> H <sub>6</sub> ) <sub>3</sub> Si(SiMe <sub>3</sub> ) <sub>3</sub>                    | 3.32–3.35(4)                    | 3.37 <sup>a</sup>        | 101.5 <sup>a</sup>    | 2.336 <sup>a</sup>   | 3   |
| K(C <sub>6</sub> D <sub>6</sub> ) <sub>3</sub> Si( <sup>t</sup> Bu) <sub>3</sub>                      | 3.378(1)                        | 3.48–3.52                | 106.0 <sup>a</sup>    | 1.995 <sup>a</sup>   | 4   |
| K(18C6)Si(SiMe <sub>3</sub> ) <sub>3</sub>  | 3.447(8)                        | 2.787–2.926              | 102.0 <sup>a</sup>    | 2.348 <sup>a</sup>   | *   |
| [K(12C4) <sub>2</sub> ][Si(SiMe <sub>3</sub> ) <sub>3</sub> ]   | N/A                             | 2.713–2.794              | 102.7 <sup>a</sup>    | 2.330 <sup>a</sup>   | *   |
| [Rb(18C6)Si(SiMe <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub> <sup>c</sup>                              | 3.436(8), 3.452(7) <sup>c</sup> | 2.826–2.984 <sup>c</sup> | 102.8 <sup>a,c</sup>  | 2.326 <sup>a,c</sup> | *   |
| [Rb(18C6) <sub>2</sub> ][Si(SiMe <sub>3</sub> ) <sub>3</sub> ] <sup>b</sup>                           | N/A <sup>d</sup>                | 3.119–3.431 <sup>d</sup> | 99.4 <sup>a,d</sup>   | 2.327 <sup>a,d</sup> |     |
| [RbSi(SiMe <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub> [C <sub>6</sub> H <sub>5</sub> Me]              | 3.52–3.62                       | 3.42–3.91                | 102.4 <sup>a</sup>    | 2.335 <sup>a</sup>   | 3   |
| [Rb(15C5) <sub>2</sub> ][Si(SiMe <sub>3</sub> ) <sub>3</sub> ]  | N/A                             | 2.905–3.014              | 100.4 <sup>a</sup>    | 2.337 <sup>a</sup>   | *   |
| [CsSi(SiMe <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub> [THF]   | 3.67–3.73                       | 3.097–3.281              | 102.3 <sup>a</sup>    | 2.332 <sup>a</sup>   | 3   |
| [CsSi(SiMe <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub> [biphen]·C <sub>5</sub> H <sub>12</sub>         | 3.68–3.81                       | 3.683–3.866 <sup>e</sup> | 101.2 <sup>a</sup>    | 2.335 <sup>a</sup>   | 3   |
|   |                                 | 3.85 <sup>f</sup>        |                       |                      |     |
| [CsSi(SiMe <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub> [C <sub>6</sub> H <sub>5</sub> Me] <sub>3</sub> | 3.77–3.85                       | 3.51–4.08                | 100.9 <sup>a</sup>    | 2.344 <sup>a</sup>   | 3   |
| [Cs(18C6) <sub>2</sub> ][Si(SiMe <sub>3</sub> ) <sub>3</sub> ] <sup>g</sup>                           | N/A                             | 3.141–3.560              | 99.5 <sup>a</sup>     | 2.336 <sup>a</sup>   | *   |

<sup>a</sup> Average. <sup>b</sup> Contact and separated ion pair in one crystal. <sup>c</sup> Contact ion pair. <sup>d</sup> Separated ion pair. <sup>e</sup> Biphenylene. <sup>f</sup> Pentane. <sup>g</sup> Two independent molecules. \* = this work.

**Table 3. Crystallographic Data for Compounds 1–6**

|   | 1   | 2   | 3   | 4   | 5  | 6   |
|---|---|---|---|---|--|---|
| formula                                       | C <sub>25</sub> H <sub>59</sub> KO <sub>8</sub> Si <sub>4</sub> | C <sub>21</sub> H <sub>51</sub> KO <sub>6</sub> Si <sub>4</sub> | C <sub>29</sub> H <sub>67</sub> O <sub>10</sub> RbSi <sub>4</sub> | C <sub>75</sub> H <sub>177</sub> O <sub>24</sub> Rb <sub>3</sub> Si <sub>12</sub> | C <sub>66</sub> H <sub>150</sub> Cs <sub>2</sub> O <sub>24</sub> Si <sub>8</sub> | C <sub>25</sub> H <sub>62</sub> K <sub>4</sub> O <sub>4</sub> Si <sub>4</sub> |
| fw  | 639.18  | 551.08  | 773.66  | 2056.66   | 1818.40  | 695.51  |
| <i>a</i> (Å)                                  | 14.5311(3)  | 9.6982(10)  | 9.2351(15)  | 16.9372(7)  | 56.700(3)  | 12.4401(10)   |
| <i>b</i> (Å)                                  | 14.0106(2)  | 19.9550(2)  | 14.916(3)   | 19.0725(8)  | 12.8789(6)   | 14.5495(2)  |
| <i>c</i> (Å)                                  | 18.7156(4)  | 17.5144(3)  | 16.355(3)   | 20.6678(9)  | 27.4749(14)  | 46.0357(3)  |
| $\alpha$ (deg)                                |   |   | 78.142(2)   | 117.098(10)   |  |   |
| $\beta$ (deg)                                 | 100.882(10)   | 90.871(1)   | 89.378(2)   | 103.628(10)   | 107.208(10)  | 94.727(10)  |
| $\gamma$ (deg)                                |   |   | 72.668(3)   | 91.172(10)  |  |   |
| <i>V</i> (Å <sup>3</sup> )                    | 3741.78(12)   | 3389.13(8)  | 2101.6(6)   | 5712.9(4)   | 19164.9(16)  | 8303.99(14)   |
| <i>Z</i>                                      | 4   | 4   | 2   | 2   | 8  | 8   |
| space group                                   | <i>P</i> 2 <sub>1</sub> / <i>c</i>                              | <i>P</i> 2 <sub>1</sub> / <i>n</i>                              | <i>P</i> $\bar{1}$  | <i>P</i> $\bar{1}$  | <i>C</i> 2/ <i>c</i>   | <i>P</i> 2 <sub>1</sub> / <i>n</i>  |
| <i>d</i> <sub>calc</sub> (g/cm <sup>3</sup> ) | 1.135   | 1.080   | 1.223   | 1.196   | 1.260  | 1.113   |
| linear abs coeff (mm <sup>-1</sup> )          | 0.307   | 0.326   | 1.336   | 1.462   | 0.921  | 0.568   |
| <i>T</i> (K)                                  | 95  | 95  | 95  | 93  | 95   | 97  |
| 2 $\theta$ range (deg)                        | 3.7–56.6  | 4.1–56.3  | 2.5–50.0  | 2.4–56.6  | 3.0–56.6   | 2.9–56.9  |
| no. of indep reflns                           | 9048  | 7809  | 7334  | 26 467  | 23 247   | 19 632  |
| no. of params                                 | 427   | 289   | 397   | 1021  | 919  | 667   |
| R1, wR2 (all data)                            | 0.0782, 0.1673  | 0.0887, 0.1163  | 0.0760, 0.1692  | 0.0780, 0.0973  | 0.0572, 0.0702   | 0.0853, 0.1236  |
| R1, wR2 (>2 $\sigma$ )                        | 0.0591, 0.1519  | 0.0512, 0.1035  | 0.0677, 0.1637  | 0.0417, 0.0867  | 0.0316, 0.0625   | 0.0636, 0.1169  |

is the result of repulsion between the crown and the sterically demanding Si(SiMe<sub>3</sub>)<sub>3</sub> ligand, and the observed metal–silicon distance of about 3.4 Å seems to be an ideal compromise between maximum interaction and minimum repulsion. Steric arguments may also be employed to explain the slightly shorter K–Si bond length in K(C<sub>6</sub>H<sub>6</sub>)<sub>3</sub>Si(SiMe<sub>3</sub>)<sub>3</sub> (3.32–3.35 Å)<sup>3</sup> as compared to 3.378(1) Å for the slightly more encumbered K(C<sub>6</sub>D<sub>6</sub>)<sub>3</sub>Si(<sup>t</sup>Bu)<sub>3</sub>.<sup>4</sup>

Geometrical features for **6** are closely related to [KO<sup>t</sup>Bu]<sub>4</sub>, with O–K–O angles close to 90°.<sup>15</sup> However, the K–O bond lengths in **6** are slightly shorter (2.59 Å *av*) than in the [KO<sup>t</sup>Bu]<sub>4</sub> tetramer (2.623(1) Å). It might be argued that the longer K–Si bond length is responsible for reduced secondary interactions between the ligand and the metal, thus shortening the K–O bonds.

### Experimental Section

All reactions were performed under a purified nitrogen atmosphere by using modified Schlenk techniques and/or a

Braun Labmaster 100 drybox. Tetrahydrofuran and *n*-hexane were distilled prior to use from a Na/K alloy and freshly degassed using two freeze–pump–thaw cycles. KO<sup>t</sup>Bu, 12-crown-4, 15-crown-5, and 18-crown-6 were obtained commercially. The crown ethers were purified by solvation in freshly distilled diethyl ether and stirred with finely cut sodium metal for 1 day. After filtration from excess metal, the crown was recrystallized at –20 °C from hexanes (18-crown-6) or distilled (12-crown-4, 15-crown-5). Li(THF)<sub>3</sub>Si(SiMe<sub>3</sub>)<sub>3</sub>,<sup>1</sup> Si(SiMe<sub>3</sub>)<sub>4</sub>,<sup>16</sup> RbO<sup>t</sup>Bu, and CsO<sup>t</sup>Bu were prepared according to literature procedures.<sup>15</sup> KO<sup>t</sup>Bu was purchased and used as received. The purity of all compounds was determined by <sup>1</sup>H NMR spectroscopy. All <sup>1</sup>H NMR and <sup>13</sup>C NMR were recorded on a Bruker DPX-300 spectrometer. <sup>29</sup>Si NMR data were recorded on a Bruker DPX-500 instrument. Reliable elemental analyses could not be obtained, even when glovebox handling was attempted, due to the extremely high moisture and oxygen sensitivity of all compounds reported. This is a well-known problem in alkali metal chemistry.<sup>9b</sup>

**General Procedure for the Synthesis of 1–5.** In a typical experiment 2 mmol (0.94 g) of Li(THF)<sub>3</sub>Si(SiMe<sub>3</sub>)<sub>3</sub> were dissolved in 20 mL of THF. In a separate flask, about 2 mmol of alkali metal *tert*-butoxide were dissolved in 30 mL of THF.

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The clear solutions were combined dropwise, affording clear, yellow solutions. After further stirring for about 30 min, crown ether dissolved in THF was added, affording clear, slightly darker colored solutions. Those were stirred for 12 h, followed by filtration over a Celite padded filter frit. Removal of the solvent in a vacuum afforded yellow-colored solids, which were washed three times with 5 mL of hexanes and dissolved in 30 mL of a solvent mixture containing 70:30 hexanes/THF. The resulting, almost clear solutions were filtered and slowly cooled to  $-20\text{ }^{\circ}\text{C}$ , upon which large, pale yellow crystals, suitable for crystallographic analysis formed.  $^1\text{H}$  NMR spectroscopy on the hexane wash solutions and the hexane/THF solutions confirmed that  $\text{LiO}^t\text{Bu}$  (1.12 ppm) was effectively separated from the target compounds.

**[K(12-crown-4)<sub>2</sub>][Si(SiMe<sub>3</sub>)<sub>3</sub>], 1.** A 0.94 g (2 mmol) sample of  $\text{Li}(\text{THF})_3\text{Si}(\text{SiMe}_3)_3$  in 20 mL of THF, 0.24 g of  $\text{KO}^t\text{Bu}$  (2.1 mmol) in 30 mL of THF, and 0.72 g of 12-crown-4 (4 mmol) in 20 mL of THF were used. Yellow crystalline rods (1.22 g, 1.9 mmol, 95% yield) were isolated. Mp: 224–226  $^{\circ}\text{C}$ .  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) 0.77 ( $\text{SiMe}_3$ ), 3.16 ( $\text{CH}_2$  crown ether).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) 7.87 ( $\text{SiMe}_3$ ), 69.23 ( $\text{CH}_2$  crown ether).  $^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm)  $-4.2$  ( $\text{Si}(\text{SiMe}_3)_3$ ),  $-196.0$  ( $\text{Si}(\text{SiMe}_3)_3$ ).

**[K(18-crown-6)Si(SiMe<sub>3</sub>)<sub>3</sub>], 2.** A 0.94 g sample of  $\text{Li}(\text{THF})_3\text{Si}(\text{SiMe}_3)_3$  (2 mmol) in 20 mL of THF, 0.24 g of  $\text{KO}^t\text{Bu}$  (2.1 mmol) in 30 mL of THF, and 0.52 g of 18-crown-6 (2 mmol) in 20 mL of THF formed a vibrant yellow solution. Pale yellow plates were obtained (1.03 g, 1.88 mmol, 94% yield). Mp: 243–245  $^{\circ}\text{C}$ .  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) 0.71 ( $\text{SiMe}_3$ ), 3.15 ( $\text{CH}_2$  crown ether).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) 8.12 ( $\text{SiMe}_3$ ), 70.58 ( $\text{CH}_2$  crown ether).  $^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm)  $-4.0$  ( $\text{Si}(\text{SiMe}_3)_3$ ),  $-191.1$  ( $\text{Si}(\text{SiMe}_3)_3$ ).

**[Rb(15-crown-5)<sub>2</sub>][Si(SiMe<sub>3</sub>)<sub>3</sub>], 3.** A 1 mmol sample of  $\text{Li}(\text{THF})_3\text{Si}(\text{SiMe}_3)_3$  (0.47 g) in 20 mL of THF, 1.1 mmol of  $\text{RbO}^t\text{Bu}$  (0.18 g) in 30 mL of THF, and 2 mmol of 15-crown-5 (0.44 g) in 20 mL of THF were used. Yellow crystalline blocks were isolated (0.7 g, 0.9 mmol, 90% yield). Mp: 219–220  $^{\circ}\text{C}$ .  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) 0.78 ( $\text{SiMe}_3$ ), 3.15 ( $\text{CH}_2$ , crown ether).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) 7.62 ( $\text{SiMe}_3$ ), 70.02 ( $\text{CH}_2$  crown ether).  $^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm)  $-4.0$  ( $\text{Si}(\text{SiMe}_3)_3$ ),  $\text{Si}(\text{SiMe}_3)_3$  not observed due to solubility problems, even with a 10 mm NMR tube and extended (72 h, depth experiment) acquisition times).

**[Rb(18-crown-6)<sub>2</sub>][Si(SiMe<sub>3</sub>)<sub>3</sub>][Rb(18-crown-6)Si(SiMe<sub>3</sub>)<sub>3</sub>], 4.** A 0.70 g sample of  $\text{Li}(\text{THF})_3\text{Si}(\text{SiMe}_3)_3$  (1.5 mmol) in 30 mL of THF, 2 mmol of  $\text{RbO}^t\text{Bu}$  (0.32 g) in 20 mL of THF, and 2 mmol (0.52 g) of 18-crown-6 in 20 mL of THF were used, resulting in 0.91 g of yellow blocks (0.44 mmol, 89% yield). Mp: 150–152  $^{\circ}\text{C}$ .  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) 0.74 ( $\text{SiMe}_3$ ), 3.31 ppm ( $\text{CH}_2$  crown ether).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) 8.02 ( $\text{SiMe}_3$ ), 70.45 ( $\text{CH}_2$  crown ether).  $^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm)  $-4.1$  ( $\text{Si}(\text{SiMe}_3)_3$ ),  $-188.9$  ( $\text{Si}(\text{SiMe}_3)_3$ ).

**[Cs(18-crown-6)<sub>2</sub>][Si(SiMe<sub>3</sub>)<sub>3</sub>], 5.** A 1 mmol sample of  $\text{Li}(\text{THF})_3\text{Si}(\text{SiMe}_3)_3$  (0.47 g) in 30 mL of THF, 1.1 mmol of  $\text{CsO}^t\text{Bu}$  (0.21 g) in 20 mL of THF, and 2 mmol 18-crown-6 (0.52 g) in 20 mL of THF were used. Yellow-green needles in 92% yield (0.84 g, 0.84 mmol) were obtained. Mp: 128–131  $^{\circ}\text{C}$ .  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) 0.78 ( $\text{SiMe}_3$ ), 3.30 ( $\text{CH}_2$  crown ether).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) 7.89 ( $\text{SiMe}_3$ ), 70.22 ( $\text{CH}_2$  crown ether).  $^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm)  $-3.8$  ( $\text{Si}(\text{SiMe}_3)_3$ ),  $-187.8$  ( $\text{Si}(\text{SiMe}_3)_3$ ).

**[[K(THF)Si(SiMe<sub>3</sub>)<sub>3</sub>][KO<sup>t</sup>Bu]<sub>3</sub>], 6.** In a typical experiment, a 10 mmol sample of  $\text{KO}^t\text{Bu}$  (1.12 g) was dissolved in 30 mL of THF. In a second flask, 10 mmol of  $\text{Si}(\text{SiMe}_3)_4$  (3.21 g) was dissolved in 30 mL of THF. The  $\text{Si}(\text{SiMe}_3)_4$  solution was slowly added to the  $\text{KO}^t\text{Bu}$  solution, yielding a clear yellow solution, which was stirred for 3.5 h, during which a black powder appeared gradually. Filtration over a Celite-padded filter frit afforded clear yellow solutions, which were stored at  $-20\text{ }^{\circ}\text{C}$  for 5 days, affording 1.194 g of colorless crystals. The yield is 17.2% based on conversion of  $\text{Si}(\text{SiMe}_3)_4$ , with a theoretical yield of 25%. Mp: 228–231  $^{\circ}\text{C}$ .  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) 3.55 (br m 4H, THF) 1.38 (br m, 4H, THF) 1.09 (s, 27H, <sup>t</sup>Bu) 0.39 (s, 27H,  $\text{SiMe}_3$ ).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm) 67.88,

66.45, 37.64, 25.6, 7.2.  $^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  (ppm)  $-4.9$  ( $\text{SiMe}_3$ )  $-194.5$  ( $\text{Si}(\text{SiMe}_3)_3$ ).

**X-ray Crystallographic Studies.** X-ray-quality crystals for all compounds were grown as described in the Experimental Section. The crystals were removed from the Schlenk tube under a stream of  $\text{N}_2$  and immediately covered with a layer of viscous hydrocarbon oil (Paratone N, Exxon). A suitable crystal was selected under the microscope, attached to a glass fiber, and immediately placed in the low-temperature nitrogen stream of the diffractometer.<sup>1817–19</sup> Due to the extreme moisture and oxygen sensitivity of compounds **3–5**, the microscope was placed inside the diffractometer enclosure, and the crystals were removed under inert gas from the mother liquor in immediate proximity to the microscope. All data sets were collected using a Siemens SMART system, complete with three-circle goniometer and CCD detector operating at  $-54\text{ }^{\circ}\text{C}$ . The data sets were collected using a custom-built low-temperature device from Professor H. Hope (UC Davis) operating at 95 K by employing graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073\text{ \AA}$ ). The data collections nominally covered a hemisphere of reciprocal space utilizing a combination of three sets of exposures, each with a different  $\omega$  angle and each exposure covering  $0.3^{\circ}$  in  $\phi$ . Repeating the initial frames at the end of the data collection and analyzing the duplicate reflections monitored crystal decay. In all cases, no decay was observed. An absorption correction was applied utilizing the program SADABS.<sup>18</sup> The crystal structures of all compounds were solved by either direct methods or Patterson synthesis, as included in the SHELX program package.<sup>19</sup> Missing atoms were located in subsequent difference Fourier maps and included in the refinement. The structures were refined by full-matrix least-squares refinement on  $F^2$  (SHELX-93).<sup>19</sup> Hydrogen atoms were placed geometrically and refined using a riding model, including free rotation about C–C bonds for methyl groups. Thermal parameters for hydrogen atoms were refined with  $U_{\text{iso}}$  constrained at 1.2 (for nonmethyl groups) and 1.5 (for methyl groups) times  $U_{\text{eq}}$  of the carrier C atom. The crystallographic programs used for structure refinement and solution were installed on a PC clone and a Silicon Graphics Indigo<sup>2</sup> R10000 Solid Impact (SHELX-93). Scattering factors were those provided with the SHELX program system.<sup>19</sup>

All non-hydrogen atoms, with the exception of some disordered or restrained positions, were refined anisotropically. Disorder was handled by including split positions for the affected groups and included the refinement of the respective occupancies. A set of restraints was applied to aid in modeling the disorder. In **1**, one of the two crown ether molecules was disordered; for **3**, a disorder model for the crown ether and silanide anions was attempted but did not result in an improved model and was therefore disregarded.

**Supporting Information Available:** Further details about the refinements and how disorder was handled are outlined in the Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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