Organometallics **2004,** *23,* 1899−1907

Small Cyclosilanes: Syntheses and Reactions toward Mono- and Dianions

Roland Fischer, Tina Konopa, Judith Baumgartner, and Christoph Marschner*

Institut für Anorganische Chemie der Technischen Universität Graz,
Stremayrgasse 16, A-8010 Graz, Österreich

Received December 22, 2003

The reaction of hexakis(trimethylsilyl)disilane with 2 equiv of potassium *tert*-butyl alcoholate and 18-crown-6 gives 1,2-dipotassiotetrakis(trimethylsilyl)disilane (**1**) in almost quantitative yield. Transmetalation with magnesium bromide allows for the derivatization of the dianion. After exchange of one or two trimethylsilyl groups for phenyl substituents in the starting material, the 1,2-dipotassio compounds (**13**, **16**) could still be obtained. Treatment of **1** with 1,2-dibromoethane gives octakis(trimethylsilyl)cyclotetrasilane (**8**), which also can be converted into a 1,3-dipotassiocyclotetrasilane (**11**).

1. Introduction

Silyl anions constitute a class of compounds which has been studied for some 50 years.[1] While disilane cleavage reactions with alkali metals, as pioneered by Gilman et al.,[1] still are the most important source of metalated silanes, a number of other synthetic routes have gained increasing importance over the last two decades.[2] Prominent among these are the reactions of oligo- and disilanes with strong nucleophiles such as alkyllithiums[3] and alkali-metal alkoxides.[4] The first examples of branched oligosilyl anions have been reported by Gilman to form in the reaction of oligosilanes with methyllithium.[5] Reports from our laboratory introduced potassium *tert*-butyl alcoholate as a reagent for the generation of branched oligosilyl anions.[6] The change from methyllithium to the potassium alkoxide allows for the preservation of the structural integrity of higher oligosilanes such as hexakis(trimethylsilyl)disilane, which is cleaved at the central silicon−silicon bond by methyllithium.[7] The high regioselectivity of the alkoxide-mediated cleavage reactions sets the stage for the preparation of higher oligosilyl anions and also dianions.[8,9]

While most of the silyl anions prepared so far are singly metalated compounds, there have been some isolated attempts to generate silanes with a 2− charge. Early reports describe the cleavage of perphenylated cyclosilanes with lithium provided to give 1,4- and 1,5-dilithiotetrasilanes and 1,4- and 1,5-dilithiopentasilanes, respectively.[10,11] Lagow et al.[12] claimed the first preparation of a 1,1-dilithiosilane, which was obtained by pyrolysis of (tris(trimethylsilyl)silyl)lithium.

Within the past decade research toward the synthesis of multiply metalated silanes was intensified; a number of examples of silyl dianions have been reported, and their molecular structures could be elucidated.[13] In this context the preparation of 1,3-, 1,4-, and 1,5-dipotassium compounds has been achieved in our laboratory.[8,9] These dianions are valuable starting materials for the synthesis of homo- and heterocyclic silanes by reaction with difunctional electrophiles.[9]

2. Results and Discussion

The reaction for the preparation of 1,3- and 1,4-dipotassium compounds using potassium *tert*-butyl alcoholate in THF or DME turned out to be a very facile

---

* To whom correspondence should be addressed. Tel: ++43-316-873-8209. Fax: ++43-316-873-8701. E-mail: marschner@anorg.tu-graz.ac.at.

[1] For accounts covering the early development of the field see: (a) Wittenberg, D.; Gilman, H. *Q. Rev. Chem. Soc.* **1959**, *13*, 116. (b) Davis, D. D.; Gray, C. E. *Organomet. Chem. Rev. A* **1970**, *6*, 283.

[2] (a) Lickiss, P. D.; Smith, C. M. *Coord. Chem. Rev.* **1995**, *145*, 75. (b) Tamao, K.; Kawachi, A. *Adv. Organomet. Chem.* **1995**, *38*, 1. (c) Belzner, J.; Dehnert U. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: New York, 1998; Vol. 2, p 779. (d) Sekiguchi, A.; Lee, V. Y.; Nanjo, M. *Coord. Chem. Rev.* **2000**, *210*, 11.

[3] (a) Still, W. C. *J. Org. Chem.* **1976**, *41*, 3063. (b) Krohn, K.; Khanbabaee, K. *Angew. Chem.* **1994**, *106*, 100; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 99.

[4] (a) Sakurai, H.; Okada, A.; Kira, M.; Yonezawa, K. *Tetrahedron Lett.* **1971**, *19*, 1511. (b) Sakurai, H.; Kondo, F. *J. Organomet. Chem.* **1975**, *92*, C46. (c) Buncel, E.; Venkatchalam, T. K.; Edlund, E. *J. Organomet. Chem.* **1992**, *437*, 85.

[5] Gilman, H.; Holmes, J. M.; Smith, C. L. *Chem. Ind. (London)* **1965**, 848.

[6] (a) Uhlig, F.; Gspaltl, P.; Trabi, M.; Hengge, E. *J. Organomet. Chem.* **1995**, *493*, 33. (b) Marschner, Ch. *Eur. J. Inorg. Chem.* **1998**, 221.

[7] Gilman, H.; Harrell, R. L., Jr. *J. Organomet. Chem.* **1967**, *9*, 67.

[8] Kayser, C.; Kickelbick, G.; Marschner, Ch. *Angew. Chem.* **2002**, *114*, 1031; *Angew. Chem., Int. Ed.* **2002**, *41*, 989.

[9] (a) Fischer, R.; Frank, D.; Gaderbauer, W.; Kayser, C.; Mechtler, C.; Baumgartner, J.; Marschner, C. *Organometallics* **2003**, *22*, 3723. (b) Fischer, R.; Konopa, T.; Ully, S.; Baumgartner, J.; Marschner, C. *J. Organomet. Chem.* **2003**, *685,* 79.

[10] (a) Jarvie, A. W.; Winkler, H. J. S.; Peterson, D. J.; Gilman, H. *J. Am. Chem. Soc.* **1961**, *83*, 1921. (b) Gilman, H.; Tomasi, R. A. *Chem. Ind. (London)* **1963**, 954.

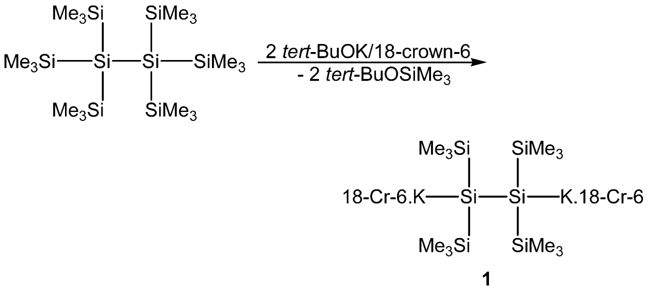
[11] (a) Hengge, E.; Wolfer, D. *J. Organomet. Chem.* **1974**, *66*, 413. (b) Becker, G.; Hartmann, H. M.; Hengge, E.; Schrank, F. *Z. Anorg. Allg. Chem.* **1989**, *572*, 63.

[12] Mehrotra, S. K.; Kawa, H.; Baran, J. R., Jr.; Ludvig, M. M.; Lagow, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 9003.

[13] (a) Sekiguchi, A.; Ichinohe, M.; Yamaguchi, S. *J. Am. Chem. Soc.* **1999**, *121*, 10231. (b) Tokitoh, N.; Hatano, K.; Sadahiro, T.; Okazaki, R. *Chem. Lett.* **1999**, 931. (c) Kira, M.; Iwamoto, T.; Yin, D.; Maruyama, T.; Sakurai, H. *Chem. Lett.* **2001**, 910. (d) Belzner, J.; Dehnert, U.; Stalke, D. *Angew. Chem.* **1994**, *106*, 2580; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2450. (e) Apeloig, Y.; Korogodsky, G.; Bravo-Zhivotovskii, D.; Bläser, D.; Boese, R. *Eur. J. Inorg. Chem.* **2000**, 1091. (f) Ando, W.; Wakahara, T.; Akasaka, T.; Nagase, S. *Organometallics* **1994**, *13*, 4683. (g) Hong, J.-H.; Boudjouk, P.; Catellino, S. *Organometallics* **1994**, *13*, 3387.

10.1021/om034396+ CCC: $27.50

Scheme 1. Synthesis of 1,2-Dipotassiotetrakis(trimethylsilyl)disilane (1)

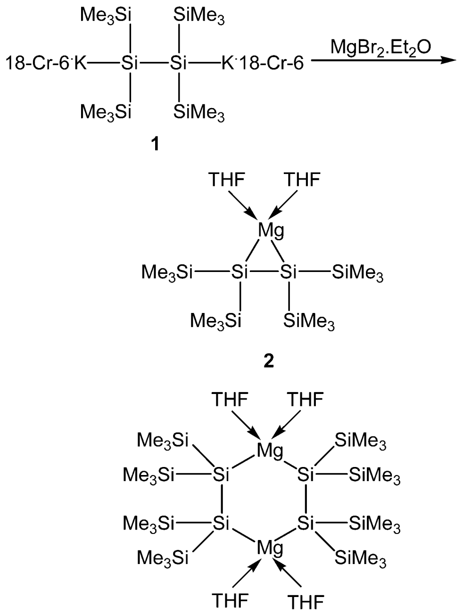


process.[6b,14] However, the respective reaction toward the analogous 1,2-dianion under the same conditions is very slow, and a number of side products, including potassium tris(trimethylsilyl)silane,[6a,15] can be detected. Considering the difficulties in obtaining 1,2-dilithio[16] or 1,2-di-Grignard compounds,[17] this does not seem to be too surprising. It was therefore rather pleasing to find that the conversion of hexakis(trimethylsilyl)disilane[18] with 2 equiv of potassium *tert*-butyl alcoholate in toluene or benzene and in the presence of 18-crown-6 occurs without any unexpected side products. The crown ether adduct (**1**; Scheme 1) can be obtained in almost quantitative yield.

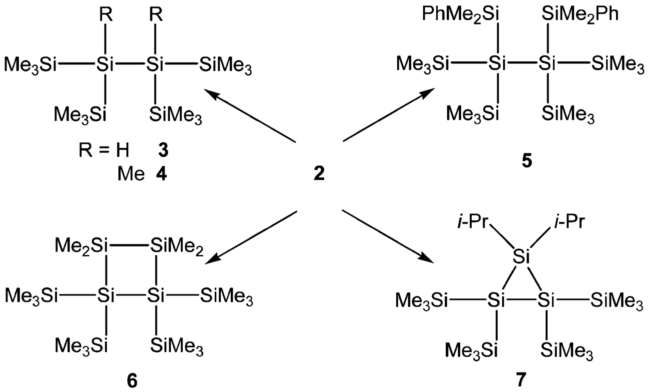
Dianion **1** is highly reactive, and no clean protonation or alkylation reaction could be achieved initially. To moderate the reactivity of **1**, conversion with magnesium bromide etherate was attempted, which led to the formation of the respective magnesium compound **2**; this compound is much easier to handle and allows a number of clean derivatization reactions.[19] So far, it has not been possible to elucidate the exact structure of **2**, to determine whether it is a magnesadisilacyclopropane or a dimeric unit (Scheme 2).

With the magnesium compound **2** protonation with sulfuric acid to the 1,2-dihydro product (**3**)[20] and also alkylation with methyl sulfate to the 1,2-dimethylsilane[21] proceed smoothly and cleanly (**4**) (Scheme 3). The same applies to the reaction with 2 equiv of dimethylphenylsilyl chloride, affording the diphenylated product **5**. In addition, **2** turned out to be also a very versatile precursor for the syntheses of three- and four-membered rings (Scheme 3). The novel cyclotetrasilane **6** was obtained by reacting **2** with 1,2-dibromotetramethyldisilane. Conversion of **2** with diisopropylsilyl dichloride led to the formation of cyclotrisilane **7**.

Scheme 2. Synthesis of Magnesium Compound 2



Scheme 3. Reactions of Magnesium Compound 2



The strategy of using 1,2-dianions for the synthesis of cyclotrisilanes offers a unique access to compounds of the structural type $(\mathrm{R^1{}_2Si})_2\mathrm{SiR^2{}_2}$, which are not easily available otherwise. An alternative route would likely involve ring closure reactions of 1,3-dihalotrisilanes,[22] which would not allow much flexibility in the choice of the $\mathrm{SiR^2{}_2}$ unit.

An effort to obtain a metal-free dianion[23] from **1** by employing a reaction with tetramethylammonium bromide failed, but this reaction eventually proved to be the sought-after alkylation method for **1** to form directly the dimethylated compound **4** (Scheme 4).

An interesting question with respect to the 1,2-dianion **1** was if it could be used as a precursor for tetrakis(trimethylsilyl)disilene.[24] By reaction of **1** with 1,2-dibromoethane and further [4 + 2] cycloadditions[25,26] with anthracene or 2,3-dimethylbutadiene or by simple dimerization of the disilene to octakis(trimethylsilyl)-cyclotetrasilane (**8**), this was shown to be possible.[24]

---

(14) Kayser, C.; Fischer, R.; Baumgartner, J.; Marschner, C. *Organometallics* **2002**, *21*, 1023.

(15) (a) Klinkhammer, K. W. *Chem. Eur. J.* **1997**, *3*, 1418. (b) Klinkhammer, K. W.; Schwarz, W. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1777.

(16) Maercker, A. In *Lithium Chemistry—A Theoretical and Experimental Overview*; Sapse, A.-M., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1995.

(17) (a) Bickelhaupt, F. *Angew. Chem.* **1987**, *99*, 1020; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 990. (b) Bickelhaupt, F. *Chem. Soc. Rev.* **1999**, *28*, 17.

(18) (a) Mallela, S. P.; Bernal, I.; Geanangel, R. A. *Inorg. Chem.* **1992**, *31*, 1, 1626. (b) Heine, A.; Herbst-Irmer, R.; Sheldrick, G. M.; Stalke, D. *Inorg. Chem.* **1993**, *32*, 2694. (c) Bock, H.; Meuret, J.; Ruppert, K. *J. Organomet. Chem.* **1993**, *445*, 19.

(19) (a) Farwell, J. D.; Lappert, M. F.; Marschner, C.; Strissel, C.; Tilley, T. D. *J. Organomet. Chem.* **2000**, *603*, 185. (b) Krempner, C.; Reinke, H.; Oehme, H. *Chem. Ber.* **1995**, *128*, 143.

(20) Baumeister, U.; Schenzel, K.; Zink, R.; Hassler, K. *J. Organomet. Chem.* **1997**, *543*, 117.

(21) Ishikawa, M.; Iyoda, J.; Ikeda, H.; Kotake, K.; Hashimoto, T.; Kumada, M. *J. Am. Chem. Soc.* **1981**, *103*, 4845.

(22) Weidenbruch, M. *Chem. Rev.* **1995**, *95*, 1479.

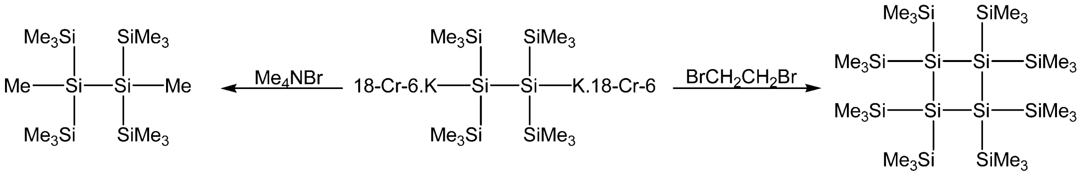
(23) Hiyama, T.; Obayashi, M.; Mori, I.; Nozaki, H. *J. Org. Chem.* **1983**, *48*, 912.

(24) (a) Shen, Y.-S.; Gaspar, P. *Organometallics* **1982**, *1*, 1410. (b) Matsumoto, H.; Yokoyama, N.; Sakamoto, A.; Aramaki, Y.; Endo, R.; Nagai, Y. *Chem. Lett.* **1986**, 1643.

(25) Nakadaira, Y.; Kobayashi, T.; Otsuka, T.; Sakurai, H. *J. Am. Chem. Soc.* **1979**, *101*, 486.

(26) Fischer, R.; Baumgartner, J.; Kickelbick, G.; Marschner, C. *J. Am. Chem. Soc.* **2003**, *125*, 3414.

Scheme 4. Reactions of the Crown Ether Adduct 1

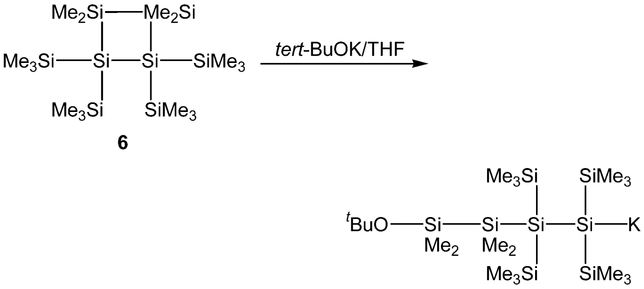


4

1

8

Scheme 5. Ring-Opening Reaction of 6



6

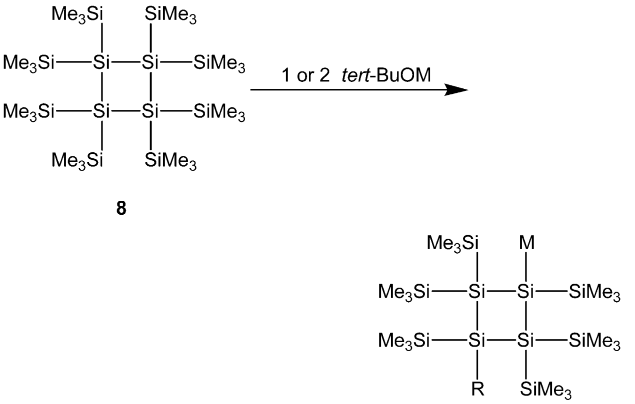
9

The two cyclotetrasilanes **6** and **8** can be treated with potassium *tert*-butyl alcoholate to convert them into anions again. Considering the work of Matyjaszewski et al.,[27] we expected to observe ring opening and perhaps even ring-opening polymerization of the strained cyclosilanes. This was true for the case of **6**, where for the first time in our studies on the synthesis of potassium silyl compounds no cleavage of a trimethylsilyl group was observed. Instead, a product that was formed via an attack at a dimethylsilyl unit, thus forming a δ-alkoxy-substituted silylpotassium compound (**9**), was obtained (Scheme 5).

It turned out that octakis(trimethylsilyl)cyclotetrasilane (**8**) behaved in a different way. Reaction of **8** with potassium *tert*-butyl alcoholate and crown ether does not effect ring opening but a trimethylsilyl group is cleaved and a cyclotetrasilanyl anion (**10a**) forms (Scheme 6).[28] Reaction of **8** with sodium *tert*-butyl alcoholate in DME causes the formation of the DME adduct of the analogous sodium compound (**10b**). Use of 2 equiv of potassium *tert*-butyl alcoholate in the presence of crown ether yielded the 1,3-*trans*-dipotassium compound **11**. A similar 1,3-cyclotetrasilane dianion was described previously by Masamune et al., but without any detailed characterization.[29,30] Compound **11** is a very interesting synthetic building block, as all remaining trimethylsilyl groups can be considered as masked functionalities for further reactions.[8,9,15]

Recently, we have demonstrated the remarkable regioselectivity of the reaction of pentakis(trimethylsilyl)phenyldisilane (**12**) with potassium *tert*-butyl alcoholate. The β-phenylsilylpotassium compound was obtained exclusively.[14] Reaction of **12** under the same conditions as required for the synthesis of **1** led to the formation of 1,2-dipotassium tris(trimethylsilyl)phenyldisilane (**13**; Scheme 7).

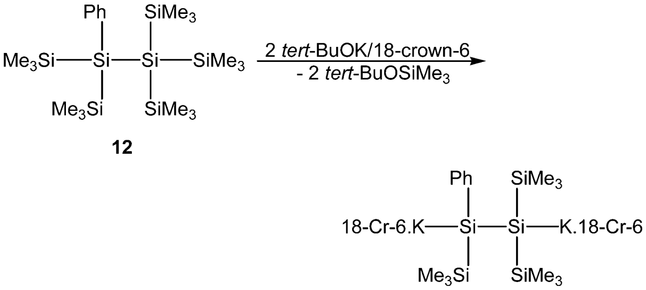
Scheme 6. Syntheses of Cyclotetrasilane Anions from 8



8

10a R = SiMe$_3$, M = K.18-Cr-6
10b R = SiMe$_3$, M = Na.DME
11 R = M = K.18-Cr-6

Scheme 7. Formation of Dipotassium Compound 13



12

13

The reactivity of tetrakis(trimethylsilyl)diphenyldisilane[20] (**14**), which can be conveniently obtained by oxidative coupling of (bis(trimethylsilyl)phenylsilyl)potassium[14] with 1,2-dibromoethane, toward potassium *tert*-butyl alcoholate resembles that of **12**. Thus, by treatment with 1 or 2 equiv of alkoxide and crown ether the respective mono- or dianions can be obtained (Scheme 8).

^{29}Si NMR Spectroscopy. ^{29}Si NMR spectra of the obtained silylpotassium compounds all show the expected high-field shift for the metalated silicon atoms. For the crown ether adduct of dipotassium compound **1** a resonance at −183.4 ppm can be found. Comparison with the respective 1,3- and 1,4-dipotassium adducts[9] shows that the resonance of the 1,4-dianion (−190.2 ppm) is close to that of (tris(trimethylsilyl)silyl)potassium,[15] whereas for the 1,3-dianion this particular resonance (−172.5 ppm) is shifted almost 20 ppm to lower field. For the monophenylated 1,2-dianion **13** the resonance for the metalated tertiary silicon atom can be observed at −176.9 ppm.

---

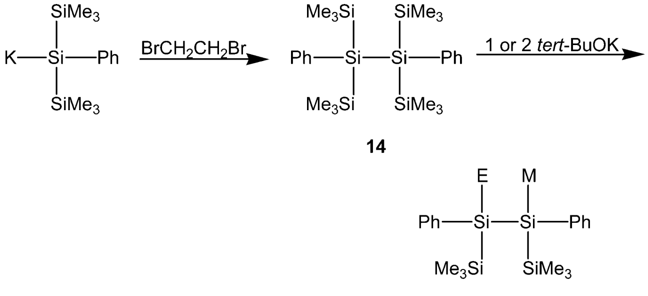
[27] (a) Fossum, E.; Matyjaszewski, K. *Macromolecules* **1995**, *28*, 1618. (b) Cypryk, M.; Gupta, Y.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1991**, *113*, 1046.

[28] The THF adduct of **10a** was reported to be obtained under almost identical reaction conditions by: Krempner, C. 1st European Organosilicon Days, Munich, Sept 6−7, 2001; Poster 38.

[29] Kawase, T.; Batcheller, S. A.; Masamune, S. *Chem. Lett.* **1987**, 227.

[30] After this paper was submitted, another report about a 1,3-dipotassiocyclotetrasilane was published: Kyushin, S.; Kawai, H.; Matsumoto, H. *Organometallics* **2004**, *23*, 311.

Scheme 8. Formation of Potassium Compounds 15 and 16



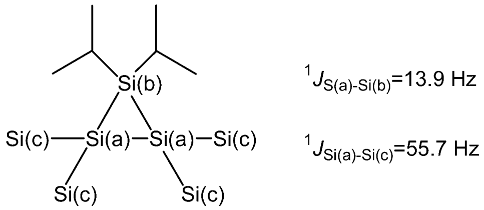
15 E = $SiMe_3$, M = K.18-Cr-6
16 E = M = K.18-Cr-6

Table 1. ^{29}Si NMR Resonances (in ppm) of Crown Ether Adducts of Metalated Disilanes of the Type $KSi(1)(R)(Si(3)Me_3)Si(2)(R')(R'')(Si(4)Me_3)$

R	R′	R″	Si(1)	Si(2)	Si(3)	Si(4)
$SiMe_3$	$SiMe_3$	$SiMe_3$	−192.6	−128.9	−5.6	−10.7
$SiMe_3$	$SiMe_3$	K	−183.4	−183.4	−5.4	−5.4
$SiMe_3$	Ph	$SiMe_3$	−186.5	−62.3	−5.6	−14.5
$SiMe_3$	Ph	K	−176.9	−81.8	−5.0	−10.5
Ph	Ph	$SiMe_3$	−93.6	−64.6	−10.0	−13.3
Ph	Ph	K	−77.2	−77.2	−11.8	−11.8

Comparison of monoanions and 1,2-dianions reveals the general trend of a shift to lower field for the resonance of the metalated silicon atom (Table 1), which occurs upon the second metalation.

The ^{29}Si NMR shift value for the silyl-substituted silicon atoms of cyclotrisilane **7** exhibits a large upfield shift of −171.4 ppm, which compares well to values obtained for other silyl-substituted cyclotrisilanes (−167.1 ppm for $((Me_3Si)_2Si)_3$[35] and −174.4 ppm for $((Et_3Si)_2Si)_3$)[31]), indicating well-shielded silicon centers. Due to the symmetric nature of most known cyclotrisilanes, data on coupling constants are scarce, the only example known to us being a value for $^1J_{Si-Si}$ of 24.1 Hz for *trans*-(*tert*-BuPhSi)$_3$.[32] For the case of **7** the endocyclic Si−Si coupling constant was determined to be 13.9 Hz. Typical ^1J coupling constants for unstrained oligosilanes usually range from 50 to 80 Hz. Evidently, in small rings the low s character of the σ-bond orbitals forming the ring skeleton is responsible for very small coupling constants. For **7** also an exocyclic ^1J coupling constant can be measured which exhibits a rather typical value of 55.7 Hz.



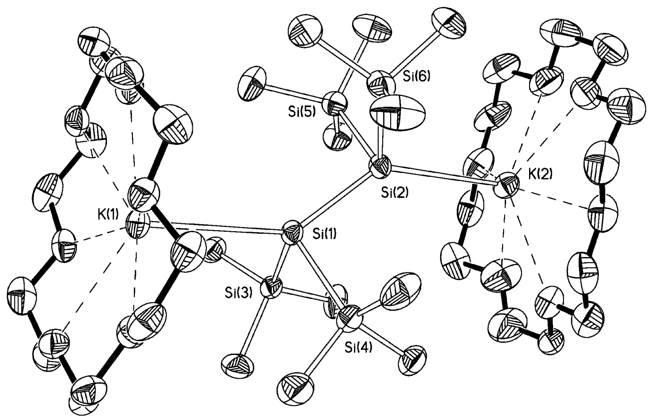
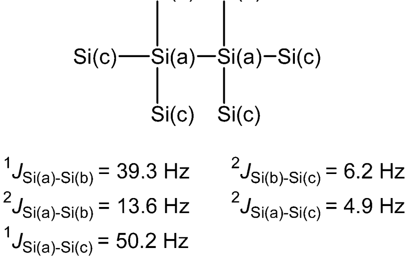


Figure 1. Molecular structure and numbering of **1** with 30% probability thermal ellipsoids. All hydrogens have been omitted for clarity. Selected bond lengths (Å) and bond angles (deg) with estimated standard deviations: K(1)−Si(1), 3.477(2); K(2)−Si(2), 3.489(2); Si(1)−Si(4), 2.358(2); Si(1)−Si(3), 2.362(2); Si(1)−Si(2), 2.448(2); Si(2)−Si(6), 2.353(2); Si(2)−Si(5), 2.361(2); Si(4)−Si(1)−Si(3), 94.51(8); Si(4)−Si(1)−Si(2), 99.43(8); Si(3)−Si(1)−Si(2), 103.41(8); Si(4)−Si(1)−K(1), 107.18(7); Si(3)−Si(1)−K(1), 102.83(7); Si(2)−Si(1)−K(1), 140.64(7); Si(6)−Si(2)−Si(5), 93.43(8); Si(6)−Si(2)−Si(1), 100.95(8); Si(5)−Si(2)−Si(1), 103.39(8); Si(6)−Si(2)−K(2), 118.59(7); Si(5)−Si(2)−K(2), 92.19(7); Si(1)−Si(2)−K(2), 136.52(7).

It is interesting to compare the strong shift to higher field, which is found for three-membered rings, to the shifts for cyclotetrasilanes such as **6** and **8**. ^{29}Si NMR spectra of **6** reveal a pronounced downfield shift compared to open-chain compounds for the dimethyl-substituted silicon atoms. While for the almost unstrained dodecamethylcyclohexasilane[33,34] a ^{29}Si NMR shift value of −41.8 ppm can be observed, for the four-membered ring of octamethylcyclotetrasilane[34] only −27.7 ppm is found. For compound **6** the dimethylsilyl groups show a distinct shift to an even lower field value of −9.7 ppm. Also, the quaternary silicon atoms of **6** exhibit a downfield shift (−114.0 ppm) compared to tetrakis(trimethylsilyl)silane (−135.6 ppm); however, this shift is not as pronounced as found for octakis(trimethylsilyl)cyclotetrasilane[24] **8** (−92.1 ppm). The exocyclic Si−Si coupling constant of **6** ($^1J_{Si-Si}$ = 50.2 Hz) is in the range of the values obtained for cyclotrisilane **7**. The substituent pattern again allows for the determination of endocyclic Si−Si coupling constants. $^1J_{Si-Si}$ was found to be 39.3 Hz, which still is significantly lower compared to ^1J coupling constants of linear oligosilanes. $^2J_{Si-Si}$ has a value of 13.6 Hz.



X-ray Crystallography. The crown ether adduct of **1** (Figure 1) has two independent molecules and four molecules of cocrystallized benzene in the unit cell. The central Si−Si bonds of the two of them are, at 2.448(2)

---

[31] Matsumoto, H.; Sakamoto, A.; Nagai, Y. *J. Chem. Soc., Chem. Commun.* **1986**, 1768.

[32] Kuroda, M.; Kabe, Y.; Hashimoto, M.; Masamune, S. *Angew. Chem.* **1988**, *100*, 1795; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1725.

[33] Stanislawski, D. A.; West, R. *J. Organomet. Chem.* **1981**, *204*, 307.

[34] Kovar, D.; Utvary, K.; Hengge, E. *Monatsh. Chem.* **1979**, *110*, 1295.

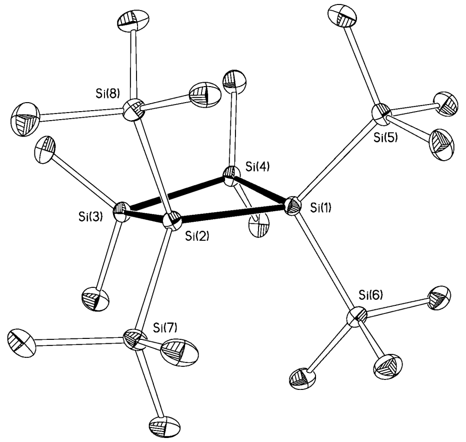


Figure 2. Molecular structure and numbering of **6** with 30% probability thermal ellipsoids. All hydrogens have been omitted for clarity. Selected bond lengths (Å) and bond angles (deg) with estimated standard deviations: Si(1)−Si(5), 2.3598(13); Si(1)−Si(6), 2.3633(13); Si(1)−Si(4), 2.3772(13); Si(1)−Si(2), 2.3940(13); Si(2)−Si(8), 2.3511(14); Si(2)−Si(7), 2.3604(13); Si(2)−Si(3), 2.3704(13); Si(3)−Si(4), 2.3630(13); Si(5)−Si(1)−Si(4), 114.98(5); Si(6)−Si(1)−Si(4), 110.29(5); Si(5)−Si(1)−Si(2), 120.76(5); Si(6)−Si(1)−Si(2), 113.80(5); Si(8)−Si(2)−Si(3), 110.71(5); Si(7)−Si(2)−Si(3), 113.20(5); Si(8)−Si(2)−Si(1), 112.66(5); Si(7)−Si(2)−Si(1), 121.65(5); Si(3)−Si(2)−Si(1), 89.09(4); Si(4)−Si(3)−Si(2), 90.05(4); Si(3)−Si(4)−Si(1), 89.67(4).

and 2.450(2) Å, explicitly elongated. The same can be observed for dianion **13**, for which an essentially identical Si−Si bond distance (2.4485(17) Å) was found (Figure 6). This is in contrast to the recently investigated compounds $(Me_3Si)_3SiSi(SiMe_3)_2K$ (Si(1)−Si(2) = 2.3745(11) Å) and $Ph(Me_3Si)_2SiSi(SiMe_3)_2K$ (Si(1)−Si(2) = 2.3677(17) Å),[14] which show a slight shortening of central Si−Si bonds. All 1,2-dianions exhibit anti conformations with torsion angles for the K−Si−Si−K arrangement ranging from 166.4 and 172.2° for the two independent molecules of **1** to 178.1° for **13**.

The X-ray diffraction analysis of **7** (Figure 3) showed different lengths of the Si−Si bonds in the three-membered ring. The distances between the $(Me_3Si)_2Si$ and the $(i\text{-}Pr)_2Si$ moieties (2.3311(15) and 2.3395(17) Å) are the shortest measured so far for cyclotrisilanes. The bond between the two $(Me_3Si)_2Si$ units is, at 2.3936(17) Å, about 0.04 Å longer than the distances in hexakis(trimethylsilyl)cyclotrisilane (2.351 Å).[35] However, if this distance is compared to the central bond in hexakis(trimethylsilyl)disilane,[18] it is found that this particular value is changing as a function of the cocrystallized solvent from 2.367 Å[18a] to 2.390 Å[18b] and 2.402 Å.[18c] Thus, our observed distance of 2.39 Å fits well into the expected range.

Compounds **6**, **10b**, and **11** were also subjected to single-crystal X-ray diffraction analysis (Figures 2, 4, and 5). **6** can be compared to octakis(trimethylsilyl)cyclotetrasilane,[24a] where the endocyclic Si−Si bonds are slightly elongated (2.405 Å), whereas the exocyclic bonds meet the expectations (2.37−2.38 Å) for ordinary Si−Si bond distances. The situation in **6** is quite comparable. The longest bond can be found between the two fully silyl substituted silicon atoms Si(1) and Si(2) (2.3940(13) Å). The other endocyclic Si−Si bond distances decrease with diminished silyl substitution, with the bond between the two dimethylsilylene groups being the shortest (2.3630(13) Å). Exocyclic Si−Si bonds in **6** range from 2.35 to 2.36 Å.

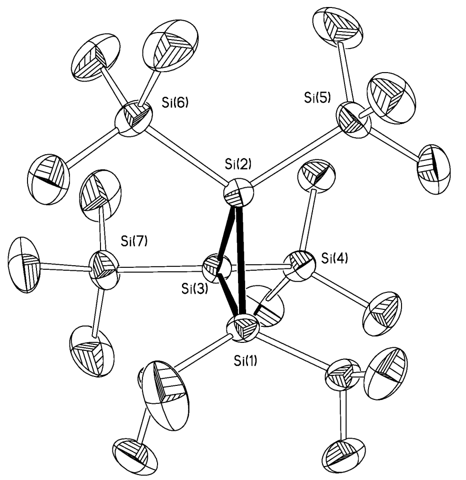


Figure 3. Molecular structure and numbering of **7** with 30% probability thermal ellipsoids. All hydrogens have been omitted for clarity. Selected bond lengths (Å) and bond angles (deg) with estimated standard deviations: Si(1)−Si(2), 2.3311(15); Si(1)−Si(3), 2.3395(17); Si(2)−Si(5), 2.3439(17); Si(2)−Si(6), 2.3507(17); Si(2)−Si(3), 2.3936(17); Si(3)−Si(7), 2.3383(18); Si(3)−Si(4), 2.3572(17); Si(2)−Si(1)−Si(3), 61.66(5); Si(1)−Si(2)−Si(3), 59.34(5); Si(1)−Si(3)−Si(2), 59.00(5).

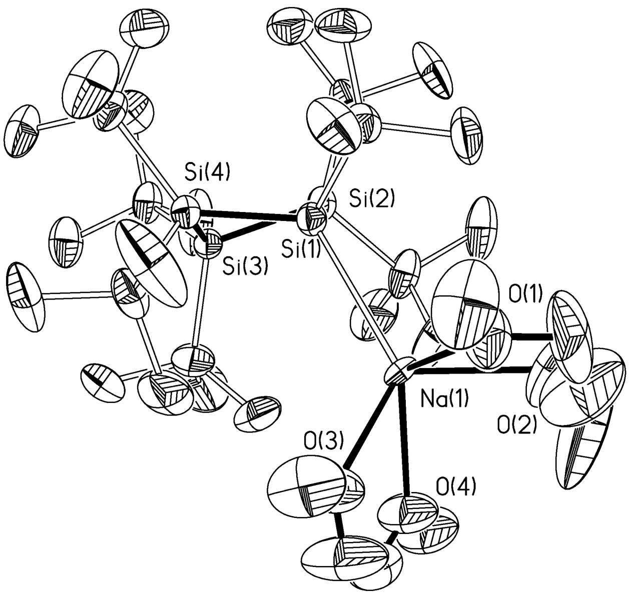


Figure 4. Molecular structure and numbering of **10b** with 30% probability thermal ellipsoids. All hydrogens have been omitted for clarity. Selected bond lengths (Å) and bond angles (deg) with estimated standard deviations: Na(1)−Si(1), 3.473(3); Si(1)−Si(5), 2.335(3); Si(1)−Si(2), 2.369(3); Si(1)−Si(4), 2.374(3); Si(2)−Si(6), 2.375(4); Si(2)−Si(7), 2.376(4); Si(2)−Si(3), 2.387(3); Si(3)−Si(9), 2.349(4); Si(3)−Si(8), 2.357(4); Si(3)−Si(4), 2.392(3); Si(4)−Si(11), 2.349(3); Si(4)−Si(10), 2.369(4); Si(1)−Si(2)−Si(3), 87.54(10); Si(2)−Si(3)−Si(4), 87.76(10); Si(1)−Si(4)−Si(3), 87.30(10); Si(2)−Si(1)−Si(4), 88.60(11).

As already found for the cases of $Ph(Me_3Si)_2SiSi(SiMe_3)_2K$ and $(Me_3Si)_3SiSi(SiMe_3)_2K$,[14] the introduction

---

(35) (a) Klinkhammer, K. W. In *Organosilicon Chemistry III: From Molecules to Materials*; Auner, N., Weis, J., Eds.; Wiley-VCH: Weinheim, Germany, 1998. (b) Structure CCDC 100906 in the Cambridge Crystallographic Data Centre.

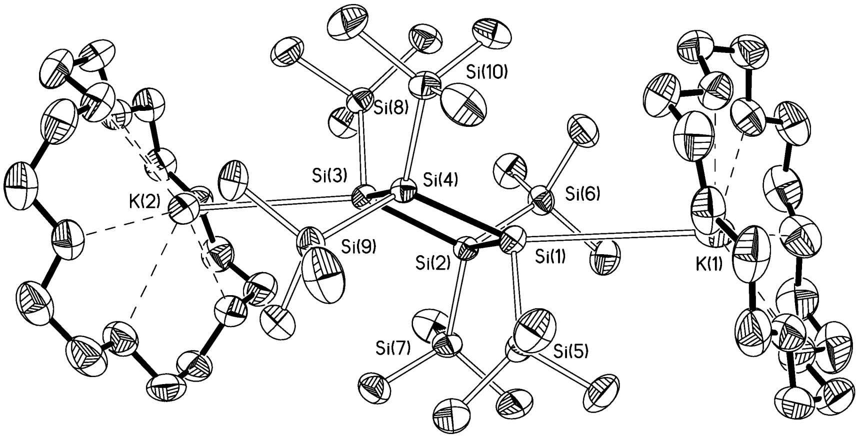


Figure 5. Molecular structure and numbering of **11** with 30% probability thermal ellipsoids. All hydrogens have been omitted for clarity. Selected bond lengths (Å) and bond angles (deg) with estimated standard deviations: K(1)−Si(1), 3.9413(18); K(2)−Si(3), 3.7203(17); Si(1)−Si(2), 2.3920(16); Si(1)−Si(4), 2.3925(13); Si(1)−Si(5), 2.3183(14); Si(2)−Si(7), 2.3444(13); Si(2)−Si(6), 2.3448(15); Si(2)−Si(3), 2.3867(13); Si(3)−Si(8), 2.3225(14); Si(3)−Si(4), 2.3858(16); Si(4)−Si(10), 2.3357(13); Si(4)−Si(9), 2.3435(15); Si(2)−Si(1)−Si(4), 83.26(5); Si(3)−Si(2)−Si(1), 96.55(5); Si(4)−Si(3)−Si(2), 83.52(5); Si(3)−Si(4)−Si(1), 96.57(5); Si(5)−Si(1)−K(1), 85.33(5); Si(8)−Si(3)−K(2), 89.33(5).

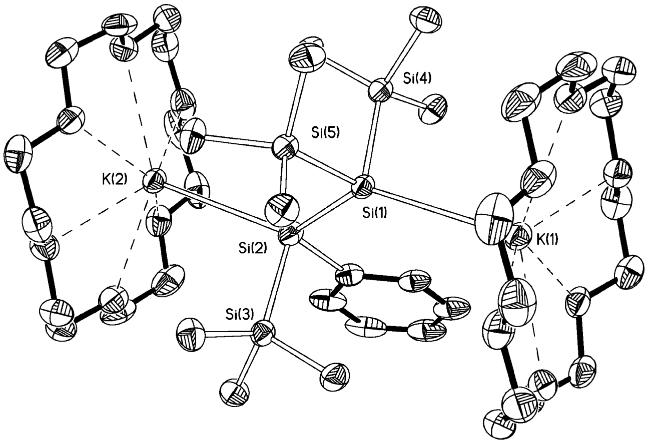


Figure 6. Molecular structure and numbering of **13** with 30% probability thermal ellipsoids. All hydrogens have been omitted for clarity. Selected bond lengths (Å) and bond angles (deg) with estimated standard deviations: K(1)−Si(1), 3.4790(16); K(2)−Si(2), 3.5895(16); Si(1)−Si(4), 2.3345(17); Si(1)−Si(5), 2.3411(17); Si(1)−Si(2), 2.4485(17); Si(2)−Si(3), 2.3550(19); Si(4)−Si(1)−Si(5), 99.31(6); Si(4)−Si(1)−Si(2), 96.21(6); Si(5)−Si(1)−Si(2), 101.99(6); Si(4)−Si(1)−K(1), 108.47(5); Si(5)−Si(1)−K(1), 109.58(5); Si(2)−Si(1)−K(1), 135.43(6); Si(3)−Si(2)−Si(1), 99.46(6); Si(3)−Si(2)−K(2), 106.32(5); Si(1)−Si(2)−K(2), 133.63(6).

of a negative charge onto a silicon atom induces a shortening of bond lengths to attached silyl substituents. This effect can also be observed for compounds **10b** and **11**. In comparison to octakis(trimethylsilyl)cyclotetrasilane[24a] we find for **10b** that the endocyclic Si−Si distances connected to the metalated atom are shortened to 2.369(3) and 2.374(3) Å. The remaining endocyclic bond distances correspond to 2.387(3) and 2.392(3) Å. All exocyclic Si−Si bond lengths in **10b** are comparably short, with the trimethylsilyl group attached to the metalated silicon atom being the shortest distance (2.335(3) Å).

The introduction of a negative charge onto a ring atom, as in **10b**, causes a folding of the previously planar ring by 31°. The introduction of another negative charge at the 1,3-position (**11**) almost restores planarity again. Only a slight folding of 3.2° can be observed.

For **11** a picture similar to that for **10b** was found. While the shortening of the endocyclic bond distances is not as pronounced, we find that all exocyclic Si−Si bonds are comparably short, with the two trimethylsilyl groups connected to the negatively charged silicon atoms exhibiting especially short Si−Si bond distances of 2.3183(14) and 2.3225(14) Å.

The distances between the negatively charged silicon atoms and the potassium ion of compounds **1** (3.477(2), 3.4890(16) Å) and **13** (3.4790(2), 3.5895(16) Å) are within the range of what we have observed so far for oligosilyl potassium crown ether adducts.[9,14] The situation is somewhat different for **11**. The distances of 3.9413(18) and 3.7203(17) Å are significantly longer. The reason for this may be some steric interaction of the crown ethers with the trimethylsilyl groups of the ring. The same is true for the silylsodium compound **10b**, which exhibits a Si−Na distance of 3.473(3) Å. This is almost 0.5 Å longer compared to what usually is found.[15a,36] Again the likely explanation seems to be interaction of the donor molecules (DME) with the trimethylsilyl groups extending from the ring.

Conclusion. We have developed a simple approach to 1,2-dipotassiodisilanes by reaction of precursors such as hexakis(trimethylsilyl)disilane with potassium *tert*-butyl alcoholate in the presence of crown ether. These 1,2-dianions can be used not only as masked disilenes but also as 1,2-dinucleophiles, permitting access to a number of small homo- and heterocyclosilanes. Applying the conditions for the formation of the dianions to octakis(trimethylsilyl)cyclotetrasilane led to the formation of *trans*-1,3-dipotassiohexakis(trimethylsilyl)cyclotetrasilane.

3. Experimental Section

All reactions were carried out under an atmosphere of dry argon or nitrogen. Solvents were dried over sodium/potassium alloy and distilled freshly before use. Potassium *tert*-butyl alcoholate was purchased from Merck, and 18-crown-6 was

---

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

Table 2. Crystallographic Data for Compounds 1, 10b, 11, and 13

	1	**10b**	**11**	**13**
empirical formula	$K_2O_{12}Si_6C_{48}H_{94}$	$NaO_4Si_{11}C_{29}H_{83}$	$K_2O_{12}Si_{10}C_{48}H_{108}$	$K_2O_{12}Si_5C_{39}H_{80}$
M_w	1109.97	827.93	1236.44	959.68
temp (K)	200(2)	213(2)	150(2)	200(2)
size (mm)	0.60 × 0.40 × 0.15	0.38 × 0.28 × 0.22	0.42 × 0.40 × 0.20	0.40 × 0.38 × 0.30
cryst syst	monoclinic	orthorhombic	triclinic	orthorhombic
space group	$P2_1/c$	$Pna2_1$	$P\bar{1}$	$Pbca$
a (Å)	24.621(5)	12.984(3)	12.577(3)	20.389(4)
b (Å)	39.049(8)	18.681(4)	15.503(3)	35.761(7)
c (Å)	14.417(3)	22.816(5)	20.319(4)	15.244(3)
α (deg)	90	90	80.16(3)	90
β (deg)	105.29(3)	90	72.47(3)	90
γ (deg)	90	90	71.57(3)	90
V (Å^3)	13370(5)	5534.3(19)	3571.7(12)	11115(4)
Z	4	4	2	8
ρ_{calcd} (g cm^{-3})	1.103	0.994	1.150	1.147
abs coeff (mm^{-1})	0.297	0.292	0.348	0.327
F(000)	4800	1816	1340	4144
θ range (deg)	0.86−24.71	1.41−24.71	1.05−24.71	1.76−26.37
no. of rflns collected/unique	64 966/22 717	37 066/9400	24 942/12 032	84 549/11 338
completeness to θ (%)	99.7	99.9	98.7	99.8
abs cor	empirical	empirical	empirical	empirical
no. of data/restraints/params	22 717/0/1249	9400/1/431	12 032/0/667	11 338/0/532
goodness of fit on F^2	0.954	1.033	1.032	1.084
final R indices ($I > 2\sigma(I)$)	R1 = 0.0830, wR2 = 0.1838	R1 = 0.0894, wR2 = 0.2032	R1 = 0.0645, wR2 = 0.1584	R1 = 0.0807, wR2 = 0.1462
R indices (all data)	R1 = 0.1719, wR2 = 0.2280	R1 = 0.1461, wR2 = 0.2370	R1 = 0.0868, wR2 = 0.1739	R1 = 0.1333, wR2 = 0.1662
largest diff peak/hole (e/Å^3)	0.468/−0.286	0.903/−0.228	1.017/−0.456	0.353/−0.206

used as purchased from Fluka. All other chemicals were used as received from chemical suppliers.

^{1}H (300 MHz), ^{13}C (75.4 MHz), and ^{29}Si (59.3 MHz) NMR spectra were recorded on a Varian Unity INOVA 300 spectrometer. Samples for ^{29}Si spectra were either dissolved in deuterated solvents or, in the cases of reaction samples, measured with a D_2O capillary in order to provide an external lock frequency signal. To compensate for the low isotopic abundance of ^{29}Si, the INEPT pulse sequence was used for the amplification of the signal.[37] The completeness of the reactions was usually controlled by NMR spectroscopy. For X-ray structure analysis, crystals were mounted onto the tip of a glass fiber, and data collection was performed with a Bruker-AXS SMART APEX CCD diffractometer (wavelength 0.710 73 Å). The data were reduced to F_o^2 and corrected for absorption effects with SAINT[38] and SADABS,[39] respectively. The structures were solved by direct methods and refined by full-matrix least-squares methods (SHELXL97).[40] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in calculated positions to correspond to standard bond lengths and angles. Crystallographic data can be found in Tables 2 and 3. More detailed information on all structures can be found in the Supporting Information. All data have been deposited at the Cambridge Crystallographic Deposition Centre: CCDC 211904 (**1**), CCDC 216727 (**6**), CCDC 211905 (**7**), CCDC 211903 (**10b**), CCDC 211906 (**11**), CCDC 216726 (**13**). The data can be retrieved via www.ccdc.cam.ac.uk/conts/retrieving.html or can be ordered at the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ (fax (+44) 1223-336-033). Pentakis(trimethylsilyl)phenyldisilane[14] and octakis(trimethylsilyl)cyclotetrasilane[26] have been prepared following previously published procedures.

No satisfactory elemental analyses of the silylpotassium compounds could be obtained. This is in accordance with our own previous observations and also those of other authors which report similar problems with alkali-metal silyl compounds.[15a,41]

Table 3. Crystallographic Data for Compounds 6 and 7

	6	**7**
empirical formula	$Si_8C_{16}H_{48}$	$Si_7C_{18}H_{50}$
M_w	465.26	463.21
temp (K)	100(2)	100(2)
size (mm)	0.45 × 0.35 × 0.02	0.65 × 0.35 × 0.30
cryst syst	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
a (Å)	10.766(2)	10.191(2)
b (Å)	9.767(2)	10.399(2)
c (Å)	29.098(6)	17.531(3)
α (deg)	90	83.09(3)
β (deg)	96.96(3)	85.08(3)
γ (deg)	90	60.68(3)
V (Å^3)	3037.2(11)	1607.4(6)
Z	4	2
ρ_{calcd} (g cm^{-3})	1.017	0.957
abs coeff (mm^{-1})	0.355	0.300
F(000)	1024	512
θ range (deg)	2.20−24.71	1.17−23.26
no. of rflns collected/unique	14 261/5155	9358/4454
completeness to θ (%)	99.5	96.3
abs cor	empirical	empirical
no. of data/restraints/params	5155/0/233	4454/0/242
goodness of fit on F^2	0.948	1.002
final R indices ($I > 2\sigma(I)$)	R1 = 0.0489, wR2 = 0.0884	R1 = 0.0553, wR2 = 0.1288
R indices (all data)	R1 = 0.0810, wR2 = 0.0985	R1 = 0.0850, wR2 = 0.1450
largest diff peak/hole (e/Å^3)	0.391/−0.262	0.274/−0.191

1,2-Dipotassio-1,1,2,2-tetrakis(trimethylsilyl)disilane 18-Crown-6 Adduct (1). To a solution of 1,1,1,2,2,2-hexakis(trimethylsilyl)disilane (1.00 g, 2.02 mmol) in benzene (10 mL) were added potassium *tert*-butyl alcoholate (464 mg,

---

[37] (a) Morris, G. A.; Freeman, R. *J. Am. Chem. Soc.* **1979**, *101*, 760. (b) Helmer, B. J.; West, R. *Organometallics* **1982**, *1*, 877.

[38] *SAINTPLUS: Software Reference Manual*, Version 5.054; Bruker-AXS: Madison, WI, 1997−1998.

[39] Blessing, R. H. *Acta Crystallogr., Sect A* **1995**, *51*, 33−38. SADABS; Bruker AXS, Madison, WI, 1998.

[40] Sheldrick, G. M. SHELX97 Programs for Crystal Structure Analysis (Release 97-2); Universität Göttingen, Göttingen, Germany, 1998.

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

4.14 mmol) and 18-crown-6 (1.09 g, 4.14 mmol). The reaction mixture turned red, and the product precipitated within 12 h at room temperature as highly air and moisture sensitive red crystals (1.85 g, 96%). Mp: >200 °C dec. NMR data (δ in ppm): ^{1}H (C_6D_6) 3.39 (s, 48H, CH_2O), 0.62 (s, 36H, $(CH_3)_3Si$); ^{13}C (C_6D_6) 70.3 (CH_2O), 8.9 (*Me*$_3$Si); ^{29}Si (C_6D_6) −5.4 (Me$_3$*Si*), −183.4 (*Si*K).

Magnesium Adduct of the 1,1,2,2-Tetrakis(trimethylsilyl)disilanyl 1,2-Dianion (2). To a solution of **1** (0.52 mmol) in THF (5 mL) was added magnesium bromide etherate (135 mg, 1.00 equiv). The solution turned from red to yellow, and KBr precipitated. After it was stirred for 1 h, the mixture was filtered, the solvent was removed, and **2** was obtained as an off-white solid (210 mg, 78%). NMR data (δ in ppm): ^{1}H (100 μL of C_6D_6/600 μL of THF-d_8) 0.31 (s, 36H, $(CH_3)_3Si$); ^{13}C (100 μL of C_6D_6/600 μL of THF-d_8) 6.7 (*Me*$_3$Si); ^{29}Si (100 μL of C_6D_6/600 μL of THF-d_8) −8.2 (Me$_3$*Si*), −162.8 (*Si*Mg).

Reactions of Compound 2. (a) 1,1,2,2-Tetrakis(trimethylsilyl)disilane (3). To an ice-cooled stirred mixture of diethyl ether (10 mL) and 2 M H_2SO_4 (10 mL) was added dropwise a solution of **2** (250 mg, 0.48 mmol) in THF (5 mL). After complete addition the reaction mixture was allowed to come to room temperature. The layers were separated, and the organic layer was dried over Na_2SO_4. After removal of the solvent **3** was obtained as a colorless oil (162 mg, 96%). NMR data (δ in ppm): ^{1}H (C_6D_6) 2.75 (s, 2H, Si−*H*, $^{1}J_{Si-H}$ = 155 Hz), 0.29 (s, 36H, $(CH_3)_3Si$); ^{13}C (C_6D_6) 1.6 (*Me*$_3$Si); ^{29}Si (C_6D_6) −11.5 (Me$_3$*Si*), −118.4 (*Si*−H). MS (70 eV; *m*/*z* (%)): 335 (1) $[M^+ - Me]$, 276 (46) $[M^+ - SiMe_3H]$, 261 (30) $[M^+ - SiMe_4H]$, 202 (100) $[M^+ - Si_2Me_6H_2]$, 187 (15) $[M^+ - Si_2Me_7H_2]$, 157 (26) $[Si_4Me_3^+]$, 73 (63) $[SiMe_3^+]$.

(b) 1,1,2,2-Tetrakis(trimethylsilyl)-1,2-(dimethylphenylsilyl)disilane (5). To a solution of **2** (1.61 mmol) in THF (15 mL) was added dimethylphenylchlorosilane (555 mg, 3.25 mmol). After it was stirred for 10 h at room temperature, the mixture was treated with 2 M H_2SO_4 (10 mL) and extracted three times with diethyl ether (3 × 10 mL); then the organic layers were dried over Na_2SO_4. After removal of the solvent the residue was recrystallized from acetone and **5** was obtained as colorless crystals (918 mg, 92%). Mp: 154−156 °C. NMR data (δ in ppm): ^{1}H ($CDCl_3$) 7.60 (m, 4H, Ar), 7.40 (m, 6H, Ar), 0.24 (s, 12H, Ph$(CH_3)_2$Si), 0.24 (s, 36H, $(CH_3)_3Si$); ^{13}C ($CDCl_3$) 141.7 (Ar), 135.2 (Ar), 128.9 (Ar), 127.7 (Ar), 4.9 (Si*Me*$_3$), 3.5 (Si*Me*$_2$); ^{29}Si ($CDCl_3$) −9.1 (*Me*$_3$*Si*), −12.5 (Ph*Me*$_2$*Si*), −124.8 ((Me$_3$Si)$_2$*Si*). Anal. Calcd for $C_{28}H_{58}Si_8$: C, 54.29; H, 9.44. Found: C, 53.91; H, 9.23.

(c) 1,1,2,2-Tetrakis(trimethylsilyl)-3,3,4,4-tetramethylcyclotetrasilane (6). Using a procedure analogous to that for the synthesis of **5**, in situ prepared **2** (0.52 mmol) in THF (5 mL) was treated with 1,2-dibromotetramethyldisilane (135 mg, 0.52 mmol) in toluene (5 mL). After aqueous workup, extraction with toluene was followed by recrystallization from diethyl ether. Colorless crystals of **6** were obtained (228 mg, 95%). Mp: 238−241 °C. NMR data (δ in ppm): ^{1}H (C_6D_6) 0.48 (s, 12H, $(CH_3)_2Si$), 0.37 (s, 36H, $(CH_3)_3Si$); ^{13}C (C_6D_6) 3.9 (*Me*$_3$Si), −1.1 (*Me*$_2$Si); ^{29}Si (C_6D_6) −8.6 (Me$_2$*Si*), −9.7 (*Me*$_3$*Si*), −114.0 ((Me$_3$Si)$_2$*Si*). MS (70 eV; *m*/*z* (%)): 464 (24) $[M^+]$, 449 (2) $[M^+ - Me]$, 391 (46) $[M^+ - SiMe_3]$, 317 (13) $[M^+ - Si_2Me_6H]$, 259 (23) $[M^+ - Si_3Me_8H]$, 243 (42) $[M^+ - Si_3Me_9H_2]$, 199 (18) $[M^+ - Si_4Me_{10}H_3]$, 131 (12) $[Si_2Me_5^+]$, 73 (63) $[SiMe_3^+]$. Anal. Calcd for $C_{16}H_{48}Si_8$: C, 41.31; H, 10.40. Found: C, 41.13; H, 10.48.

(d) 1,1,2,2-Tetrakis(trimethylsilyl)-3,3-diisopropylcyclotrisilane (7). To a solution of **2** (0.52 mmol) in THF (15 mL) was added dichlorodiisopropylsilane (97 mg, 0.52 mmol). The solution almost immediately decolorized. After it was stirred for 4 h at room temperature, the mixture was filtered, the solvent was removed, and **7** was obtained after recrystallization from diethyl ether as a colorless solid (220 mg, 92%). Mp: 188−190 °C. NMR data (δ in ppm): ^{1}H (C_6D_6) 1.44 (d, 12H, $(CH_3)_2CHSi$, $^{3}J_{H-H}$ = 7.5 Hz), 1.14 (heptet, 2H, $(CH_3)_2CH$Si, $^{3}J_{H-H}$ = 7.5 Hz), 0.39 (s, 36H, $(CH_3)_3Si$); ^{13}C (C_6D_6) 23.1 ($(CH_3)_2CHSi$), 17.2 ($(CH_3)_2CHSi$), 3.7 (*Me*$_3$Si); ^{29}Si (C_6D_6) −7.4 (*Me*$_3$*Si*), −35.3 (*iso*-Pr$_2$ *Si*) −171.7 ((Me$_3$Si)$_2$*Si*). MS (70 eV; *m*/*z* (%)): 462 (26) $[M^+]$, 388 (18) $[M^+ - SiMe_3H]$, 332 (38) $[M^+ - i\text{-}Pr_2MeSiH]$, 303 (43) $[M^+ - Si_3Me_5]$, 259 (27) $[M^+ - i\text{-}PrSi_3Me_5H]$, 73 (100) $[SiMe_3^+]$. Anal. Calcd for $C_{18}H_{50}Si_7$: C, 46.67; H, 10.88. Found: C, 46.51; H, 10.91.

1-Potassio-4-*tert*-butoxy-1,1,2,2-tetrakis(trimethylsilyl)-3,3,4,4-tetramethyltetrasilane 18-Crown-6 Adduct (9). A mixture containing **6** (100 mg, 0.22 mmol), potassium *tert*-butyl alcoholate (24 mg, 0.22 mmol), and 18-crown-6 (57 mg, 0.22 mmol) was dissolved in benzene (2 mL). After 3 h the solvent was removed and **9** was obtained as a yellow oil. NMR data (δ in ppm): ^{1}H (C_6D_6) 3.25 (s, 24H, CH_2O), 1.34 (s, 9H, $(CH_3)_3C$), 0.68 (s, 6H, $(CH_3)_2Si$), 0.67 (s, 18H, $(CH_3)_3Si$), 0.66 (s, 18H, $(CH_3)_3Si$), 0.14 (s, 6H, $(CH_3)_2Si$); ^{13}C (C_6D_6) 73.1 (Me$_3$*C*O), 70.0 (CH_2O), 32.5 (*Me*$_3$CO), 9.2 (*Me*$_3$Si), 5.0 (*Me*$_2$Si), 4.9 (*Me*$_3$Si), 0.5 (*Me*$_2$Si); ^{29}Si (C_6D_6) 9.1 (Me$_3$CO*Si*), −6.4 ((Me$_3$*Si*)$_2$SiK), −10.8 ((Me$_3$*Si*)$_2$Si), −41.9 (Me$_2$*Si*), −120.8 ((Me$_3$Si)$_2$*Si*), −186.4 ((Me$_3$Si)$_2$*Si*K).

Reactions of 8 with Potassium (10a, 11) or Sodium (10b) *tert*-Butyl Alcoholates. (a) 1-Potassio-1,2,2,3,3,4,4-heptakis(trimethylsilyl)cyclotetrasilane 18-Crown-6 Adduct (10a). By the same procedure as for the synthesis of **9**, **8** (100 mg, 0.14 mmol) was treated with potassium *tert*-butyl alcoholate (16 mg, 0.14 mmol) and 18-crown-6 (37 mg, 0.14 mmol). **10a** was obtained as red crystals (125 mg, 96%). NMR data (δ in ppm): ^{1}H (C_6D_6/THF-d_8) 3.49 (s, 24H, CH_2O), 0.38 (s, 18H, $(CH_3)_3Si$), 0.34 (s, 36H, $(CH_3)_3Si$), 0.24 (s, 9H, $(CH_3)_3Si$); ^{13}C (C_6D_6/THF-d_8) 70.3 (CH_2O), 6.0 ((*Me*$_3$Si)SiK), 4.3 ((*Me*$_3$Si)$_2$Si), 3.8 ((*Me*$_3$Si)$_2$Si); ^{29}Si (C_6D_6/THF-d_8) −10.3 ((Me$_3$*Si*)SiK), −12.4 ((Me$_3$*Si*)$_2$Si), −13.0 ((Me$_3$*Si*)$_2$Si), −95.6 ((Me$_3$Si)$_2$*Si*), −101.1 ((Me$_3$Si)$_2$*Si*), −156.7 ((Me$_3$Si)*Si*K).

(b) 1-Sodio-1,2,2,3,3,4,4-heptakis(trimethylsilyl)cyclotetrasilane Dimethoxyethane Adduct (10b). Sodium *tert*-butyl alcoholate (14 mg, 0.14 mmol) and **8** (100 mg, 0.14 mmol) were dissolved in DME (0.60 mL). After 2 h the mixture was cooled to −35 °C and yellow crystals of **10b** precipitated. NMR data (δ in ppm): ^{1}H (C_6D_6/DME) 3.25 (s, 8H, CH_2O), 3.09 (s, 12H, CH_3O), 0.26 (s, 18H, $(CH_3)_3Si$), 0.21 (s, 36H, $(CH_3)_3Si$), −0.06 (s, 9H, $(CH_3)_3SiNa$); ^{13}C (C_6D_6/DME) 71.8 (CH_2O), 58.1 (CH_3O), 6.1 ((*Me*$_3$Si)SiNa), 4.4 ((*Me*$_3$Si)$_2$Si), 3.9 ((*Me*$_3$Si)$_2$Si); ^{29}Si (C_6D_6/DME), −10.3 ((Me$_3$*Si*)SiNa), −12.4 ((Me$_3$*Si*)$_2$Si), −13.0 ((Me$_3$*Si*)$_2$Si), −95.5 ((Me$_3$Si)$_2$*Si*), −101.1 ((Me$_3$Si)$_2$*Si*), −156.7 ((Me$_3$Si)*Si*Na).

(c) 1,3-Dipotassio-1,2,2,3,4,4-hexakis(trimethylsilyl)cyclotetrasilane 18-Crown-6 Adduct (11). Potassium *tert*-butyl alcoholate (32 mg, 0.29 mmol), **8** (100 mg, 0.14 mmol), and 18-crown-6 (76 mg, 0.29 mmol) were dissolved in benzene (2 mL). Red crystals of **11** were obtained after 24 h at room temperature (158 mg, 98%). NMR data (δ in ppm): ^{1}H (C_6D_6/THF-d_8) 3.53 (s, 48H, CH_2O), 0.28 (s, 36H, $(CH_3)_3Si$), 0.17 (s, 18H, $(CH_3)_3Si$); ^{13}C (C_6D_6/THF-d_8) 70.4 (CH_2O), 6.8 ((*Me*$_3$Si)SiK), 3.2 ((*Me*$_3$Si)$_2$Si); ^{29}Si (C_6D_6/THF-d_8) −11.8 ((Me$_3$*Si*)SiK), −14.3 ((Me$_3$*Si*)$_2$Si), −115.8 ((Me$_3$Si)$_2$*Si*), −166.5 ((Me$_3$Si)*Si*K).

1,2-Dipotassio-1,1,2-tris(trimethylsilyl)-2-phenyldisilane 18-Crown-6 Adduct (13). 1,1,1,2,2-Pentakis(trimethylsilyl)-2-phenyldisilane[14] (250 mg, 0.50 mmol), potassium *tert*-butyl alcoholate (112 mg, 1.0 mmol), and 18-crown-6 (264 mg, 1.0 mmol) were dissolved in benzene (4 mL). Upon standing for 24 h, the solution turned deep red. Upon addition of *n*-pentane **13** precipitated at room temperature as deep red crystals (426 mg, 89%). NMR data (δ in ppm): ^{1}H (C_6D_6) 8.42 (m, 2H, Ar), 7.13 (m, 3H, Ar), 3.23 (s, 24H, CH_2O), 0.75 (s, 18H, $(CH_3)_3Si$), 0.69 (s, 9H, $(CH_3)_3Si$). ^{13}C (C_6D_6) 169.4 (Ar), 139.1 (Ar), 124.3 (Ar), 119.2 (Ar), 70.1 (CH_2O), 8.8 ((*Me*$_3$Si)$_2$Si), 5.8 (*Me*$_3$Si); ^{29}Si (C_6D_6) −5.0 ((Me$_3$*Si*)$_2$SiK), −10.5 ((Me$_3$*Si*)SiPh), −81.8 (*Si*Ph), −176.9 (*Si*K). Acidic hydrolysis derivative: MS (70 eV; *m*/*z* (%)): 324 (13) $[M^+]$, 251 (8) $[M^+ - SiMe_3]$, 236 (10) [$\mathrm{M}^+ - \mathrm{SiMe}_4$], 174 (80) [$(\mathrm{SiMe}_3)_2\mathrm{Si}^+$], 159 (30) [$\mathrm{SiMe}_3\mathrm{SiSiMe}_2{}^+$], 135 (64) [$\mathrm{PhMe}_2\mathrm{Si}^+$], 105 (11) [$\mathrm{PhSi}^+$], 73 (100) [$\mathrm{SiMe}_3{}^+$]

1,1,2,2-Tetrakis(trimethylsilyl)-1,2-diphenyldisilane (14). A solution of potassium bis(trimethylsilyl)phenylsilane[14] (20 g, 68.8 mmol) in diethyl ether (200 mL) was cooled to −80 °C. Within 1.5 h a solution of 1,2-dibromoethane (13.1 g, 70.0 mmol) in diethyl ether (50 mL) was added. During the addition a white precipitate was formed and ethene evolution was observed. After complete addition the reaction mixture was stirred for 2 h at −80 °C and then for 12 h at room temperature before trimethylchlorosilane (2 mL) was added. The reaction mixture was subjected to an aqueous workup with diethyl ether/2 M $\mathrm{H_2SO_4}$. The solvent was removed, and **14** was obtained after Kugelrohr distillation (0.02 mbar, 160 °C) as a colorless, waxy solid (13.2 g, 75%). NMR data (δ in ppm): ^{1}H ($\mathrm{C_6D_6}$) 7.63 (m, 4H, Ar), 7.14 (m, 6H, Ar), 0.26 (s, 36H, $(\mathrm{C}\mathit{H}_3)_3\mathrm{Si}$); ^{13}C ($\mathrm{C_6D_6}$) 137.6 (Ar), 136.2 (Ar), 128.2 (Ar), 128.0 (Ar), 2.1(*Me*$_3$Si); ^{29}Si ($\mathrm{C_6D_6}$) −12.1 (Me$_3$*Si*), −70.8 (*Si*Ph). MS (70 eV; *m*/*z* (%)): 352 (12) [$\mathrm{M}^+ - \mathrm{SiMe}_3\mathrm{Ph}$], 278 (72) [$\mathrm{M}^+ - \mathrm{Si}_2\mathrm{Me}_6\mathrm{PhH}$], 251 (24) [$\mathrm{M}^+ - \mathrm{Si}_3\mathrm{Me}_6\mathrm{Ph}$], 135 (69) [$\mathrm{Me}_2\mathrm{PhSi}^+$], 73 (100) [$\mathrm{SiMe}_3{}^+$].

Reaction of 14 with Potassium *tert*-Butyl Alcoholate. (a) 1-Potassio-1,2,2-tris(trimethylsilyl)-1,2-diphenyldisilane 18-Crown-6 Adduct (15). 1,2-Diphenyl-1,1,2,2-tetrakis(trimethylsilyl)disilane (200 mg, 0.40 mmol), potassium *tert*-butyl alcoholate (45 mg, 0.40 mmol), and 18-crown-6 (106 mg, 0.40 mmol) were dissolved in toluene (2 mL). After complete dissolution a bright orange reaction mixture was obtained, from which **15** precipitated as orange crystals (274 mg, 94% yield) upon addition of 5 mL of *n*-pentane and cooling to −35 °C. NMR data (δ in ppm): ^{1}H ($\mathrm{C_6D_6}$) 8.17 (m, 2H, *Ar*), 7.98 (m, 2H, *Ar*), 7.21 (m, 4H, *Ar*), 7.06 (m, 1H, *Ar*), 6.96 (m, 1H, *Ar*), 3.16 (s, 24H, $\mathrm{C}\mathit{H}_2\mathrm{O}$), 0.57 (s, 9H, $(\mathrm{C}\mathit{H}_3)_3\mathrm{Si}$), 0.51 (s, 18H, $(\mathrm{C}\mathit{H}_3)_3\mathrm{Si}$); ^{13}C ($\mathrm{C_6D_6}$) 157.7 (*Ar*), 147.7 (*Ar*), 138.6 (*Ar*), 138.0 (*Ar*), 126.7 (*Ar*), 125.9 (*Ar*), 125.6 (*Ar*), 122.3 (*Ar*), 70.0 ($\mathit{C}\mathrm{H}_2\mathrm{O}$), 5.5 (*Me*$_3$Si)SiK, 2.8 (*Me*$_3$Si)$_2$Si; ^{29}Si ($\mathrm{C_6D_6}$) −10.0 ((Me$_3$*Si*)PhSiK), −13.3 ((Me$_3$*Si*)$_2$SiPh), −64.6 (*Si*Ph), −93.6 (*Si*K). Acidic hydrolysis derivatives: MS (70 eV; *m*/*z* (%)) 430 (3) [M^+], 356 (17) [$\mathrm{M}^+ - \mathrm{SiMe}_3\mathrm{H}$], 297 (8) [$\mathrm{M}^+ - \mathrm{SiMe}_5\mathrm{H}_2$], 282 (53) [$\mathrm{M}^+ - \mathrm{SiMe}_6\mathrm{H}_2$], 220 (100) [$\mathrm{M}^+ - \mathrm{PhSi}_2\mathrm{Me}_5$], 206 (96) [$\mathrm{M}^+ - \mathrm{PhSi}_2\mathrm{Me}_6\mathrm{H}$], 135 (89) [$\mathrm{SiMe}_2\mathrm{Ph}^+$], 73 (67) [$\mathrm{SiMe}_3{}^+$].

(b) 1,2-Dipotassio-1,2-bis(trimethylsilyl)-1,2-diphenyldisilane 18-Crown-6 Adduct (16). **14** (250 mg, 0.50 mmol), potassium *tert*-butyl alcoholate (112 mg, 1.0 mmol), and 18-crown-6 (264 mg, 1.0 mmol) were dissolved in benzene (4 mL), giving a clear deep red reaction mixture. After 24 h *n*-pentane was added until the solution became cloudy. A vial filled with *n*-pentane was placed into the reaction vessel, to induce the growth of crystals by gas-phase diffusion. **16** was obtained as deep red crystals (918 mg, 95%). NMR data (δ in ppm): ^{1}H ($\mathrm{C_6D_6}$) 8.16 (m, 4H, Ar), 7.02 (m, 4H, Ar), 6.87 (m, 2H, Ar), 3.28 (s, 48H, $\mathrm{C}\mathit{H}_2\mathrm{O}$), 0.76 (s, 18H, $(\mathrm{C}\mathit{H}_3)_3\mathrm{Si}$); ^{13}C ($\mathrm{C_6D_6}$) 169.4 (Ar), 137.4 (Ar), 125.1 (Ar), 117.8 (Ar), 70.1 ($\mathit{C}\mathrm{H}_2\mathrm{O}$), 6.3 (*Me*$_3$Si; ^{29}Si ($\mathrm{C_6D_6}$) −11.8 (Me$_3$*Si*), −77.2 (*Si*K). Acidic hydrolysis derivative (2 isomers with virtually identical MS fragmentation pattern), one isomer: MS (70 eV; *m*/*z* (%)) 358 (22) [M^+], 284 (51) [$\mathrm{M}^+ - \mathrm{SiMe}_3\mathrm{H}$], 239 (100) [$\mathrm{M}^+ - \mathrm{SiC}_7\mathrm{H}_7$], 206 (32) [$\mathrm{M}^+ - \mathrm{SiMe}_3\mathrm{PhH}_2$], 163 (41) [$\mathrm{Si}_2\mathrm{Me}_2\mathrm{Ph}^+$], 135 (76) [$\mathrm{SiMe}_2\mathrm{Ph}^+$], 105 (57) [$\mathrm{SiPh}^+$], 73 (52) [$\mathrm{SiMe}_3{}^+$].

Acknowledgment. This study was supported by the Austrian Science Foundation (FWF) and the START project *Chiral polysilanes* (Y120), funded by the Austrian Ministry of Education, Science, and Culture.

Supporting Information Available: Tables giving crystallographic data for **1**, **6**, **7**, **10b**, **11**, and **13**; these data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

OM034396+