A New and Easy Route to Polysilanylpotassium Compounds☆[1]

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A method is presented for the synthesis of tertiary, secondary, and primary polysilylpotassium compounds. Reaction of potassium *tert*-butoxide, in either DME or THF, with a suitable precursor molecule, proceeds by cleavage of a trimethylsilyl–polysilanyl bond, and formation of trimethylsilyl *tert*-butyl ether and a polysilanylpotassium compound. This route allows easy and flexible access to a number of novel polysilanylpotassium compounds, avoiding the hitherto common use of poisonous mercury compounds.

As is known from the pioneering work of Gilman and coworkers tetrakis(trimethylsilyl)silane can react with methyllithium to form tetramethylsilane and tris(trimethylsilyl)-silyllithium.[2]

$$(Me_3Si)_4Si + MeLi \rightarrow (Me_3Si)Me + \underset{\mathbf{1}}{(Me_3Si)_3SiLi} \quad (1)$$

The latter compound has been rapidly accepted as a prototype of a bulky nucleophilic polysilyl anion and, only recently, has been referred to as "hypersilyl" group.[3] It has been used for the synthesis of transition metal silyl compounds,[4] for the generation of silenes by means of sila-Peterson reaction,[5] and for a number of other purposes.[6] However, it is noticeable that this reagent, although so widely accepted, has rarely been the subject of variation. Only very recently have Klinkhammer[7] and Oehme[8] reported on the synthesis of the potassium and magnesium analogs, however the isotetrasilanyl moiety has almost never been varied. Nevertheless, Apeloig et al. have recently shown that variation of this moiety can be of some advantage. They have been able to show that an increase in the size of ligand gives rise to the formation of stable silenes.[9][5g]

Although it would be interesting to have a set of bulky polysilyl groups differing in reactivity and, especially, in size,[10] in order to achieve different degrees of steric hindrance, this problem has not so far been systematically addressed. The reason for this becomes obvious if one looks at a fact that was first pointed out by Gilman,[11] and then recently studied in more detail by Apeloig et al.,[12] namely that if polysilanes with "inner" Si–Si bonds react with methyllithium there is a pronounced tendency for these "inner" Si–Si bonds to undergo scission. This means that, for example, hexakis(trimethylsilyl)disilane yields **1** and tris(trimethylsilyl)methylsilane in the reaction with methyllithium (Eq. 2).

$$(Me_3Si)_6Si_2 + MeLi \rightarrow \underset{\mathbf{1}}{(Me_3Si)_3SiLi} + MeSi(SiMe_3)_3 \quad (2)$$

The results described in this paper show that this is not a primary limitation, and that it can be easily overcome by the correct choice of the transmetalating agent.

Results and Discussion

Our studies on the synthesis of dendritic and branched polysilanes[13] led to the investigation of some aspects of the chemistry of polysilyl anions. In reactions directed towards the formation of polysilanes with monosilyl anions and silyl halides we often found that the use of the potassium compound was superior to the use of lithium anions. So it was reasonable to also address the use of lithium vs. potassium in the case of the "hypersilyl" anion. Although this compound was already known from the work of Klinkhammer,[7] transmetalation from the corresponding bis-"hypersilyl" mercury, zinc, or cadmium compounds with potassium did not seem to be a real alternative to the use of the readily available "hypersilyllithium" **1**.[2] We felt that a really competitive synthesis must introduce the potassium in as easy a fashion as the lithium. So the obvious reagent of choice was potassium *tert*-butylate, which very effectively transforms dodecamethylcyclohexasilane into the corresponding undecamethylcyclohexasilanylpotassium.[14]

Indeed initial experiments showed that the conversion of tetrakis(trimethylsilyl)silane with *tert*-butylate in DME or THF, in a clean and almost quantitative reaction, gives "hypersilylpotassium" **1a** accompanied by the formation of trimethylsilyl *tert*-butyl ether (Eq. 3).

$$(Me_3Si)_4Si + KO\mathit{t}Bu \rightarrow \underset{\mathbf{1a}}{(Me_3Si)_3SiK} + (Me_3Si)O\mathit{t}Bu \quad (3)$$

Changing the solvent to toluene or pentane gives **1a** as a crystalline compound, with one or two molecules of the

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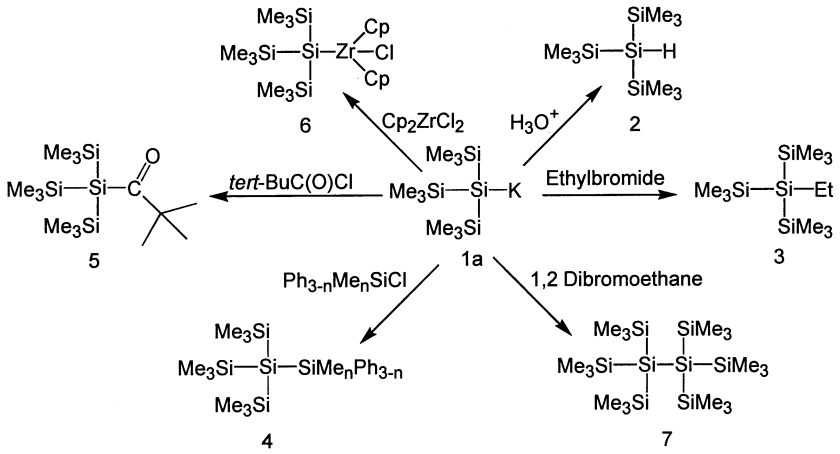
etheral solvent still present, as can be seen from ^{1}H- and ^{13}C-NMR data. This synthesis of **1a** can be regarded as a significant improvement, avoiding the use of poisonous heavy metal compounds which are in turn prepared from **1** or tris(trimethylsilyl)silane.[7] It is an interesting alternative to use **1a** instead of **1** because the reactivities are comparable, the potassium compound being slightly more reactive. We found that the stoichiometry of the potassium reaction is easier to control dealing with potassium *tert*-butylate, which is a weightable solid, compared to methyllithium solutions which may have more or less well defined concentrations.

Treatment of **1a** with a variety of electrophiles proceeded as smoothly as expected (Scheme 1). Reaction with aqueous sulfuric acid gives the hydrosilane **2**, reaction with ethyl bromide yielded the ethylated product **3**, and silylation with a number of phenylated silyl chlorides was easily achieved (**4a,b,c**). Syntheses of an acylsilane (**5**),[15] and of the known zirconocene hypersilyl chloride (**6**),[16] can be achieved in a straightforward manner. The reaction of **1a** with 1,2-dibromoethane at −78°C proceeds in an analogous manner to that of the corresponding lithium compound **1**, and yields the dimerisation product **7**.

Scheme 1



4a can be converted quantitatively to the corresponding bromosilane **8** by a protodesilylation reaction in neat hydrogen bromide at −78°C. The reaction of **8** with another equivalent of **1a** gives bis-"hypersilyl"-dimethylsilane **9** (Eq. 4). The latter compound was found first by Sakurai et al. as one of the products in the aluminum trichloride catalyzed isomerisation of linear permethylnonasilane,[17] and was recently synthesized by Apeloig et al.[12][18]

$$\underset{\mathbf{4a}}{(Me_3Si)_3SiSiMe_2Ph} + HBr \rightarrow \underset{\mathbf{8}}{(Me_3Si)_3SiSiMe_2Br} \rightarrow \underset{\mathbf{9}}{[(Me_3Si)_3Si]_2SiMe_2} \quad (4)$$

Compounds **7** and **9** were chosen to test the reaction with potassium *tert*-butylate for its ability to differentiate between "inner" and "outer" Si−Si bonds. From Gilmans work it is known that the reaction of **7** with methyllithium leads to the formation of **1** and tris(trimethylsilyl)methylsilane.[11] Similarly Apeloig et al. also found, in the reaction of **9** with methyllithium, exclusive cleavage of one of the "inner" Si−Si bonds.[12]

In contrast to these findings the reaction to give the potassium polysilanyl, using potassium *tert*-butylate, exhibits the opposite selectivity, splitting exclusively one of the "outer" Si−$SiMe_3$ bonds (**10**, **11**).

$$RSi(SiMe_3)_3 + KO\mathit{t}Bu \rightarrow RSi(SiMe_3)_2K + (Me_3Si)O\mathit{t}Bu \quad (5)$$

R = $(Me_3Si)_3Si$ **7** **10**
R = $(Me_3Si)_3SiSiMe_2$ **9** **11**

These results open the door for the synthesis of higher polysilyl anions. Both of the anions **10** and **11** are already known as lithium analogs. The lithium analog of **10** was observed by Gilman in the reaction of **7** with **1**.[11] The lithium derivative of **11** was found by Apeloig et al. in a reaction that they describe as the addition of methyllithium to a disilene.[12]

The polysilyl anions **10** and **11** are candidates for experiments in which the polysilyl moiety is required to be of increased size compared to the "hypersilyl" unit in order to fulfill its stabilizing function. It also should be mentioned that in both cases we attempted to obtain the dianionic species by the addition of another equivalent of potassium *tert*-butylate, but failed under normal reaction conditions. However, experiments to obtain such compounds are still in progress in our laboratory. The results reported so far have demonstrated that the potassium polysilanyls are serious competitors to their lithium analogs when higher polysilyl anions are required. The following section will show that this chemistry is also able to yield smaller polysilyl anions.

When ethylated **3** was subjected to standard treatment with potassium *tert*-butylate the reaction proceeded as expected and secondary potassium trisilane **12** was formed.

$$\underset{\mathbf{3}}{(Me_3Si)_3SiEt} + KO\mathit{t}Bu \rightarrow \underset{\mathbf{12}}{(Me_3Si)_2Si(Et)K} + (Me_3Si)O\mathit{t}Bu \quad (6)$$

As **12** can as easily be treated with electrophiles, as was demonstrated for **1a**, the sequence: tetrakis(trimethylsilyl)si-

lane → $(Me_3Si)_3SiK$ (**1a**) → $(Me_3Si)_3SiE$ (**3**) → $(Me_3Si)_2Si(E)K$ (**12**) → $(Me_3Si)_2Si(E)E'$ offers an interesting method of access to 2,2′-disubstituted trisilanes.[19]

Even more interesting, but unfortunately less selective, is the conversion of **2**. Under analogous conditions a secondary potassium trisilane **13** was formed with hydrogen and potassium attached to the same silicon atom. The reaction is accompanied by the formation of **1a**, which seems to be the result of a deprotonation reaction. The ratio of these two products is about 7:3 in favor of **13**.

$$\underset{\mathbf{2}}{(Me_3Si)_3SiH} + KO\mathit{t}Bu \rightarrow 0.7\ \underset{\mathbf{13}}{(Me_3Si)_2Si(H)K} + 0.3\ \underset{\mathbf{1a}}{(Me_3Si)_3SiK} + 0.7\ (Me_3Si)O\mathit{t}Bu + 0.3\ HO\mathit{t}Bu \quad (7)$$

While it has been shown so far that tertiary and secondary potassium silanyls are easily available from the reaction of suitable precursors with potassium *tert*-butylate, and it is also known that monosilyl potassium compounds are accessible from disilanes by reaction with C_8K,[20] primary potassium silanyls are not so easy to obtain.

The reaction of octamethyltrisilane with potassium *tert*-butylate in DME shows some rather complex chemistry, which we are currently studying in more detail, but which does not provide a suitable route to pentamethyldisilanylpotassium. Since 1,1-diphenyltrimethyldisilanyl alkali compounds are known to form from the reaction of 2,2-diphenylhexamethyltrisilane with methyllithium or sodium potassium alloy,[21] it was decided to test our reaction conditions on 2-phenylheptamethyltrisilane. However addition of one equivalent of potassium *tert*-butylate to the latter gave not only the desired disilanylpotassium compound **14**, but also a substantial amount of trimethylsilylpotassium, which was detected by ^{29}Si NMR. Changing the solvent to THF slowed down the reaction rate and did improve the ratio, but only slightly. It was finally found that optimum reaction conditions could be achieved by gradual addition of potassium *tert*-butylate to a THF solution of the starting material.

Analysis of ^{29}Si-NMR data from the experiments described and from the literature (see Table 1) shows some interesting details. Comparison of the shift values of the silicon atom with a trimethylsilyl substituent and the analog bearing a negative charge shows a high field shift of about 60 ppm, for tertiary alkali silanyls (entries 1−3), and of 33 ppm for the generation of a secondary potassium silanyl compound with one alkyl group (entry 4). Interestingly the substitution of a trimethylsilyl group by hydrogen (cf. entry 5) also gives a $\Delta\delta_{Si}$ value similar to the tertiary alkali silanyl (entry 1). Comparison of the known ^{29}Si-NMR value of H_3SiK (entry 10) with that of the respective trimethylsilylated compound shows that even a trihydrogenated silicon atom shifts some 60 ppm to higher field when the trimethylsilyl substituent is replaced by potassium.

While the change from secondary alkali silanyls to primary ones (entry 4 vs. 6) is not so pronounced, the influence of a phenyl group on the silicon atom bearing the negative charge is indicative, as can be seen by comparison of entries 6 and 7. In the case of the permethylated molecule (entry 6) a 26 ppm higher field shift is observed, while the molecule with one phenyl group shows only a 16 ppm shift. Obviously some of the negative charge can be transferred onto the phenyl group, resulting in a weaker deshielding effect. A very similar case is that of the monosilyl alkali compounds. While trimethylsilylpotassium shows an even weaker shift (only 14 ppm) compared to hexamethyldisilane (entry 8), dimethylphenylsilyllithium (entry 9) shows the weakest shift in the entire series (about 6 ppm) compared to the trimethylsilylated compound.

Table 1. Comparison of ^{29}Si-NMR shift values of polysilyl alkali compounds with the respective trimethylsilylated molecules

Entry	Oligosilane	$\delta_{Si-SiMe_3}$	Alkali silanyl	δ_{Si-M}	$\Delta\delta_{Si}$
1	$(Me_3Si)_4Si$[a]	−135.6	$(Me_3Si)_3SiK$[a]	−195.8	60.2
2	$(Me_3Si)_3SiSi(SiMe_3)_3$[a]	−129.5	$(Me_3Si)_3SiSi(SiMe_3)_2K$[a]	−192.7	63.2
3	$(Me_3Si)_3SiSiMe_2Si(SiMe_3)_3$[a]	−117.8	$(Me_3Si)_3SiSiMe_2Si(SiMe_3)_2K$[a]	−187.0	69.2
4	$(Me_3Si)_3SiEt$[a]	−78.6	$(Me_3Si)_2EtSiK$[a]	−111.7	33.1
5	$(Me_3Si)_3SiH$[a]	−115.4	$(Me_3Si)_2HSiK$[a]	−181.1	65.7
6	$Me_3SiSiMe_2SiMe_3$[b]	−48.7	$Me_3SiSiMe_2Li$[c]	−74.9	26.2
7	$Me_3SiSiMePhSiMe_3$[d]	−46.0	$Me_3SiSiMePhK$[d]	−62.9	16.9
8	$Me_3SiSiMe_3$[b]	−20.5	Me_3SiK[e]	−34.4	13.9
9	$PhMe_2SiSiMe_3$[b]	−21.7	$PhMe_2SiLi$[b]	−27.3	5.6
10	Me_3SiSiH_3[f]	−97.7	H_3SiK[b]	−165.0	67.3

[a] Measured in DME. − [b] Value taken from ref.[26]. − [c] Value taken from ref.[27]. − [d] measured in THF. − [e] Value taken from ref.[22]. − [f] A sample of Me_3SiSiH_3 was kindly provided by Dr. Robert Zink.

From the comparison of these data it is evident that the silicon atom bearing the negative charge can gain a release of charge which depends on the kind of substituents attached. While hydrogen and silyl groups, in accordance with their respective electropositive characters, do not take a great deal of the charge, charge can be transferred to methyl and, to an even greater extent, to phenyl groups,[22] which in turn leads to smaller values of $\Delta\delta_{Si}$.

One should mention here that analysis of these NMR data has to be undertaken with some caution with respect to the solvents used in the measurement. While the shifts of the uncharged compounds are relatively independent of solvent effects the silyl potassium compounds show a rather pronounced dependence on the solvent. Compared to the reported ^{29}Si-NMR data of $\delta = -185$ for **1a** in deuterobenzene, we found that a complexing solvent such as DME causes an additional upfield shift of 11 ppm, indicating a less covalent character for the Si−K bond. Formation of **1a** in THF results in a signal at −194 ppm. Subsequent crystallization from pentane shows the presence of two molecules of THF in the ^{1}H-NMR spectrum, and a value of $\delta = -189.5$ in the ^{29}Si-NMR spectrum. So we can observe, for one compound, a difference in the shift value of some 10 ppm depending on the solvent. However, it was considered that, as the data compared in Table 1 always refer to compounds in etheral solvents, this comparison was valid. Also the tendencies discussed are so pronounced that the solvent effects are relatively small.

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Experimental Section

All reactions were carried out in flame-dried glassware under an inert atmosphere of dry argon or nitrogen. Solvents were distilled prior to use from either sodium or sodium potassium alloy. Starting materials tetrakis(trimethylsilyl)silane[23] and 2-phenylheptamethyltrisilane[24] were prepared according to literature procedures. $PhMe_2SiCl$, $Ph_2MeSiCl$, Ph_3SiCl, potassium *tert*-butylate, 1,2-dibromoethane, and ethyl bromide were used without further purification.

^1H-, ^{13}C-, and ^{29}Si-NMR spectra were recorded on a Bruker MSL 300 at the indicated frequencies. ^{29}Si-NMR spectra were measured either in C_6D_6 or directly from the reaction mixture using a D_2O capillary providing an external lock signal. In all cases, except for **2** and **13**, the INEPT pulse sequence was employed. − GC/MS was performed on an HP 5890/II gas chromatgraph with an HP 5971/A MSD, an HP1 (Cross-linked methyl silicone) column and helium as a carrier gas. − Elemental analyses of the branched polysilanes were done using a Heraeus elementar vario EL apparatus. For some reason the carbon values found in the elemental analyses are too low when certain compounds were analyzed with quarternary silicon atoms. While the hydrogen values correspond nicely to the calculated numbers we attribute the low carbon values to the formation of silicon carbide, which seems to be very favorable in the cases of the compounds mentioned.

General Procedure: Starting material and one equivalent of potassium *tert*-butylate were mixed together in a flask and either DME or THF added. Almost immediately the solution turned yellow and, after some time, sometimes orange. Completion of the reaction was detected either by ^{29}Si-NMR spectroscopy (D_2O capillary as external lock) and/or by obtaining a derivative and subsequent GC/MS or GC analysis. The derivative was obtained 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_2SO_4 mixture followed by mixing of the layers.

Tris(trimethylsilyl)silylpotassium (**1a**): In a typical experiment tetrakis(trimethylsilyl)silane (3.10 g, 9.66 mmol) was treated with *tert*-BuOK (1.14 g, 10.14 mmol) in 5 ml of either DME or THF following the general procedure. While the conversion in DME was usually complete within 10 min the use of THF sometimes required reaction times up to 60 min. − ^{29}Si NMR (59.6 MHz, DME, D_2O lock): δ = −3.93, −195.83, (59.6 MHz, THF, D_2O lock): δ = −4.55, −194.10.

A sample of **1a** prepared in THF on the same scale as described above, which was isolated by removal of solvent in vacuo and crystallization from toluene and pentane (3.20 g, 7.71 mmol, 80%), was identified by ^1H NMR and ^{13}C NMR as a complex containing two molecules of THF. − ^1H NMR (300 MHz, C_6D_6): δ = 3.42 (m, 8 H), 1.47 (m, 8 H), 0.47 (s, 27 H). − ^{13}C NMR (75.4 MHz, C_6D_6): δ = 68.33, 25.93, 7.67. − ^{29}Si NMR (59.6 MHz, C_6D_6): δ = −5.35, −189.56.

Tris(trimethylsilyl)silane (**2**): **1a** was generated in THF from tetrakis(trimethylsilyl)silane (1.00 g, 3.11 mmol) following the general procedure. After complete conversion the solution of **1a** in THF was slowly poured into a mixture of ethyl ether (30 ml), aqueous H_2SO_4 (1 M solution, 50 ml), and ice. The organic layer was dried over Na_2SO_4 and evaporated in vacuo. The remaining oil (720 mg, 2.90 mmol, 93%) was pure by GC/MS. − ^{29}Si NMR (59.6 MHz, pentane, D_2O lock): δ −10.92, −115.36 (d, J = 156 Hz). − MS (70 eV): *m/z* (%): 248 (33) [M^+], 233 (27) [M^+ − Me], 174 (82) [M^+ − $HSiMe_3$], 160 (100) [M^+ − $SiMe_4$], 159 (88) [MH − $SiMe_4$], 73 (80) [$SiMe_3$]. − IR, ^1H and ^{13}C NMR data in accordance to the literature.[25]

Tris(trimethylsilyl)ethylsilane (**3**): Compund **3** was prepared from tetrakis(trimethylsilyl)silane (2.00 g, 6.22 mmol) by essentially the same method as for **2** with the difference that the solution of **1a** was poured into a mixture of ethyl ether (30 ml) and ethyl bromide (5 ml). After complete addition the solution was stirred for 5 min at room temp. and aqueous H_2SO_4 (1 M solution, 50 ml) was added. The workup was the same as for **2**. The remaining white solid (1.43 g, 5.17 mmol, 83%) was found, using GC/MS and NMR, to be pure. An analytical sample was recrystallized from ethanol (mp: 136−138°C). − ^1H NMR (300 MHz, $CDCl_3$): δ = 1.10 (t, J = 8.0 Hz, 3 H), 0.82 (q, J = 7.9 Hz, 2 H), 0.17 (s, 27 H). − ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 13.11, 1.39, 0.00. − ^{29}Si NMR (59.6 MHz, pentane, D_2O lock): δ −12.35, −78.81. − MS (70 eV): *m/z* (%): 276 (20) [M^+], 261 (4) [M^+ − Me], 203 (19) [M^+ − $SiMe_3$], 188 (30) [M^+ − $SiMe_4$], 175 (27) [M^+ − $EtSiMe_3$], 73 (100) [$SiMe_3$]. − $C_{11}H_{32}Si_4$ (276.72) calcd. C 47.75, H 11.66; found C 47.46, H 11.71.

1,1,1-Tris(trimethylsilyl)dimethylphenyldisilane (**4a**): **1a** was prepared from tetrakis(trimethylsilyl)silane (3.10 g, 9.66 mmol) and *tert*-BuOK (1.14 g, 10.1 mmol) in THF by the general procedure. After complete reaction the solvent was removed in vacuo and toluene (15 ml) was added. The mixture was cooled to −78°C and chlorodimethylphenylsilane (1.81 g, 10.6 mmol) was added in toluene (10 ml) gradually over 5 min. The reaction was stirred for further 12 h at room temp.. The workup was done by the addition of aqueous H_2SO_4 (1 M solution, 20 ml), extraction of the aqueous phase with two portions of ether, and drying of the combined organic phases over Na_2SO_4. After removal of the solvent by evaporation the white residue was crystallized from ethanol to give **4a** (3.00 g, 7.83 mmol, 81%) as white crystals (mp: 156−157°C). − ^1H NMR (300 MHz, $CDCl_3$): δ = 7.56 (m, 2 H), 7.36 (m, 3 H), 0.54 (s, 6 H), 0.18 (s, 27 H). − ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 141.46, 134.32, 128.68, 127.86, 3.02, 1.42. − ^{29}Si NMR (59.6 MHz, pentane, D_2O lock): δ = −8.92, −12.48, −133.23. − MS (70 eV): *m/z* (%): 382 (14) [M^+], 367 (7) [M^+ − Me], 294 (4) [M^+ − $SiMe_4$], 232 (93) [$Me_2Si_2(SiMe_3)_2$], 135 (79) [$SiMe_2Ph$], 73 (100) [$SiMe_3$]. − $C_{17}H_{38}Si_5$ (382.92) calcd. C 53.32, H 10.00; found C, 53.04 H 9.93.

1,1,1-Tris(trimethylsilyl)methyldiphenyldisilane (**4b**): **4b** was prepared following the procedure for the synthesis of **4a**, and on the same scale, using methyldiphenylchlorosilane (2.47 g, 10.6 mmol) as an electrophile. White crystals of **4b** (3.06 g, 6.88 mmol, 71%) were isolated after crystallization from ethanol (mp: 161−164°C). − ^1H NMR (300 MHz, $CDCl_3$): δ = 7.56 (m, 4 H), 7.33 (m, 6 H), 0.79 (s, 3 H), 0.14 (s, 27 H). − ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 138.90, 135.41, 128.97, 127.86, 3.10, 0.58. − ^{29}Si NMR (59.6 MHz, pentane, D_2O lock): δ = −8.95, −11.95, −132.84. − MS (70 eV): *m/z* (%): 444 (4) [M^+], 429 (2) [M^+ − Me], 294 (4) [M^+ − $PhSiMe_3$], 232 (100) [$Me_2Si_2(SiMe_3)_2$], 197 (75) [$SiMePh_2$], 135 (34) [$SiMe_2Ph$], 73 (47) [$SiMe_3$]. − $C_{22}H_{40}Si_5$ (444.99) calcd. C 59.38, H 9.09; found C 59.32, H 9.01.

1,1,1-Tris(trimethylsilyl)triphenyldisilane (**4c**): **4c** was prepared following the procedure for the synthesis of **4a**, and on the same

scale, using triphenylchlorosilane (3.13 g, 10.5 mmol) as an electrophile. White crystals of **4c** (3.74 g, 7.37 mmol, 76%) were yielded after crystallization from ethanol (mp: 263−266°C). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.52 (m, 6 H), 7.37 (m, 9 H), 0.18 (s, 27 H). − ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 137.71, 136.71, 129.26, 127.99, 3.19. − ^{29}Si NMR (59.6 MHz, pentane, D_2O lock): δ = −9.17, −10.22, −130.84. − MS (70 eV): *m/z* (%): 297 (1) [M^+ − $SiPhMe_2$ − $HSiMe_3$], 282 (8) [M^+ − $SiPhMe_2$ − $SiMe_4$], 259 (93) [$SiPh_3$)], 232 (100) [$Me_2Si_2(SiMe_3)_2$], 135 (28) [$SiMe_2Ph$], 73 (47) [$SiMe_3$]. − $C_{27}H_{42}Si_5$ (507.06) calcd. C 63.96, H 8.35; found C 63.81, H 8.39.

Tris(trimethylsilyl)silylpivaloate (**5**): **1a** was generated following the general procedure from tetrakis(trimethylsilyl)silane (3.00 g, 9.35 mmol) in THF. After removal of the solvent toluene (10 ml) was added and the solution was added slowly to an ice cold solution of pivaloyl chloride (1.16 g, 9.63 mmol) in toluene (10 ml). After complete conversion, which was checked by GC/MS, the reaction mixture was poured into an ice/sulfuric acid mixture (10%). The aqueous layer was extracted with ether (2 × 20 ml) and the combined organic layer dried over Na_2SO_4. After removal of the solvent final purification was achieved by chromatography on silica with toluene/heptane, 10:1. Spectral data of the compound (2.17 g, 6.52 mmol, 70%) were in accordance with the literature.[15]

Tris(trimethylsilyl)silylchlorozirconocene (**6**): **1a** was generated following the general procedure from tetrakis(trimethylsilyl)silane (2.00 g, 6.23 mmol) in DME. After complete conversion the solution was added, using a syringe pump, over a period of 40 min to a suspension of Cp_2ZrCl_2 (1.82 g, 6.22 mmol) in pentane (10 ml). Complete conversion was detected by ^{29}Si NMR after another 60 min stirring at room temp. Crystallization was achieved by removal of the solvent, addition of 20 ml of pentane and storage at −75°C. Extremely air-sensitive red crystals (3.12 g, 5.78 mmol, 93%) were obtained. − Spectral data in accordance to literature values.[16]

Hexakis(trimethylsilyl)disilane (**7**): **1a** was generated following the general procedure from tetrakis(trimethylsilyl)silane (5.00 g, 15.6 mmol) in THF. After complete conversion the solution was cooled to −78°C and 1,2-dibromoethane (1.63 g, 8.67 mmol) in ethyl ether (30 ml) was added dropwise over a period of 30 min. The solution then was allowed to come to room temp. and was poured into an ice/aqueous H_2SO_4 mixture. The organic layer was dried over Na_2SO_4 and the solvent removed in vacuo. The remaining white crystals (3.80 g) were shown by ^{29}Si NMR to be 90% pure **7**, with tetrakis(trimethylsilyl)silane being the only impurity. Sublimation (120°C, 1 mbar) removed about 300 mg of tetrakis(trimethylsilyl)silane. Finally pure **7** was obtained by recrystallization from acetone and ethanol which gave **7** (3.16 g 6.38 mmol, 82%) as white crystals. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.20 (s). − ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 4.60. − ^{29}Si NMR (59.6 MHz, pentane, D_2O lock): δ = −9.04, −129.49. − MS (70 eV): *m/z* (%): 406 (0.2) [M^+ − $SiMe_4$], 247 (6) [M^+ − $Si(SiMe_3)_3$], 232 (29) [M^+ − $MeSi(SiMe_3)_3$], 73 (100) [$SiMe_3$].

1,1,1-Tris(trimethylsilyl)dimethylbromodisilane (**8**): A flask equipped with a reflux condenser cooled to −80°C and charged with a sample of **4a** (2.40 g, 6.27 mmol) was cooled to −80°C and approx. 10 ml of hydrogen bromide was condensed on under a pressure of 200−500 mbar. After 30 min the cooling bath was removed and the solution of **4a** in hydrogen bromide was refluxed for 90 min. Then hydrogen bromide was removed in vacuo and pentane was distilled onto the residue (10 ml). The solution was filtered over a plug of glass wool and the solvent of the filtrate was removed in vacuo. The remaining white powder of **8** (2.40 g, 6.22 mmol, 99%) was pure by GC and NMR. − ^{1}H NMR (300 MHz, C_6D_6): δ = 0.71 (s, 6 H), 0.26 (s, 27 H). − ^{13}C NMR (75.4 MHz, C_6D_6): δ = 8.08, 2.90. − ^{29}Si NMR (59.6 MHz, C_6D_6): δ = 25.81, −9.61, −127.92; MS (70 eV): *m/z* (%): 369/371 (4/5) [M^+ − Me], 311/313 (1/2) [M^+ − $SiMe_3$], 232 (45) [M^+ − $BrSiMe_3$], 73 (100) [$SiMe_3$]. − $C_{11}H_{33}BrSi_5$ (385.71) calcd. C 34.25, H 8.62; found C 33.97, H 8.57.

1,1,1,3,3,3-Hexakis(trimethylsilyl)dimethyltrisilane (**9**): A solution of **1a** [prepared from tetrakis(trimethylsilyl)silane (1.66 g, 5.17 mmol) in DME] in toluene (5 ml) was added slowly at −50°C to a solution of **8** (1.81 g, 4.70 mmol) in toluene (5 ml). The reaction was allowed to reach room temp. and was followed by ^{29}Si NMR. After complete conversion a workup was performed by the addition of aqueous H_2SO_4 (1 M solution, 20 ml), extraction of the aqueous layer with two portions of ether, and drying of the combined organic layers over Na_2SO_4. Solvent was removed in vacuo and the residue was subjected to Kugelrohr distillation (1 mbar, 250°C) to remove volatile components. Finally crystallization of the remaining solid was achieved from ethanol/ethyl acetate to yield **9** (1.62 g, 2.92 mmol, 62%) as white crystals (mp: 168−171; ref.[17] 170−172°C). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.50 (s, 6 H), 0.23 (s, 54 H). − ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 5.81, 4.10. − ^{29}Si NMR (59.6 MHz, pentane, D_2O lock): δ = −8.64, −25.19, −117.70. − MS (70 eV): *m/z* (%): 537 (1) [M^+ − Me], 305 (97) [M^+ − $Si(SiMe_3)_3$], 232 (100) [$Me_2Si_2(SiMe_3)_2$], 73 (95) [$SiMe_3$]. − $C_{20}H_{60}Si_9$ (553.47) calcd. C 43.40, H 10.93; found C 41.94, H 10.92.

Pentakis(trimethylsilyl)disilanylpotassium (**10**): Compound **10** was prepared from **7** (200 mg, 0.40 mmol) and *tert*-BuOK (44 mg, 0.40mmol) in DME following the general procedure. The only product after complete consumption of **7**, as detected by NMR and GC/MS of derivatives of the samples, was **10**. − ^{29}Si NMR (59.6 MHz, DME, D_2O lock): δ = −5.58, −10.68, −128.92, −192.62. − H_3O^+ quench: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.81 (s, 1 H), 0.33 (s, 18 H), 0.32 (s, 27 H). − ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 3.74, 3.54. − ^{29}Si NMR (59.6 MHz, pentane, D_2O lock): δ = −11.84, −13.38, −118.02, −135.04. − MS (70 eV): *m/z* (%): 407 (3) [M^+ − Me], 348 (18) [M^+ − $HSiMe_3$], 333 (2) [M^+ − $HSiMe_4$], 259 (4) [M^+ − $H_2Si_2Me_7$], 73 (100) [$SiMe_3$]. − Ethyl bromide quench: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.13 (t, *J* = 7.0 Hz, 3 H), 0.97 (q, *J* = 7.0 Hz, 2 H), 0.26 (s, 27 H), 0.24 (s, 18 H). − ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 13.52, 5.11, 4.18, 3.01. − ^{29}Si NMR (59.6 MHz, pentane, D_2O lock): δ = −8.94, −11.73, −68.92, −130.43. − MS (70 eV): *m/z* (%): 377 (6) [M^+ − $SiMe_3$], 275 (4), [M^+ − 2 $SiMe_3$, − Et], 232 (26) [$Me_2Si_2(SiMe_3)_2$], 73 (100) [$SiMe_3$]. The experiment was repeated in THF with essentially the same results. Removal of solvent and crystallization from pentane gave white crystals solvated with two molecules of THF in an almost quantitative yield (220 mg, 0.37 mmol, 93%). − ^{1}H NMR (300 MHz, C_6D_6): δ = 3.41 (m, 8 H), 1.46 (m, 8 H), 0.51 (s, 18 H), 0.46 (s, 27 H). − ^{13}C NMR (75.4 MHz, C_6D_6): δ = 68.28, 25.94, 8.82, 4.78.

1,1,3,3,3-Pentakis(trimethylsilyl)-2,2-dimethyltrisilanylpotassium (**11**): Compound **11** was prepared from **9** (95 mg, 0.17 mmol) and *tert*-BuOK (19 mg, 0.17 mmol) in DME following the general procedure. The reaction was followed directly by ^{29}Si NMR and GC/MS of the quenched samples. Conversion was complete after 60 min. Addition of another equivalent of *tert*-BuOK (19 mg, 0.17 mmol) did not result in a second splitting reaction but led to the slow decomposition of the product after two days. − ^{29}Si NMR (59.6 MHz, DME, D_2O lock): δ = −3.21, −8.80, −16.12, −127.09, −186.99. − H_3O^+ quench: MS (70 eV): *m/z* (%): 480 (0.1) [M^+], 406 (3) [M^+ − $HSiMe_3$], 305 (63) [M^+ − $HSi(SiMe_3)_3$], 231 (25) [$Me_2Si_2(SiMe_3)_2$ − H], 73 (100) [$SiMe_3$]. − Ethyl bromide quench:

MS (70 eV): *m/z* (%): 493 (0.2) [M^+ − Me], 305 [M^+ − EtSi(SiMe$_3$)$_2$], 232 (30) [$Me_2Si_2(SiMe_3)_2$], 188 (24) [EtSi(SiMe$_3$) − Me], 73 (100) [SiMe$_3$)].

Bis(trimethylsilyl)ethylsilylpotassium (**12**): Compound **12** was prepared from **3** (89 mg, 0.36 mmol) and *tert*-BuOK (40 mg, 0.36 mmol) in DME following the general procedure. The reaction was followed directly by ^{29}Si NMR and GC/MS of the quenched samples. It was found to be complete after 25 min. − ^{29}Si NMR (59.6 MHz, DME, D_2O lock): δ = −6.82, −111.68. − H_3O^+ quench: MS (70 eV): *m/z* (%): 204 (14) [M^+], 189 (7) [M^+ − Me], 161 (8) [M^+ − SiMe$_3$], 130 (29) [M^+ − HSiMe$_3$], 102 (65) [M^+ − EtSiMe$_3$)], 73 (100) [SiMe$_3$]. − Ethyl bromide quench: MS (70 eV): *m/z* (%): 232 (12) [M^+], 159 (16) [M^+ − SiMe$_3$], 131 (27) [MH^+ − EtSiMe$_3$], 73 (100) [SiMe$_3$]. Repeating the experiment the same scale in THF led to the same results with some increased reaction time. Removals of solvent and crystallization from pentane gave white crystals (56 mg, 0.20 mmol, 56%), which were shown by NMR to contain half a molecule of THF coordinated to the silyl potassium compound. − ^{1}H NMR (300 MHz, C_6D_6): δ = 3.37 (m, 2 H), 1.37 (m, 2 H), 1.24 (t, *J* = 7.8 Hz, 3 H), 0.86 (q, *J* = 7.8 Hz, 2 H), 0.32 (s, 18 H). − ^{13}C NMR (75.4 MHz, C_6D_6): δ = 68.42, 25.82, 19.57, 5.03, 3.69.

Bis(trimethylsilyl)silylpotassium (**13**): Compound **13** was prepared from **2** (775 mg, 3.11 mmol) and *tert*-BuOK (385 mg, 3.43 mmol) in DME following the general procedure. The reaction was followed directly by ^{29}Si NMR and GC/MS of the quenched samples. Complete conversion was reached after 2 h and gave **13** and **1a** in a ratio of about 7:3. − IR $\tilde{\nu}$: 1891 cm^{-1} (Si−H). − ^{29}Si NMR (59.6 MHz, DME, D_2O lock): δ = −4.02, −181.14 (d, *J* = 82 Hz). − H_3O^+ quench: MS (70 eV): *m/z* (%):, 176 (11) [M^+], 161 (16) [M^+ − Me], 101 (9) [M^+ − H_2SiMe_3], 88 (21) [M^+ − SiMe$_4$], 73 (100) [SiMe$_3$]. − Ethyl bromide quench: MS: vide supra. The experiment was repeated in THF on larger scale and gave essentially the same results. Removal of the solvent and crystallization from pentane gave a mixture of **13** and **1a** with THF coordinated to the alkali silanyl compounds. − ^{1}H NMR (300 MHz, C_6D_6): δ = 3.51 (m), 1.38 (m), 1.29 (s, 1 H), 0.47 (s, 18 H), 0.43 (s, 27 H).

1-Phenyltetramethyldisilanylpotassium (**14**): Compound **14** (200 mg, 0.75 mmol) was prepared from 2-phenylheptamethyltrisilane in THF following the general procedure, with the variation that *tert*-BuOK (85 mg, 0.75 mmol) was added in several portions over two hours. − ^{29}Si NMR (59.6 MHz, THF, D_2O lock): δ = −12.33, −62.96. − H_3O^+ quench: MS (70 eV): *m/z* (%): 194 (21) [M^+], 179 (15) [M^+ − Me], 135(83) [M^+ − HSiMe$_2$], 121 (21) [M^+ − SiMe$_3$], 105 (28) [M^+ − HSiMe$_4$], 73 (100) [SiMe$_3$]. − Ethyl bromide quench: MS (70 eV): *m/z* (%): 222 (20) [M^+], 207 (4) [M^+ − Me], 193 (14) [M^+ − Et], 149 (39) [M^+ − SiMe$_3$], 135 (44) [SiPhEt], 121 (100) [HSiPhMe], 105 (17) [SiPh], 73 (27) [SiMe$_3$].

☆ In memoriam Prof. *Edwin Hengge*.

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