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Articles

Tailor-made Oligosilyl Potassium Compounds

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A number of differently substituted oligosilyl potassium compounds have been prepared by reaction of the respective trimethylsilylated precursors with potassium *tert*-butoxide. It has been demonstrated that in the presence of larger trialkylsilyl groups always trimethylsilyl groups are removed selectively. This selectivity enables the syntheses of oligosilylanions with different sterical demand. By transmetalation of the oligosilyl potassium compounds with halides of less electropositive metals also the reactivity of the silyl anions can be controlled.

Introduction

The chemistry of silicon is due to its electropositive character dominated by electrophilic silicon species. Nevertheless, also the silicon congeners of carbanions are known and of synthetic value. These silyl anions now constitute a rapidly growing area of organosilicon chemistry.[1] However, research concentrates mainly on monosilyl anions. A survey of known oligosilyl anions shows that only tris(trimethylsilyl)silyllithium enjoys a peculiar popularity. Since the tris(trimethylsilyl)silyl group is able to kinetically stabilize a huge number of otherwise unstable structural types in transition metal[2] and main group[3] chemistry, this is not surprising. However, even considering all the merits of this group, the possibility of sterical[4] and electronical tuning would be highly desirable. Apeloig et al. for example have shown that the replacement of one trimethylsilyl by a *tert*-butyldimethylsilyl group in the sila-Peterson reaction of adamantanone with tris(trimethylsilyl)silyllithium leads to the formation of stable silenes.[5] For these reasons it is astonishing that almost no studies so far have addressed the systematic variation of the tris(trimethylsilyl)silyl anion. After the landmark studies of Gilman et al. on oligosilyllithium compounds[6] only very recently have investigations in this direction been resumed.[7,8]

In this connection we have reported the syntheses of oligosilyl potassium compounds by reaction of suitable trimethylsilylated precursors with potassium *tert*-butoxide.[8] As our studies continue, we wish to report on the selective synthesis of oligosilyl anions with different steric demand and reactivity as well as some mechanistic insight into the reaction.

Results and Discussion

Isotetrasilanyl Potassiums of Different Steric Demand. We have reported that tris(trimethylsilyl)silyl potassium[9] can easily be silylated with phenylated silylchorides ($Me_{3-n}Ph_nSiCl$, $n = 0-3$) (**1**−**3**).[8] In addition also the sterically demanding triisopropylsilyl (**4**), *tert*-butyldimethylsilyl (**5**),[5] and thexyldimethylsilyl (**6**) groups were introduced by reaction with the respective chlorides (Scheme 1).

All these neopentasilanes again can be subjected to the reaction with potassium *tert*-butoxide. It was hoped

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[1] (a) Lickiss, P. D.; Smith, C. M. *Coord. Chem. Rev.* **1995**, *145*, 75−124. (b) Tamao, K.; Kawachi, A. *Adv. Organomet. Chem.* **1995**, *39*, 1−58. (c) Belzner, J.; Dehnert, U. Alkaline and alkaline earth silyl compounds−preparation and structure. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig,Y., Eds.; John Wiley & Sons: New York, 1998; Vol. 2, Chapter 14, pp 779−825. (d) Sekiguchi, A.; Lee, V. Y.; Nanjo, M. *Coord. Chem. Rev.* **2000**, *210*, 11−45.

[2] (a) Tilley, T. D. Transition-metal silyl derivatives. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons Ltd: Chichester, 1989; Chapter 24, pp 1415−1477. (b) Tilley, T. D. Appendix to transition-metal silyl derivatives. In *The Silicon-Heteroatom Bond*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons Ltd: Chichester, 1991; Chapter 10, pp 309−364. (b) Eisen, M. S. Transition-metal silyl complexes. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig,Y., Eds.; John Wiley & Sons Ltd: Chichester, 1998; Vol. 2, Chapter 35, pp 2037−2119.

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[5] Apeloig, Y.; Bendikov, M.; Yuzefovich, M.; Nakash, M.; Bravo-Zhivotovskii, D.; Blaser, D.; Boese, R. *J. Am. Chem. Soc.* **1996**, *118*, 12228−12229.

[6] (a) Gilman, H.; Holmes, J. M.; Smith, C. L. *Chem. Ind. (London)* **1965**, 848−849. (b) Gilman, H.; Harrell, R. L., Jr. *J. Organomet. Chem.* **1967**, *9*, 67−76.

[7] (a) Apeloig, Y.; Yuzefovich, M.; Bendikov, M.; Bravo-Zhivotovskii, D.; Klinkhammer, K. *Organometallics* **1997**, *16*, 1265−1269. (b) Apeloig, Y.; Korogodsky, G.; Bravo-Zhivotovskii, D.; Bläser, D.; Boese, R. *Eur. J. Inorg. Chem.* **2000**, 1091−1095.

[8] Marschner, Ch. *Eur. J. Inorg. Chem.* **1998**, 221−226.

[9] (a) Klinkhammer, K. W.; Schwarz, W. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1777−1789. (b) Klinkhammer, K. W. *Chem. Eur. J.* **1997**, *3*, 1418−1431.

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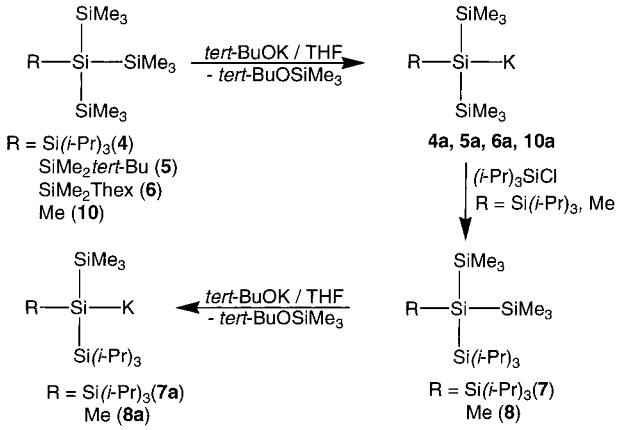
Scheme 1 . Selective Removal of Trimethylsilyl Groups versus Sterically More Demanding Silyl Groups

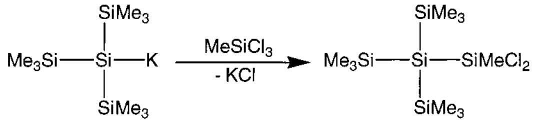


that the introduction of steric bulk on one substituent would selectively differentiate between the silyl groups on the central silicon atom. The experiments proved this only in part to be true, since there was found a distinct difference in reactivity between the phenylated and the alkylated compounds. In the latter cases our expectation was fully met and only trimethylsilyl groups were cleaved off (**4a**, **5a**, **6a**), while the bulkier silyl groups were not touched. This leads to the formation of a number of sterically more hindered analogues of tris(trimethylsilyl)silyl potassium. For the triisopropylsilylated compound (**4a**) this scheme was repeated, and thus bis(triisopropylsilyl)(trimethylsilyl)silyl potassium (**7a**)[10] was obtained. This demonstrates the possibility of subsequent buildup of steric bulk in oligosilyl anions.

The selective removal of trimethylsilyl groups also holds for isotetrasilanes, and as an example (triisopropylsilyl)bis(trimethylsilyl)methylsilane (**8**) (easily obtained by reaction of bis(trimethylsilyl)methylsilyl potassium (**10a**) with triisopropylsilyl chloride or alternatively by methylation of **4a** with dimethyl sulfate) was converted to (triisopropylsilyl)(trimethylsilyl)methylsilyl potassium (**8a**) (Scheme 1).

In contrast to the just described selectivity pattern the reactions with the phenylated compounds **(1−3)** do not exhibit a pronounced preference for attack at the trimethylsilyl groups. In the case of tris(trimethylsilyl)(phenyldimethylsilyl)silane (**1**), where a statistically evenly distributed attack of the alkoxide on the silyl groups should result in the formation of 3 equiv of bis(trimethylsilyl)(phenyldimethylsilyl)silyl potassium (**1a**) and 1 equiv of tris(trimethylsilyl)silyl potassium, a ratio of 1:1 of the expected products is found. This indicates that the probability for the alkoxide to attack the phenylated silyl group is 3 times higher than for the trimethylsilyl group. The situation for the double- and triple-phenylated neopentasilanes (**2**,**3**) is more complicated. While also there is found a preference for attack at the phenylated silicon, in addition, the enhanced stability of the phenylated monosilyl anions also leads to the formation of diphenylmethylsilyl and triphenylsilyl potassium and a number of follow-up products.

Scheme 2 . Direct Synthesis of (Dichloromethylsilyl)tris(trimethylsilyl)silane



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The phenyl groups in compounds **1**−**3** can be regarded as masked functionalities. Facile protodesilylation with neat hydrogen bromide at low temperatures leads to the respective silyl bromides.[11] Besides this route also the direct synthesis of silyl halides is possible employing silyl potassium compounds as was demonstrated by the reaction of tris(trimethylsilyl)silyl potassium with trichloromethylsilane. In a remarkably clean reaction tris(trimethylsilyl)(dichloromethylsilyl)silane (**9**) was obtained (Scheme 2).[12] **Secondary Silyl Potassiums.** Alkylated tris(trimethylsilyl)silanes can easily be obtained by alkylation of tris(trimethylsilyl)silyl potassium.[8] However, problems can occur when alkyl iodides are used as the alkylating agents. The reaction of tris(trimethylsilyl)silyl potassium with methyl iodide results in a mixture of the expected methyltris(trimethylsilyl)silane[6a] (**10**) and tris(trimethylsilyl)silyl iodide[13] in a ratio of about 1:1. If the silyl potassium compound is even more sterically demanding, as in the case of (triisopropylsilyl)bis(trimethylsilyl)silyl potassium (**4a**), the silyl iodide is formed selectively. Metal halogen exchange becomes the dominant reaction pathway if the sterics make the nucleophilic substitution more difficult. This phenomenon is only observed with alkyl iodides. Routine reaction monitoring by quenching reaction aliquots with ethyl bromide did not indicate a similar behavior as a notable reaction (**11**). However, using dimethyl sulfate as an alternative alkylating agent, methylation of silyl potassium compounds proceeds very cleanly. The isopropyl group can be introduced via isopropyl chloride (**12**).

To obtain the phenylated tris(trimethylsilyl)silane[14] (**13**), we reacted tris(trimethylsilyl)silyl chloride with phenyllithium. Although this is a relatively clean reaction, it produces pentakis(trimethylsilyl)phenyldisilane[15] (**15**) as a side product. All the mentioned isotetrasilanes (**10**−**13**) could be converted into the corresponding silyl potassiums (**10a**−**13a**) by treatment with potassium *tert*-butoxide in very clean reactions in essentially quantitative yields (Scheme 3).

Higher Silyl Potassiums. A main advantage of the use of potassium alkoxides compared to alkyllithiums is the preservation of inner Si−Si bonds. We have demonstrated this for hexakis(trimethylsilyl)disilane (**14**), where the use of methyllithium results in clean

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[10] For a similar approach, where two trimethysilyl groups of tris(trimethylsilyl)silyllithium have been replaced by *tert*-butyldimethylsilyl groups, see ref 5.

[11] Marschner, Ch. Unpublished results.

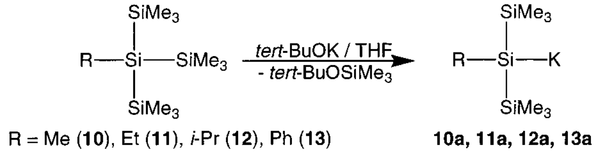
[12] For a recent example of the reaction of tris(trimethylsilyl)silyl potassium with hexachlorodisilane see: Ackerhans, C.; Bötcher, P.; Müller, P.; Roesky, H. W.; Uson, I.; Schmidt, H.-G.; Noltemeyer, M. *Inorg. Chem.* **2001**, *40*, 3766−3773.

[13] Bürger, H.; Kilian, W.; Burczyk, K. *J. Organomet. Chem.* **1970**, *21*, 291−301.

[14] (a) Gilman, H.; Atwell, W. H.; Sen, P. K.; Smith, C. L. *J. Organomet. Chem.* **1965**, *4*, 163−167. (b) Brough, L. F.; West, R. *J. Organomet. Chem.* **1982**, *229*, 113−118. (c) Herzog, U.; Roewer, G. *J. Organomet. Chem.* **1997**, *544*, 217−223. (d) Baumeister, U.; Schenzel, K.; Zink, R.; Hassler, K. *J. Organomet. Chem.* **1997**, *543*, 117−124.

[15] Kusukawa, T.; Ando, W. *J. Organomet. Chem.* **1998**, *559*, 11−22.

Scheme 3 . Preparation of Secondary Silyl Potassium Compounds from Substituted Isotetrasilanes



cleavage of the central Si−Si bond, thus generating tris(trimethylsilyl)silyllithium and tris(trimethylsilyl)-methylsilane.[6b,7] In contrast to this, potassium *tert*-butoxide cleanly removes a trimethylsilyl group and generates pentakis(trimethylsilyl)disilanyl potassium (**14a**).[8] The size of the metalating agent seems to have some influence at least for the reaction with alkyllithiums. This was shown by the reaction of hexakis-(trimethylsilyl)disilane with *tert*-butyllithium, which leads to a mixture of tris(trimethylsilyl)silyllithium and pentakis(trimethylsilyl)disilanyllithium in a ratio of about 2:3. An attempt in the opposite direction, to employ a smaller alkoxide, namely, potassium methoxide,[16] however, again led to the clean formation of pentakis(trimethylsilyl)disilanyl potassium (**14a**).[8]

These results are surprising and seem to indicate that we have to differentiate with respect to mechanisms between the two reactions. While the alkoxide reaction seems to be a nucleophilic attack at a trimethylsilyl group, the alkyllithium reaction maybe can be regarded more as an electron-transfer reaction, similar to the cleavage of Si−Si bonds with lithium. Subsequently, we investigated also a number of other potassium alkoxides for their ability to promote the cleavage of trimethylsilyl groups. It was found that potassium methoxide, ethoxide, and isopropoxide promote the reaction all more or less equally well. For reasons of convenience we still use *tert*-butoxide as the reagent of choice.

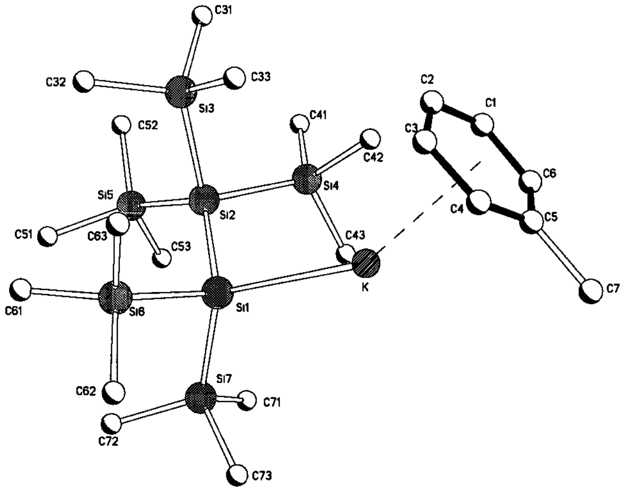


Figure 1. Molecular structure of compound **14a**.

Table 1. Crystal Data for 14a and 15b

	14a	15b
formula	$C_{22}H_{53}KSi_7$	$C_{36}H_{71}KO_6Si_6$
fw	553.37	807.57
temp (K)	293(2)	223(2)
cryst syst	monoclinic	monoclinic
space group	$P2(1)/n$	$P2(1)/c$
a (Å)	11.964(2)	11.962(2)
b (Å)	22.277(5)	19.363(4)
c (Å)	13.739(3)	21.633(4)
α (deg)	90	90
β (deg)	97.89(3)	92.65(3)
γ (deg)	90	90
volume (Å^3)	3627.1(13)	5005.(17)
Z	4	4
D(calc) (g/cm^3)	1.013	1.072
μ (mm^{-1})	0.387	0.285
F(000)	1208	1752
λ(Mo Kα) (Å)	0.71073	0.71073
cryst size (mm)	0.22 × 0.18 × 0.12	0.99 × 0.62 × 0.21
θ range (deg)	2.99−25.00	1.41−20.81
completeness (%)	99.3	99.9
no. of unique reflns	6336	5224
no. of params	329	450
R_1/R_{w2} [$I>2\sigma(I)$]	0.0494 (0.1041)	0.0634 (0.1624)
R_1/R_{w2} [all data]	0.0959 (0.1162)	0.0746 (0.1725
goodness-of-fit on F^2	1.233	1.028

Table 2. Selected Bond Lengths (Å) and Angles (deg) of 14a

Si(1)−K	3.3147(12)	Si(7)−Si(1)−K	121.24(4)
Si(1)−Si(2)	2.3745(11)	Si(6)−Si(1)−Si(7)	99.23(4)
Si(1)−Si(6)	2.3497(11)	Si(6)−Si(1)−Si(2)	109.16(4)
Si(1)−Si(7)	2.3477(12)	Si(6)−Si(1)−K	106.60(4)
Si(2)−Si(3)	2.3626(12)	Si(7)−Si(1)−Si(2)	109.82(4)
Si(2)−Si(4)	2.3574(11)	Si(2)−Si(1)−K	109.78(4)
Si(2)−Si(5)	2.3534(11)	Si(3)−Si(2)−Si(1)	109.77(4)
K−C(62)#1	3.197(4)	Si(3)−Si(2)−Si(4)	102.08(4)
K−C(43)#2	3.511(4)	Si(3)−Si(2)−Si(5)	106.05(4)
K−C(1−6)	3.20−3.41	Si(4)−Si(2)−Si(1)	108.19(4)
		Si(4)−Si(2)−Si(5)	105.23(4)
		Si(5)−Si(2)−Si(1)	123.44(4)

In connection with the formation of pentakis(trimethylsilyl)disilanyl potassium (**14a**) we also encountered another interesting feature of these oligosilyl potassium compounds. While the tetrahydrofurane (THF) donor molecules are bound rather firmly to tris-(trimethylsilyl)silyllithium,[3b] the interaction between the silyl potassium compounds and the donor is less strong. We have reported two molecules of THF coordinating to tris(trimethylsilyl)silyl potassium but different amounts coordinating to other compounds.[8] In general the coordination of two molecules seems to be a preferred coordination mode for this class of compounds; however, the donor molecules can easily, partially or completely, be removed in a vacuum for example during the removal of solvent at the end of reaction. For example, pentakis(trimethylsilyl)disilanyl potassium (**14a**) was generated in THF, and the solvent removed and crystallized from toluene. The resulting crystals do not contain THF but pentakis(trimethylsilyl)disilanyl potassium coordinating to one molecule of toluene, as can be seen in the obtained crystal structure (Figure 1, Table 2). This structure resembles the donor-free tris(trimethylsilyl)silanides investigated by Klinkhammer.[9] However, it does not exist as a dimer with a four-membered ring built by the Si−K units. Since in a monomeric structure (Figure 1) the potassium would be coordinatively unsaturated, we find additional coordination to the methyl groups of two neighbor molecules. Interestingly, these methyl groups are situated on different trimethysilyl groups. One (C43) is attached to the silicon atom coordinating to potassium. The other one (C63), which is about as close [3.197(4) Å] to the potassium as the closest toluene carbon [3.203-(7) Å], is part of a trimethylsilyl group bonded to the other silicon atom of the disilanyl unit. These intermo-

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[16] Sakurai, H.; Kondo, F. *J. Organomet. Chem.* **1975**, *92*, C46−C48.

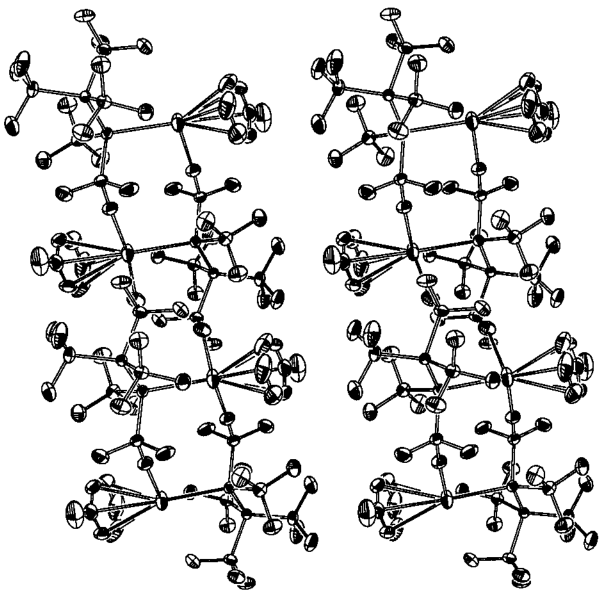


Figure 2. Band-shaped arrangement of **14a** in the crystal.

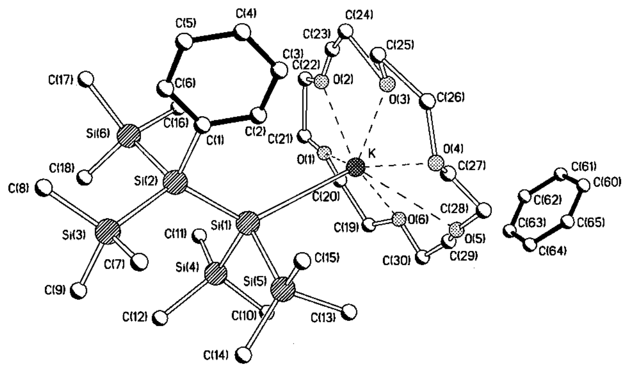
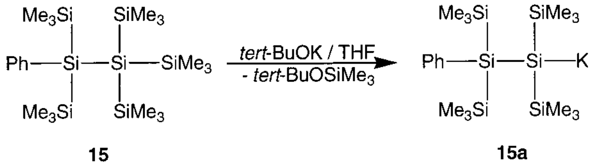


Figure 3. Molecular structure of compound **15b**.

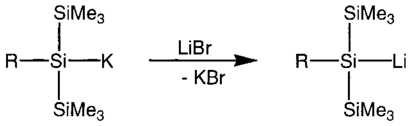
Table 3. Selected Bond Lengths (Å) and Angles (deg) of 15b

Si(1)−K	3.5994(19)	Si(5)−Si(1)−K	104.63(6)
Si(1)−Si(2)	2.3677(17)	Si(4)−Si(1)−Si(5)	100.92(8)
Si(1)−Si(4)	2.3428(19)	Si(4)−Si(1)−Si(2)	108.64(7)
Si(1)−Si(5)	2.352(2)	Si(4)−Si(1)−K	102.50(6)
Si(2)−Si(3)	2.3686(18)	Si(5)−Si(1)−Si(2)	106.48(7)
Si(2)−Si(6)	2.3612(18)	Si(2)−Si(1)−K	130.11(6)
Si(2)−C(1)	1.932(4)	Si(3)−Si(2)−Si(1)	123.48(7)
		Si(3)−Si(2)−Si(6)	107.21(7)
		Si(3)−Si(2)−C(1)	103.72(15)
		Si(6)−Si(2)−Si(1)	108.80(7)
		Si(6)−Si(2)−C(1)	103.24(15)
		C(1)−Si(2)−Si(1)	108.55(16)

Scheme 4 . Regioselective Removal of a Trimethylsilyl Group in β-Position to the Phenyl Group



Scheme 5 . Transmetalation of a Silyl Potassium to the Corresponding Lithium Compound



lecular interactions lead to the formation of a polymeric band-shaped arrangement of the oligosilyl potassium structures (Figure 2).

In another experiment we reacted the above-mentioned pentakis(trimethylsilyl)phenyldisilane (**15**) with potassium *tert*-butoxide. It could be expected that the regiochemistry of the attack would reveal some information about the ability of trimethylsilyl versus phenyl groups to stabilize a negative charge in the α-position. The metalation also in this case proceeded completely selective and occurred at the nonphenylated silicon atom (**15a**). The regioselectivity was confirmed by the crystal structure of the 18-crown-6 adduct of the silanide (**15b**) (Figure 3, Table 3). This compound was obtained in the reaction of **15** with potassium *tert*-butoxide in benzene in the presence of 1 equiv of 18-crown-6. We found that running reactions under these conditions avoids the use of etheral solvents and facilitates the access to single crystals of the respective silyl anions. As we find frequently in structures such as **15b**, the crown ether part was heavily disordered while the silanide fragment was very well resolved.

Other Metals. When we started to investigate the reactions of oligosilanes with potassium *tert*-butoxide, the question arose whether this method can also be used employing the alkoxides of other alkali metals. While we found that reactions of oligosilanes with cesium *tert*-butoxide behave very similarly to ones with potassium, the use of lithium *tert*-butoxide in DME or THF did not result in any cleavage of a silicon−silicon bond and formation of an oligosilyllithium compound. However, the use of sodium *tert*-butoxide in DME or THF is a feasible reaction when carried out at elevated temperature. This means for example that the treatment of tetrakis(trimethylsilyl)silane with sodium *tert*-butoxide in DME at reflux yields the respective tris(trimethylsilyl)silylsodium DME adduct, which precipitates out of solution when the reaction solution is allowed to cool to room temperature. This compound can be seen as an interesting alternative to tris(trimethylsilyl)silyllithium since it is very easy to obtain as a storable reagent.

The mentioned failure to obtain the lithium compound does not limit the value of the method at all since it is easily possible to transmetalate the highly electropositive potassium against less electropositive cations such as lithium, zinc,[17] or, as we have demonstrated recently, magnesium.[18] This strategy offers the possibility to moderate the reactivity of the rather reactive potassium silyls via the lithium and magnesium derivatives to the zinc silyl compounds (Scheme 5).

^{29}Si NMR Spectroscopy. ^{29}Si NMR studies of oligosilyl anions are especially indicative. Besides the chemical shift values, coupling constants are of main interest. Among these, coupling over one bond is most relevant. Depending on the type of compound, this means J_{SiC}, J_{SiH},[19] J_{SiSi}, or J_{SiM} coupling. In our study we were most interested in ^{29}Si−^{29}Si couplings. Since the natural abundance of the ^{29}Si isotope is only 4.7%

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(17) Arnold, J.; Tilley, T. D.; Rheingold, A. L.; Geib, S. *J. Inorg. Chem.* **1987**, *26* , 2106−2109.

(18) Farwell, J. D.; Lappert, M. F.; Marschner, Ch.; Strissel, Ch.; Tilley, T. D. *J. Organomet. Chem.* **2000**, *603*, 185−188.

(19) For H(Me$_3$Si)$_2$SiK a comparingly small value of 82 Hz for J_{SiH} was found. Cf. ref 8.

and the probability of two neighboring ^{29}Si isotopes in a chain is only 0.24%, we employed the INEPT-INADEQUATE[20] experiment.

According to Bent's rule, the coupling constant should reflect the electronegativity of the substituents at the involved atoms.[21] Typical values for neopentasilanes are around 50 Hz.[22] Very electropositve substituents therefore should lead to very small values for J_{SiSi}. Sekiguchi et al. could show a strong dependence of J_{SiSi} from solvents.[23] Tris(trimethylsilyl)silyllithium exhibits a value of 17.4 Hz in THF-d_8. For the more electropositive potassium compound we found a smaller value of 10.3 Hz. A change to toluene in the absence of coordinating THF led to increasing values of 28.6 Hz for the lithium but only 11.7 Hz for the potassium compound.

The differences in the magnitude of the coupling constant indicate a strongly ionic character of the silicon alkali bond in polar solvents. The absence of strong donors therefore seems to cause a more covalent interaction between the anionic silicon atom and the cation. Silyl potassium compounds seem to exhibit this effect to a much lower extent than their lithium counterparts. The more electropositive character of potassium makes the compounds even in the donor-free state more ionic. Therefore, only a slight increase of ionicity is caused by the addition of THF, as reflected in the small increase of the coupling constant. The smaller change in ionicity seems also to be the reason for the mentioned phenomenon of easy removal of THF molecules from the adducts of the potassium silyls.

For compound **14a**, where a trimethylsilyl group is replaced by a tris(trimethylsilyl)silyl group, we find an even smaller value of only 3.9 Hz for the Si−Si coupling constant in THF. If the amount of THF is reduced, as in the adduct containing two donor molecules, or THF is removed completely, then again the value for J_{SiSi} increases to 6.8 or 11.7 Hz, respectively. For Et(Me$_3$Si)$_2$SiK we observe a similar behavior of the coupling constants depending on donor solvents. Interesting is also the case of the magnesium compounds (Me$_3$Si)$_3$SiMgBr·2THF and [(Me$_3$Si)$_3$Si]$_2$Mg·2THF,[18] where the two different Si−Si coupling constants of 40.0 and 34.7 Hz, respectively, reflect the different electronegativity of bromine versus the tris(trimethylsilyl)silyl group. That chemical shifts of compounds with similar Si−Si coupling constant are sometimes very different can be seen by comparison of the tris(trimethylsilyl)silylmagnesium compounds with Cp$_2$Zr(Cl)Si(SiMe$_3$)$_3$.[24]

Mechanism. There can be said a few things concerning the mechanism of the metalation and the difference between an alkoxide and an lithium alkyl as metallating agents.

Usually we carry out our reactions so that to the starting material is added potassium *tert*-butoxide and the solvent and the product then forms within, depending on the substrate, a few minutes to a couple of hours. In this setup we cannot say anything about interaction of the product with the starting material. However, if we do a crossover experiment with two starting materials with different silyl groups (i.e., the trimethylsilyl and the dimethylphenylsilyl group), we observe after initial formation of the two expected products another product that carries two different silyl groups.This third compound stems from the interaction of a silyl potassium compound with the other starting material and subsequent transformation of the newly formed isotetrasilane to the potassium compound (Schemes 6 and 7). The same kind of interaction also takes place in the conventional setup, as can be seen from exchange NMR spectroscopy. For example an EXSY spectrum of the reaction of tetrakis(trimethylsilyl)silane with potassium *tert*-butoxide reveals that there is chemical exchange between the starting material and the product, as well as, although to a much lesser extent, between the product and the trimethylsilyl-*tert*-butyl ether.

Table 4. ^{29}Si NMR Spectroscopic Shifts and Coupling Constants of the Central Silicon Atom of Tris(trimethylsilyl)silyl Derivatives: (Me$_3$Si)$_2$R′SiR

R	δ_{Si^1}	$^1J_{SiSiMe_3}$[a]	solvent	R′
SiMe$_3$	−135.5[b]	52.5[b]	toluene	SiMe$_3$
SiMe$_3$	−129.9[b]	50.6[b]	toluene	Si(SiMe$_3$)$_3$
Li	−190.7[c]	17.4[c]	THF-d_8	SiMe$_3$
Li	−181.7[c]	28.6[c]	toluene-d_8	SiMe$_3$
K	−194.4	10.3	THF	SiMe$_3$
K·2THF	−189.6	15.0	toluene	SiMe$_3$
K	−188.8	15.4	toluene	SiMe$_3$
K	−190.7	3.9	THF	Si(SiMe$_3$)$_3$
K·2THF	−187.3	6.8	toluene	Si(SiMe$_3$)$_3$
K	−185.0	11.7	toluene	Si(SiMe$_3$)$_3$
K	−111.0	9.7	THF	Et
K·2THF	−110.2	13.5	toluene	Et
K	−109.5	16.3	toluene	Et
MgBr·2THF	−169.7[d]	40.0	toluene	SiMe$_3$
MgSi(SiMe$_3$)$_3$·2THF	−171.1[d]	34.3	toluene	SiMe$_3$
Zr(Cl)Cp$_2$[e]	−82.6	39.9	toluene	SiMe$_3$

[a] All values for $^1J_{SiSi}$ are ±0.6 Hz· [b] Ref 22. [c] Ref 23. [d] Ref 18. [e] Ref 24.

Experimental Part

All manipulations involving air-sensitive materials were performed either under a nitrogen or argon atmosphere using standard Schlenk techniques or in a nitrogen-filled glovebox. All solvents were dried over sodium/potassium alloy under nitrogen and distilled prior to use. NMR spectra were recorded either on a Bruker MSL 300 (^{1}H 300.13 MHz, ^{13}C 75.47 MHz, ^{29}Si 59.63 MHz) or a Varian INOVA 500 (^{1}H 499.82 MHz, ^{13}C 125.89 MHz, ^{29}Si 99.30 MHz) spectrometer. Samples were dissolved in CDCl$_3$, in C$_6$D$_6$, or in the case of ^{29}Si NMR in a nondeuterated solvent using a capillary filled with D$_2$O for deuterium lock. Shifts are reported in ppm downfield from TMS (tetramethylsilane). Besides the usual abbreviations for the signal multiplicities (s, d, t) the term *pd* is used for pseudodoublets, which are frequently found in compounds with the triisopropylsilyl group. GC analyses were carried out on a HP 5890 series II (capillary column DB-1HT; 15 m × 0.251 mm; 0.1 μm; flame ionization detector). Mass spectra were obtained with either a HP 5971 or a Kratos Profile spectrometer.

The degree of conversion in the syntheses of the silyl potassium compounds was followed by derivatization of a reaction aliquot and subsequent GC/MS or GC analysis. This was achieved by adding a 20 μL sample of the reaction mixture into a solution of 100 μL of ethyl bromide in 2 mL of ether or by addition of the sample into the etheral phase of a 2 mL ether/2 mL 2 M H$_2$SO$_4$ mixture followed by mixing of the layers. The etheral layer was used to carry out the GC/MS or GC analysis. The MS fragmentation patterns of the derivatives

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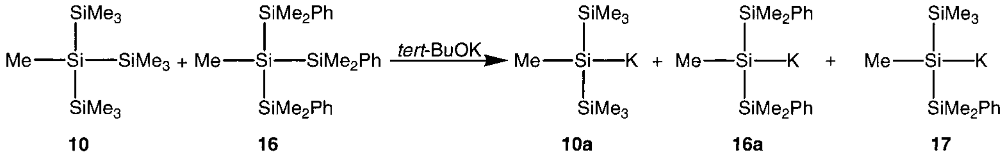
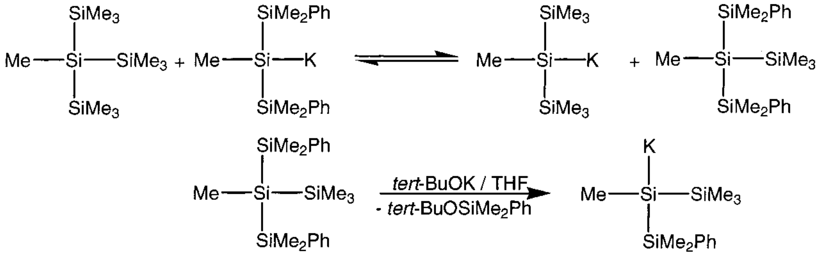
Scheme 6. Crossover Experiment between Trimethylsilyl and Dimethylphenylsilyl Groups



Scheme 7. Intermolecular Metalation of Different Starting Materials



are reported for each silyl potassium compound. Both derivatization reactions are usually quantitative by their nature so that we do not observe any other products.

Tris(trimethylsilyl)silyl Potassium. Tetrakis(trimethylsilyl)silane and the respective amount of potassium *tert*-butoxide (5% excess) were mixed, and so much THF or DME was added that everything dissolves. The solution turns yellow immediately and subsequently orange or green. Conversion normally is complete after 2 h, but usually the reaction was allowed to run overnight.

The course of the reaction to the silyl potassium is quantitative, and the resulting solution in THF or DME can be used for most purposes. Isolation of the silanide can be achieved by removal of the solvent in a vacuum, dissolving the residue in pentane, and crystallization at −70 °C. The compound crystallizes with two molecules of THF, which can be removed completely by mild heating (50−60 °C) under vacuum (0.1 mbar). The scale of the reaction can be varied from a few milligrams to more than 100 g. The degree of conversion is controlled as described above by GLC analysis of derivatized aliquots or ^{29}Si NMR spectroscopy.

(Phenyldimethylsilyl)bis(trimethylsilyl)silyl Potassium (1a). (Phenyldimethylsilyl)tris(trimethylsilyl)silane (360 mg, 0.940 mmol) and potassium *tert*-butoxide (112 mg, 1.00 mmol) were mixed, and THF was added. The reaction was followed by ^{29}Si NMR of aliquots and GLC/MS analysis of derivatized aliquots. After about 60 min a mixture of (phenyldimethylsilyl)bis(trimethylsilyl)silyl potassium (**1a**) and tris(trimethylsilyl)silyl potassium in a ratio of about 1:1 was detected.

1a: ^{29}Si (THF, D_2O capillary) −4.8, −5.0, −193.7. Ethyl bromide derivatization: MS (70 eV) *m*/*z* (%) 338 (27) [M^+], 265 (12) [$M^+ - SiMe_3$], 188 (74) [$M^+ - PhSiMe_3$], 135 (100) [$SiMe_2Ph^+$]. Acidic hydrolysis derivatization: MS (70 eV) *m*/*z* (%): 310 (4) [M^+], 295 (11) [$M^+ - Me$], 236 (100) [$M^+ - HSiMe_3$], 135 (71) [$SiMe_2Ph^+$].

(Triisopropylsilyl)tris(trimethylsilyl)silane (4). To a cooled (−70 °C) solution of triisopropylchlorosilane (0.96 g, 5.00 mmol) in toluene (10 mL) was slowly added a solution of tris(trimethylsilyl)silyl potassium (4.90 mmol) in toluene (5 mL). The solution was allowed to warm to room temperature, stirred for 16 h, and then subjected to an aqueous workup (diluted sulfuric acid, drying over sodium sulfate). The obtained solution was evaporated and the remaining solid crystallized from ether: white crystals (mp 315−320 °C) (1.59 g, 3.93 mmol, 80%). NMR data (δ in ppm): ^{1}H (C_6D_6) 1.30 (m, 3H), 1.19 (pd, 18H), 0.26 (s, 27H); ^{13}C ($CDCl_3$) 20.39, 14.73, 4.22; ^{29}Si (pentane, D_2O capillary) 14.24, −9.34, −135.62. MS (70 eV): *m*/*z* (%) 362 (1) [$M^+ - C_3H_6$], 232 (100) [$M^+ - (i\text{-}Pr)_3SiMe$], 157 (37) [$Si(i\text{-}Pr)_3^+$], 73 (42) [$SiMe_3^+$]. Anal. Calcd for $C_{18}H_{48}Si_5$: C, 53.38; H, 11.95. Found: C, 53.02; H, 11.94.

(Triisopropylsilyl)bis(trimethylsilyl)silyl Potassium (4a). 4a was obtained as described for tris(trimethylsilyl)silyl potassium above in almost quanitative yield as a light gray powder. Crystallization was achieved from pentane at −35 °C. NMR data (δ in ppm): ^{1}H (C_6D_6) 3.42 (m, 4H), 1.45 (pd and m, 21H), 1.39 (m, 4H), 0.58 (s, 18H); ^{13}C (C_6D_6) 67.96, 25.47, 21.82, 15.84, 8.54; ^{29}Si (THF, D_2O capillary) 21.3, −6.1, −198.6. Ethyl bromide derivatization: MS (70 eV) *m*/*z* (%) 360 (3) [M^+], 345 (1) [$M^+ - Me$], 188 (100) [$M^+ - (i\text{-}Pr)_3SiMe$], 157 (45) [$Si(i\text{-}Pr)_3^+$], 115 (54) [$HSi(i\text{-}Pr)_2^+$], 73 (39) [$SiMe_3^+$]. Acidic hydrolysis derivatization: MS (70 eV) *m*/*z* (%): 332 (7) [M^+], 289 (31) [$M^+ - i\text{-}Pr$], 160 (100) [$M^+ - (i\text{-}Pr)_3SiMe$], 115 (65) [$HSi(i\text{-}Pr)_2^+$].

(*tert*-Butyldimethylsilyl)bis(trimethylsilyl)silyl Potassium (5a). 5a was obtained as described above for tris(trimethylsilyl)silyl potassium in almost quanitative yield as a light gray powder. Crystallization was achieved from pentane at −35 °C. NMR data (δ in ppm): ^{1}H (C_6D_6) 3.41 (m, 4H), 1.41 (m, 4H), 1.25 (s, 9H), 0.56 (s, 18H), 0.53 (s, 6H); ^{13}C (C_6D_6) 67.84, 29.02, 25.57, 19.08, 8.04, 2.00; ^{29}Si (THF, D_2O capillary) 9.8, −4.6, −197.6. Ethyl bromide derivatization: MS (70 eV) *m*/*z* (%) 318 (8) [M^+], 261 (41) [$M^+ - CMe_3$], 233 (12) [$M^+ - SiCMe_3$], 187 (37) [$M^+ - EtSi(H)SiMe_3$], 73 (100) [$SiMe_3^+$]. Acidic hydrolysis derivatization: MS (70 eV) *m*/*z* (%) 290 (4) [M^+], 233 (37) [$M^+ - CMe_3$], 159 (39) [$M^+ - Me_3SiCMe_3 - H$], 73 (100) [$SiMe_3^+$].

(Dimethylthexylsilyl)tris(trimethylsilyl)silane (6). The synthesis of **6** (using dimethylthexylchlorosilane (0.89 g, 4.98 mmol)) was achieved analogously to the preparation of **4**. The product was obtained after aqueous workup and evaporation of the toluene as a colorless oil (1.40 g, 3.58 mmol, 73%). NMR data (δ in ppm): ^{1}H ($CDCl_3$) 1.81 (heptet, 1H, $J = 3.9$ Hz), 0.94 (s, 6H), 0.87 (d, 6H, $J = 3.9$ Hz), 0.28 (s, 6H), 0.27 (s, 27H); ^{13}C ($CDCl_3$) 35.59, 25.04, 22.40, 19.13, 3.91, 1.82; ^{29}Si (pentane, D_2O capillary) 9.45, −9.03, −133.68. MS (70 eV): *m*/*z* (%) 390 (4) [M^+], 232 (75) [$M^+ - Me_3SiCMe_2CHMe_2$], 143 (18) [$M^+ - Si(SiMe_3)_3$], 73 (100) [$SiMe_3^+$]. Anal. Calcd for $C_{17}H_{46}Si_5$: C, 52.22; H, 11.86. Found: C, 51.96; H, 11.90.

(Dimethylthexylsilyl)bis(trimethylsilyl)silyl Potassium (6a). Compound **6a** was prepared as described above for tris(trimethylsilyl)silyl potassium and obtained in quantitative yield as a light gray powder, which was crystallized at −35 °C from pentane. NMR data (δ in ppm): ^{1}H (C_6D_6) 3.42 (m, 4H), 2.18 (m, 1H), 1.46 (m, 4H), 1.14 (s, 6H), 1.09 (d, 6H, $J = 9.2$ Hz), 0.52 (s, 6H), 0.50 (s, 18H); ^{13}C (C_6D_6) 67.89, 35.11, 25.62, 24.76, 22.17, 19.59, 8.09, 4.64; ^{29}Si (THF, D_2O capillary) −4.82, −11.16, −193.12. Ethyl bromide derivatization: MS (70 eV) *m*/*z* (%) 346 (1) [M^+], 261 (30) [$M^+ - CMe_2CHMe_2$], 233 (10) [$M^+ - HSiCMe_2CHMe_2$], 187 (29) [$M^+ - Me_3SiCMe_2CHMe_2 - H$], 73 (100) [$SiMe_3^+$]. Acidic hydrolysis derivatization: MS (70 eV) *m/z* (%): 318 (0.8) [$M^{+\bullet}$], 233 (38) [$M^+ - CMe_2CHMe_2$], 160 (29) [$M^+ - Me_3SiCMe_2CHMe_2$], 73 (100) [$SiMe_3^+$].

Bis(triisopropylsilyl)bis(trimethylsilyl)silane (7). To a solution of **4a** (7.41 mmol) in toluene (20 mL) was added triisopropylchlorosilane (1.74 mL, 8.15 mmol) in toluene (20 mL). The solution was heated to 100 °C for 18 h and then was subjected to an aqueous workup. After evaporation the remaining solid was crystallized from 2-propanol at 0 °C to give **7** (2.60 g, 5.33 mmol, 72%) as white needles (mp 287−290 °C). NMR data (δ in ppm): ^1H (C_6D_6) 1.43 (heptet, 6H); 1.22 (pd, 36H, $J = 6.9$ Hz); 0.43 (s, 18H); ^{13}C ($CDCl_3$) 21.25, 16.12, 6.01; ^{29}Si (THF, D_2O capillary) 9.76; −10.14; −129.50. Anal. Calcd for $C_{24}H_{60}Si_5$: C, 58.93; H, 12.36. Found: C, 58.61; H, 12.47.

Bis(triisopropylsilyl)(trimethylsilyl)silyl Potassium (7a). **7** (0.50 g, 1.03 mmol) and potassium *tert*-butoxide (122 mg, 1.03 mmol) were dissolved in THF (15 mL) in a Schlenk flask and heated for 5 days to 70 °C. Quantitative conversion was detected by ^{29}Si NMR of an aliquot: ^{29}Si (THF, D_2O capillary) 22.2; −6.9; −210.3.

A sample of **7a** was quenched with aqueous sulfuric acid to give the corresponding hydrosilane in quantitative yield: ^1H (C_6D_6) 2.74 (s, 1H); 1.26 (m, 6H); 1.18 (d, 18H, $J = 6.9$ Hz); 1.16 (d, $J = 7.0$ Hz, 18H), 0.33 (s, 9H); ^{13}C (C_6D_6) 20.15, 20.10, 14.53, 3.47; ^{29}Si (C_6D_6) 14.5; −10.2; −136.4 ($J_{Si-H} = 137.5$ Hz).

Methyl(triisopropysilyl)bis(trimethylsilyl)silane (8). **4a** was generated from **4** (1.50 g, 3.70 mmol) and potassium *tert*-butoxide (436 mg, 3.89 mmol) in THF as described above. After complete conversion the solvent was removed in a vacuum, and pentane (10 mL) was added. Dimethyl sulfate (0.40 mL) dissolved in hexanes (2 mL) was added to the silyl potassium solution, whereupon the solution immediately decolorized and a white precipitate appeared. After aqueous workup the solvent was evaporated and **8** was left as a colorless oil: ^1H ($CDCl_3$) 1.27 (heptet, 3H); 1.15 (pd, 18H, $J = 7.0$ Hz); 0.32 (s, 3H), 0.24 (s, 18H); ^{13}C ($CDCl_3$) 20.21, 15.35, 4.03, 1.18; ^{29}Si (toluene, D_2O capillary) 9.3; −11.4; −89.2; MS (70 eV) *m/z* (%) 346 (4) [M^+], 303 (12) [$M^+ -$ i-Pr], 261 (7) [$M^+ - C_6H_{13}$], 219 (29) [$M^+ - C_9H_{19}$], 73 (100) [$SiMe_3^+$].

An attempt to alkylate **4a** with methyl iodide led to the quantitative formation of (triisopropysilyl)bis(trimethylsilyl)silyl iodide: ^1H ($CDCl_3$) 1.36 (heptet, 3H); 1.17 (d, 18H, $J = 7.0$ Hz); 0.32 (s, 18H); ^{13}C ($CDCl_3$) 19.43, 12.72, 0.40; ^{29}Si (toluene, D_2O capillary) 7.0; −12.8; −59.0.

Methyl(triisopropylsilyl)(trimethylsilyl)silyl Potassium (8a). Compound **8a** was prepared from **8** as described above for tris(trimethylsilyl)silyl potassium and obtained in quantitative yield. NMR data (δ in ppm): ^1H (C_6D_6) 3.48 (m, 4H), 1.41 (m, 7H), 1.37 (pd, 18H), 0.46 (s, 9H), 0.38 (s, 3H); ^{13}C (C_6D_6) 67.77, 25.49, 21.42, 15.35, 4.58, −7.02; ^{29}Si (C_6D_6) 13.1, −8.5, −128.3. Ethyl bromide derivatization: MS (70 eV) *m/z* (%) 302 (13) [M^+], 259 (32) [$M^+ -$ i-Pr], 217 (18) [$M^+ - C_6H_{13}$], 175 (39) [$M^+ - C_9H_{19}$], 73 (100) [$SiMe_3^+$]. Acidic hydrolysis derivatization: MS (70 eV) *m/z* (%) 274 (12) [M^+], 231 (27) [$M^+ -$ i-Pr], 189 (40) [$M^+ - C_6H_{13}$], 73 (100) [$SiMe_3^+$].

1,1,1-Tris(trimethylsilyl)-2,2-dichloro-2-methyldisilane (9). To a cooled (−50 °C) solution of methyltrichlorosilane (0.500 g, 3.50 mmol) in toluene (5 mL) was added slowly dropwise tris(trimethylsilyl)silyl potassium (3.50 mmol) in toluene (5 mL). After warming to room temperature the reaction was stirred for an additional 2 h. The solvent was removed in a vacuum, and to the residue was added pentane (20 mL). After filtering off the salts the solvent was evaporated and the product was obtained as a noncrystalline white solid, which was pure as judged by ^1H NMR. NMR data (δ in ppm): ^1H (C_6D_6) 0.81 (s, 3H), 0.27 (s, 27H); ^{13}C (C_6D_6) 13.16, 2.57; ^{29}Si (C_6D_6) 43.32; −9.58; −120.44. MS (70 eV): *m/z* (%) 345/347 (11) [$M^+ -$ Me], 325 (5) [$M^+ -$ Cl], 252 (82) [$M^+ - Me_3SiCl$], 73 (100) [$SiMe_3^+$]. Anal. Calcd for $C_{10}H_{30}Cl_2Si_5$: C, 33.21; H, 8.36. Found: C, 32.77; H, 8.35.

Methylbis(trimethylsilyl)silyl Potassium (10a). Methyltris(trimethylsilyl)silane (**10**) was converted to the corresponding silyl potassium compound (**10a**) as described above for tris(trimethylsilyl)silyl potassium. NMR data (δ in ppm): ^1H (C_6D_6) 3.46 (m, 4H), 1.46 (m, 4H), 0.46 (s, 18H), 0.30 (s, 3H); ^{13}C (C_6D_6) 67.85, 25.35, 3.54, −9.09; ^{29}Si (C_6D_6) −7.81, −127.37. Ethyl bromide derivatization: MS (70 eV) *m/z* (%) 218 (26) [M^+], 203 (8) [$M^+ -$ Me], 145 (35) [$M^+ - SiMe_3$], 117 (80) [$M^+ - SiMe_3 - C_2H_4$], 73 (100) [$SiMe_3^+$]. Acidic hydrolysis derivatization: MS (70 eV) *m/z* (%) 190 (13) [M^+], 175 (14) [$M^+ -$ Me], 116 (38) [$M^+ - HSiMe_3$], 73 (100) [$SiMe_3^+$].

Isopropyltris(trimethylsilyl)silane (12). A solution of tris(trimethylsilyl)silyl potassium (17.2 mmol) in toluene (30 mL) was added dropwise to a solution of isopropyl chloride (7.8 mL, 86 mmol) in toluene (20 mL) cooled to −70 °C. After complete addition the reaction mixture was allowed to warm to room temperature and stirring was continued for another 2 h. Afterward the reaction mixture was poured on ice/dilute sulfuric acid. The aqueous layer was extracted with toluene, and the combined organic phases were dried over $MgSO_4$. After removal of the solvent 4.86 g of a crude product was obtained, which were further purified by means of bulb-to-bulb distillation, affording 3.96 g (13.6 mmol, 79%) of **12** as a colorless solid. NMR data (δ in ppm): ^1H (C_6D_6) 1.26 (heptet, 1H, $J = 6.6$ Hz), 1.17 (d, 6H, $J = 6.6$ Hz), 0.24 (s, 27H); ^{13}C (C_6D_6) 23.70, 11.59, 1.93; ^{29}Si (C_6D_6) −10.99, −68.63. MS (70 eV): *m/z* (%) 290 (13) [M^+], 247 (8) [$M^+ -$ i-Pr], 217 (7) [$M^+ - SiMe_3$], 202 (15) [$M^+ - SiMe_4$], 175 (44) [$M^+ - SiMe_3 - C_3H_6$], 117 (14) [H(i-Pr)$SiMe_3^+$], 73 (100) [$SiMe_3^+$]. Anal. Calcd for $C_{12}H_{34}Si_4$ C, 49.57; H, 11.79. Found: C, 49.23; H, 11.81.

Isopropylbis(trimethylsilyl)silyl Potassium (12a). Isotetrasilane **12** was converted into the corresponding potassium compound **12a** as described for tris(trimethylsilyl)silyl potassium above. NMR data (δ in ppm): ^1H (C_6D_6) 1.79 (heptet 1H, $J = 7.1$ Hz), 1.53 (d, 6H, $J = 7.1$ Hz), 0.55 (s, 18H); ^{13}C (C_6D_6) 29.00, 13.05, 5.38; ^{29}Si (C_6D_6) −10.09, −91.56. Ethyl bromide derivatization: MS (70 eV) *m/z* (%) 246 (20) [M^+], 231 (2) [$M^+ -$ Me], 203 (13) [$M^+ -$ i-Pr], 175 (19) [$M^+ -$ Si(i-Pr)], 173 (17) [$SiMe_3$i-PrEtSi$^+$], 131 (39) [$SiMe_3SiMe_2^+$], 73 (100) [$SiMe_3^+$]. Acidic hydrolysis derivatization: MS (70 eV) *m/z* (%) 218 (12) [M^+], 175 (3) [$M^+ -$ i-Pr], 144 (20) [$SiMe_3$i-PrSi$^+$], 129 (13) [$SiMe_2$i-PrSi$^+$], 102 (100) [$SiMe_3HSi^+$], 73 (72) [$SiMe_3^+$].

Phenyltris(trimethylsilyl)silane (13). A solution of phenyllithium (47.4 g, 560 mmol) in diethyl ether was added dropwise to the solution of tris(trimethylsilyl)silyl chloride (155 g, 550 mmol) in diethyl ether (700 mL) at −20 °C. During the addition precipitation of a white solid occurred, and after the addition was complete, the reaction mixture was allowed to warm to room temperature and stirring was continued for another 24 h. Acidic hydrolysis with diluted sulfuric acid was followed by extractive workup with diethyl ether. The combined organic layers were dried over $MgSO_4$, the solvent was removed in a vacuum, and the crude product was purified by vacuum distillation (bp 110 °C at 0.1 mmHg) to yield noncrystalline colorless **13 (**128 g, 394 mmol, 72%), identical in all respects with reported spectral data.[14] The residue contained compound **15**, which was further purified by crystallization from 2-propanol **(**9.8 g, 19.6 mmol, 7.1%).

15. NMR data (δ in ppm): ^1H ($CDCl_3$) 7.58 (m, 2H), 7.26 (m, 3H), 0.34 (s, 18H), 0.20 (s, 27H); ^{13}C ($CDCl_3$) 137.72, 137.15, 127.82, 127.78, 3.93, 3.02; ^{29}Si ($CDCl_3$) −9.19, −12.22, −68.95, −127.86. MS (70 eV): *m/z* (%) 483 (0.5) [$M^+ -$ Me], 425 (2) [$M^+ - SiMe_3$], 348 (43) [$(SiMe_3)_4Si_2^+$], 251 (24) [$(SiMe_3)_2PhSi^+$], 232 (46) [$(SiMe_3)_2Si_2Me_2^+$], 177 (14) [$SiMe_3SiPh^+$], 135 (39) [Me_2PhSi^+], 73 (100) [$SiMe_3^+$]. Anal. Calcd for $C_{21}H_{50}Si_7$: C, 50.52; H, 10.10. Found: C, 50.43; H, 10.02.

Phenylbis(trimethylsilyl)silyl potassium (13a). Isotetrasilane **13** was converted into the corresponding potassium compound **13a** as described above for tris(trimethylsilyl)silyl potassium. NMR data (δ in ppm): ^1H (C_6D_6) 7.71 (d, 2H), 7.06 (t, 2H), 6.86 (t, 1H), 0.53(s, 18H); ^{13}C (C_6D_6) 157.20, 136.33, 127.84, 123.15, 4.36; ^{29}Si (C_6D_6) −9.78, −99.28. Ethyl bromide derivatization: MS (70 eV) *m*/*z* (%) 280 (28) [M$^+$], 265 (6) [M$^+$ − Me], 237 (7) [M$^+$ − SiMe], 207 (37) [M$^+$ − SiMe$_3$], 179 (100) [M$^+$ − SiMe$_3$ − C$_2$H$_4$], 163 (15) [PhSiSiMe$_2$$^+$], 135 (66) [PhMe$_2Si^+$], 105 (22) [PhSi$^+$], 102 (26) [HSi$_2Me_3$$^+$], 73 (47) [SiMe$_3$$^+$]. Acidic hydrolysis derivatization: MS (70 eV) *m*/*z* (%) 252 (16) [M$^+$], 237 (10) [M$^+$ − Me], 178 (58) [M$^+$ − HSiMe$_3$], 163 (100) [PhSiSiMe$_2$$^+$], 135 (60) [PhMe$_2Si^+$], 105 (21) [PhSi$^+$], 73 (69) [SiMe$_3$$^+$].

Pentakis(trimethylsilyl)disilanyl potassium (14a). Hexakis(trimethylsilyl)disilane was converted into the corresponding potassium compound **14a** as described above for tris(trimethylsilyl)silyl potassium. After complete conversion the solvent was removed in a vacuum and toluene was added. Once again the solution was evaporated to remove residual THF. The residue was dissolved in toluene and crystallized at −30 °C. From this solution single crystals were obtained suitable for X-ray structure analysis. The crystal was mounted in a thin-wall glass capillary, which then was flame sealed. The data were collected on a Nonius Kappa CCD diffractometer with Mo Kα radiation.

2-Phenyl-1,1,2,2-tetrakis(trimethylsilyl)disilanyl potassium (15a). Compound **15a** was prepared as described above for tris(trimethylsilyl)silyl potassium and obtained in quantitative yield as a light yellow powder which was crystallized at −35 °C from pentane. In contrast to most other reactions of this type a clearly exothermic reaction could be observed, which caused the reaction solution to warm. NMR data (δ in ppm): ^{1}H (C_6D_6) 7.88 (d, 2H), 7.15 (t, 2H), 7.01 (t, 1H), 3.35 (m, 4H), 1.37 (m, 4H), 0.52 (s, 18H), 0.50 (s, 18H); ^{13}C (C_6D_6) 147.93, 137.30, 127.46, 126.24, 67.74, 25.44, 7.91, 2.86; ^{29}Si (THF, D$_2$O capillary) −6.3, −14.5,−62.3, −184.0. Ethyl bromide derivatization: MS (70 eV) *m*/*z* (%) 439 (2) [M$^+$ − Me], 381 (4) [M$^+$ − SiMe$_3$], 304 (92) [M$^+$ − PhSiMe$_3$], 73 (100) [SiMe$_3$$^+$]. Acidic hydrolysis derivatization: MS (70 eV) *m*/*z* (%) 426 (0.1) [M$^+$], 352 (9) [M$^+$ − HSiMe$_3$], 278 (90) [M$^+$ − 2 HSiMe$_3$], 219 (26) [M$^+$ − Si(SiMe$_3$)PhH], 73 (100) [SiMe$_3$$^+$].

2-Phenyl-1,1,2,2-tetrakis(trimethylsilyl)disilanyl Potassium. 18-Crown-6 (15b). 15 (200 mg, 0.40 mmol), potassium *tert*-butoxide (47 mg, 0.42 mmol), and 18-crown-6 (110 mg, 0.42 mmol) were reacted in benzene (1.00 mL) to rapidly afford a yellow solution of **15b** in quantitative yield. After addition of *n*-pentane yellow crystals precipitate upon standing at room temperature within 24 h. NMR data (δ in ppm): ^{1}H (C_6D_6) 8.16 (m, 2H), 7.17 (m, 2H), 7.03 (m, 1H), 3.23 (s, 24H), 0.52 (s, 18H), 0.50 (s, 18H); ^{13}C (C_6D_6) 146.21, 138.02, 126.55, 125.64, 70.01, 8.39, 2.98; ^{29}Si (C_6D_6) −5.6, −14.4, −62.3, −186.5.

A crystal suitable for X-ray structure analysis was mounted on a glass fiber in paratone N oil and cooled to −60 °C in a cold nitrogen stream. The data were collected on a Bruker SMART Apex diffractometer with Mo Kα radiation.

X-ray Structure Analyses. The structures of **14a** and **15b** were determined and refined using direct methods and least-squares refinement as implemented in SHELXTL-5.1. Crystal and refinement data are listed in Table 1. Selected angles and bond lengths are given in Tables 2 (**14a**) and 3 (**15b**). Detailed crystal structure and refinement data can be found in the Supporting Information. The data have also been deposited at the Cambridge Crystallographic Deposition Centre (CCDC 167978 for **14a**, CCDC 174658 for **15b**).

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Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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