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Structural Aspects of Trimethylsilylated Branched Group 14 Compounds

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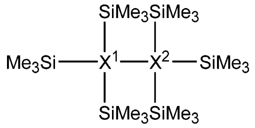
Some newly synthesized compounds of the type $[(Me_3Si)_3X^1X^2(SiMe_3)_3]$ (X^1, X^2 = Si, Ge, or Sn) together with some related compounds bearing triisopropylsilyl or -stannyl groups are characterized by single-crystal X-ray crystallography. The structural data are compared to similar compounds already known. The interaction of silyl groups connected to different central atoms such as Si, Ge, and Sn is analyzed.

1. Introduction

Over the last decades polysilanes have attracted attention for their interesting features comprising thermochromic behavior, UV absorption, and nonlinear optic (NLO) properties.[1] Most of these characteristics derive from the occurrence of σ-bond conjugation, which is highly dependent on the conformation of the molecules. As polygermanes and polystannanes[2] are also interesting materials for the same reasons, copolymers of the types organosilane/organogermane and organosilane/organostannane have been prepared and studied in some detail. Most of these synthetic endeavors have utilized either Wurtz-type coupling conditions of diorganodichloro compounds with alkali metals[3] or electrochemical[4] methods. Over the past few years our group has been involved in the chemistry of oligosilyl anions[5] and dianions, which allows the selective construction of medium-sized polysilanes with chain lengths up to 20 silicon atoms with completely defined structure. As most of the compounds are rather constricted in their conformational flexibility, conformation−property relationships can be studied.

Scheme 1. Analyzed Hexakis(trimethylsilyl)-Substituted Compounds



2 $X^1 = X^2 = Ge$
3 $X^1 = X^2 = Sn$
4 $X^1 = Si$, $X^2 = Ge$
5 $X^1 = Si$, $X^2 = Sn$
6 $X^1 = Ge$, $X^2 = Sn$

Recently the chemistry was expanded to silylated germyl[6] and stannyl anions.[7] These compounds are available from common starting materials such as tetrakis(trimethylsilyl)silane, -germane, or -stannane, which can be reacted with potassium alkoxides to the respective anions. Most substrates investigated share a tris(trimethylsilyl)silyl or similar space-filling group. As we started to employ these compounds to prepare defined polysilanes with tin or germanium atoms in the chains, we also became interested in the structural and UV-spectroscopic features of these compounds. Despite their simplicity, good availability, and frequent occurrence, surprisingly little is known about their structural aspects.

In this account we report on new crystal structures of the type $[(Me_3Si)_3X^1X^2(SiMe_3)_3]$ [X^1, X^2 = Si, Ge, or Sn] (Scheme 1). In another approach we studied variations of tetrakis(trimethylsilyl)silane, -germane, or -stannane where trimethylsilyl groups were replaced by more space demanding triisopropylsilyl or -stannyl groups (Scheme 2).

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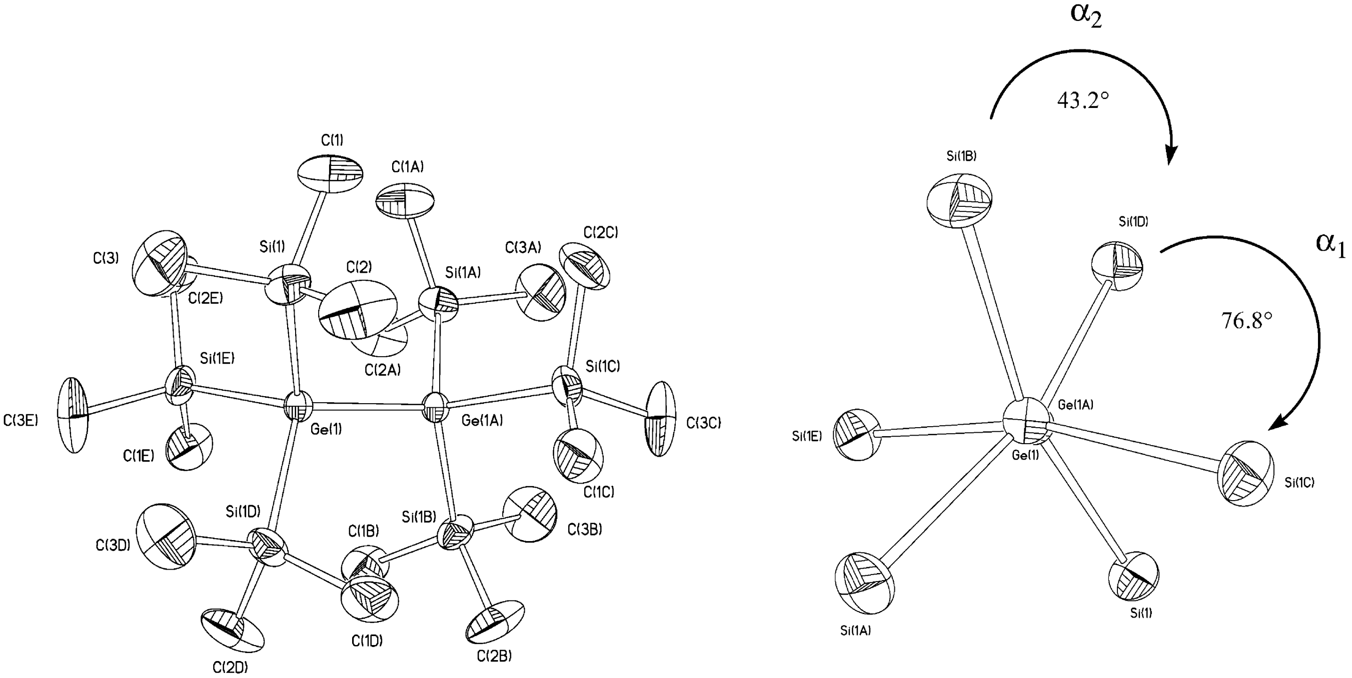
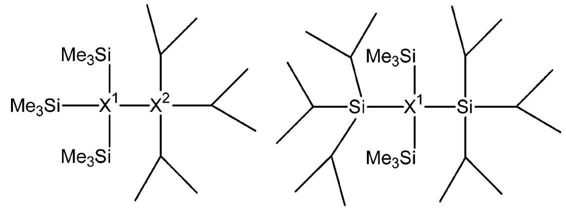


Figure 1. Left: Molecular structure and numbering of **2**. Right: Newman projection of **2** along the Ge−Ge bond. Selected bond lengths [Å] and bond angles [deg] with SD's: Ge(1)−Si(1) 2.4062(6), Ge(1)−Ge(1A) 2.4787(7), Si(1)−C(1) 1.861(2), Si(1)−C(2) 1.866(2), Si(1)−C(3) 1.875(2), Si(1)−Ge(1)-Si(1D) 105.646(18), Si(1)−Ge(1)-Ge(1A) 113.067(16).

Scheme 2. Analyzed Compounds with Triisopropylsilyl and -stannyl Groups



7 $X^1 = X^2 = Si$
8 $X^1 = Ge, X^2 = Si$
9 $X^1 = Sn, X^2 = Si$
10 $X^1 = Si, X^2 = Sn$
11 $X^1 = Ge, X^2 = Sn$

12 $X_1 = Si$
13 $X_1 = Ge$
14 $X_1 = Sn$

The crystal structure of hexakis(trimethylsilyl)disilane (**1**)[8] was determined more than a decade ago.[9] An elongation of the distance between the central Si atoms from the average value of 2.35 to 2.40 Å was found. In addition an interpenetration of methyl groups belonging to different $(Me_3Si)_3Si$ groups was concluded from the fact that the intramolecular methyl clearances were found to be as close as 3.51 Å, which was considered to be less than the sum of the van der Waals radii of two methyl groups, 2.00 Å each. A more recent solid-state NMR study of **1** pointed out various reorientation processes in the crystal even at low temperature.[10]

By exchanging the central silicon atoms in hexakis(trimethylsilyl)disilane we wanted to study the influence on the crystal structures and the intra- and intermolecular interactions.

2. Results and Discussion

Hexakis(trimethylsilyl)disilane (**1**) crystallizes in the trigonal space group *R*-3*c*. Half of a molecule is in the asymmetric unit, and the central Si−Si bond is located on a 3-fold axis. Not only the *intra*molecular but also the *inter*molecular contacts between the carbon atoms of methyl groups were found to be as short as 3.89 Å. As a consequence of the sterically demanding substituents, deviations from the ideal tetrahedral bond angle (109.5°) were found frequently (angles between 114° and 105°).[9]

Hexakis(trimethylsilyl)digermane[11] (**2**) crystallizes as **1** in *R*-3*c*, and as expected all structural parameters are very similar (Figure 1). The distances between carbon atoms belonging to different $(Me_3Si)_3Ge$ groups are as close as 3.61 Å, and the shortest *inter*molecular contacts between the carbon atoms were found to be 3.96 Å. Also tetrahedral bond angles are similar to what was found for **1**. Unfortunately, no crystal structures of acyclic compounds bearing a $Si_3Ge{-}GeSi_3$ or $Si_2Ge{-}GeSi_2$ unit have been reported so far, which makes direct comparison of the lengths of the Ge−Ge bond (2.48 Å) difficult. Bond lengths of 2.46 Å for open chain tetragermane[12] $Ge_4Ph_{10}{\cdot}2C_6H_6$ or 2.42 Å for digermane[13] $[(Me_3Si)_3Si{-}GeCl_2]_2$ have been reported.

Hexakis(trimethylsilyl)distannane[14] (**3**) crystallizes in the space group *R*32 (Figure 2) and shows some interesting, maybe unexpected, differences. The structure

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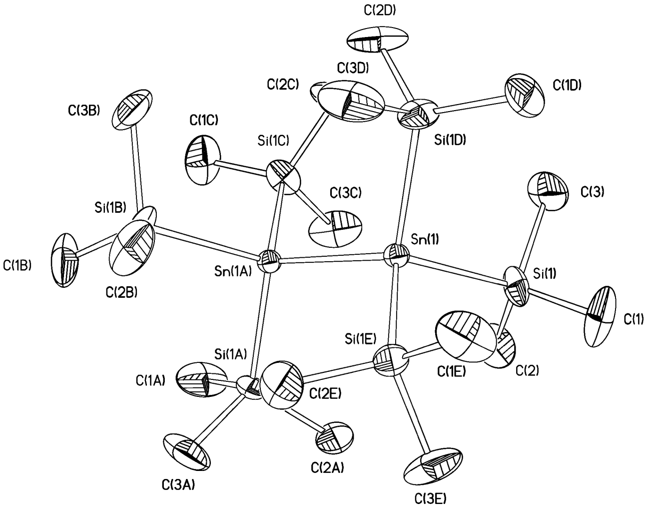

Figure 2. Molecular structure and numbering of **3**; selected bond lengths [Å] and bond angles [°] with SD's: Sn(1)−Si(1) 2.5707(17), Sn(1)−Sn(1A) 2.7930(12), Si(1)−C(1) 1.801(11), Si(1)−C(2) 1.835(11), Si(1)−C(3) 2.020(14), Si(1A)−Sn(1)−Si(1E) 106.53(5), Si(1)−Sn(1)−Sn(1A) 112.27(5).

has been reported previously but with trimethylsilyl groups so strongly disordered that only tin and silicon atoms could be refined anisotropically.[14] The Sn−Sn bond length of 2.79 Å is slightly shorter than found for other open chain distannanes such as $[(Me_2ClSi)(tBu)_2Sn]_2$[15] (2.84 Å) and $[(Me_2PhSi)(tBu)_2Sn]_2$[16] (2.88 Å), but structurally characterized examples with a Si−Sn−Sn−Si skeleton are rare. The Sn−Si bond length (2.57 Å) is close to the two given examples. The Si−C bond lengths differ from 1.80 to 2.02 Å. This is likely to be caused by the measurement at 253 K as the crystals undergo a phase transition when cooled to lower temperature, which destroyed the crystal (the same is true for all crystals in the study measured at temperatures higher than 100 K). The higher temperature is responsible for higher anisotropic displacement parameters obtained for the methyl groups, so that the differences in the Si−C bonds lengths are a consequence of the inaccuracy of the carbon atom positions. *Intra*molecular carbon−carbon contacts between the two $(Me_3Si)_3Sn$ groups were found to be as small as 3.46 Å, thus somewhat shorter than in compounds **1** and **2**. The same is true for *inter*molecular contacts, where the shortest distance between the carbon atoms of the methyl groups was found to be 3.22 Å, which is a reduction of some 0.6 Å compared to contacts in **1**. Even if the before mentioned inaccuracy of the carbon atom positions is considered, the distances are shorter than in **1**.

For the next step of our investigation one of the central silicon atoms of hexakis(trimethylsilyl)disilane was substituted by a germanium atom in **4**, a tin atom in **5**, or both central silicon atoms by a germanium and a tin atom in **6**. Compounds **4** (Figure 3) and **5** (Figure 4) crystallized in the rhombohedric space group *R*-3*c* and **6** in *R*3 (Figure 5). Because of the small difference of the atom radii of silicon and germanium, the two atoms in **4** share the same site, whereas in the silicon−tin compound **5** the two atom positions could be treated independently. This means that in compound **5** all atomic positions could be determined exactly, whereas in compound **4** the only exact distance information can be obtained for the central Ge−Si bond. All other bond distances in **4** correspond to averaged values over the two occupation possibilities.

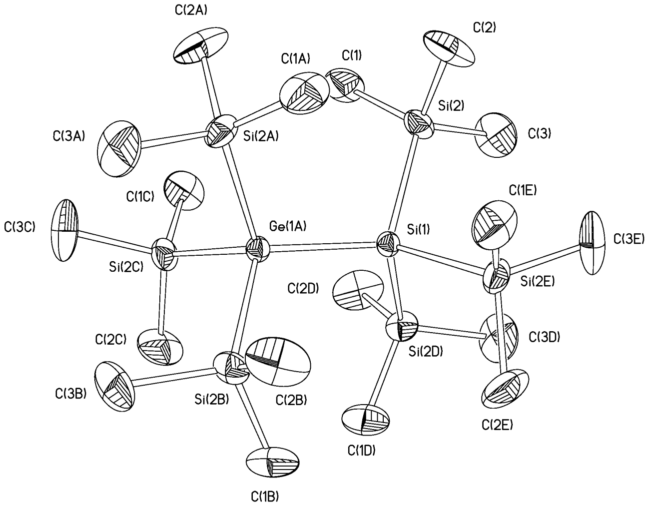

Figure 3. Molecular structure and numbering of **4**. Selected bond lengths [Å] and bond angles [deg] with SD's: Ge(1)−Si(1) 2.4256(9), Ge(1)−Si(2) 2.3922(7), Si(2)−C(2) 1.859(3), Si(2)−C(1) 1.860(3), Si(2)−C(3) 1.875(3), Si(2C)−Ge(1)−Si(2A) 105.19(2), Ge(1)−Si(1)−Si(2D) 113.47(2), Si(2D)−Si(1)−Si(2E) 105.19(2).

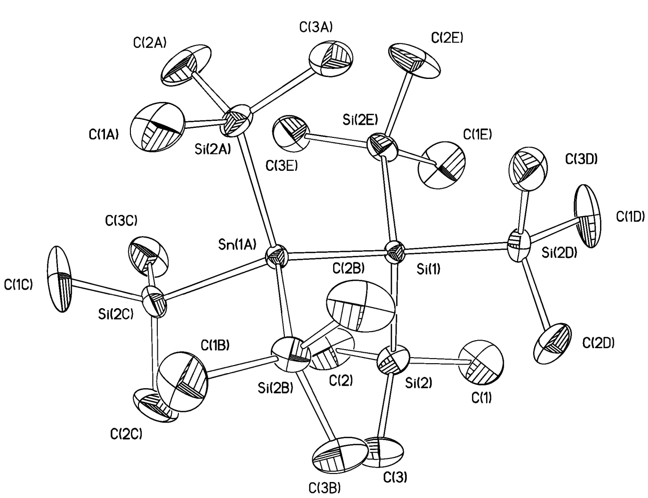

Figure 4. Molecular structure and numbering of **5**. Selected bond lengths [Å] and bond angles [deg] with SD's: Sn(1A)−Si(1) 2.614(2), Sn(1A)−Si(2A) 2.519(2), Si(1)−Si(2) 2.421(6), Si(2)−C(2) 1.832(3), Si(2)−C(1) 1.868(4), Si(2)−C(3) 1.878(3), Si(2)−Si(1)−Si(2D) 109.3(4), Sn(1A)−Si(1)−Si(2D) 109.6(4), Si(2C)−Sn(1A)−Si(2A) 103.3(6).

In **6** the germanium and tin atoms share the same site, but the attached silicon atoms can be resolved. In **4** the central Si−Ge bond length is 2.43 Å, which is slightly larger than the sum of the covalent radii (2.40 Å).[17] The average of Me_3Si−Ge and Me_3Si−Si bonds in **4** amounts to 2.39 Å, whereas the Me_3Si−Ge bonds in **6** are substantially elongated to 2.49 Å. The central Si−

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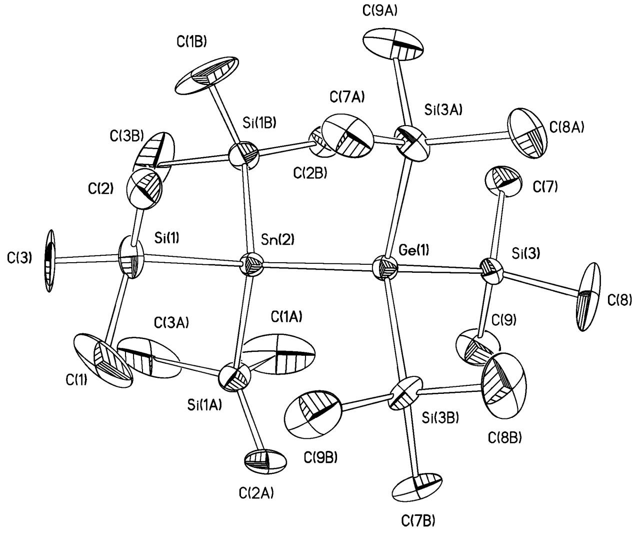


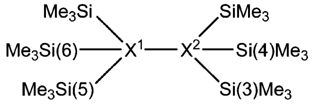
Figure 5. Molecular structure and numbering of **6**. Selected bond lengths [Å] and bond angles [deg] with SD's: Ge(1)–Si(3) 2.496(9), Ge(1)–Sn(2) 2.5887(7), Sn(2)–Si(1) 2.522(14), Si(1)–C(3) 1.86(3), Si(3)–C(8) 1.855(19), Si(3A)–Ge(1)–Si(3) 105.7(3), Si(3A)–Ge(1)–Sn(2) 113.0(2), Si(1B)–Sn(2)–Si(1) 106.9(4), Si(1)–Sn(2)–Ge(1) 112.0(3).

Table 1. Torsion Angles of Compounds 1–6[a]

compound	α_1	α_2
1[9e]	77.2	42.8
2	76.8	43.2
3	62.1	57.9
4	76.6	43.4
5	76.8	43.2
6	61.9	58.1

[a] Angles as indicated in Figure 1.

Table 2. Bond Angles of Compounds 1–6



	X^1–X^2–Si(3)	Si(3)–X^2–Si(4)	Si(5)–X^1–Si(6)
1[9e] (X^1 = X^2 = Si)	113.6	105.0	
2 (X^1 = X^2 = Ge)	113.1	105.7	
3 (X^1 = X^2 = Sn)	112.3	106.5	
4 (X^1 = Ge; X^2 = Si)	113.5	105.2	105.2
5 (X^1 = Sn; X^2 = Si)	109.6	109.3	103.2
6 (X^1 = Sn; X^2 = Ge)	113.0 X^2–X^1–Si(5) = 112.0	105.7	106.9

Sn bond distance in **5** is 2.61 Å, elongated by 0.1 Å compared to the Me_3Si–Sn bond length of 2.52 Å, found for **5** and **6**. The closest *intra*molecular carbon–carbon contacts between the $(Me_3Si)_3Si$ and the $(Me_3Si)_3X$ (X = Ge or Sn) units were found to be 3.57 Å for **4** and 3.66 Å for **5**. The closest contact between the two $(Me_3Si)_3X$ shells in **6** is 3.51 Å. The shortest *inter*molecular contacts between carbon atoms are 3.97 Å for **4**, 4.02 Å for **5**, and 3.88 Å for **6**.

The torsional angles Me_3Si–X^1–X^2–$SiMe_3$ should be 60° for a perfectly staggered conformation, and further theoretical energetic minima can be expected for the *cisoid* (~40°) and *ortho* (~90°) conformers.[18] This dihedral angle was determined for **1** to be 77.2° and 42.8°, thus differing substantially from the ideal values expected for a strain-free conformation.[9e] For the above-discussed compounds **2**, **4**, and **5** these values are very similar, and the only exceptions are the tin compounds **3** and **6** with an approximately staggered conformation (Table 1).

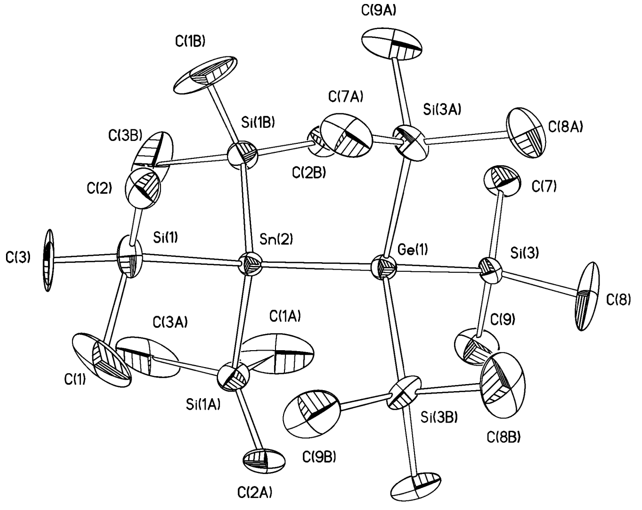


Figure 6. Molecular structure and numbering of **8**. Selected bond lengths [Å] and bond angles [deg] with SD's: Ge(1)–Si(2) 2.4032(10), Ge(1)–Si(1) 2.4261(15), Si(1)–C(1) 1.900(5), Si(2)–C(4) 1.877(6), C(1)–C(3) 1.557(7), Si(2A)–Ge(1)–Si(2) 105.50(3), Si(2A)–Ge(1)–Si(1) 113.20(3).

As a consequence of the steric overcrowding in the above-discussed cases, deviations of the ideal tetrahedral bond angles were found frequently (Table 2). The steric strain widens the bond angles along the central atoms to 113° and minimizes the angles in the two hemispheres to about 105°. Compound **5** is an exception because here the bond angles around the tin atom are almost at the ideal value of 109.5°.

Exchanging one trimethylsilyl group in tetrakis(trimethylsilyl)silane by one triisopropylsilyl group (**7**)[19] lowers the symmetry from cubic to trigonal (space group *R*3), and the same applies accordingly to **8** (Figure 6), **9** (Figure 7), **10** (Figure 8), and **11** (Figure 9). The lengths of the Si–$SiMe_3$ bonds are elongated from 2.34 Å[20] in tetrakis(trimethylsilyl)silane to 2.38 Å in **7**, which is about 0.02 Å shorter than the central Si–Si bond in **1**. The lengths of the Ge–$SiMe_3$ (**8**) and Sn–$SiMe_3$ (**9** and **10**) bonds are the same as for the hexakis(trimethylsilyl) compounds **4** and **5**. The Si–Ge (2.37 Å) and Ge–Sn (2.61 Å) bonds in **11** are both close to the expected distances for Si–Ge bond lengths, which were reported to range from 2.38 to 2.41 Å,[21] and Ge–Sn bond lengths in $Me_3GeSnPh_3$, $Ph_3GeSnMe_3$, $[(Me_3Si)_3Ge]_2SnCl_2$, and $Ph_3SnGeMe_2SiMe_2{}^tBu$, which range from 2.60 to 2.63 Å.[22] The shortest *inter*molecular C–C clearances for **7** are all greater than 3.90 Å, and they are similar for **8** (C6–C3, 3.74 Å), **9** (C1–C5, 3.68 Å), **10** (C3–C6, 3.73 Å), and **11** (C3–C6, 3.72 Å). The *intra*molecular C–C

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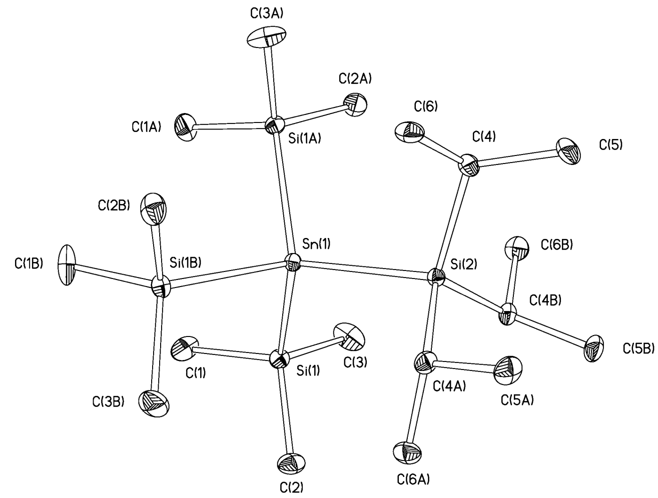

Figure 7. Molecular structure and numbering of **9**. Selected bond lengths [Å] and bond angles [deg] with SD's: Sn(1)−Si(1) 2.5799(6), Sn(1)−Si(2) 2.5868(11), Si(1)−C(1) 1.873(3), Si(2)−C(4) 1.901(2), C(4)−C(6) 1.535(3), Si(1A)−Sn(1)−Si(1) 106.196(16), Si(1A)−Sn(1)−Si(2) 112.575(14).

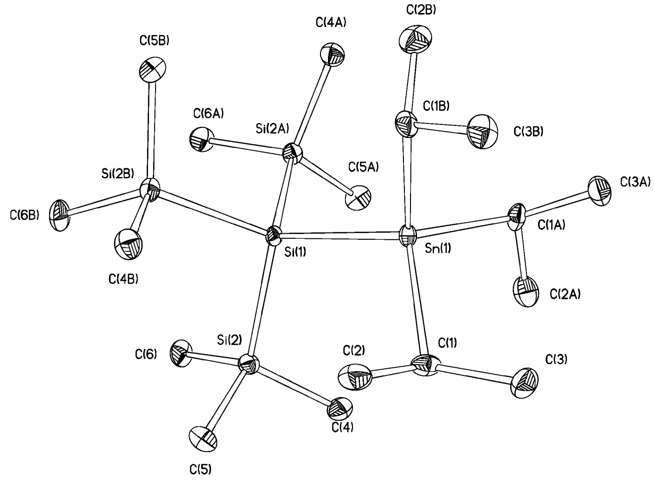

Figure 8. Molecular structure and numbering of **10**. Selected bond lengths [Å] and bond angles [deg] with SD's: Sn(1)−C(1) 2.208(6), Sn(1)−Si(1) 2.573(4), Si(1)−Si(2) 2.360(2), Si(2)−C(6) 1.858(9), C(1)−C(2) 1.497(10), C(1)−Sn(1)−C(1B) 108.0(2), Si(2A)−Si(1)−Si(2) 107.84(10), Si(2)−Si(1)−Sn(1) 111.06(10).

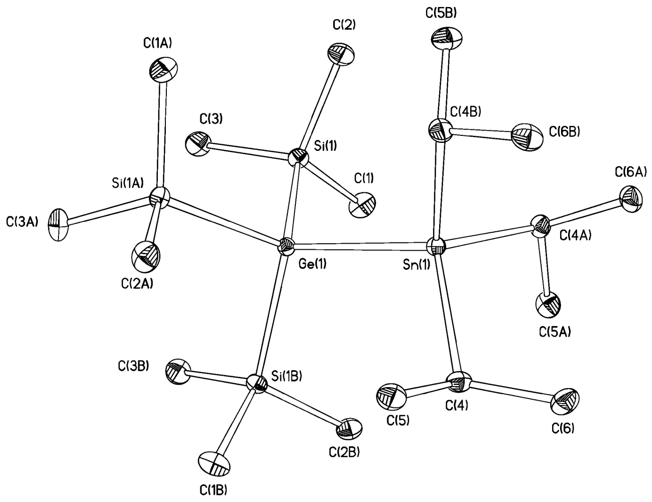

Figure 9. Molecular structure and numbering of **11**. Selected bond lengths [Å] and bond angles [deg] with SD's: Sn(1)−C(4) 2.186(2), Sn(1)−Ge(1) 2.6109(6), Ge(1)−Si(1) 2.3864(7), Si(1)−C(1) 1.873(2), C(4)−C(5) 1.522(3), C(4)−Sn(1)−Ge(1) 110.19(6), Si(1)−Ge(1)−Si(1A) 108.105(18), Si(1)−Ge(1)−Sn(1) 110.804(18).

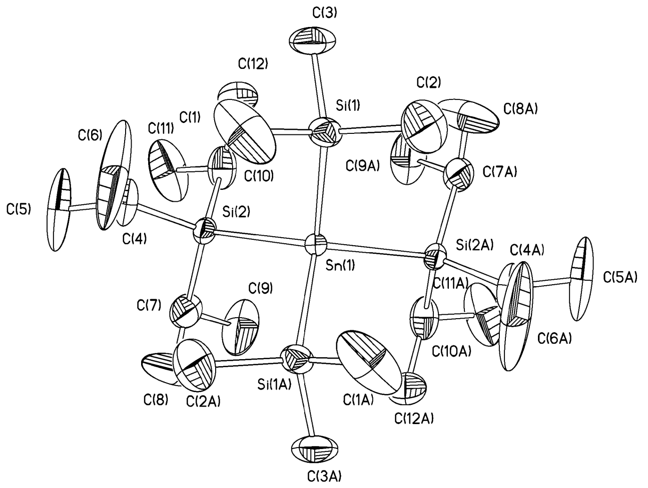

Figure 10. Molecular structure and numbering of **14**. Selected bond lengths [Å] and bond angles [deg] with SD's: Sn(1)−Si(1) 2.611(2), Sn(1)−Si(2A) 2.6416(19), Si(1)−C(1) 1.844(12), Si(1)−C(2) 1.880(12), Si(1)−C(3) 1.888(11), Si(1)−Sn(1)−Si(1A) 101.18(10), Si(1)−Sn(1)−Si(2A) 108.93(7), Si(1A)−Sn(1)−Si(2A) 109.93(7), Si(1)−Sn(1)−Si(2) 109.93(7), Si(1A)−Sn(1)−Si(2) 108.93(7), Si(2A)−Sn(1)−Si(2) 116.81(10).

minimum distance is 2.91 Å[20] for tetrakis(trimethylsilyl)silane and 3.35 Å for **7**[19] between the C atoms of Si(CH$_3$)$_3$ and CH(CH$_3$)$_2$. This distance increases further to 3.72 Å (C2−C5) for **8**, 3.84 Å (C2−C4) for **10**, 3.87 Å (C2−C5) for **11**, and 3.91 Å (C6−C3) for **9**. The bond angles (Si−Si−Si) in **1** are 109.3° and 109.7°,[20] whereas in **7** and **8** the bond angles change to 105.6° for Me$_3$Si−Si−SiMe$_3$ and 113.1° for Me$_3$Si−Si−Si^{i}Pr$_3$. The elongation of the central bond obtained by the introduction of the tin atom in **9**, **10**, and **11** leads to an approximation of both bond angles toward ideal values (to 106.2° in **9** for Me$_3$Si−Sn−SiMe$_3$, 107.8° in **10** for Me$_3$Si−Si−SiMe$_3$, 108.1° in **11** for Me$_3$Si−Ge−SiMe$_3$ and 112.6° in **9** for Me$_3$Si−Sn− Si^{i}Pr$_3$, 111.1° in **10** for Me$_3$Si−Si−Sn^{i}Pr$_3$, and 110.8° in **11** for Me$_3$Si−Ge−Sn^{i}Pr$_3$).

Displacing another trimethylsilyl group by a second triisopropylsilyl group in **7** leads to the last explored series of related compounds, namely, **12**, **13**, and **14**. The symmetry is further brought down to monoclinic space group *C*2/*c* for **12**[19] and **14** (Figure 10). Unfortunately, we were not able to obtain single crystals for **13** at all, and on one hand the quality of **14** was poor and on the other the crystals did not tolerate low temperature; therefore, we could obtain structural data only at room temperature. The Si−Si bond distance is elongated from 2.38 Å in **7** to 2.44 Å in **12**. In the case of the tin compounds a likewise elongation for the Si−Sn Bond length can be observed from 2.57 Å in **10** to 2.61 Å in

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(22) (a) Pannell, K. H.; Parkanyi, L.; Sharma, H. K.; Cervantes-Lee, F. *Inorg. Chem.* **1992**, *31*, 522−524. (b) Parkanyi, L.; Kalman, A.; Pannell, K. H.; Sharma, H. K. *J. Organomet. Chem.* **1994**, *484*, 153−159. (c) Mallela, S. P, Geanangel, R. A. *Inorg. Chem.* **1994**, *33*, 1115−1120. (d) Sharma, H. K.; Cervantes-Lee, F.; Parkanyi, L.; Pannell, K. H. *Organometallics* **1996**, *15*, 429−435.

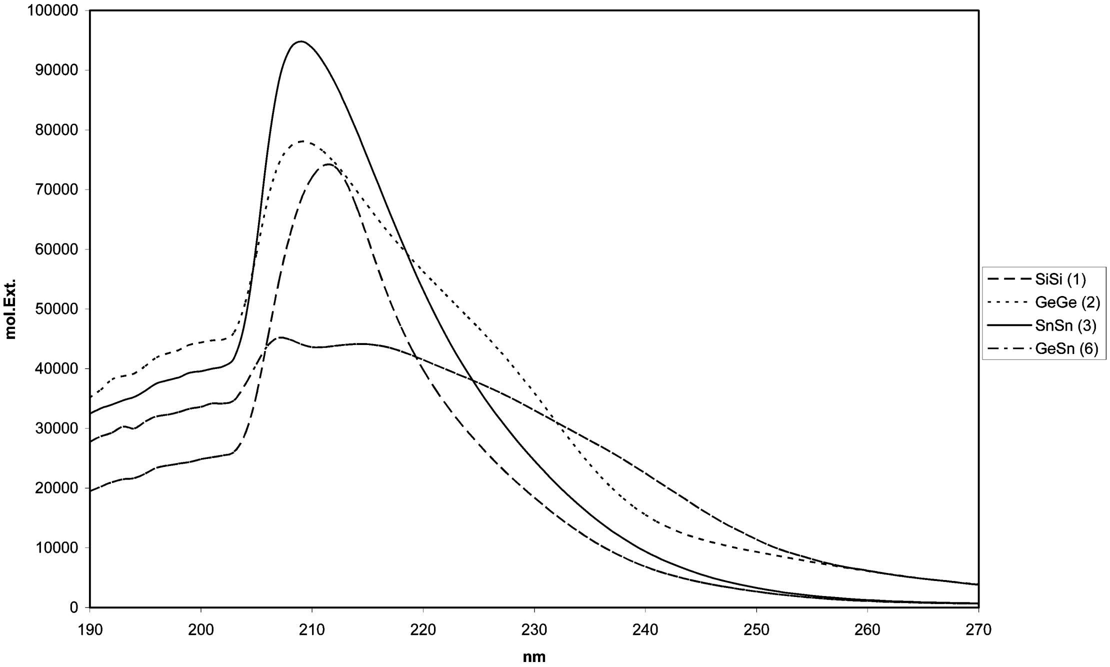

Figure 11. UV spectra of hexakis(trimethylsilyl) compounds **1**, **2**, **3**, and **6**.

Table 3. Selected Bond Lengths of Compounds of Type $(Me_3Si)_3X^1X^2(SiMe_3)_3$ [Å]

compound	Me_3Si-X^1	X^1-X^2	X^2-SiMe_3
1 ($X^1 = X^2 = Si$)[a]	2.372(2)	2.405(5)	
2 ($X^1 = X^2 = Ge$)	2.4062(6)	2.4787(7)	
3 ($X^1 = X^2 = Sn$)	2.5707(17)	2.7930(12)	
4 ($X^1 = Si$, $X^2 = Ge$)	2.3922(7)*	2.4256(9)	2.3922(7)
5 ($X^1 = Si$, $X^2 = Sn$)	2.421(6)	2.614(2)	2.519(2)
6 ($X^1 = Ge$, $X^2 = Sn$)	2.496(9)	2.5887(7)	2.522(14)

[a] Data taken from ref 9b.

Table 4. Selected Bond Lengths of Compounds of Types $(Me_3Si)_3X^1X^2(^iPr)_3$ and $(Me_3Si)_2X^1[Si(^iPr)_3]_2$ [Å]

compound	Me_3Si-X^1	$X_1-X^2(^iPr)_3$
7 ($X^1 = X^2 = Si$)[a]	2.3668(12)	
8 ($X^1 = Ge$, $X^2 = Si$)	2.4032(10)	2.4261(15)
9 ($X^1 = Sn$, $X^2 = Si$)	2.5799(6)	2.5868(11)
10 ($X^1 = Si$, $X^2 = Sn$)	2.360(2)	2.573(4)
11 ($X^1 = Ge$, $X^2 = Sn$)	2.3864(7)	2.6109(6)
12 ($X^1 = Si$)[a]	2.3948(17)	2.4228(13)
	2.4015(14)	2.4402(13)
14 ($X^1 = Sn$)	2.611(2)	2.6416(19)

[a] Data taken from ref 19.

14. The steric strain of the two Si^iPr_3 groups in **14** increases the bond angle of $Si^iPr_3-Sn-Si^iPr_3$ to 116.8° (compared to 115.8° for Si^iPr_3-Si- Si^iPr_3 in **12**) and reduces the $Me_3Si-Sn-SiMe_3$ angle to 101.2° (compared to 101.8° for $Me_3Si-Si-SiMe_3$ in **12**).

In the UV spectrum of **1** it was noted[8] that the absorption near 210 nm (Figure 11) is surprisingly low (Table 7) for a tetrasilane compared to the position for λ_{max} of 235 nm for decamethyltetrasilane.[23] An explanation for this blue shift would be both the conformational constraint and also the silyl substituents. The UV spectra of **2** and **3** (Figure 11) are very similar to **1** but display a larger degree of absorption. This indicates that conjugation between the trimethylsilyl groups and the two heteroatoms seems to be comparable to the trisilane unit in **1**. Finally the UV spectrum of **6** displays two maxima at 207 and 214 nm of similar absorption. This reflects the different absorbing structural units: Si−Ge−Sn and Si−Sn−Ge.

Conclusion

The investigation of a number of compounds of the type $(Me_3Si)_3X^1X^2(SiMe_3)_3$ revealed some interesting conformational behavior. As was already pointed out for hexakis(trimethylsilyl)disilane (**1**), the attachment of sterically demanding ligands on a disilane causes an elongation of the central silicon−silicon bond and in addition a twist to avoid the staggered conformation and to adopt a conformation with approximate dihedral angles of 77/43°. This orientation was found also for $^tBu_3SiSi^tBu_3$[24] and seems to minimize steric interaction of the bulky ligands, which are as close as 3.51 Å in **1**. The situation is very similar for compounds **2**, **4**, and **5**. X^1-X^2 bonds are elongated, and the 77/43° conformation is adopted. Methyl groups on different trimethylsilyl groups approach each other to distances of 3.61 Å (**2**), 3.57 Å (**4**), and 3.66 Å (**5**). The tin-containing compounds **3** and **6**, however, show a different pattern. The conformation switches back to a staggered one with dihedral angles of approximately 60°. There is also no more elongation of the central bond. The closest nonbonding distances between methyl groups on different trimethylsilyl groups are still in the same range as observed for the other compounds (3.46 Å (**3**), 3.51 Å (**6**)). This indicates that **3** and **6** can achieve the same degree of intramolecular interaction between the substituents on the central atoms even in a staggered conformation. The increased covalent radius of tin causes longer bond lengths and therefore seems to be responsible for this behavior. If the staggered conformation is engaged, the central bond is no longer elongated. This leads to the strange situation that the Sn−Ge bond in **6** (2.59 Å) is

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Table 5. Crystallographic Data for Compounds 2, 3, 4, 5, and 6

	2	**3**	**4**	**5**	**6**
empirical formula	$Ge_2Si_6C_{18}H_{54}$	$Sn_2Si_6C_{18}H_{54}$	$GeSi_7C_{18}H_{54}$	$SnSi_7C_{18}H_{54}$	$SnGeSi_6C_{18}H_{54}$
M_w	584.33	676.53	539.83	585.93	621.36
temperature [K]	253(2)	253(2)	294(2)	233(2)	233(2)
size [mm]	0.38 × 0.28 × 0.20	0.38 × 0.26 × 0.20	0.44 × 0.36 × 0.18	0.42 × 0.30 × 0.18	0.46 × 0.32 × 0.22
cryst syst	rhombohedral	rhombohedral	rhombohedral	rhombohedral	rhombohedral
space group	*R*-3*c*	*R*32	*R*-3*c*	*R*-3*c*	*R*3
a [Å]	16.176(2)	16.290(2)	16.149(2)	16.222(2)	16.257(2)
b [Å]	16.176(2)	16.290(2)	16.149(2)	16.222(2)	16.257(2)
c [Å]	22.921(5)	11.578(2)	22.881(5)	23.099(5)	11.580(2)
α [deg]	90	90	90	90	90
β [deg]	90	90	90	90	90
γ [deg]	120	120	120	120	120
V [Å^3]	5194(2)	2660(7)	5168(2)	5264(2)	2650(7)
Z	6	3	6	6	3
ρ_{calc} [g cm^{-3}]	1.121	1.267	1.041	1.109	1.168
absorp coeff [mm^{-1}]	1.948	1.615	1.137	0.971	1.764
F(000)	1860	1038	1752	1860	957
θ range	$2.30 < \theta < 26.37$	$2.28 < \theta < 26.33$	$2.30 < \theta < 26.36$	$2.28 < \theta < 26.35$	$2.28 < \theta < 26.34$
no. of reflns collected/ unique	16 024/1183	9370/1218	12 850/1180	17 594/1201	9465/2419
completeness to *θ* [%]	99.7	99.7	100	99.9	99.9
no. of data/restraints/ params	1183/0/43	1218/0/44	1180/0/44	1201/0/42	2419/1/154
goodness of fit on F^2	0.90	1.17	1.13	1.11	1.03
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.022, wR2 = 0.054	R1 = 0.035, wR2 = 0.093	R1 = 0.032, wR2 = 0.085	R1 = 0.033, wR2 = 0.101	R1 = 0.027, *w*R2 = 0.057
R indices (all data)	R1 = 0.034, wR2 = 0.056	R1 = 0.036, wR2 = 0.094	R1 = 0.037, wR2 = 0.088	R1 = 0.040, wR2 = 0.104	R1=0.035, *w*R2=0.059
largest diff peak/hole [e$^-$/Å^3]	0.25/−0.18	0.92/−0.62	0.32/−0.14	0.53/−0.27	0.70/−0.17

Table 6. Crystallographic Data for Compounds 8, 9, 10, 11, and 14

	8	**9**	**10**	**11**	**14**
empirical formula	$GeSi_4C_{18}H_{48}$	$SnSi_4C_{18}H_{48}$	$SnSi_4C_{18}H_{48}$	$SnGeSi_3C_{18}H_{48}$	$SnSi_4C_{24}H_{60}$
M_w	449.51	495.61	495.61	540.11	579.77
temperature [K]	293(2)	100(2)	100(2)	100(2)	293(2)
size [mm]	0.38 × 0.27 × 0.18	0.38 × 0.28 × 0.18	0.44 × 0.28 × 0.20	0.36 × 0.30 × 0.20	0.40 × 0.20 × 0.20
cryst syst	rhombohedral	rhombohedral	rhombohedral	rhombohedral	monoclinic
space group	*R*3	*R*3	*R*3	*R*3	*C*2/*c*
a [Å]	14.714(2)	14.617(2)	14.663(4)	14.701(2)	20.353(4)
b [Å]	14.714 (2)	14.617(2)	14.663(4)	14.701(2)	9.826(2)
c [Å]	10.906(2)	11.024(2)	10.990(7)	11.021(2)	18.581(4)
α [deg]	90	90	90	90	90
β [deg]	90	90	90	90	113.82(3)
γ [deg]	120	120	120	120	90
V [Å ^{3}]	2044.9(6)	2039.8(6)	2046.3(2)	2062.7(6)	3399.2(12)
Z	3	3	3	3	4
ρ_{calc} [g cm^{-3}]	1.095	1.210	1.207	1.304	1.133
absorp coeff [mm^{-1}]	1.299	1.116	1.112	2.132	0.902
F(000)	732	786	786	840	1240
θ range	$2.46 < \theta < 26.37$	$2.45 < \theta < 24.99$	$2.45 < \theta < 26.41$	$2.44 < \theta < 26.33$	$2.19 < \theta < 25.00$
no. of reflns collected/unique	5301/1849	4749/1588	4156/1736	5462/1867	11 600/2999
completeness to *θ* [%]	99.8	100	96.3	99.9	99.8
no. of data/restraints/params	1849/1/76	1588/1/76	1736/1/76	1867/1/76	2999/0/144
goodness of fit on F^2	1.02	1.04	1.05	0.89	1.05
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.034, wR2 = 0.077	R1 = 0.016, wR2 = 0.037	R1 = 0.049, wR2 = 0.111	R1 = 0.015, wR2 = 0.037	R1 = 0.061, wR2 = 0.160
largest diff peak/hole [e$^-$/Å^3]	0.48/−0.21	0.51/−0.23	1.61/−0.76	0.66/−0.35	0.80/−0.59

Table 7. UV Absorption Data for Compounds 1, 2, 3, and 6 in Pentane at Room Temperature

compound	λ_1 [nm]	ϵ_1 [M^{-1} cm^{-1}]	λ_2 [nm]	ϵ_2 [M^{-1} cm^{-1}]
Si−Si (**1**)	211	7.4×10^4		
Ge−Ge (**2**)	209	7.8×10^4		
Sn−Sn (**3**)	209	9.5×10^4		
Ge−Sn (**6**)	207	4.5×10^4	214	4.4×10^4

shorter than the Sn−Si bond in **5** (2.61 Å) (Table 3). However, some bond elongation is also found for the staggered molecules **3** (Si−Sn bond length: 2.57 Å) and **6** (Si−Ge bond length: 2.49 Å).

In general alkylsilylated main group compounds are fairly nonpolar and can be considered to resemble alkanes to some degree as the surface is peralkylated. Investigations on the crystal structures of alkanes have shown that intermolecular distances between terminal carbon atoms are around 3.60 Å.[25] Therefore, this behavior that methyl groups approach each other to distances closer than the sum of the methyl van der Waals radii[26] should not be considered to be unusual at all. The spherical shape of the investigated compounds and the ease of structural reorganization are responsible for the frequent occurrence of methyl groups

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approaching each other closely. In addition intermolecular distances in the crystals are also frequently less than 4 Å.

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. All solvents besides $CDCl_3$ were dried over sodium/potassium alloy under nitrogen and were freshly distilled prior to use. Potassium *tert*-butyl alcoholate was purchased from Merck. All other chemical were bought from different suppliers and were used without further purification.

^{1}H (300 MHz), ^{13}C (75.4 MHz), ^{119}Sn (111.8 MHz), and ^{29}Si (59.3 MHz) NMR spectra were recorded on a Varian INOVA 300 spectrometer. Samples for ^{29}Si spectra were either dissolved in a deuterated solvent or measured with a D_2O capillary in order to provide an external lock frequency signal. To compensate for the low isotopic abundance of ^{29}Si, the INEPT pulse sequence was used for the amplification of the signal.[27] Elementary analysis was carried out using a Heraeus Vario Elementar.

Tetrakis(trimethylsilyl)germane,[11] **2**,[28,29] **3**,[28,30] **4**,[29] **5**,[30] **6**,[30] **9**,[30] and **14**[30] have been prepared according to literature procedures.

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 Kα radiation (0.71073 Å). The data were reduced to F_o^2 and corrected for absorption effects with SAINT[31] and SADABS[32] (except **3**), respectively. The structures were solved by direct methods and refined by the full-matrix least-squares method (SHELXL97).[33] If not noted otherwise 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. All diagrams were drawn with 30% probability thermal ellipsoids, and all hydrogen atoms were omitted for clarity.

In compounds **4** and **6** the central Sn, Ge, and Si atoms are sharing the same site and were treated with PART instructions. The *xyz* and U_{ij} parameters were equated using EXYZ and EADP. The values for the free variables were set using the FVAR instruction and were set free to refine. The obtained factors show Ge:Si and Ge:Sn occupancies for both compounds of 50:50.

Crystallographic data (excluding structure factors) for the structures of compounds **2**, **3**, **4**, **5**, **6**, **8**, **9**, **10**, **11**, and **14** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-273402 (**2**), 273403 (**3**), 273400 (**4**), 273401 (**5**), 173396 (**6**), 273399 (**8**), 273397 (**9**), 273404 (**10**), 273405 (**11**), and 273398 (**14**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (internat.) +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk].

Tris(trimethylsilyl)triisopropylsilylgermane (8). To a solution of tetrakis(trimethylsilyl)germane (400 mg, 1.1 mmol) in benzene were added potassium *tert*-butoxide (124 mg, 1.1 mmol) and 18-crown-6 (290 mg, 1.1 mmol). After stirring for 30 min the solution was added dropwise to a solution of chlorotriisopropylsilane (211 mg, 1.1 mmol) in benzene. After stirring for 5 h the reaction was poured into aqueous sulfuric acid (1 M) and extracted several times with diethyl ether. The combined organic layers were dried over Na_2SO_4, and the solvent was removed in vacuo. The residue was recrystallized from ether/acetone (1:1), and white crystals (mp: 272−276 °C.) were obtained (404 mg, 82%). ^{29}Si NMR (C_6D_6, δ ppm): 20.3; −5.7. ^{13}C NMR (C_6D_6, δ ppm): 20.3; 15.1; 4.6. ^{1}H NMR (C_6D_6, δ ppm): 1.23 (m, 3H); 1.15 (vd, 18H); 0.42 (s, 27H). Anal. Calcd for $C_{18}H_{48}Si_4Ge$ (449.53): C 48.09, H 10.76. Found: C 48.04, H 10.81.

Triisopropyl[tris(trimethylsilyl)silyl]stannane (10). Preparation of **10** was carried out similarly to the procedure for the synthesis of **8** starting from tetrakis(trimethylsilyl)-silane (500 mg, 1.56 mmol). After addition of chlorotriisopropylstannane[34] (442 mg, 1.56 mmol) the reaction was complete within 2 h, yielding **10** (627 mg, 81%) as a light yellow solid (mp: 272−276 °C). ^{119}Sn (C_6D_6, δ ppm): −42.7. ^{29}Si NMR (C_6D_6, δ ppm): −8.6; −138.6. ^{13}C NMR (C_6D_6, δ ppm): 23.4; 16.5; 3.8. ^{1}H NMR (C_6D_6, δ ppm): 1.61 (m, 3H); 1.41 (vd, 18H); 0.33 (s, 27H). Anal. Calcd for $C_{18}H_{48}Si_4Sn$ (495.63): C 43.62, H 9.76. Found: C 43.58, H 9.78.

Triisopropyl[tris(trimethylsilyl)germyl]stannane (11). Preparation of **11** was carried out analogously to the procedure for the synthesis of **10** starting from tetrakis(trimethylsilyl)-germane (500 mg, 1.37 mmol). After addition of chlorotriisopropylstannane[34] (388 mg, 1.37 mmol) the reaction was complete within 1 h, yielding **11** (614 mg, 83%) as a light yellow solid. ^{119}Sn NMR (C_6D_6, δ ppm): −25.3. ^{29}Si NMR (C_6D_6, δ ppm): −4.0. ^{13}C NMR (C_6D_6, δ ppm): 23.4; 16.7; 4.4. ^{1}H NMR (C_6D_6, δ ppm): 1.57 (m, 3H); 1.38 (vd, 18H); 0.33 (s, 27H). Anal. Calcd for $C_{18}H_{48}Si_3GeSn$ (540.18): C 40.02, H 8.96. Found: C 39.98, H 9.00.

Bis(trimethylsilyl)bis(triisopropylsilyl)germane (13). Preparation of the potassium compound was analogous to the procedure for the synthesis of **8** starting with 0.47 mmol of **8**. After 3 h the solution was added dropwise to a cooled toluene solution (−70 °C) of chlorotris(isopropyl)silane (0.47 mmol). The reaction mixture was stirred for another 5 h at rt, and the aqueous workup was done according to the procedure for **8**. White semicrystalline material was obtained in 67% yield. ^{29}Si NMR (C_6D_6, δ ppm): 20.22; −5.77. ^{13}C NMR (C_6D_6, δ ppm): 20.3; 15.0; 4.6. ^{1}H NMR (C_6D_6, δ ppm): 1.42 (m, 6H); 1.16 (pd, 36H); 0.34 (s, 18H). Anal. Calcd for $GeSi_4C_{24}H_{60}$: C, 54.01; H, 11.33. Found: C, 53.62; H, 11.02.

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

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