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# Silylgermylpotassium Compounds

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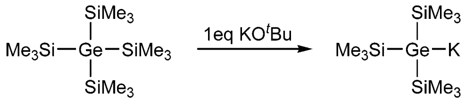
By the reactions of potassium *tert*-butoxide with a number of oligosilylgermanes, oligosilylgermylpotassium compounds were generated. Their chemistry very much resembles that of the analogous oligosilylsilylpotassium compounds. However, the ease of formation is even more pronounced in the case of the germyl anions. Again potassium *tert*-butoxide proved to be a highly selective metalation reagent, leading to no unwanted cleavage of Si−Ge or Ge−Ge bonds. A number of new and potentially useful oligosilylgermyl mono- and dianions have been prepared in this manner.

## Introduction

While the chemistry of oligosilyl anions has received increasing attention over the last few years,[1] the analogous chemistry of silyl-substituted germanium compounds was very much limited to the chemistry of the tris(trimethylsilyl)germyl fragment.[2] Brook et al. introduced this moiety in an attempt to obtain germenes via photolytic rearrangement of acylgermanes.[3] For the synthesis of tris(trimethylsilyl)germyllithium they utilized a route pioneered by Gilman et al. for the synthesis of tris(trimethylsilyl)silyllithium.[4] Starting from tetrakis(trimethylsilyl)germane, reaction with methyllithium cleaved a trimethylsilyl group and formed tris(trimethylsilyl)germyllithium and tetramethylsilane. Some structural investigations of this germyllithium reagent were carried out, and it eventually became the reagent of choice for the introduction of this particular germyl substituent into transition metal[5] and main group[6] compounds. While tris(trimethylsilyl)germyllithium usually is coordinated by three THF molecules, recently the unsolvated reagent became available and was shown to exist as a trimer in solid state.[7]

**Scheme 1. Formation of Tris(trimethylsilyl)germylpotassium (1)**



(**1**)

## Results and Discussion

Recent work by Teng and Ruhlandt-Senge concerning the synthesis of tris(trimethylsilyl)germylpotassium[8] prompts us to report our own results of research in this area. In analogy with the above-mentioned work, we reacted tetrakis(trimethylsilyl)germane with potassium *tert*-butoxide to obtain tris(trimethylsilyl)germylpotassium (**1**) (Scheme 1). In accordance with our experiences with the tris(trimethylsilyl)silylpotassium chemistry,[9] the reaction could be conducted either in THF or in an aromatic solvent. The latter case, though, required the presence of crown ether.

The reactivity of **1** very much resembles that of tris(trimethylsilyl)silylpotassium. Reactions with electrophiles gave the expected products (Scheme 2). Simple hydrolysis with aqueous sulfuric acid gave the respective germanium hydride (**2**);[3] reaction with ethyl bromide yielded tris(trimethylsilyl)ethylgermane (**3**). Re-

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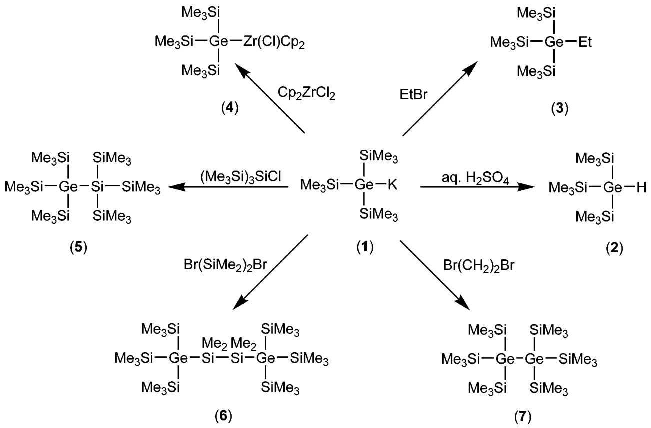
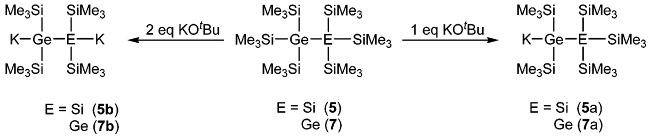
10.1021/om0491894 CCC: $30.25

**Scheme 2. Reactions of Tris(trimethylsilyl)germylpotassium (1)**



**Scheme 3. Formation of Germylsilyl and Digermyl Mono- and Dipotassium Compounds**

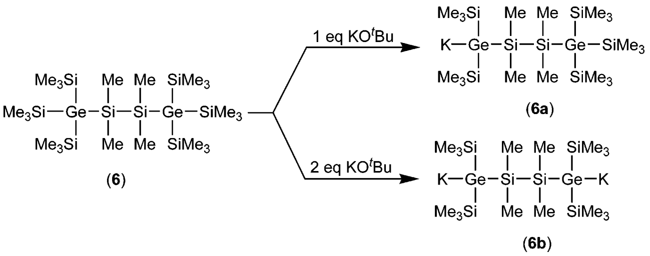


action with zirconocene dichloride gave tris(trimethylsilyl)germylzirconocene chloride (**4**), a substance previously prepared by Tilley and co-workers using the germyllithium reagent.[10] Reaction with tris(trimethylsilyl)silyl chloride gave tris(trimethylsilyl)[tris(trimethylsilyl)silyl]germane (**5**). To introduce two tris(trimethylsilyl)germyl units in one molecule, 2 equiv of **1** was reacted with 1,2-dibromotetramethyldisilane to obtain 1,2-bis[tris(trimethylsilyl)germyl]tetramethyldisilane (**6**). Also, in close analogy with the chemistry of the tris(trimethylsilyl)silyl anion, the formation of hexakis(trimethylsilyl)digermane (**7**)[3] was achieved by reaction of **1** with 1,2-dibromoethane. All these reactions proceeded cleanly, giving the expected products in good to excellent yields.

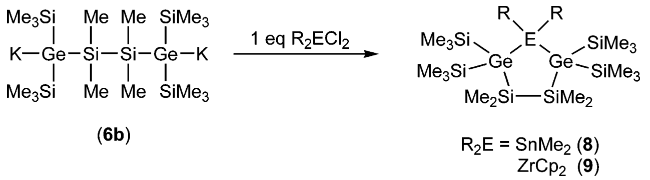
As we have studied the formation of numerous oligosilylpotassium compounds by reaction of oligosilanes with potassium *tert*-butoxide, it was of interest to investigate analogous chemistry with **5**, **6**, and **7**. Especially **5** was considered an interesting molecule with respect to this. The fact that there are three trimethylsilyl groups at each of the central silicon and germanium atoms should exclude any kinetic preferences for one side of the molecule. Surprisingly, reaction of **5** with 1 equiv of potassium *tert*-butoxide afforded metalation exclusively at the germanium atom (**5a**) (Scheme 3). While it seems evident that thermodynamic reasons favor the formation of a germanide over that of a silanide, it could be likely that at an early stage of the reaction both **5a** and the respective silylpotassium compounds are formed. Attempts to detect such mixtures by means of NMR spectroscopy, however, were not successful. At least at room temperature the reaction seems to be too fast to observe any kinetically controlled product ratio.

Reaction of **5** with 2 equiv of potassium *tert*-butoxide in the presence of crown ether gave the 1,2-dipotassium compound **5b**, with the second metalation step being much slower (Scheme 3). Again, this behavior is in accordance with our previous observations on the synthesis of oligosilyl dianions.[11] The potassium *tert*-butoxide cleavage of hexakis(trimethylsilyl)digermane (**7**) was also examined. Depending on the amount of potassium alkoxide used, either the mono- (**7a**) or di- (**7b**) potassium compound was obtained (Scheme 3).

**Scheme 4. Formation of Germyl Mono- (6a) and 1,4-Dianion (6b)**



**Scheme 5. Use of 6b for the Synthesis of Germa-Sila-Heterocycles**



In a further attempt to compare the germanium chemistry to that of silicon also the mono- (**6a**) and di- (**6b**) anions of **6** were generated by reaction with either 1 or 2 equiv of potassium *tert*-butoxide (Scheme 4). Both reactions proceeded smoothly in full accordance with what had been observed before in the case of the silicon analogues. The second metalation step was comparably fast, and it was found that for the formation of **6b** the use of crown ether can be avoided if the reaction was carried out in THF.

The silicon analogue of **6b** had served as a versatile precursor for the syntheses of a number of homo- and heterocyclosilanes.[9c,12] Accordingly, **6b** also was used for the preparation of stanna- (**8**) and a zirconocena- (**9**) disilacyclogermanes (Scheme 5). Both reactions proceeded as expected to give the five-membered rings in good yield.

**X-ray Crystallography.** The two dianons **6b** and **7b** as well as the 1-stanna-2,5-digermacyclopentasilane **8** were studied by single-crystal structure analysis (Table 1). **7b** (Figure 1) could be compared to the analogous 1,2-dipotassium disilane.[11] Due to a different content of solvent (benzene) in the crystal, the compounds did not belong to the same space group. In addition to one and a half molecules of **7b**, one benzene molecule was found in the asymmetric unit. As had already been observed for the 1,2-dipotassiodisilane,[11] in the case of **7b** the central Ge−Ge bond is also elongated by 0.1 Å to 2.5805(9) Å. The elongation of the Si−Ge bonds is less pronounced but still significant to values from 2.4017(17) to 2.4062(13) Å. The degree of pyramidization is relatively high, as can be judged from the small angles for Si(1)−Ge(1)−Si(2) (92.52(5)°) and Si(3)−Ge(2)−Si(4) (95.47(5)°).

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**Table 1. Crystallographic Data for Compounds 6b, 7b, and 8**

| | **6b** | **7b** | **8** |
|---|---|---|---|
| empirical formula | $C_{52}H_{108}Ge_2K_2O_{12}Si_6$ | $C_{60}H_{132}Ge_3K_3O_{18}Si_6$ | $C_{18}H_{54}Ge_2Si_6Sn$ |
| $M_w$ | 1317.30 | 1645.27 | 703.02 |
| temp [K] | 100(2) | 100(2) | 100(2) |
| size [mm] | 0.55 × 0.38 × 0.20 | 0.50 × 0.35 × 0.24 | 0.44 × 0.32 × 0.02 |
| cryst syst | monoclinic | triclinic | monoclinic |
| space group | $P2(1)/c$ | $P\bar{1}$ | $C2/c$ |
| $a$ [Å] | 17.911(4) | 11.906(2) | 15.901(3) |
| $b$ [Å] | 18.560(4) | 19.793(4) | 9.5497(19) |
| $c$ [Å] | 11.320(2) | 20.304(4) | 22.498(5) |
| α [deg] | 90 | 114.50(3) | 90 |
| $\beta$ [deg] | 105.69(3) | 91.99(3) | 92.68(3) |
| $\gamma$ [deg] | 90 | 102.03(3) | 90 |
| $V$ [Å$^3$] | 3623.1(13) | 4219.0(15) | 3412.7(12) |
| $Z$ | 2 | 2 | 4 |
| $\rho_{calc}$ [g cm$^{-3}$] | 1.207 | 1.295 | 1.368 |
| abs coeff [mm$^{-1}$] | 1.092 | 1.351 | 2.692 |
| $F$(000) | 1404 | 1746 | 1440 |
| $\theta$ range | 1.61 to 25.00 | 1.77 to 25.00 | 1.81 to 24.00 |
| no. of reflns collected/unique | 25 315/6373 [$R$(int) = 0.1147] | 30 078/14 665 [$R$(int) = 0.0417] | 10 582/2658 [$R$(int) = 0.0706] |
| completeness to $\theta$ [%] | 25.00 [99.9] | 25.00 [98.7] | 24.00 [99.2] |
| abs corr | SADABS | SADABS | SADABS |
| no. of data/restraints/params | 6373/0/342 | 14 665/3/829 | 2658/0/132 |
| goodness of fit on $F^2$ | 1.073 | 1.031 | 1.219 |
| final $R$ indices [$I > 2\sigma(I)$] | R1 = 0.0846, wR2 = 0.1947 | R1 = 0.0522, wR2 = 0.1399 | R1 = 0.0918, wR2 = 0.2229 |
| $R$ indices (all data) | R1 = 0.1128, wR2 = 0.2120 | R1 = 0.0707, wR2 = 0.1506 | R1 = 0.0958, wR2 = 0.2252 |
| largest diff peak/hole [e$^-$/Å$^3$] | 1.288 and −1.557 | 1.735 and −1.666 | 3.041 and −1.395 |

The structure of **6b** (Figure 2) exhibited a similar but less distinct picture. Half of a molecule was found in the asymmetric unit together with one benzene molecule. Again the Ge−Si bond along the main chain is the longest: Ge(1)−Si(3) 2.4291(18) Å. The bond distances to the trimethylsilyl groups (2.3924(19) and 2.413(2) Å), however, are close to this value. The central Si−Si bond (2.378(3) Å) is not affected by the anionic character. The deviation from the perfect tetrahedral angle around the germanium is still obvious (Si(1)−Ge(1)−Si(2) 97.77(7)°, Si(1)−Ge(1)−Si(3) 105.83(7)°, Si(2)−Ge(1)−Si(3) 100.53(6)°), but considerably smaller than for **7b**.

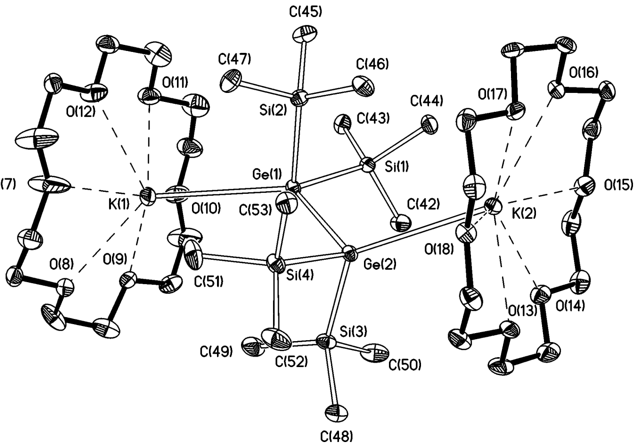

**Figure 1.** Molecular structure and numbering of **7b** with 30% probability thermal ellipsoids; all hydrogen atoms have been omitted for clarity. Only one molecule of two in the asymmetric unit is drawn. Selected bond lengths [Å] and bond angles [deg] with estimated standard deviations: K(1)−Ge(1) 3.5223(17), K(2)−Ge(2) 3.4968(16), Ge(1)−Si(1) 2.4017(17), Ge(1)−Si(2) 2.4062(13), Ge(1)−Ge(2) 2.5805(9), Ge(2)−Si(3) 2.4049(13), Ge(2)−Si(4) 2.4057(18), Si(1)−Ge(1)−Si(2) 92.52(5), Si(1)−Ge(1)−Ge(2) 98.28(4), Si(2)−Ge(1)−Ge(2) 98.75(4), Si(1)−Ge(1)−K(1) 134.23(4), Si(2)−Ge(1)−K(1) 99.65(4), Ge(2)−Ge(1)−K(1) 122.72(3), Si(3)−Ge(2)−Si(4) 95.47(5), Si(3)−Ge(2)−Ge(1) 97.30(4), Si(4)−Ge(2)−Ge(1) 98.73(4), Si(3)−Ge(2)−K(2) 126.59(4), Si(4)−Ge(2)−K(2) 115.68(4), Ge(1)−Ge(2)−K(2) 117.62(3), K(1)−Ge(1)−Ge(2)−K(2) −159.15(3).

Compound **8** was found to exhibit a $C_2$ symmetric half-chair conformation (Figure 3). This is similar to what was found for a related compound with a diphenylstannylene unit and silicon instead of the germanium atoms.[9b] The Sn(1)−Ge(1) distance of 2.6120(16) Å is in the range of values observed for similar compounds.[6g,13] The same can be said about the germanium−silicon bond lengths, which range from 2.37 to 2.39 Å.

**NMR Spectroscopy.** For the chemistry of trifold silylated silylpotassium compounds it was found that the $^{29}$Si NMR resonances of the negatively charged silicon atoms undergo a pronounced upfield shift of

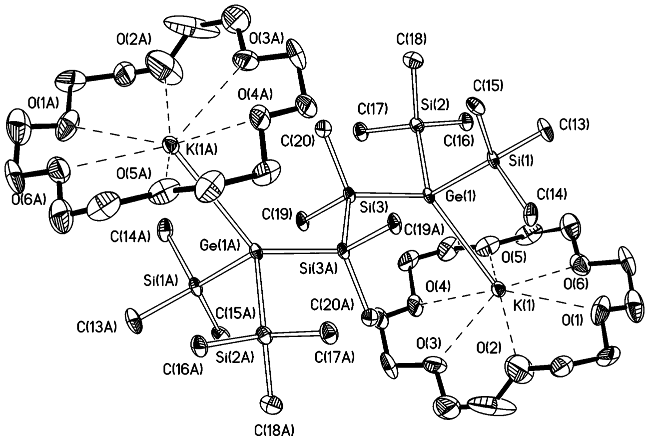

**Figure 2.** Molecular structure and numbering of **6b** with 30% probability thermal ellipsoids; all hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and bond angles [deg] with estimated standard deviations: K(1)−Ge(1) 3.4208(17), Ge(1)−Si(1) 2.3924(19), Ge(1)−Si(2) 2.413(2), Ge(1)−Si(3) 2.4291(18), Si(3)−Si(3A) 2.378(3), Si(1)−Ge(1)−Si(2) 97.77(7), Si(1)−Ge(1)−Si(3) 105.83(7), Si(2)−Ge(1)−Si(3) 100.53(6), Si(1)−Ge(1)−K(1) 96.99(6), Si(2)−Ge(1)−K(1) 117.62(6), Si(3)−Ge(1)−K(1) 132.10(5), Si(3A)−Si(3)−Ge(1) 116.05(10).

**Table 2. $^{29}$Si NMR Shifts for $Me_3Si$ and ($Me_2Si$) Groups ($\delta$ in ppm)**

| compound | E = Si | E = Ge | $\Delta_{Si-Ge}$ |
|---|---|---|---|
| $(Me_3Si)_4\mathit{E}$ | −9.6 | −5.5 | 4.1 |
| $(Me_3Si)_3\mathit{E}K$ | −3.9 | −3.3 | 0.6 |
| $(Me_3Si)_3\mathit{E}H$ | −10.9 | −6.5 | 4.4 |
| $(Me_3Si)_3\mathit{E}Et$ | −12.3 | −7.4 | 4.9 |
| $(Me_3Si)_3\mathit{E}Zr(Cl)Cp_2$ | −6.1 | −2.1 | 4.0 |
| $(Me_3Si)_3\mathit{EE}(SiMe_3)_3$ | −9.0 | −5.0 | 4.0 |
| $K(Me_3Si)_2\mathit{EE}(SiMe_3)_3$ | −8.9/ −11.7 | −4.9/ −6.8 | 4.0/4.9 |
| $K(Me_3Si)_2\mathit{EE}(SiMe_3)_2K$ | −5.4 | −5.3 | 0.1 |
| $(Me_3Si)_3\mathit{SiGe}(SiMe_3)_3$ | −9.9 | −4.9 | 5.0 |
| $(Me_3Si)_3\mathit{SiGe}(SiMe_3)_2K$ | −10.5 [$(Me_3\mathit{Si})_3Si$] | −5.4 [$(Me_3\mathit{Si})_2Ge$] | |
| $K(Me_3Si)_2\mathit{SiGe}(SiMe_3)_2K$ | −5.6[a] | −4.8[a] | 0.8 |
| $(Me_3Si)_3\mathit{E}(SiMe_2)_2\mathit{E}(SiMe_3)_3$ | −9.6 (−29.8) | −5.0 (−24.4) | 4.6 |
| $K(Me_3Si)_2\mathit{E}(SiMe_2)_2\mathit{E}(SiMe_3)_2K$ | −3.7 (−24.5) | −3.4 (−22.4) | 0.3 |
| $Cp_2Zr[E(SiMe_3)_2SiMe_2]_2$ | −2.4 (−29.2) | −5.0 (−24.4) | 2.6 |
| $Me_2Sn[E(SiMe_3)_2SiMe_2]_2$ | −5.4 (−22.2) | −1.0 (−16.8) | 3.8 |

[a] Unambiguous assignment was not possible.

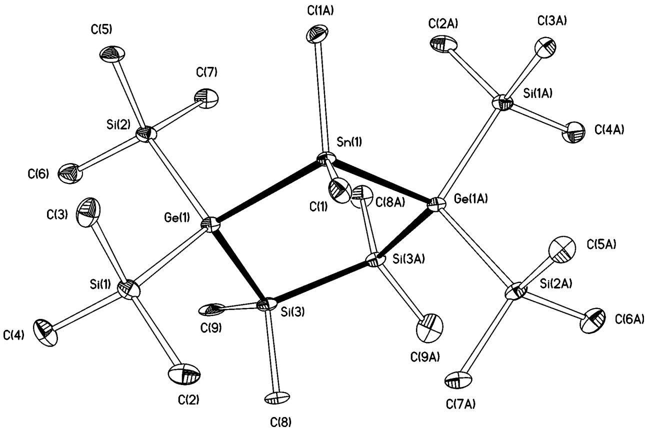

**Figure 3.** Molecular structure and numbering of **8** with 30% probability thermal ellipsoids; all hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and bond angles [deg] with estimated standard deviations: Sn(1)−Ge(1) 2.6120(16), Ge(1)−Si(2) 2.375(4), Ge(1)−Si(1) 2.383(4), Ge(1)−Si(3) 2.390(4), Si(3)−Si(3A) 2.358(8), C(1A)−Sn(1)−C(1) 105.2(8), Ge(1)−Sn(1)−Ge(1A) 104.78(8), Si(2)−Ge(1)−Si(1) 111.09(15), Si(2)−Ge(1)−Si(3) 112.24(14), Si(1)−Ge(1)−Si(3) 112.93(15), Si(2)−Ge(1)−Sn(1) 107.90(11), Si(1)−Ge(1)−Sn(1) 108.89(11), Si(3)−Ge(1)−Sn(1) 103.34(11).

about 60 ppm, while the trimethylsilyl groups attached to these atoms move approximately 5 ppm to lower field. For the germyl anions studied in this report we were restricted to the observation of the trimethylsilyl resonances. A comparison of the neutral silyl and germyl compounds showed that the trimethylsilyl signals of the germanium congeners are shifted about 4−5 ppm to lower field compared to the silicon series (Table 2). If, however, anionic derivatives were compared, the shift differences decreased to values most times smaller than 1 ppm. This effect is caused by the very slight change in chemical shift upon metalation of the germanium compounds. This indicates a greatly reduced participation of the trimethylsilyl groups in the localization of the negative charge for the germanium anions. For the case of **7b** an even smaller upfield shift compared to **7** can be observed.

## Conclusion

The chemistry of the investigated oligosilylgermylpotassium compounds very much resembled that of the previously studied oligosilylpotassium compounds. Compared to silicon, the increased ability of germanium to stabilize negative charge clearly facilitates the formation of the germanides. As a consequence, the use of a crown ether, which is a real necessity for a rapid formation of silyl-dianions, is not required for the rapid formation of **6b**. The reactivity of the obtained oligosilylgermylpotassium compounds is comparable to that of the analogous all-organosilicon compounds. Thus, the described mono- and dipotassium compounds widely extend the repertoire of existing nucleophilic bulky germylation reagents. They can be considered interesting reagents for further studies on the chemistry of germanium transition metal and main group compounds.

## Experimental Part

All reactions were carried out under an atmosphere of dry argon or nitrogen. Solvents were dried using a column solvent purification system.[14] Potassium *tert*-butoxide was purchased exclusively from Merck. All other chemicals were used as received from several different 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 cases of reaction samples measured with a $D_2O$ capillary in order to provide a 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.[15] The completeness of 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 0.71073 Å). The data were reduced to $F_o^2$ and corrected for absorption effects with SAINT[16] and SADABS,[17] respectively. Structures were solved using direct

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methods and refined by full-matrix least-squares method (SHELXL97).[18] 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 Table 1. More detailed information for all structures can be found in the Supporting Information. All data have been deposited at the Cambridge Crystallographic Deposition Centre: CCDC 253310 (**6b**), CCDC 253311 (**7b**), CCDC 258956 (**8**). 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 CB21Ez; fax: (+44) 1223-336-033.

Elemental analyses were performed with a Heraeus VARIO ELEMENTAR EL analyzer. No satisfactory elemental analyses of the germyl- and silylpotassium compounds could be obtained. This is in accordance with our own previous observations and also those of other authors which report about similar problems with alkali silyl compounds.[19] Tetrakis(trimethylsilyl)germane,[3] tris(trimethylsilyl)silyl chloride,[20] and 1,2-dibromotetramethyldisilane[21] have been prepared following previously published procedures.

**General Procedure A for the Synthesis of Germylpotassium Compounds in THF.** To a solution of the respective silylgermane in THF was added potassium *tert*-butoxide (1 molar equiv). The reaction usually turned yellow immediately and was stirred at room temperature until complete conversion was reached (monitored either by $^{29}$Si NMR spectroscopy or GC/MS of a derivatized aliquot). The obtained germylpotassium compound was either used for further reaction as obtained in THF solution or isolated by removal of the solvent in a vacuum.

**General Procedure B for the Synthesis of Germylpotassium Compounds in the Presence of 18-crown-6.** To a solution of the respective silylgermane and 18-crown-6 (1 or 2 molar equiv for mono- or dianions, respectively) in toluene or benzene potassium *tert*-butoxide was added 1 or 2 molar equiv of the germane for mono- or dianions, respectively, and the reaction was stirred at room temperature until complete conversion was reached (monitored either by $^{29}$Si NMR spectroscopy or GC/MS of a derivatized aliquot). The obtained potassium compound either was used for further reaction as obtained in solution or in the case of the dianions precipitates from solution.

**Tris(trimethylsilyl)germylpotassium (1). 1** was prepared as the crown ether adduct according to general procedure B. NMR ($\delta$ in ppm): $^1$H ($C_6D_6$): 3.20 (s, 24H); 0.64 (s, 27H). $^{13}$C ($C_6D_6$): 70.0; 8.1. $^{29}$Si ($C_6D_6$): −3.3.

**Tris(trimethylsilyl)germane (2).** A solution of **1** in THF (0.27 mmol) was added to an ether/dilute sulfuric acid mixture. After separating the layers, the ether phase was dried over sodium sulfate and concentrated in a vacuum. The product (78 mg, 98%) was obtained as a colorless oil with spectroscopic properties identical to published data.[3] NMR ($\delta$ in ppm): $^1$H ($C_6D_6$): 2.17 (s, 1H); 0.28 (s, 27H). $^{13}$C ($C_6D_6$): 2.6. $^{29}$Si ($C_6D_6$): −6.5.

**Ethyltris(trimethylsilyl)germane (3).** A solution of **1** (0.41 mmol) in benzene was added dropwise to a benzene solution of ethyl bromide (109 mg, 1.0 mmol). The mixture was stirred for 15 min, and the solvent was then removed in a vacuum, after which pentane was added to extract the product. The mixture was filtered to remove the salts, and after removal of pentane a colorless low-melting solid was obtained (124 mg, 95%). NMR ($\delta$ in ppm): $^1$H ($C_6D_6$): 1.23 (t, 3H, $J$ = 7.6 Hz); 1.05 (q, 2H, $J$ = 7.6 Hz); 0.25 (s, 27H). $^{13}$C ($C_6D_6$): 14.7; 1.9; 1.5. $^{29}$Si ($C_6D_6$): −7.4.

**Tris(trimethylsilyl)germylzirconocene Chloride (4).** To a solution of **1** (0.82 mmol) in THF (4 mL) was added zirconocene dichloride (240 mg, 0.82 mmol). The red color of the solution turned dark red, and after another 30 min the solvent was removed in a vacuum, pentane was added, and insoluble salts were removed by filtration. The product was crystallized from pentane at −30 °C. Red crystals (378 mg, 84%) with spectroscopic properties identical to published data were obtained.[10] NMR ($\delta$ in ppm): $^1$H ($C_6D_6$): 6.01 (s, 10H); 0.40 (s, 27H). $^{29}$Si ($C_6D_6$): −2.1. Anal. Calcd for $C_{19}H_{37}ClGeSi_3Zr$ (549.02): C 41.60, H 6.79. Found: C 41.66, H 6.58.

Reaction of **4** (50 mg, 0.09 mmol) with 2,6-dimethylphenyl isonitrile (13 mg, 0.1 mmol) in $C_6D_6$ (0.6 mL) proceeded according to NMR spectroscopy in a quantitative manner to give the isonitrile insertion product. NMR ($\delta$ in ppm): $^1$H ($C_6D_6$): 6.74 (m, 1H); 6.60 (m, 2H); 5.90 ($C_5H_5$); 2.06 (s, 6H); 0.22 (s, 27H). $^{13}$C ($C_6D_6$): 269.2; 148.4; 129.6; 128.9; 125.7; 110.3; 20.4; 3.6. $^{29}$Si ($C_6D_6$): −4.7.

**Tris(trimethylsilyl)[tris(trimethylsilyl)silyl]germane (5).** A solution of **1** in benzene (0.55 mmol) was added dropwise to a solution of chlorotris(trimethylsilyl)silane (155 mg, 0.55 mmol) in benzene. The mixture was stirred for another 30 min. The solvent was removed in a vacuum, after which pentane was added to extract the product. After filtration and removal of pentane in a vacuum, a yellow solid was obtained (266 mg, 90%). Mp: 156−160 °C (subl), 280 °C (dec). NMR ($\delta$ in ppm): $^1$H ($C_6D_6$): 0.36 (s, 27H); 0.32 (s, 27H). $^{13}$C ($C_6D_6$): 4.9; 4.3. $^{29}$Si ($C_6D_6$): −4.9; −9.9; −122.3. Anal. Calcd for $C_{18}H_{54}GeSi_7$ (539.83): C 40.05, H 10.08. Found: C 39.82, H 10.21.

**1,2-Bis[tris(trimethylsilyl)germyl]tetramethyldisilane (6).** From a solution of **1** (8.21 mmol) in THF the solvent was removed in a vacuum and toluene (10 mL) was added. The solution was cooled to −78 °C, and a solution of 1,2-dibromotetramethyldisilane (1.16 g, 0.5 equiv, 4.10 mmol) in toluene (40 mL) was added dropwise. The reaction mixture was allowed to warm to room temperature and was stirred overnight. After quenching with dilute sulfuric acid and extraction with ether, the organic phase was dried over sodium sulfate and the solvent was removed in a vacuum. White crystals of pure product were obtained by recrystallization from acetone at −80 °C (1.90 g, 66%). Mp: 208−213 °C. NMR ($\delta$ in ppm): $^1$H ($C_6D_6$): 0.36 (s, 54H); 0.57 (s, 12H). $^{13}$C ($C_6D_6$): 4.2; 2.1. $^{29}$Si ($C_6D_6$): −5.0; −24.4. Anal. Calcd for $C_{22}H_{66}Ge_2Si_8$ (700.63): C 37.71, H 9.49. Found: C 37.11, H 9.36.

**Hexakis(trimethylsilyl)digermane (7). 7** was obtained in a procedure completely analogous to the preparation of **6** using ether instead of toluene as solvent and 1,2-dibromoethane (770 mg, 0.5 equiv, 4.10 mmol) as the electrophilic component. White crystals of pure product were obtained (1.80 g, 75%). Mp: 167−170 °C (subl), 285 °C (dec). NMR ($\delta$ in ppm): $^1$H ($C_6D_6$): 0.39 (s, 54H). $^{13}$C ($C_6D_6$): 4.7. $^{29}$Si ($C_6D_6$): −5.0. Anal. Calcd for $C_{18}H_{54}Si_6Ge_2$ (584.32): C 36.99, H 9.30. Found: C 37.50, H 9.17.

**Bis(trimethylsilyl)[tris(trimethylsilyl)silyl]germylpotassium 18-Crown-6 (5a). 5a** was obtained from **5** (220 mg, 0.41 mmol) according to general procedure B employing 1 equiv of potassium *tert*-butoxide. NMR ($\delta$ in ppm): $^1$H ($C_6D_6$): 0.64 (s, 18H); 0.56 (s, 27H). $^{13}$C ($C_6D_6$): 70.3; 9.2; 4.6. $^{29}$Si ($C_6D_6$): −5.4; −10.5; −132.2.

**Bis(trimethylsilyl)[potassiobis(trimethylsilyl)silyl]germylpotassium 2 × 18-Crown-6 (5b). 5b** was obtained from **5** (220 mg, 0.41 mmol) according to general procedure B employing 2 equiv of potassium *tert*-butoxide. NMR ($\delta$ in ppm): $^1$H ($C_6D_6$): 3.38 (s, 48H); 0.60 (s, 18H); 0.59 (s, 18H). $^{13}$C ($C_6D_6$): 70.2; 9.3; 8.9. $^{29}$Si ($C_6D_6$): −4.8; −5.6; −178.0.

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**1,1,4,4,4-Pentakis(trimethylsilyl)-2,2,3,3-tetramethyl-2,3-disila-1,4-digermanyl-1-potassium 18-Crown-6 (6a).** **6a** was obtained from **6** (150 mg, 0.22 mmol) according to general procedure B employing 1 equiv of potassium *tert*-butoxide. NMR ($\delta$ in ppm): $^1$H ($C_6D_6$): 3.20 (s, 24H); 0.83 (s, 6H); 0.74 (s, 6H); 0.65 (s, 18H); 0.49 (s, 27H). $^{13}$C ($C_6D_6$): 69.7; 8.6; 5.2; 4.4; 2.6. $^{29}$Si ($C_6D_6$): −3.5; −5.3; −20.9; −25.1.

**1,1,4,4-Tetrakis(trimethylsilyl)-2,2,3,3-tetramethyl-2,3-disila-1,4-digermanyl-1,4-dipotassium 2 × 18-Crown-6 (6b).** **6b** was obtained from **6** (150 mg, 0.22 mmol) according to general procedure B employing 2 equiv of potassium *tert*-butoxide. Yellow crystals of the product precipitated from the benzene solution rapidly. The crystals were dissolved in a $C_6D_6$/THF mixture and subjected to NMR analysis. NMR ($\delta$ in ppm): $^1$H ($C_6D_6$/THF): 3.40 (s, 48H); 0.44 (s, 12H); 0.49 (s, 18H). $^{13}$C ($C_6D_6$): 70.1; 8.6; 5.3. $^{29}$Si ($C_6D_6$): −3.4; −22.4.

**Pentakis(trimethylsilyl)digermylpotassium 18-Crown-6 (7a).** **7a** was obtained from **7** (300 mg, 0.51 mmol) according to general procedure B employing 1 equiv of potassium *tert*-butoxide. NMR ($\delta$ in ppm): $^1$H ($C_6D_6$): 3.19 (s, 24H); 0.67 (s, 18H); 0.62 (s, 27H). $^{13}$C ($C_6D_6$): 69.9; 9.0; 5.1. $^{29}$Si ($C_6D_6$): −4.9; −6.8.

**Tetrakis(trimethylsilyl)digermyl-1,2-dipotassium 2 × 18-Crown-6 (7b).** **7b** was obtained from **7** (300 mg, 0.51 mmol) according to general procedure B employing 2 equiv of potassium *tert*-butoxide. Red crystals of **7b** that precipitated from the benzene solution were dissolved in a $C_6D_6$/THF mixture for NMR analysis. NMR ($\delta$ in ppm): $^1$H ($C_6D_6$/THF): 3.40 (s, 48H); 0.42 (s, 36H). $^{13}$C ($C_6D_6$): 70.0; 8.9. $^{29}$Si ($C_6D_6$): −5.3.

**2,2,5,5-Tetrakis(trimethylsilyl)-1,1,3,3,4,4-hexamethyl-1-stanna-2,5-digermacyclopentasilane (8).** A solution of **6b** (starting from 0.22 mmol **6**) in toluene (3 mL) was added dropwise to a solution of dimethyltin dichloride (49 mg, 0.22 mmol) in toluene (3 mL). The solution turned deep yellow and was stirred overnight. After quenching with dilute sulfuric acid and extraction with ether, the organic phase was dried over sodium sulfate and the solvent was removed in a vacuum. White crystals of **8** (131 mg, 87%) were obtained from a pentane extract at −30 °C. Mp: 104−105 °C. NMR ($\delta$ in ppm): $^1$H ($C_6D_6$): 0.59 (s, 6H); 0.39 (s, 12H); 0.31 (s, 36H). $^{13}$C ($C_6D_6$): 4.3; −1.0; −7.5. $^{29}$Si ($C_6D_6$): −1.0; −16.8 [$^2J$(Si−Sn) = 30.0 Hz]. $^{119}$Sn ($C_6D_6$): −101.9. Anal. Calcd for $C_{18}H_{54}Ge_2Si_6Sn$ (703.06): C 30.75, H 7.74. Found: C 30.75, H 7.78.

**2,2,5,5-Tetrakis(trimethylsilyl)-3,3,4,4-tetramethyl-1-zirconocena-2,5-digermacyclopentasilane (9).** A solution of **6b** (starting from 0.15 mmol **6**) in benzene (3 mL) was added dropwise to a solution of zirconocene dichloride (43 mg, 0.15 mmol) in benzene (3 mL). The solution turned deep red. The reaction mixture was stirred overnight, after which the solvent was removed in a vacuum. Pentane was then added, and the salts were removed by filtration. After crystallization at −30 °C, red crystals were obtained (84 mg, 75%). NMR ($\delta$ in ppm): $^1$H ($C_6D_6$): 6.32 (s, 10H), 0.39 (s, 12H); 0.35 (s, 36H). $^{13}$C ($C_6D_6$): 108.5; 6.8; 4.1. $^{29}$Si ($C_6D_6$): −5.0; −24.4. Anal. Calcd for $C_{26}H_{58}Ge_2Si_6Zr$ (775.70): C 40.26, H 7.54. Found: C 39.89, H 7.45.

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

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