

Polygermane Building Blocks[†]

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Tetrakis(trimethylgermyl)germane was prepared by the reaction of chlorotrimethylgermane and tetrabromogermane with lithium at -78 °C. Reaction with potassium *tert*-butoxide/18-crown-6 gave (Me₃Ge)₃GeK · 18-crown-6, which displayed typical reactivity with electrophiles. In the reaction of (Me₃Ge)₃GeSiMe₃ with *tert*-butoxide/18-crown-6 exclusive attack at the trimethylsilyl group was observed. Attempts to obtain a dimetalated species from (Me₃Ge)₃GeGe(GeMe₃)₃ and 2 *tert*-butoxide/2 18-crown-6 failed due to cleavage of the central Ge–Ge bond. The respective dianion was, however, accessible employing (Me₃Si)(Me₃Ge)₂GeGe(GeMe₃)₂(SiMe₃) as the precursor.

Introduction

Despite the multifaceted applications of germanium in physics, its chemistry is clearly underestimated. While the synthesis of compounds containing Si–Si bonds can be achieved by numerous methods in good yields, only few routes to compounds containing catenated germanium atoms are known and are often characterized by low yields or complex product mixtures. Compared to the already modest interest in the organometallic chemistry of germanium, the field of polygermanes (i.e., compounds with Ge–Ge bonds) is even more neglected.¹ A recently published review reflects this situation perfectly:² covering the field of polygermanes over the last 80 years, it lists less than 250 references.

In recent years our group was involved in the development of oligosilyl potassium chemistry, which provided us with versatile building blocks for the synthesis of compounds composed of all-silicon scaffolds.³ In particular the tris-(trimethylsilyl)silyl⁴ group, which is a very common structural motif in organosilicon chemistry, can easily be introduced using the corresponding anion. Analogous isotetragermanyl groups, (R₃Ge)₃Ge, on the other hand are only scarcely known.⁵ The related tris(trimethylsilyl)germyl moiety,⁶ where germanium occupies only the central position, was introduced by Brook et al. more than 20 years ago in an attempt

(3) Marschner, C. Organometallics 2006, 25, 2110–2125.

to obtain germenes via photolytic rearrangement of acylgermanes.⁷ Also this group can easily be transformed into its anionic form, ^{6–8} and the chemistry of $(Me_3Si)_3GeLi$ was studied on several occasions.⁹ Work from our laboratory featured $(Me_3Si)_3GeK$ and related germylpotassium compounds,¹⁰ which for example could be used to obtain some single-source precursors for the synthesis of germanium nanowires containing a crystalline germanium core with a silicon oxide shell.¹¹

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⁽¹⁾ Voronkov, M. G.; Abzaeva, K. A. In *The Chemistry of Organic Germanium, Tin and Lead Compounds*; Rappoport, Z., Ed.; Wiley: New York, 2002; Vol. 2, Chapter 1.

⁽²⁾ Amadoruge, M. L.; Weinert, C. S. Chem. Rev. 2008, 108, 4253–4294.

⁽⁴⁾ Kornev, A. N. Russ. Chem. Rev. 2004, 73, 1065-1089.

^{(5) (}a) Glockling, F.; Hooton, K. A. J. Chem. Soc. 1963, 1849–1854.
(b) Bulten, E. J.; Noltes, J. G. J. Organomet. Chem. 1971, 29, 409–417.
(c) Leung, W.-P.; So, C.-W.; Chong, K.-H.; Kan, K.-W.; Chan, H.-S.; Mak, T. C. W. Organometallics 2006, 25, 2851–2858.

T. C. W. Organometallics 2006, 25, 2851–2858.
 (6) (a) Freitag, S.; Herbst-Irmer, R.; Lameyer, L.; Stalke, D. Orga-

⁽b) (a) Filing, S., Herbstermer, K., Laneyer, L., Statke, D. Organometallics 1996, 15, 2839–2841. (b) Heine, A.; Statke, D. Angew. Chem. 1994, 106, 121–123. Angew. Chem., Int. Ed. Engl. 1994, 33, 113–115.

⁽⁷⁾ Brook, A. G.; Abdesaken, F.; Söllradl, H. J. Organomet. Chem. 1986, 299, 9–13.

 ^{(8) (}a) Nanjo, M.; Nanjo, E.; Mochida, K. Eur. J. Inorg. Chem. 2004, 2961–2967.
 (b) Naka, A.; Ueda, S.; Ishikawa, M. J. Organomet. Chem. 2007, 692, 2357–2360.

^{(9) (}a) Nanjo, M.; Oda, T.; Mochida, K. *Bull. Chem. Soc. Jpn.* **2003**, 76, 1261–1264. (b) Nanjo, M.; Oda, T.; Mochida, K. *J. Organomet. Chem.* 2003, 672, 100-108. (c) Farwell, J. D.; Fernandes, M. A.; Hitchcock, P. B.; Lappert, M. F.; Layh, M.; Omondi, B. Dalton Trans. 2003, 1719-1729. (d) Braunschweig, H.; Colling, M.; Kollann, C.; Englert, U. J. Chem. Soc., Dalton Trans. 2002, 2289–2296. (e) Nanjo, M.; Oda, T.; Mochida, K. Chem. Lett. 2002, 108-109. (f) Linti, G.; Rodig, A. Chem. Commun. 2000, 127-128. (g) Sekiguchi, A.; Fukaya, N.; Ichinohe, M.; Takagi, N.; Nagase, S. J. Am. Chem. Soc. **1999**, *121*, 11587–11588. (h) Mallela, S. P.; Saar, Y.; Hill, S.; Geanangel, R. A. Inorg. Chem. 1999, 38, 2957-2960. (i) Mallela, S.; Su, W.-P.; Chen, Y.-S.; Korp, J. D.; Geanangel, R. A. Main Group Chem. 1998, 2, 315-322. (j) Hitchcock, P. B.; Lappert, M. F.; Layh, M. Chem. Commun. 1998, 2179–2180. (k) Mallela, S. P.; Hill, S.; Geanangel, R. A. Inorg. Chem. 1997, 36, 6247-6250. (l) Casty, G. L.; Tilley, T. D.; Yap, G. P. A.; Rheingold, A. L. Organometallics 1997, 16, 4746-4754. (m) Schwan, F.; Mallela, S. P.; Geanangel, R. A. J. Chem. Soc., Dalton Trans. 1996, 4183-4187. (n) Mitchell, G. P.; Tilley, T. D. Organometallics 1996, 15, 3477-3479. (o) Mallela, S. P.; Schwan, F.; Geanangel, R. A. *Inorg. Chem.* **1996**, *35*, 745–748. (p) Bravo-Zhivotovskii, D.; Zharov, I.; Kapon, M.; Apeloig, Y. J. Chem. Soc., Chem. Commun. 1995, 1625-1626. (q) Mallela, S. P.; Geanangel, R. A. Inorg. Chem. 1994, 33, 6357-6360. (r) Mallela, S. P.; Geanangel, R. A. Inorg. Chem. 1994, 33, 1115-1120. (s) Mallela, S. P.; Geanangel, R. A. Inorg. Chem. 1993, 32, 5623-5625. (t) Campion, B. K.; Heyn, R. H.; Tilley, T. D. Organometallics 1993, 12, 2584–2590. (u) Bonasia, P. J.; Christou, V.; Arnold, J. J. Am. Chem. Soc. 1993, 115, 6777-6781. (v) Preuss, F.; Wieland, T.; Perner, J.; Heckmann, G. Z. Naturforsch. B 1992, 47, 1355-1362. (w) Arnold, J.; Roddick, D. M.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. Inorg. Chem. 1988, 27, 3510-3514. (x) Maerkl, G.; Wagner, R. Tetrahedron Lett. 1986, 27, 4015-4018.

⁽¹⁰⁾ Fischer, J.; Baumgartner, J.; Marschner, C. Organometallics 2005, 24, 1263–1268.

⁽¹¹⁾ Arnold, D. C.; Hobbs, R. G.; Zirngast, M.; Marschner, C.; Hill, J. J.; Ziegler, K. J.; Morris, M. A.; Holmes, J. D. J. Mater. Chem. 2009, 19, 954–961.

With respect to structures composed entirely of germanium as the heavy group 14 element the synthesis of a mixture of tetrakis(trimethylgermyl)germane and hexakis-(trimethylgermyl)digermane by reaction of trimethylgermyllithium and tetrachlorogermane was reported some 40 years ago but without much characterization.¹²

Another point worth raising here concerns the commodity prices of germanium reagents: while the starting materials for oligosilane chemistry are relatively inexpensive, the materials for analogous oligogermanium chemistry are nearly unaffordable. For this reason we want to present here an affordable access to tetrakis(trimethylgermyl)germane, hexakis(trimethylgermyl)digermane, and the corresponding potassium compounds as convenient building blocks. Their somewhat different reactivity compared to their pure silicon or silicon/germanium analogues will briefly be discussed.

Results and Discussion

For the synthesis of (Me₃Si)₄Ge we found Brook's synthesis starting from Me₃SiCl, GeCl₄, and Li⁷ quite satisfactory¹⁰ but noted that GeCl₄ is quite expensive. For an analogous synthesis of (Me₃Ge)₄Ge the even more expensive Me₃GeCl is required. The latter can be prepared from Me₄Ge by reaction with SnCl₄.¹³ Me₄Ge is available from GeCl₄ and MeMgI.¹⁴ Searching for a more affordable starting material we came across GeBr₄, which can be obtained in a most convenient way by reaction of germanium powder with bromine.¹⁵

In contrast to the only reported synthesis of $(Me_3Ge)_4Ge$,¹² which utilized trimethylgermyllithium, we decided to adapt Gilman's procedure for the synthesis of $(Me_3Si)_4Si$.¹⁶ However, also the reaction of chlorotrimethylgermane and tetrabromogermane with lithium wire at rt gave a mixture of $(Me_3Ge)_4Ge$ (1) and $(Me_3Ge)_3GeGe(GeMe_3)_3$ (3). If alternatively the reaction was carried out at -78 °C, it gave the expected tetrakis(trimethylgermyl)germane (1) exclusively in 40% yield (eq 1).



In analogy with the syntheses of (Me₃Si)₃SiK¹⁷ and (Me₃Si)₃-GeK¹⁰ we attempted the conversion of neopentagermane **1** to the potassium salt of the respective tris(trimethylgermyl)-germanide (**2**) by means of reaction with potassium *tert*-butoxide. While this reaction worked perfectly fine in toluene or benzene in the presence of 1 equiv of 18-crown-6, it did not proceed

Scheme 1. Reactions of the Crown-Ether Adduct of (Me₃Ge)₃GeK (2) with Electrophiles



cleanly in THF in the absence of crown ether. Alternatively, also potassium diisopropylamide (KDA) could be used as metalation reagent (eq 2).



As expected, compound **2** is a strong nucleophile, which easily reacts with all sorts of electrophiles. Reaction of **2** with 1,2-dibromoethane led to the formation of hexakis(trimethylgermyl)digermane (**3**).¹⁸ Reaction with 0.5 equiv of dichlorodimethylgermane gave bis{tris(trimethylgermyl)germyl}dimethylgermane (**4**), containing a linear pentagermane substructure. Silylation of **2** was another facile reaction. By treatment with chlorotrimethylsilane and chlorotriisopropylsilane the respective silylated isotetragermanes **5** and **6** were obtained (Scheme 1).

The trimethylsilylated compound 5 was reacted with potassium *tert*-butoxide in order to compare the selectivity of alkoxide attack on trimethylsilyl and trimethylgermyl groups. The fact that exclusive attack on the trimethylsilyl group was observed is probably caused by the stronger Si-O compared to Ge-O bond (Scheme 1).

Finally, also hydrolysis of **2** with dilute sulfuric acid was studied. Rigorous exclusion of oxygen was required for clean conversion to obtain the respective hydrogermane (7). Precautions were also required for the analogous reaction of $(Me_3Si)_3GeK$.¹⁰

With hexakis(trimethylgermyl)digermane (**3**) in hand, synthesis of mono- and dianions thereof was the logical next step. However, reaction of **3** under the usual conditions (with KO^tBu in either THF or benzene/18-crown-6) indicated formation of **2** as the only formed anionic species. Mass spectroscopic analysis provided additional evidence for the formation of $(Me_3Ge)_3$ -GeO^tBu. These results clearly suggest cleavage of the internal Ge–Ge bond. While the reasons for this are not completely clear, we assume that the increased steric accessibility through longer Ge–Ge bonds and the diminished oxophilicity of germanium are the major contributors.

This course of reaction was somewhat surprising, as we previously were able to demonstrate the clean formation

 ^{(12) (}a) Glockling, F.; Light, J. R. C.; Strafford, R. G. J. Chem. Soc. A
 1970, 426–432. (b) Glockling, F.; Light, J. R. C. J. Chem. Soc., Chem.
 Commun. 1968, 1052–1053.

^{(13) (}a) Baines, K.; Mueller, K. A.; Sham, T. K. Can. J. Chem. **1992**, 70, 2884–2886. (b) Barrau, J.; Rima, G.; El Amine, M.; Satge, J. Synth. React. Inorg. Met.-Org. Chem. **1988**, 18, 21–28.

^{(14) (}a) Herrmann, W. A.; Brauer, G., Eds. *Synthetic Methods of Organometallic and Inorganic Chemistry*; Thieme: Stuttgart, 1996, Vol. 2, p 251. (b) Job, R. C.; Curtis, M. D. *Inorg. Nucl. Chem. Lett.* **1972**, *8*, 251–255.

⁽¹⁵⁾ Modified Procedure of: *Handbuch der Präparativen Anorga*nischen Chemie; Brauer, G., Ed.; F. Enke Verlag: Stuttgart, 1978; p 723.

^{(16) (}a) Gilman, H.; Holmes, J. M.; Smith, C. L. *Chem. Ind. (London)* **1965**, 848–849. (b) Gilman, H.; Smith, C. L. *J. Organomet. Chem.* **1968**, *14*, 91–101.

⁽¹⁷⁾ Marschner, C. Eur. J. Inorg. Chem. 1998, 221-226.

⁽¹⁸⁾ For the analogous synthesis of hexakis(trimethylsilyl)disilane see: Gilman, H.; Harrell, R. L., Jr. J. Organomet. Chem. **1967**, *9*, 67–76.

Scheme 2. Successive Replacement of Trimethylsilyl against Trimethylgermyl Groups Provides Access to K(Me₃Ge)₂GeGe(GeMe₃)₂K (11)



of $K(Me_3Si)_2GeGe(SiMe_3)_2K$ starting from $(Me_3Si)_3GeGe-(SiMe_3)_3$.¹⁰ Therefore it was of interest to study whether a compound like $K(Me_3Ge)_2GeGe(GeMe_3)_2K$ would be stable if prepared by another route.

For this reason we reacted $K(Me_3Si)_2GeGe(SiMe_3)_2K^{10}$ with 2 equiv of Me_3GeCl to obtain 2,2,3,3-tetrakis(trimethylsilyl)hexamethyltetragermane (8) (Scheme 2). Reaction of 8 with 2 equiv of KO^tBu proceeded again under selective cleavage of the Si–Ge bonds, and the respective 1,2-dipotassium compound 9 was obtained. Germylation with Me_3GeCl led to the required precursor (Me_3Si)(Me_3Ge)_2GeGe(GeMe_3)_2(SiMe_3) (10) for the synthesis of K(Me_3Ge)_2GeGe(GeMe_3)_2K, which still has two trimethylsilyl groups to be removed in the final step. The last reaction step eventually provided the desired dianion K(Me_3Ge)_2GeGe(GeMe_3)_2K (11) as the crown ether adduct (Scheme 2). Its formation could be unambiguously demonstrated by single-crystal X-ray structure analysis.

X-ray Crystallography. Compounds 2, 3, 4, 6, and 11 of this study could be characterized by X-ray single-crystal structure analysis. With numerous related polysilane structures determined previously, these compounds provide an excellent opportunity to compare structural properties of organooligosilanes and -germanes.

While $(Me_3Si)_3SiK \cdot 18$ -crown-6¹⁹ and $(Me_3Si)_3GeK \cdot 18$ crown-6²⁰ both crystallize in the monoclinic space group P2(1)/n, the analogous all-germanium compound 2 was found in P2(1)/c. Measurement of the crystal at higher temperature (233) K) was required, as loss of structural integrity was observed at 100 K. Similar to what was found for (Me₃Si)₃SiK and (Me₃Si)₃-GeK the potassium of 2 exhibits an additional coordination to a methyl group of a neighboring molecule. This increases the coordination number of potassium from seven to eight. The Ge-Ge bond distances are not affected much by the anionic character and are close to the values found in 3 and 6. Hexakis(trimethylsilyl)disilane,²¹ hexakis(trimethylsilyl)digermane,²² and tris(trimethylsilyl)[tris(trimethylsilyl)silyl]germane²² all crystallize in the trigonal space group $R\overline{3}c$ in contrast to the all-germanium analogue 3, for which the lower $R\overline{3}$ space group was found. The central Ge-Ge bond distance in



Figure 1. Molecular structure of 2 (thermal ellipsoid plot drawn at the 30% probability level). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ge(1)-Ge(3) 2.4369(7), Ge(1)-Ge(2) 2.4393(6), Ge(1)-Ge(4) 2.4503(7), Ge(1)-K(1) 3.4213(11), Ge(2)-C(3) 1.989(4), Ge(4)-C(9) 1.966(4), Ge(3)-Ge(1)-Ge(2) 96.81(3), Ge(3)-Ge(1)-Ge(4) 98.00(2), Ge(2)-Ge(1)-Ge(4) 97.50(2), Ge(3)-Ge(1)-K(1) 120.38(2), Ge(2)-Ge(1)-K(1) 126.35(2), Ge(4)-Ge(1)-K(1) 112.30(3).

hexakis(trimethylsilyl)digermane was reported to be 2.48 Å, whereas in **3** it is only 2.46 Å. This slightly shorter distance is in accordance with the differences of the torsional angles $Me_3X^1-X^2-X^3-X^1Me_3$: While 3 adopts a perfectly staggered conformation with a dihedral angle of 60° (Figure 2), for the three other above-mentioned compounds the respective angles were determined to be 76.6-77.2° and 42.8-43.4°, thus differing substantially from the ideal values expected for a strain-free alignment. 1,1,1,3,3,3-Hexakis(trimethylsilyl)-2,2-dimethyltrisilane²³ and the analogous all-germanium compound 4 both crystallize in the monoclinic space group C2/c with half a molecule in the asymmetric unit. In both structures, one trimethylsilyl or trimethylgermyl group is disordered and the central Ge-Ge as well as the Si-Si bond distances are all almost minimized to normal values. The dihedral angles Me₃Ge-Ge-Ge(Me)₂- $Ge(A)-Ge(A)Me_3$ in 4 show a strong deviation from the 60° of a

⁽¹⁹⁾ Jenkins, D. M.; Teng, W.; Englich, U.; Stone, D.; Ruhlandt-Senge, K. Organometallics 2001, 20, 4600–4606.

 ⁽²⁰⁾ Teng, W.; Ruhland-Senge, K. Chem.—Eur. J. 2005, 11, 2462–2470.
 (21) (a) Fronczek, F. R.; Lickiss, P. D. Acta Crystallogr. C 1993, 49, 331–333. (b) Mallela, S. P.; Bernal, I.; Geanangel, R. A. Inorg. Chem. 1992,

³¹, 1626–1627.

⁽²²⁾ Baumgartner, J.; Fischer, R.; Fischer, J.; Wallner, A.; Marschner, C. *Organometallics* **2005**, *24*, 6450–6457.

⁽²³⁾ Baumgartner, J.; Frank, D.; Kayser, C.; Marschner, C. Organometallics 2005, 24, 750–761.



Figure 2. Left: Molecular structure of 3 (thermal ellipsoid plot drawn at the 30% probability level). Hydrogen atoms are omitted for clarity. Right: Newman projection of 3 along the Ge(1)-Ge(1A) bond. Selected bond distances (Å) and angles (deg): Ge(1)-Ge(2) 2.4418(4), Ge(1)-Ge(1A) 2.4571(8), Ge(2)-C(2) 1.950(2), Ge(2)-C(1) 1.963(2), Ge(2)-Ge(1)-Ge(2A) 105.130(12), Ge(2)-Ge(1)-Ge(1A) 113.526(10).

perfectly staggered conformation (Figure 3) but have nearly the same values as were found for the corresponding Si compound. Tris(trimethylsilyl)triisopropylsilylsilane²³ and 6 both crystallize in the same space group (trigonal R3) with nearly the same cell dimensions. The distances of the Ge–Ge bonds at 2.44 Å in 6 are in the range published for a couple of linear perphenylated germanium compounds.²⁴ The bond angles are 105.1° for Me₃Ge-Ge-GeMe₃ and 113.5° for Me₃Ge-Ge-Si^{*i*}Pr₃ and thus practically identical with the ones in tris(trimethylsilyl)triisopropylsilylsilane. The dipotassium compound 11 crystallizes in the triclinic space group $P\overline{1}$ with one and a half molecules and an additional toluene in the asymmetric unit. The central Ge-Ge bond is elongated by about 0.1 to 2.58 Å, as it had been observed before for the 1,2-dipotassiumdisilane²⁵ and also for tetrakis(trimethylsilyl)digermyl-1,2-dipotassium.10 As all the other 1,2-dianions, 11 also exhibits an anti-conformation with a torsion angle for the K-Ge-Ge-K arrangement of 158.1°. In close analogy with what was found for tetrakis(trimethylsilyl)digermyl-1,2-dipotassium the degree of pyramidalization of the anionic germanium atoms is relatively high, as can be seen from the small angles for Ge(6)-Ge(2)-Ge(5) (91.5°) and Ge(3)-Ge(1)-Ge(4) (93.0°).

NMR Spectroscopy. While ²⁹Si NMR spectroscopy provides a very convenient handle to interpret the chemical situation at silicon, the situation for germanium is quite different. ⁷³Ge, with a natural abundance of 7.76%, is a spin 9/2 isotope with very low resonance frequencies. ⁷³Ge NMR spectroscopy is therefore not commonly available. For this reason NMR spectroscopic characterization relies heavily on ¹H and ¹³C.

Generally the range for the chemical shifts of trimethylgermyl groups in proton spectra is between 0.80 and 0.30 ppm. Increasing the steric pressure on a compound usually results in a slight downfield shift such as from 0.40 ppm in **1** to 0.50 ppm in **3** and **6**. Compared to the resonance behavior of trimethylsilyl the trimethylgermyl groups can be found at slightly lower field, as exemplified in **5**, where resonance for the Me₃Ge is found at

0.35 ppm compared to that of Me₃Si at 0.28 ppm. Similar situations are found for compounds 8 and 10. If the trimethylgermyl group is attached to a negatively charged germanium, a shift to values close to 0.80 ppm is observed, such as in compounds 2, 9, and 11. Compound 9 is especially interesting, as its negatively charged germanium atoms are chiral. As we have two chiral atoms, we can expect two types of isomers: a *meso*-form and a racemic mixture of enantiomers. Assuming that both forms should be energetically similar, a mixture in a ratio close to 1:1 can be expected. The fact that indeed a double signal set (four singlets in the ¹H and also four resonances in the ¹³C) is observed indicates configurational stability of the germyl anions at rt.²⁶

The situation for the 13 C NMR chemical shifts of trimethylgermyl groups parallels the situation described for the respective proton spectra. Shifts around 3 ppm for unstrained compounds (1, 5) are followed by a slight move to lower field (to values close to 4.5 ppm) for more crowded compounds (3, 6, 8, 10) and eventually a further move downfield for charged species (2, 9, 11) to values in the range between 7 and 9 ppm.

Our experience with silyl anions has shown us that the ²⁹Si NMR resonances of trimethylsilyl groups attached to negatively charged silicon atoms usually experience a downfield shift of approximately 4-6 ppm compared to the neutral species. Interestingly enough, we find that in cases where trimethylsilyl groups are attached to negatively charged germanium atoms (9) this shift behavior is not observed.¹⁰

Conclusion

While the tris(trimethylsilyl)silyl⁴ and to a lesser extent also the tris(trimethylsilyl)germyl⁹ groups have captured their spots in the organometallic chemistry of main group and transition metals, the chemistry of the structurally related tris(trimethylgermyl)germyl group has been barely addressed.¹² To provide an entry into this area, we describe the synthetic access to tetrakis(trimethylgermyl)germane (1) and further to tris(trimethylgermyl)germylpotassium (2), which serves as a convenient

⁽²⁴⁾ Roller, S.; Simon, D.; Dräger, M. J. Organomet. Chem. 1986, 301, 27-40.

⁽²⁵⁾ Fischer, R.; Konopa, T.; Baumgartner, J.; Marschner, C. Organometallics 2004, 23, 1899–1907.

⁽²⁶⁾ For a related example of a configurationally stable germyl anion see: Fischer, J. Doctoral Thesis, TU Graz, 2005.



Figure 3. Molecular structure of 4 (thermal ellipsoid plot drawn at the 30% probability level). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): C(1)–Ge(2) 1.882(9), Ge(1)–Ge(4) 2.4215(8), Ge(1)–Ge(2) 2.4362(8), Ge(1)–Ge(3) 2.4372(8), Ge(1)–Ge(5) 2.4480(8), Ge(4)–Ge(1)–Ge(2) 110.78(3), Ge(4)–Ge(1)–Ge(3) 105.90(3), Ge(2)–Ge(1)–Ge(3) 105.70(3), Ge(4)–Ge(1)–Ge(5) 114.83(3), Ge(2)–Ge(1)–Ge(5) 113.11(3), Ge(3)–Ge(1)–Ge(5) 105.69(3), Ge(1A)–Ge(5)–Ge(1) 123.66(4).

tris(trimethylgermyl)germyl transfer reagent. In the context of this study it was found that trimethylgermyl abstraction with potassium *tert*-butoxide is less facile compared to the cleavage of trimethylsilyl groups. This leads to the unexpected situation that 1,2-dipotassiumtetrakis(trimethylgermyl)digermane (11) cannot be prepared starting from hexakis(trimethylgermyl)digermane (3) but requires 1,2-bis(trimethylsilyl)tetrakis(trimethylgermyl)digermane (10) as the precursor for the reaction with 2 equiv of potassium *tert*-butoxide.

Experimental Section

General Remarks. All reactions involving air-sensitive compounds were carried out under an atmosphere of dry nitrogen or argon using either Schlenk techniques or a glovebox. Solvents were dried using a column solvent purification system.²⁷ Potassium *tert*-butanolate was purchased exclusively from Merck, and lithium was used as wire with sodium content between 0.5% and 1.0%. All other chemical were obtained from different



Figure 4. Molecular structure of 6 (thermal ellipsoid plot drawn at the 30% probability level). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ge(1)-Si(1) 2.4172(14), Ge(1)-Ge(2A) 2.4406(4), Ge(1)-Ge(2) 2.4406(4), Ge(2)-C(6) 1.960(3), Si(1)-C(1) 1.890(3), Si(1)-Ge(1)-Ge(2) 113.514(11), Ge(2A)-Ge(1)-Ge(2) 105.143(13).

suppliers and used without further purification. Tetrakis-(trimethylsilyl)digermyl-1,2-dipotassium¹⁰ was prepared according to a published procedure, whereas the preparation of chlorotrimethylgermane was carried out in two steps, forming tetramethylgermane from GeBr₄ and methyl magnesium iodide¹⁴ followed by reaction with SnCl₄.¹³ ¹H (300 MHz), ¹³C (75.4 MHz), and ²⁹Si (59.3 MHz) NMR

¹H (300 MHz), ¹³C (75.4 MHz), and ²⁹Si (59.3 MHz) NMR spectra were recorded on a Varian Unity INOVA 300. To compensate for the low isotopic abundance of ²⁹Si, the INEPT pulse sequence was used for the amplification of the signal.²⁸ If not noted otherwise, the used solvent was C_6D_6 and all samples were measured at rt. Elementary analyses were carried using a Heraeus Vario Elementar EL apparatus. UV spectra were measured on a Perkin-Elmer Lambda 35 spectrometer using spectroscopy grade pentane as solvent. GC-MS measurements were carried out using an Agilent 7890A GC equipped with a 5975C VL MSD.

X-ray Structure Determination. For X-ray structure analyses the crystals were mounted onto the tip of glass fibers, and data collection was performed with a Bruker-AXS SMART APEX CCD diffractometer using graphite-monochromated Mo Ka radiation (0.71073 Å). The data were reduced to F_0^2 and corrected for absorption effects with SAINT²⁹ and SADABS,³⁰ respectively. Structures were solved by direct methods and refined by a fullmatrix least-squares method (SHELXL97).³¹ All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in calculated positions to correspond to standard bond lengths and angles. Detailed crystallographic data on the structures of compounds 2, 3, 4, and 6 are compiled in Table S-1 and in the cif files provided in the Supporting Information. The latter have also been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC 760794 (2), 760795 (3), 760797 (4), 760796 (6), and 764851 (11). Copies of data can be obtained free of charge at http://www. ccdc.cam.ac.uk/products/csd/request/.

⁽²⁷⁾ Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.

^{(28) (}a) Morris, G. A.; Freeman, R. J. Am. Chem. Soc. **1979**, *101*, 760–762. (b) Helmer, B. J.; West, R. Organometallics **1982**, *1*, 877–879.

⁽²⁹⁾ SAINTPLUS: Software Reference Manual, Version 6.45; Bruker-AXS: Madison, WI, 1997–2003.

⁽³⁰⁾ Blessing, R. H. Acta Crystallogr. A 1995, 51, 33–38. SADABS: Version 2.1; Bruker AXS, 1998.

⁽³¹⁾ Sheldrick, G. M. Acta Crystallogr. A 2008, 64, 112-122.



Figure 5. Molecular structure of **11** (thermal ellipsoid plot drawn at the 30% probability level). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): K(1)–Ge(1) 3.488(4), K(2)–Ge(2) 3.521(4), Ge(1)–Ge(3) 2.464(2), Ge(1)–Ge(2) 2.574(2), Ge(2)–Ge(6) 2.463(2), Ge(3)–C(1) 1.940(16), Ge(3)–Ge(1)–Ge(4) 93.04(8), Ge(3)–Ge(1)–Ge(2) 94.74(8), Ge(4)–Ge(1)–Ge(2) 97.02(8), Ge(3)–Ge(1)–K(1) 127.17(9), Ge(4)–Ge(1)–K(1) 115.71(9), Ge(2)–Ge(1)–K(1) 121.98(8), Ge(6)–Ge(2)–Ge(5) 91.47(8), Ge(6)–Ge(2)–Ge(1) 96.90(8), Ge(5)–Ge(2)–Ge(1) 96.05(8), Ge(6)–Ge(2)–K(2) 126.46(9).

Tetrakis(trimethylgermyl)germane, 1. To a mixture of chopped lithium wire (600 mg, 86 mmol) in THF (100 mL) at -78 °C was added dropwise chlorotrimethylgermane (5.70 g,

37.2 mmol) within 5 min followed by the dropwise addition of tetrabromogermane (3.65 g, 9.30 mmol) in THF (15 mL) within 7 min. The reaction mixture turned yellow. After slowly warming to rt the mixture was stirred for further 14 h, after which it turned black and almost all lithium was consumed. Reaction progress was monitored by ¹H NMR spectroscopy. The solution was hydrolyzed by transfer via a filter paper-capped canula into a mixture of H₂SO₄ (0.5 M), diethyl ether, and ice, followed by extraction with diethyl ether. The combined organic layers were dried over Na₂SO₄ and the solvent removed under vacuum. The residue was crystallized from acetone to obtain 1 as colorless crystals [2.00 g, 40%, mp 255–281 °C (subl)]. ¹H NMR (δ ppm): 0.42 (s, 36H). ¹³C NMR (δ ppm): 2.8. MS (70 eV): *m/z* (%) 529.0 (93) [M⁺ – Me], 426.9 (100) [M⁺ – GeMe₃], 322.9 (83) [(Me₃Ge)₂-MeGe⁺], 218.9 (64) [Me₅Ge₂⁺], 119.0 (94) [GeMe₃⁺]. Anal. Calcd for C₁₂H₃₆Ge₅ (543.46): C 26.52, H 6.68. Found: C 26.86, H 6.67. UV absorption: $\lambda = 212 \text{ nm} (\varepsilon = 3.3 \times 10^4 \text{ [M}^{-1} \text{ cm}^{-1})$

Tris(trimethylgermyl)germylpotassium 18-Crown-6, 2. Tetrakis-(trimethylgermyl)germane (150 mg, 0.276 mmol), KO¹Bu (33 mg, 0.290 mmol), and 18-crown-6 (77 mg, 0.290 mmol) were dissolved in toluene (3 mL) and stirred at rt. The solution turned pink immediately. Reaction progress was monitored by ¹H NMR spectroscopy. After 4 h complete conversion was observed and the solution of the compound could be used directly without further purification. For NMR characterization the solvent was removed under vacuum and the residue dissolved in C₆D₆. ¹H NMR (δ ppm): 3.14 (s, 24H, 18-crown-6), 0.79 (s, 27H). ¹³C NMR (δ ppm): 70.0 (18-crown-6), 7.0. MS (70 eV) (bromoethane quench): *m/z* (%) 453.9 (46) [M⁺], 334.9 (45) [M⁺ – GeMe₃], 308.9 (100) [(Me₃Ge)₂-HGe⁺], 119.0 (83) [GeMe₃⁺].

Hexakis(trimethylgermyl)digermane, **3.** To a solution of **2** (1.84 mmol) in toluene (20 mL) at -80 °C was added dropwise a solution of 1,2-dibromoethane (182 mg, 0.97 mmol) in toluene (2 mL) within 5 min. The reaction mixture was allowed to warm to rt and after 2 h was hydrolyzed with sulfuric acid (0.5 M) and extracted with diethyl ether. The combined organic layers were dried over Na₂SO₄ and the solvent was removed under vacuum. Impurities of tetrakis(trimethylgermyl)germane were removed by sublimation, and colorless crystals (547 mg, 70%, mp 166–190 °C) of **3** were obtained. ¹H NMR (δ ppm): 0.50 (s, 54H). ¹³C NMR (δ ppm): 4.3. MS (70 eV): m/z (%) 528.9 (78) [(Me₃Ge)₃GeGeMe₂⁺], 427.0 (91) [(Me₃Ge)₃Ge⁺], 323.0 (70) [(Me₃Ge)₂MeGe⁺], 118.9 (100) [GeMe₃⁺]. Anal. Calcd for C₁₈H₅₄Ge₈ (851.50): C 25.39, H 6.39. Found: C 24.98, H 6.44. UV absorption: $\lambda_1 = 213$ nm ($\varepsilon_1 = 5.6 \times 10^4$ [M⁻¹ cm⁻¹]), $\lambda_2 = 221$ nm ($\varepsilon_2 = 5.9 \times 10^4$ [M⁻¹ cm⁻¹]).

Bis{tris(trimethylgermyl)germyl}dimethylgermane, 4. To a solution of dichlorodimethylgermane (42 mg, 0.241 mmol) in toluene (5 mL), cooled to -30 °C, was added dropwise a toluene solution of 2 (0.460 mmol) within 15 min. After 14 h the reaction mixture was treated with aqueous sulfuric acid (0.5 M) and extracted with diethyl ether. The combined organic layers were dried over Na₂SO₄ and the solvent removed under reduced pressure. Impurities of tetrakis(trimethylgermyl)germane were removed via sublimation, and colorless crystals (150 mg, 68%, mp 205–219 °C) of 4 were obtained. ¹H NMR (δ ppm): 0.77 (s, 6H), 0.50 (s, 54H). ¹³C NMR (δ ppm): 7.1, 4.1(Me₂Ge). MS (70 eV): m/z (%) 528.9 (89) [(Me₃Ge)₃GeGeMe₂⁺], 409.8 (100) [(Me₃Ge)₂GeGeMe₂⁺], 220.8 (44) [Me₃Ge₂⁻], 118.9 (78) [GeMe₃⁺]. Anal. Calcd for C₂₀H₆₀Ge₉ (954.18): C 25.17, H 6.34. Found: C 25.37, H 6.42. UV absorption: $\lambda_1 = 202 \text{ nm} (\epsilon_1 = 7.8 \times 10^4 [\text{M}^{-1} \text{ cm}^{-1}]), \lambda_2 = 252 \text{ nm} (\epsilon_2 = 4.7 \times 10^4 [\text{M}^{-1} \text{ cm}^{-1}]).$

Trimethylsilyltris(trimethylgermyl)germane, 5. To a solution of chlorotrimethylsilane (42 mg, 0.386 mmol) in toluene (5 mL) was added dropwise a toluene solution of 2 (42 mg, 0.386 mmol) within 5 min. After 14 h the reaction mixture was treated with aqueous sulfuric acid (0.5 M) and extracted with diethyl ether. The combined organic layers were dried over Na₂SO₄, and the solvent was removed under reduced pressure. Yield: 180 mg (98%, mp 214–217 °C), colorless crystals. ¹H NMR (δ ppm): 0.28 (s, 9H), 0.35 (s, 27H). ¹³C NMR (δ ppm): 2.8, 3.2. ²⁹Si NMR

(δ ppm): -3.3. MS (70 eV): m/z (%) 483.0 (93) [M⁺ – Me], 381.0 (100) [(Me₃Ge)₂(Me₃Si)Ge⁺], 279 (83) [(Me₃Ge)(Me₃Si)Me-Ge⁺], 177.0 (59) [Me₅SiGe⁺], 118.9 (63) [GeMe₃⁺], 73.1 (67) [SiMe₃⁺]. Anal. Calcd for C₁₂H₃₆Ge₄Si (498.94): C 28.89, H 7.27. Found: C 29.11, H 7.32. UV absorption: λ = 198 nm (ε = 5.6 × 10⁴ [M⁻¹ cm⁻¹]).

Triisopropylsilyltris(**trimethylgermyl)germane**, **6**. To a solution of chlorotriisopropylsilane (38 mg, 0.193 mmol) in toluene (5 mL) was added dropwise within 10 min a toluene solution of **2** (0.184 mmol). After 14 h the reaction mixture was treated with aqueous sulfuric acid (0.5 M) and extracted with diethyl ether. The combined organic layers were dried over Na₂SO₄, and the solvent was removed under reduced pressure. The residue was crystallized from acetone to yield colorless crystals (96 mg, 89%, mp 260 °C) of **6**. ¹H NMR (δ ppm): 1.18–1.27 (m, 3H), 1.14 (d, 18H), 0.50 (s, 27H). ¹³C NMR (δ ppm): 4.3, 14.6, 20.3. ²⁹Si NMR (δ ppm): 22.6. MS (70 eV): *m/z* (%): 539.0 (2) [M⁺ - ⁱPr], 409.0 (100) [M⁺ - MeSi(ⁱPr)₃], 157.1 (23) [ⁱPr₃Si⁺], 118.9 (21) [GeMe₃⁺], 115.0 (42) [ⁱPr₂HSi⁺]. Anal. Calcd for C₁₈H₄₈Ge₄Si (583.10): C 37.08, H 8.30. Found: C 36.96, H 7.90. UV absorption: $\lambda = 211$ nm ($\varepsilon = 3.3 \times 10^4$ [M⁻¹ cm⁻¹]).

Tris(trimethylgermyl)germane, 7. A solution of **2** (0.92 mmol) was added dropwise to a vigorously stirred mixture of degassed H₂SO₄ (20 mL, 0.5 M) and ether (20 mL). After 30 min the organic phase was separated and the aqueous phase extracted with pentane. The combined organic layers were dried over Na₂SO₄, and the solvent was removed under reduced pressure, leaving a colorless liquid (286 mg, 73%). ¹H NMR (δ ppm): 2.81 (s, 1H), 0.41 (s, 27H). ¹³C NMR (δ ppm): 2.0. MS (70 eV): m/z (%): 427.9 (18) [M⁺], 410.9 (23) [M⁺ - Me], 307.9 (98) [(Me₃Ge)₂HGe⁺], 220.9 (54) [Me₅Ge₂⁺], 118.9 (100 [GeMe₃⁺]. Anal. Calcd for C₉H₂₈Ge₄ (426.76): C 25.33, H 6.61. Found: C 25.44, H 6.54. UV absorption: $\lambda = 198$ nm ($\varepsilon = 5.0 \times 10^4$ [M⁻¹ cm⁻¹]).

1,2-Bis(trimethylgermyl)-1,1,2,2-tetrakis(trimethylsilyl)digermane, 8. A solution of 1,1,2,2-tetrakis(trimethylsilyl)digermyl-1,2-dipotassium [prepared from hexakis(trimethylsilyl)digermane (1.00 g, 1.71 mmol), KOtBu (403 mg, 3.59 mmol), and 18crown-6 (950 mg, 3.59 mmol)] in toluene (4 mL) was added dropwise to a stirred solution of chlorotrimethylgermane (550 mg, 3.59 mmol) in toluene (10 mL). After 3 h the reaction mixture was treated with aqueous sulfuric acid (0.5 M) and extracted with diethyl ether. The combined organic layers were dried over Na₂SO₄, and the solvent was removed under reduced pressure, yielding 8 as a white solid (1.14 g, 99%, mp > 320 °C). ¹H NMR (δ ppm): 0.52 (s, 18H), 0.37 (s, 36H). ¹³C NMR (δ ppm): 4.7 (6 Me), 4.6 (12 Me). ²⁹Si NMR $(\delta \text{ ppm}): -4.0. \text{ MS} (70 \text{ eV}): m/z (\%) 497.1 (7) [M^+ -2 \text{ SiMe}_4], 395.0$ (11) $[M^+ - Me_5SiGe]$, 322.0 (100) $[(Me_3Ge)_2MeGe^+]$, 235.0 (41) $[(Me_3Si)_2MeGe^+]$, 118.9 (8) $[GeMe_3^+]$, 73.1 (72) $[SiMe_3^+]$. Anal. Calcd for $C_{18}H_{54}Ge_4Si_4$ (673.40): C 32.10, 8.08. Found: C 31.97, H 8.05. UV absorption: $\lambda_1 = 211 \text{ nm} (\varepsilon_1 = 6.5 \times 10^4 [\text{M}^{-1} \text{ cm}^{-1}]), \lambda_2 = 217 \text{ nm shoulder} (\varepsilon_2 = 5.9 \times 10^4 [\text{M}^{-1} \text{ cm}^{-1}]).$

1,2- Bis(trimethylgermyl)-1,2-bis(trimethylsilyl)digermyl-1,2-dipotassium, 9. Compound **8** (500 mg, 0.742 mmol), KO^tBu (175 mg, 1.56 mmol), and 18-crown-6 (412 mg, 1.56 mmol) were dissolved in toluene (2 mL) and stirred at rt. The solution turned orange immediately. Reaction progress was monitored by ¹H NMR spectroscopy. After 4 h complete conversion was

observed and the solution of the compound could be used directly without further purification. For NMR characterization the solvent was removed under vacuum and the residue dissolved in C₆D₆. ¹H NMR (δ ppm): 3.33 (s, 48H, 18-crown-6), 0.81 (s, 9H), 0.80 (s, 9H), 0.77 (s, 9H), 0.75 (s, 9H). ¹³C NMR (δ ppm): 70.1 (18-crown-6), 9.0, 8.9, 8.2, 8.1. ²⁹Si NMR (δ ppm): -3.3, -3.5. MS (70 eV) (bromoethane quench): m/z (%) 512.9 (3) [M⁺ – SiMe₃], 467.0 (67) [M⁺ – GeMe₃], 364.9 (29) [(Me₃Ge)(Me₃Si)EtGe₂⁺], 264.9 (61) [(Me₃Ge)(Me₃Si)HGe⁺], 119.0 (27) [GeMe₃⁺], 73.1 (100) [SiMe₃⁺].

1,1,2,2-Tetrakis(trimethylgermyl)-1,2-bis(trimethylsilyl)digermane, 10. A solution of 9 (0.742 mmol) in toluene (2 mL) was added dropwise to a stirred solution of chlorotrimethylgermane (239 mg, 1.56 mmol) in toluene (5 mL). After 3 h the reaction mixture was treated with aqueous sulfuric acid (0.5 M) and extracted with diethyl ether. The combined organic layers were dried over Na₂SO₄ and the solvent removed under reduced pressure, yielding a white solid (470 mg, 83%, mp > 320 °C). ¹H NMR (δ ppm): 0.47 (s, 36H), 0.33 (s, 18H). ¹³C NMR (δ ppm): 4.6 (12 Me), 4.5 (6 Me). ²⁹Si NMR (δ ppm): -3.0. MS (70 eV): m/z (%) 541.0 (7) $[M^+ - Me_5Ge_2]$, 439.0 (15) $[(Me_3Si)(Me_3Ge)_2GeSi Me_2^+$], 365.9 (100) [(Me_3Si)(Me_3Ge)Me_2Ge_2^+], 278.9 (36) [(Me_3-Ge)(Me₃Si)MeGe⁺], 177.1 (38 [Me₅SiGe⁺], 119.0 (28) [GeMe₃⁺], 73.1 (44) [SiMe₃⁺]. Anal. Calcd for C₁₈H₅₄Ge₆Si₂ (762.45): C 28.35, H 7.14. Found: C 28.02, H 6.96. UV absorption: $\lambda = 213$ nm ($\varepsilon =$ $6.3 \times 10^4 \,[\text{M}^{-1} \,\text{cm}^{-1}]).$

Tetrakis(trimethylsilyl)digermyl-1,2-dipotassium 2 × 18-crown-6, 11. Compound 10 (130 mg, 0.171 mmol), KO^tBu (40 mg, 0.358 mmol), and 18-crown-6 (95 mg, 0.358 mmol) were dissolved in toluene (4 mL) and stirred at rt. The solution turned yellow immediately. Reaction progress was monitored by ¹H NMR spectroscopy. After 14 h complete conversion was observed and the solution of the compound could be used directly without further purification. For NMR characterization the solvent was removed under vacuum and the residue dissolved in C₆D₆. ¹H NMR (δ ppm): 3.35 (s, 48H, 18-crown-6), 0.78 (s, 36H). ¹³C NMR (δ ppm): 70.3 (18-crown-6), 7.1. MS (70 eV) (bromoethane quench): *m/z* (%) 494.8 (40) [(Me₃Ge)₃Ge₂⁺], 306.9 (67) [(Me₃Ge)₂HGe⁺], 206.9 (38) [Me₄HGe₂⁺], 119.0 (100) [GeMe₃⁺].

Tetrabromogermane.¹⁵ In a flask equipped with reflux condenser a mixture of germanium powder (18.5 g, 255 mmol) and bromine (89.6 g, 561 mmol) was heated to 75 °C. After 3 days at this temperature all germanium powder was consumed. Excess of bromine was removed under reduced pressure, leaving a light orange residue. From the residue colorless crystals of tetrabromogermane (96 g, 96%, mp 26 °C) started forming.

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Supporting Information Available: A table containing combined crystallographic data and X-ray crystallographic information in CIF format are available free of charge via the Internet at http://pubs.acs.org.