New Cyclic and Acyclic Silicon–Germanium and Silicon–Germanium–Tin Derivatives

S. P. Mallela and R. A. Geanangel*

Department of Chemistry, University of Houston, Houston, Texas 77204-5641

Received September 14, 1993[⊛]

New Si–Ge and Si–Ge–Sn compounds bearing the bulky groups $-E(SiMe_3)_3$ (E = Si, Ge) were obtained by treatment of MCl_4 (M = Ge, Sn) with either $(THF)_3LiSi(SiMe_3)_3$ or $(THF)_{2.5}LiGe(SiMe_3)_3$. The cyclic tetragermane $[(Me_3Si)_3SiGeCl]_4{\cdot}C_6H_6$ crystallizes in the monoclinic space group *C*2/*c* with $a = 21.835(7)$ Å, $b = 26.342(9)$ Å, $c = 14.464(4)$ Å, $\beta = 103.45°$, $V = 8092$ Å^3, and $Z = 4$. The Ge_4 ring was nonplanar with an average torsion angle of 17.2°. The tetragermane $[(Me_3Si)_3GeGeCl_2]_2$ was characterized by elemental analyses and NMR spectra, which were consistent with a linear tetragermane backbone for the molecule. Dichlorobis(tris(trimethylsilyl)germyl)tin(IV), $((Me_3Si)_3Ge)_2SnCl_2$, crystallizes in the monoclinic space group *C*2/*c* with $a = 16.106(4)$ Å, $b = 10.034(2)$ Å, $c = 47.375(11)$ Å, $\beta = 90.02°$, $V = 7656$ Å^3, and $Z = 8$. The coordination geometry around tin is extremely distorted with Ge–Sn–Ge = 142.1° and Cl–Sn–Cl = 98.8°. The three compounds were stable in air except $((Me_3Si)_3Ge)_2SnCl_2$ was mildly hygroscopic. Reactions of the compounds with Li, $LiAlH_4$, and $(THF)_{2.5}LiGe(SiMe_3)_3$ were carried out, but no new products were identified. Treatment of $LaCl_3$ with 3 equiv of $(THF)_3LiSi(SiMe_3)_3$ afforded $(THF)La(Si(SiMe_3)_3)_2Cl$ as a very hygroscopic white solid. All attempts to substitute more than two $-Si(SiMe_3)_3$ groups on a central atom were unsuccessful.

Introduction

Recent reviews regarding the influence of bulky silyl substituents on the structure and reactivity of main group compounds recognized the importance of such groups in stabilizing labile structures.[1] Structural evidence was presented that groups such as "trisyl" ($-C(SiMe_3)_3$) have enough flexibility to help reduce steric strain in very crowded molecules but that, beyond a certain point, steric strain can destabilize a structure such as that of the diphosphine $((Me_3Si)_2CH)_2P{-}P(CH(SiMe_3)_2)_2$, which dissociates into phosphinyl free radicals in solution and in the gas phase.[2] We have suggested the use of cone angles to compare the steric demands of $-M(EMe_3)_3$ (M and E are group 14 elements) substituents.[3] The large cone angle of the trisyl group apparently inhibits the synthesis of bis(trisyl)silicon(IV) derivatives,[4] and the extreme distortion of the tetrahedral geometry around tin in $((Me_3Si)_3Si)_2SnCl_2$[5] testifies to the bulkiness of the $-Si(SiMe_3)_3$ substituent. Our attempts to prepare $((Me_3Si)_3Si)_2GeCl_2$ yielded instead a digermane with only one $-Si(SiMe_3)_3$ group on each Ge.[6] Further studies of the reaction between $GeCl_4$ and 2 equiv of $(THF)_3LiSi(SiMe_3)_3$ showed it to be more complex than originally supposed. In order to better understand the effect of the size of the entering substituent in such reactions, we have prepared new group 14 derivatives bearing the $-Ge(SiMe_3)_3$ substituent. Since the greater radius of Ge should cause a decreased cone angle in $M{-}Ge(SiMe_3)_3$ structures compared to their silicon counterparts described above, it was of interest to determine what effect that group has on the structure and stability of such molecules.

Experimental Section

Except as noted below, all manipulations were conducted under argon as described previously.[5] Diethyl ether and tetrahydrofuran (THF) were distilled from $LiAlH_4$ under dry nitrogen. Pentane and hexane were distilled off sodium just before use. Benzene was distilled from CaH_2. Germanium tetrachloride was supplied by Strem Products, and tin tetrachloride, by Aldrich. The lithium silyl, $(THF)_3LiSi(SIMe_3)_3$, and germyl, $(THF)_{2.5}LiGe(SiMe)_3$, reagents were prepared using literature procedures[7,8] with the modification of using low-halide (chloride) methyllithium obtained from Aldrich. Elemental analyses were performed by Atlantic Microlabs. NMR, IR, and UV–visible spectra were recorded as described earlier.[6,9]

Syntheses. 1,2,3,4-Tetrachloro-1,2,3,4-tetrakis(tris(trimethylsilyl)silyl)cyclotetragermane, $[(Me_3Si)_3SiGeCl]_4{\cdot}C_6H_6$ (I). To a hexane solution (200 mL) of $(THF)_3LiSi(SiMe)_3$ (13 080.6 mg, 27.77 mmol) held at −78 °C, $GeCl_4$ (2977.1 mg, 13.909 mmol) dissolved in 50 mL of hexane was added dropwise over a period of 1 h with vigorous stirring. Stirring was continued for 12 h at −78 °C, followed by slow warming to ambient temperature. After 36 h of additional stirring, hexane was removed *in vacuo*. The residue obtained was extracted with 2 × 30 mL portions of pentane. The combined filtrate (orange yellow) was concentrated to ~30 mL and cooled to −78 °C for 4 to 5 h, and the solution was cannulated, separating the precipitated solid. A minimum amount of pentane was added to this solid so as to just dissolve the entire precipitate. Upon standing for 2 h at room temperature, the pentane solution afforded bright yellow, transparent crystals that were isolated and washed with a minimal amount of pentane (935 mg, isolated yield 19.0%). On drying *in vacuo*, the crystals turned to a yellow powder.

Crystals suitable for an X-ray structure determination were obtained by redissolving the yellow powder in a small volume of benzene and holding the solution at room temperature overnight. Lemon yellow crystals were isolated, washed with benzene, and dried *in vacuo* for 2 to 3 h at room temperature. Mp: changed to red at 125 °C, melted at 150 °C. NMR (C_6D_6): ^1H, δ 0.533; ^{13}C, δ 4.89. UV–visible: λ_{max} 365 nm. IR (Nujol, cm^{-1}): 1470 sh, 1360 sh, 1320 w, 1261 vs, 1070 br, s, 860 vs, br, 780 w, 730 m, 660 s, 650 sh, 525 m, 510 sh, 380 w.

X-ray Structure Determination of I. A bright lemon yellow prismatic block having approximate dimensions 0.48 × 0.42 × 0.28 mm was mounted in a random orientation on a Nicolet R3m/V automated diffractometer. The radiation used was Mo Kα monochromatized by a highly ordered graphite crystal. Final cell constants, as well as other information pertinent to data collection and refinement, are listed in Table 1. The Laue

---

[⊛] Abstract published in *Advance ACS Abstracts*, February 15, 1994.

(1) (a) Rankin, D. W. H. *Frontiers in Organosilicon Chemistry* (Proc. 9th Int. Symp. Organosilicon Chem.); Royal Soc. Chem.: London, 1990; p 253. (b) Wiberg, N. *Frontiers in Organosilicon Chemistry* (Proc. 9th Int. Symp. Organosilicon Chem.); Royal Soc. Chem.: London, 1990; p 263.

(2) Wiberg, N.; Kühnel, E.; Schurz, K.; Borrmann, H. Simon, A. *Z. Naturforsch.* **1988**, *43b*, 1075.

(3) Aggarwal, M.; Ghuman, M. A.; Geanangel, R. A. *Main Group Met. Chem.* **1991**, *14*, 263.

(4) Dua, S. S.; Eaborn, C.; Happer, D. A. R.; Hopper, S. P.; Safa, K. D.; Walton, D. R. M. *J. Organomet. Chem.* **1979**, *178*, 75.

(5) Mallela, S. P.; Geanangel, R. A. *Inorg. Chem.* **1990**, *29*, 3525.

(6) Mallela, S. P.; Geanangel, R. A. *Inorg. Chem.* **1991**, *30*, 1480.

(7) Gutekunst, G.; Brook, A. G. *J. Organomet. Chem.* **1982**, *225*, 1.

(8) Brook, A. G.; Abdesaken, F.; Söllradl, H. *J. Organomet. Chem.* **1986**, *299*, 9.

(9) Mallela, S. P.; Geanangel, R. A. *Inorg. Chem.* **1993**, *32*, 602.

0020-1669/94/1333-1115$04.50/0

symmetry was determined to be $2/m$, and from the systematic absences noted, the space group was shown to be either $C2/c$ or Cc. Intensities were measured using the ω scan technique, with the scan rate depending on the count obtained in rapid prescans of each reflection. Two standard reflections were monitored after every 2 h or every 100 data collected, and these showed no significant change during the course of the experiment. During data reduction Lorentz and polarization corrections were applied; however, no correction for absorption was made due to equipment failure.

The structure was solved by use of the SHELXTL direct methods program, which revealed most of the atoms in the asymmetric unit, consisting of one-half molecule situated about a 2-fold axis which bisects two Ge–Ge bonds. Remaining non-hydrogen atoms were located in subsequent difference Fourier syntheses. The usual sequence of isotropic and anisotropic refinement was followed, after which all hydrogen atoms were entered in ideal calculated positions and constrained to riding motion, with a single variable isotropic temperature factor for all of them. A molecule of benzene solvent was also located, which is disordered about a 2-fold axis. This molecule was refined as a rigid body and gave a reasonable overall isotropic temperature factor when the population factor was fixed at 40% (indicating 80% occupancy at the disordered site). For all calculations in Table 1 an occupancy of 100% was used, under the assumption that there are one or more minor orientations of the solvent which were not located. After all shift/esd ratios were less than 0.1, convergence was reached at the agreement factors listed in Table 1. No unusually high correlations were noted between any of the variables in the last cycle of full-matrix least-squares refinement, and the final difference density map showed a maximum peak of about 0.6 e/Å^3. All calculations were made using Nicolet's SHELXTL PLUS (1987) series of crystallographic programs.

Another reaction of $(THF)_3LiSi(SiMe)_3$ (13 186.8 mg, 28.00 mmol) in 200 mL of hexane with $GeCl_4$ (3000 mg, 13.99 mmol) in 50 mL of hexane at −78 °C for 10 h and then at room temperature for 10 days yielded copious amounts of $Si(SiMe_3)_4$ and $HSi(SiMe_3)_3$ and a small amount of I but no new polygermane oligomers.

2,2,3,3-Tetrachloro-1,1,1,4,4,4-hexakis(trimethylsilyl)tetragermane, $[(Me_3Si)_3GeGeCl_2]_2$ (II). Germanium tetrachloride (1277.4 mg, 5.968 mmol), dissolved in 50 mL of hexane, was cooled to −78 °C, and a hexane solution (200 mL) of $(THF)_{2.5}LiGe(SiMe_3)_3$ (5712.9 mg, 11.916 mmol) was added dropwise with vigorous agitation. A light yellow color developed after the addition was complete (2.5 h). The reaction mixture was stirred for 7 h at −78 °C and then allowed to warm to ambient temperature and stirred for another 46 h. After hexane was removed *in vacuo*, the residue was stirred with 50 mL of pentane. Upon concentration to ∼25 mL and standing at ambient temperature for 3 h, the yellow filtrate afforded transparent, colorless crystals of II, which were washed three times with mininal amounts of pentane and dried *in vacuo* (2203.7 mg, isolated yields 85%). Mp: 215 °C (dec; melts at 235 °C). Anal. Calcd for $C_{18}H_{54}Cl_4Ge_4Si_6$: C, 24.81; H, 6.25. Found: C, 24.82; H, 6.25. NMR (C_6D_6): ^1H, δ 0.448; ^{13}C, δ 3.129. IR (neat and Nujol, cm^{-1}): 3000 vw, 2940 vw, 1420 sh, 1340 w, 1265 vs, 1020 vw, 1070 sh, 1005 w, 860 vs br, 790 w, 785 sh, 740 sh, 740 s, 665 s, 665 sh, 465 w, 405 s, 395 sh.

Dichlorobis(tris(trimethylsilyl)germyl)tin(IV), $[(Me_3Si)_3Ge]_2SnCl_2$ (III). Hexane solutions of $SnCl_4$ (678.4 mg, 2.603 mmol) and $(THF)_{2.5}LiGe(SiMe_3)_3$ (2497 mg, 5.208 mmol) were combined as described above for II. Workup afforded 1645.3 mg (isolated yield 82%) of III as colorless, transparent crystals. Mp: begins to decompose at 176 °C; melts to black liquid at 185 °C. Anal. Calcd for $C_{18}H_{54}Cl_2Ge_2Si_6Sn$: C, 27.93, H, 7.03. Found: C, 28.08; H, 7.05. NMR (C_6D_6): ^1H, δ 0.446; ^{13}C, δ 3.95. IR (neat and Nujol, cm^{-1}): 3002, sh, 2942 w, 1422 sh, 1342 w, 1262 vs, 1152 sh, 862 vs, br, 802 sh, 786 w, 735 m, 667 s, 557 sh, 397 m.

X-ray Structure Determination of III. A clear colorless block having approximate dimensions 0.50 × 0.35 × 0.30 mm was mounted in a random orientation on the same diffractometer. Final cell constants, as well as other information pertinent to data collection and refinement, are listed in Table 4. Although all three angles are 90°, on the basis of the analysis of equivalent reflections, the Laue symmetry was determined to be $2/m$, and from the systematic absences noted, the space group was shown to be either Cc or $C2/c$. Intensities were measured as described for I. Two standard reflections were monitored after every 2 h or every 100 data collected, and these showed a 35% decay over the 6 days of the experiment. A normalizing factor as a function of X-ray exposure time was applied to account for this. Upon visual examination, large portions of the sample surface were seen to have turned milky white, as if the material was mildly hygroscopic. During data reduction Lorentz and polarization corrections were applied, as well as an empirical absorption correction based on ψ scans of 10 reflections having χ values between 70 and 90°. The very long c axis caused a certain amount of interference between neighboring peaks at low angles. Therefore, the data had to be carefully scrutinized for signs of peak overlap, and any affected reflections discarded due to mismeasurement. Approximately 2% of the data had to be eliminated on this basis. Since the unitary structure factors displayed centric statistics, space group $C2/c$ was assumed from the outset. The structure was solved by use of the Patterson technique, which revealed the position of the Sn atom. Remaining non-hydrogen atoms were located in subsequent difference Fourier syntheses. The usual sequence of isotropic and anisotropic refinement was followed, after which all hydrogens were entered in ideal calculated positions and constrained to riding motion, as described for I. After all shift/esd ratios were less than 0.1, convergence was reached at the agreement factors listed in Table 4. No unusually high correlations were noted between any of the variables in the last cycle of full-matrix least-squares refinement, and the final difference density map showed a maximum peak of about 0.5 e/Å^3.

Attempt to Prepare 1,2,3,4-Tetrachloro-1,2,3,4-tetrakis(tris(trimethylsilyl)germyl)cycloteragermane, $[(Me_3Si)_3GeGeCl]_4$. To a cold (−78 °C) hexane solution of $(THF)_{2.5}LiGe(SiMe_3)_3$ (3882.3 mg, 8.1 mmol) was added a hexane solution of $GeCl_4$ (866.6 mg, 4.05 mmol) using the procedure described for I. After workup, the products consisted of a mixture of crystals of II (major), and the NMR spectrum of the solution exhibited signals for $(Me_3Si)_4Ge$ (major), $(Me_3Si)_3GeH$ (minor), and $(Me_3Si)_3GeGe(SiMe_3)_3$ (δ 0.393, minor) along with unidentified minor signals at δ 0.497 and 0.551 in C_6D_6. No evidence for the germyl-substituted cyclotetragermane was found.

Attempt To Further Substitute II. Combination of a hexane (50 mL) solution of II (486.3 mg, 0.558 mmol) with $(THF)_{2.5}LiGe(SiMe_3)_3$ (535.2 mg, 1.11 mmol) in hexane (50 mL) at −78 °C followed by the usual workup resulted only in recovery of unreacted II along with some $(Me_3Si)_4Ge$, identified by its ^1H NMR signal.

Reaction of II with Lithium and $LiAlH_4$. To an ether (30 mL) suspension of Li powder (38.0 mg, 5.47 g atom) at ambient temperature was added a solution of II (384.2 mg, 0.441 mmol) in ether (30 mL). After the mixture was stirred for 48 h, workup in pentane resulted in recovery of II along with $(Me_3Si)_3GeGe(SiMe_3)_3$ and an unidentified minor product with ^1H at δ 0.738. In a similar reaction of II with $LiAlH_4$, after 5 days at room temperature and hydrolysis with 10% HCl(aq), and ether extract contained unreacted II, $(Me_3Si)_4Ge$ (major), $(Me_3Si)_3GeH$ (minor), and $(Me_3Si)_3GeGe(SiMe_3)_3$ (major) along with several unidentified products with ^1H resonances at δ 0.268 (major), 0.162, 0.177, 0.197, 0.301, and 0.340 (minor).

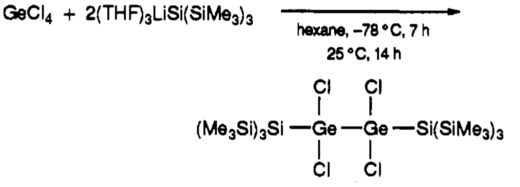
Reaction of $(THF)_3LiSi(SiMe_3)_3$ with $LaCl_3$. To an ether (50 mL) suspension of $LaCl_3$ (1042.7 mg, 4.25 mmol) held at −78 °C was added dropwise an ether solution (200 mL) of $(THF)_3LiSi(SiMe_3)_3$ (6007.5 mg, 12.75 mmol), and stirring was continued 8 h at −78 °C and then 84 h at room temperature. After removal of ether, the residue was stirred 1 h in pentane (100 mL) and filtered. The filtrate was concentrated and held at 4 °C producing 3095.2 mg (98%) of an hygroscopic, white solid, believed to be $(THF)La[Si(SiMe_3)_3]_2Cl$, that was washed with a small volume of pentane and recrystallized from the same solvent (mp 128 °C). Anal. Calcd for $C_{22}H_{62}ClOSi_8La$: C, 35.64; H, 8.42. Found: 35.04; H, 9.47. NMR (C_6D_6): ^1H, δ 0.54 ($-Si(SiMe_3)_3$), 1.450 (mult., THF), 3.54 (mult., THF); ^{13}C, δ 6.994 ($-Si(SiMe_3)_3$), 25.5 (THF), 68.38 (THF).

Attempts To Introduce More Than Two $Si(SiMe_3)_3$ Groups on Tin(IV). A hexane solution of $SnCl_4$ was treated with 4 equiv of $(THF)_3LiSi(SiMe_3)_3$ at −78 °C. After workup, only $((Me_3Si)_3Si)_2SnCl_2$ (major), $Si(SiMe_3)_4$ (major), $HSi(SiMe_3)_3$ (minor), and $(Me_3Si)_3Si–Si(SiMe_3)_3$ were detected by their NMR spectra. Reaction of $Cl_2Sn[Si(SiMe_3)_3]_2$ with 2 equiv of $(THF)_3LiSi(SiMe_3)_3$ gave similar results.

Results and Discussion

Kinetic stabilization of low-coordinate central atoms usually requires bulky substituents to sterically crowd the coordination sphere of the central atom enough to prevent dimerization, disproportionation, solvolysis, etc. but not so much that attachment of the appropriate number of bulky groups during synthesis is inhibited. One approach to comparing the spacial requirements of substituents is the use of the cone angle generated by the group when attached to the central atom being considered. When $-E(SiMe_3)_3$ (E = C, Si) groups are attached to group 14 central atoms, cone angles approaching and, in some cases, exceeding 180° are generated.[3] Such large cone angles are probably the reason that efforts to introduce more than one

–C(SiMe$_3$)$_3$ substituent into a Si(IV) central atom failed[4] and that a similar conclusion was reached concerning –Si(SiMe$_3$)$_3$ groups.[10] We were successful in preparing the disubstituted Sn(IV) derivative, ((Me$_3$Si)$_3$Si)$_2$SnCl$_2$,[5] but the molecule exhibited extreme distortion from tetrahedral geometry about tin (∠Si–Sn–Si = 142.5°) and our efforts to prepare the analogous Ge(IV) derivative were unsuccessful. Structural characterization of the product initially isolated from that reaction revealed it to be a digermane (eq 1) with one –Si(SiMe$_3$)$_3$ and two chlorines per Ge, perhaps indicating that attachment of two of the bulky groups to the smaller Ge atom is sterically unfavorable.[6]



$$\mathrm{GeCl_4} + 2(\mathrm{THF})_3\mathrm{LiSi(SiMe_3)_3} \xrightarrow[\substack{\text{hexane, }-78\,^\circ\mathrm{C},\ 7\ \mathrm{h}\\ 25\,^\circ\mathrm{C},\ 14\ \mathrm{h}}]{} (\mathrm{Me_3Si})_3\mathrm{Si}-\underset{\mathrm{Cl}}{\overset{\mathrm{Cl}}{\mathrm{Ge}}}-\underset{\mathrm{Cl}}{\overset{\mathrm{Cl}}{\mathrm{Ge}}}-\mathrm{Si(SiMe_3)_3}\quad (49\%) \qquad (1)$$

The presence of unidentified ^{1}H NMR signals in the reaction mixture (eq 1) led us to investigate the system further. From a reaction stirred 36 h at room temperature, we were able to isolate a second product as a yellow powder which turned red at 125 °C and melted at 150 °C. Because of its utility in identifying the digermane noted above,[6] field desorption mass spectroscopy was again used for this product, exhibiting a parent ion isotopic envelope of m/z = 1415–1436, which may be compared to an envelope of m/z = 1411–1436 expected for a composition of $C_{36}H_{108}Cl_4Ge_4Si_{16}$. This composition corresponds to the cyclotetragermane, [(Me$_3$Si)$_3$Si(Cl)Ge]$_4$ (**I**). Fragment ion envelopes centered at m/z = 1142 (M$^+$ – (Me$_3$Si)$_3$Si – Cl), 1069 (M$^+$ – (Me$_3$Si)$_3$Si – (Me$_3$Si) – Cl) and 1032 (M$^+$ – (Me$_3$Si)$_3$Si – (Me$_3$Si) – 2Cl) were consistent with the progressive fragmentation of substituents from the Ge$_4$ core. The best yield obtained for **I** was 19%, but isolated yields varied widely depending on conditions. Although **I** was reasonably stable in the solid phase and was unaffected by atmospheric moisture, in benzene solution its NMR signal decayed markedly over 24 h and a turbid solution formed.

Because of the unexpected structure indicated for **I**, an X-ray structure determination was undertaken on crystals obtained by recrystallization from benzene. The molecular structure of **I** as a monobenzene solvate (Figure 1a) confirms the presence of a ring of four germanium atoms that is nonplanar with an average internal torsion angle of 17.2°. Crystallographic data, atomic positions, and selected bond lengths and angles are given in Tables 1–3, respectively. Each Ge bears one chlorine and one tris(trimethylsilyl)silyl group, and Si(SiMe$_3$)$_3$ groups on neighboring Ge atoms occupy positions on opposite sides of the ring plane. Those Si(SiMe$_3$)$_3$ groups on diagonally opposed Ge atoms are twisted differently minimizing steric strain (Figure 1b). The crowding around the ring is evident in the SiMe$_3$ group that is most nearly above the ring (Si8) by its enlarged Ge–Si–Si angle (116.5°). The Ge–Ge bond lengths (2.558 and 2.509 Å) are both significantly longer than that in the open chain tetragermane, Ge$_4$Ph$_{10}$·2C$_6$H$_6$ (2.46 Å)[11] and also longer than that in the digermane [(Me$_3$Si)$_3$SiGeCl$_2$]$_2$ (2.421(13) Å).[6] The mean Ge–Ge distances in **I** are exceeded only by those in hexakis(2,6-dimethylphenyl)cyclotrigermane,[12] among comparable structures. The average Ge–Si distance in **I** is 2.460(2) Å, which exceeds those in Me$_3$SiGePh$_3$ (2.384(1) Å),[13] Ph$_3$SiGeMe$_3$ (2.394(1) Å),[14] and even the very crowded (Me$_3$Si)$_3$SiGePh$_3$ (2.416(1) Å).[15] The average Si–Ge–Cl angle is 103.9°, a compression that probably also reflects the crowding present near the ring in **I**.

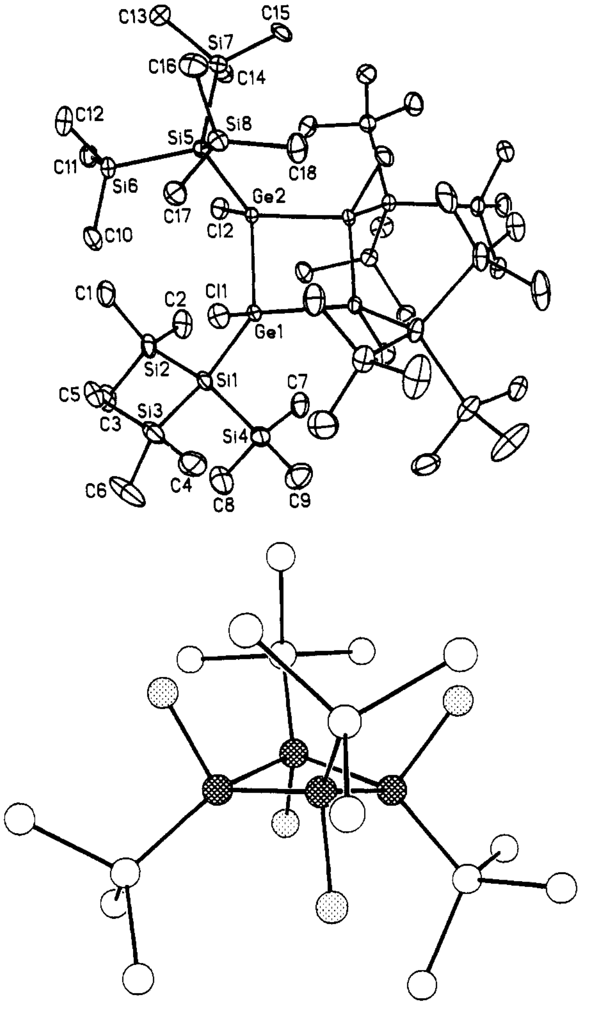


Figure 1. (a) Top: Molecular structure of **I**, showing the atom-numbering scheme. Hydrogen atoms are omitted for clarity. (b) Bottom: Skeleton of **I** with methyl groups omitted to show alternating positions of substituents.

Table 1. Crystallographic Data for [(CH$_3$)$_3$Si)$_3$SiGeCl]$_4$·C$_6$H$_6$ (I·C$_6$H$_6$)

$C_{36}H_{108}Si_{16}Cl_4Ge_4\cdot C_6H_6$	$C2/c$ (monoclinic)
fw = 1501.16	T = –60 °C
a = 21.835(7) Å	λ = 0.710 73 Å
b = 26.342(9) Å	ρ(calc) = 1.23 g·cm^{-3}
c = 14.464(4) Å	μ = 18.4 cm
β = 103.45(2)	$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\| = 0.037$
V = 8092 Å^3	$R_w = [\sum w^2(\|F_o\| - \|F_c\|)^2/\sum\|F_o\|^2]^{1/2} = 0.038$
Z = 4	

Several cyclotetragermanes, [R$_2$Ge]$_4$, are known including R = Me,[16] *i*-Pr,[17] Ph,[17,18] *p*-Tol,[19] and Me$_3$SiCH$_2$;[17] however, **I** is apparently the first example of an [R(X)Ge]$_4$ type and the only one incorporating a substituent as bulky as –Si(SiMe$_3$)$_3$. In prior syntheses involving reductive coupling of R$_2$GeX$_2$ species, the presence of bulky R groups has often led to formation of cyclotrigermanes such as [Mes$_2$Ge]$_3$ instead of cyclotetragermanes.[17] Given the conditions in the preparation of **I**, two pathways to the formation of the Ge$_4$ ring can be suggested. First, it could result from cyclopolymerization of an [(Me$_3$-

---

[10] Derouiche, Y.; Lickis, P. D. *J. Organomet. Chem.* **1991**, *407*, 41.

[11] Roller, S.; Simon, D.; Dräger, M. *J. Organomet. Chem.* **1986**, *301*, 27.

[12] Masamune, S.; Hanzawa, Y. *J. Am. Chem. Soc.* **1982**, *104*, 6136.

[13] Parkanyi, L.; Hernandez, C.; Pannel, K. H. *J. Organomet. Chem.* **1986**, *301*, 145.

[14] Pannel, K. H.; Kapoor, R. N.; Raptis, R.; Parkanyi, L.; Fulop, V. *J. Organomet. Chem.* **1991**, *384*, 1480.

[15] Mallela, S. P.; Ghuman, M. A.; Geanangel, R. A. *Inorg. Chim. Acta* **1992**, *202*, 211.

[16] Sakurai, H.; Sakamoto, K.; Kira, M. *Chem. Lett.* **1984**, 1379.

[17] Ando, W.; Tsumuraya, T. *J. Chem. Soc., Chem. Commun.* **1987**, 1514.

[18] Neumann, W. P.; Kuhlein, K. *Liebigs Ann. Chem.* **1965**, *683*, 1.

[19] Richter, M.; Neumann, W. P. *J. Organomet. Chem.* **1969**, *20*, 81.

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times$ 10^3) for I

	x	*y*	*z*	*U*(eq)[a]
Ge(1)	5478(1)	7301(1)	2130(1)	29(1)
Ge(2)	5554(1)	6360(1)	2396(1)	26(1)
Cl(1)	6259(1)	7561(1)	3307(1)	48(1)
Cl(2)	5500(1)	6009(1)	987(1)	43(1)
Si(1)	5650(1)	7766(1)	726(2)	37(1)
Si(2)	5998(1)	7253(1)	–407(2)	48(1)
Si(3)	6430(1)	8391(1)	1287(2)	56(1)
Si(4)	4733(1)	8196(1)	–100(2)	49(1)
Si(5)	6459(1)	5940(1)	3429(1)	29(1)
Si(6)	7341(1)	6060(1)	2767(2)	39(1)
Si(7)	6243(1)	5059(1)	3453(2)	36(1)
Si(8)	6752(1)	6229(1)	5022(2)	39(1)
C(1)	6667(4)	6827(3)	123(6)	61(4)
C(2)	5358(4)	6874(4)	–1147(5)	65(4)
C(3)	6304(4)	7694(4)	–1229(6)	79(5)
C(4)	6263(4)	8801(3)	2243(7)	82(5)
C(5)	7228(3)	8109(3)	1733(6)	59(4)
C(6)	6463(5)	8839(4)	283(7)	113(6)
C(7)	4054(3)	7777(3)	–577(6)	61(4)
C(8)	4885(4)	8513(4)	–1197(6)	95(5)
C(9)	4532(4)	8685(3)	692(7)	82(5)
C(10)	7466(4)	6748(3)	2588(6)	51(4)
C(12)	8057(3)	5828(3)	3642(6)	62(4)
C(11)	7273(4)	5693(3)	1642(6)	54(4)
C(13)	7010(3)	4699(3)	3804(6)	60(4)
C(14)	5821(4)	4821(3)	2268(5)	52(4)
C(15)	5782(3)	4919(3)	4376(5)	45(3)
C(16)	7224(4)	5717(3)	5758(5)	58(4)
C(17)	7267(3)	6805(3)	5181(5)	47(3)
C(18)	6033(4)	6350(3)	5485(6)	60(4)
C(19)	4648(12)	69(7)	799(11)	136(5)
C(20)	4188	76	1326	136(5)
C(21)	4365	96	2317	136(5)
C(22)	5001	109	2779	136(5)
C(23)	5461	103	2252	136(5)
C(24)	5284	83	1261	136(5)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

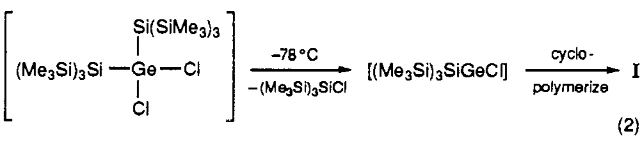
Table 3. Selected Bond Lengths (Å) and Angles (deg) for I

Ge(1)–Ge(2)	2.509(1)	Ge(1)–Cl(1)	2.218(2)
Ge(1)–Si(1)	2.474(2)	Ge(1)–Ge(1′)	2.558(2)
Ge(2)–Cl(2)	2.215(2)	Ge(2)–Si(5)	2.446(2)
Ge(2)–Ge(2′)	2.507(2)	Si(1)–Si(2)	2.381(3)
Si(1)–Si(3)	2.373(3)	Si(1)–Si(4)	2.367(3)
Si(5)–Si(7)	2.371(3)	Si(5)–Si(8)	2.368(3)
Si(5)–Si(6)	2.364(3)	Si–C(av)	1.869

Ge(2)–Ge(1)–Cl(1)	100.1(1)	Ge(2)–Ge(1)–Si(1)	126.7(1)
Cl(1)–Ge(1)–Si(1)	104.0(1)	Ge(2)–Ge(1)–Ge(1′)	88.1(1)
Cl(1)–Ge(1)–Ge(1′)	103.6(1)	Si(1)–Ge(1)–Ge(1′)	129.6(1)
Ge(1)–Ge(2)–Cl(2)	106.5(1)	Ge(1)–Ge(2)–Si(5)	123.7(1)
Cl(2)–Ge(2)–Si(5)	103.7(1)	Ge(1)–Ge(2)–Ge(2′)	89.3(1)
Cl(2)–Ge(2)–Ge(2′)	105.3(1)	Si(5)–Ge(2)–Ge(2′)	126.3(1)
Ge(1)–Si(1)–Si(2)	114.7(1)	Ge(1)–Si(1)–Si(3)	107.3(1)
Si(2)–Si(1)–Si(3)	108.1(1)	Ge(1)–Si(1)–Si(4)	112.3(1)
Si(2)–Si(1)–Si(4)	107.0(1)	Si(3)–Si(1)–Si(4)	107.2(1)
Si(1)–Si(2)–C(1)	113.9(3)	Si(1)–Si(2)–C(2)	112.7(3)
Si(1)–Si(2)–C(3)	107.4(3)	Si(1)–Si(3)–C(4)	114.1(3)
Si(1)–Si(3)–C(5)	112.3(3)	Si(1)–Si(3)–C(6)	108.9(3)
Si(1)–Si(4)–C(7)	114.4(3)	Si(1)–Si(4)–C(8)	110.0(3)
Si(1)–Si(4)–C(9)	108.5(3)	Ge(2)–Si(5)–Si(6)	108.1(1)
Ge(2)–Si(5)–Si(7)	108.4(1)	Si(6)–Si(5)–Si(7)	108.6(1)
Ge(2)–Si(5)–Si(8)	116.5(1)	Si(6)–Si(5)–Si(8)	106.9(1)
Si(7)–Si(5)–Si(8)	108.0(1)	C–Si–C(av)	108.0

Cl(1)–Ge(1)–Ge(2)–Cl(2)	–133.7	Ge(2)–Si(5)–Si(6)–C(12)	171.5
Cl(1)–Ge(1)–Ge(2)–Si(5)	–14.1	Ge(2)–Si(5)–Si(6)–Cl(1)	–69.7
Cl(1)–Ge(1)–Ge(2)–Ge(2′)	120.6	Si(7)–Si(5)–Si(6)–C(10)	172.7
Si(1)–Ge(1)–Ge(2)–Cl(2)	–17.7	Si(7)–Si(5)–Si(6)–C(12)	–71.0
Si(1)–Ge(1)–Ge(2)–Si(5)	102.0	Si(7)–Si(5)–Si(6)–Cl(1)	47.8
Si(1)–Ge(1)–Ge(2)–Ge(2′)	–123.4	Si(8)–Si(5)–Si(6)–C(10)	–71.0
Ge(1′)–Ge(1)–Ge(2)–Cl(2)	122.8	Si(8)–Si(5)–Si(6)–C(12)	45.3
Ge(1′)–Ge(1)–Ge(2)–Si(5)	–117.5	Si(8)–Si(5)–Si(6)–Cl(1)	164.1
Ge(1′)–Ge(1)–Ge(2)–Ge(2′)	17.1	Ge(2)–Si(5)–Si(7)–C(13)	157.3
Ge(2)–Ge(1)–Si(1)–Si(2)	–5.0	Ge(2)–Si(5)–Si(7)–C(14)	38.6
Ge(2)–Ge(1)–Si(1)–Si(3)	–125.1	Ge(2)–Si(5)–Si(7)–C(15)	–85.1
Ge(2)–Ge(1)–Si(1)–Si(4)	117.4	Si(6)–Si(5)–Si(7)–C(13)	40.0
Cl(1)–Ge(1)–Si(1)–Si(2)	109.3	Si(6)–Si(5)–Si(7)–C(14)	–78.7
Cl(1)–Ge(1)–Si(1)–Si(3)	–10.8	Si(6)–Si(5)–Si(7)–C(15)	157.6
Cl(1)–Ge(1)–Si(1)–Si(4)	–128.3	Si(8)–Si(5)–Si(7)–C(13)	–75.6
Ge(1′)–Ge(1)–Si(1)–Si(2)	–129.3	Ge(1′)–Ge(1)–Si(1)–Si(3)	110.6
Ge(1′)–Ge(1)–Si(1)–Si(4)	–7.0		

$Si)_3SiGeCl]$ intermediate in the same way as is believed to take place in the formation of cyclopolygermanes by reduction of R_2GeX_2 species.[17] Another plausible pathway to I involves the cyclization of two digermane molecules. Tests of this pathway were carried out by following the NMR spectra of $[(Me_3Si)_3SiGeCl_2]_2$ for extended periods in benzene or pentane and by treating the digermane with $(THF)_3LiSi(SiMe_3)_3$, as might happen in the reaction mixture. In the former test, no change was seen in the NMR spectrum of $[(Me_3Si)_3SiGeCl_2]_2$, and in the latter, no I was detected, suggesting that the second pathway is unlikely, thus favoring the first involving a Ge(II) intermediate. A plausible source of the $[(Me_3Si)_3SiGeCl]$ precursor is the elimination of $(Me_3Si)_3SiCl$ from the presumably unstable disubstituted monogermane intermediate (eq 2). Evidence which

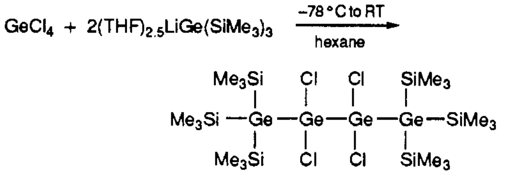


$$\left[(Me_3Si)_3Si\text{—}\overset{\displaystyle Si(SiMe_3)_3}{\underset{\displaystyle Cl}{Ge}}\text{—}Cl\right] \xrightarrow[-(Me_3Si)_3SiCl]{-78\,°C} [(Me_3Si)_3SiGeCl] \xrightarrow[\text{polymerize}]{\text{cyclo-}} \mathbf{I} \qquad (2)$$

supports this scenario is the presence of an ^1H NMR signal at δ 0.225 in spectra of the reaction mixture that does not match those of any of the usual side products of such reactions but does resemble that reported for $(Me_3Si)_3SiCl$ (δ 0.24 in $CDCl_3$[20]).

Since several cyclotrigermanes are known[17] and at least one has been structurally characterized,[12] the absence of any cyclotrigermane product at first seems inconsistent with this pathway, since its formation might be expected to precede that of the tetrameric cyclooligomer.[17] However, the three-membered ring would require neighboring $Si(SiMe_3)_3$ groups to be on the same side of the ring, which is not seen in the structure of **I**, and this steric conflict would probably inhibit cyclization at the cyclotrigermane stage or cause that oligomer to decompose, if formed.

The availability of the lithium germyl reagent $(THF)_{2.5}LiGe(SiMe_3)_3$ permitted us to compare the steric influence of the $Ge(SiMe_3)_3$ group to that of its silyl counterpart. Since the radius of Ge is larger than that of Si (1.223 Å *vs* 1.176 Å[21]), the cone angle generated by $Ge(SiMe_3)_3$ should be somewhat less than that of $Si(SiMe_3)_3$ for a given central atom.[3] We carried out the reaction of 2 equiv of the lithium germyl with $GeCl_4$ under the conditions used for the lithium silyl[6] to determine whether the smaller steric demands of $Ge(SiMe_3)_3$ would permit disubstitution on germanium. The air-stable product was identified by elemental analyses and ^1H and ^{13}C NMR spectra as the tetragermane, $(Me_3Si)_3GeGeCl_2GeCl_2Ge(SiMe_3)_3$ (**II**) (eq 3), the germanium



$$GeCl_4 + 2(THF)_{2.5}LiGe(SiMe_3)_3 \xrightarrow[\text{hexane}]{-78\,°C\text{ to RT}} Me_3Si\text{—}\overset{\displaystyle Me_3Si}{\underset{\displaystyle Me_3Si}{Ge}}\text{—}\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{Ge}}\text{—}\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{Ge}}\text{—}\overset{\displaystyle SiMe_3}{\underset{\displaystyle SiMe_3}{Ge}}\text{—}SiMe_3 \quad (85\%) \qquad (3)$$

analogue of $[(Me_3Si)_3siGeCl_2]_2$.[6] Although we were not able to carry out a structure determination on **II**, close parallels between its melting point (235 *vs* 195 °C), ^1H NMR (s, δ 0.448, *vs* s, δ 0.420) and ^{13}C NMR (s, δ 3.129, *vs* s, δ 2.61) and those of $[(Me_3$-

---

(20) Bock, H.; Meuret, J.; Ruppert, K. *J. Organomet. Chem.* **1993**, *445*, 19.

(21) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon: Oxford, Great Britain, 1984.

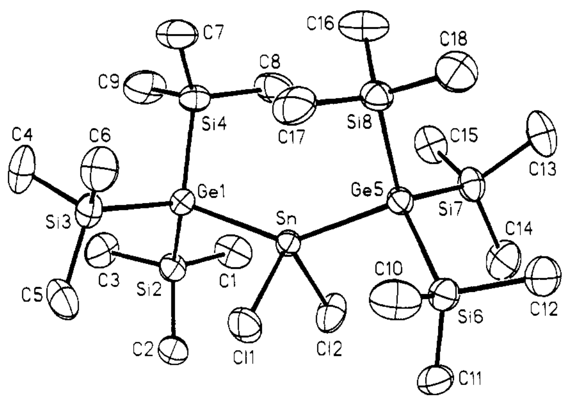


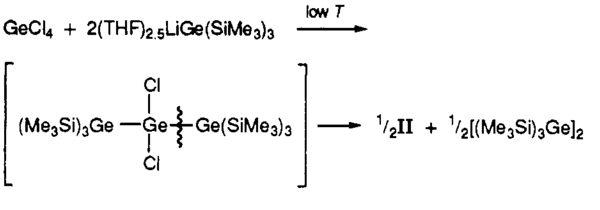
Figure 2. Molecular structure of **III**, showing the atom-numbering scheme. Hydrogen atoms are omitted for clarity.

Table 4. Crystallographic Data for III

$C_{18}H_{54}Si_6Cl_2Ge_2Sn$	$C2/c$ (monoclinic)
fw = 774.03	$T = 27$ °C
$a = 16.106(4)$ Å	$\lambda = 0.710\ 73$ Å
$b = 10.034(2)$ Å	ρ(calc) = 1.34 g·cm^{-3}
$c = 47.375(11)$ Å	$\mu = 25.2$ cm
$\beta = 90.02\ (2)°$	$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\| = 0.037$
$V = 7656$ Å^3	$R_w = [\Sigma w^2(\|F_o\| - \|F_c\|)^2/\Sigma\|F_o\|^2]^{1/2} = 0.032$
$Z = 8$	

$Si)_3SiGeCl_2]_2$ support the proposed structure of **II** as based on a chain of four Ge atoms. Aside from Ge_4H_{10}, few acyclic tetragermanes have been reported.[22,23]

The high yield of **II** is consistent with an uncomplicated pathway to its synthesis. One credible route (eq 4) involves a disubstituted



$$GeCl_4 + 2(THF)_{2.5}LiGe(SiMe_3)_3 \xrightarrow{\text{low } T} \left[(Me_3Si)_3Ge - \overset{Cl}{\underset{Cl}{Ge}} - Ge(SiMe_3)_3 \right] \longrightarrow {}^1/_2\mathbf{II} + {}^1/_2[(Me_3Si)_3Ge]_2 \qquad (4)$$

product, formed at low temperature, dissociating because of steric crowding by cleavage of a Ge–Si bond. Coupling of the larger Ge-based radical would afford **II**. The abstraction by the radical of a proton from the solvent is not favored because of the low Ge–H bond dissociation energy,[24] so coupling of the Ge radicals may prevail. The presence of NMR signals for the expected coproduct, $(Me_3Si)_3Ge–Ge(SiMe_3)_3$ (δ 0.391),[25] and for $(Me_3Si)_3GeH$ (δ 0.295)[26] was consistent with this pathway. Notable by its absence, even after long stirring times at room temperature, was any evidence for the tetragermyl–cyclotetragermane counterpart of **I** that might have been expected to form under such conditions.

Another approach to comparing the effect of the smaller cone angle assumed for $-Ge(SiMe_3)_3$ (compared to $-Si(SiMe_3)_3$) was to prepare and structurally characterize the disubstituted tin(IV) derivative, $[(Me_3Si)_3Ge]_2SnCl_2$ (**III**). The Si–Sn–Si bond angle in $[(Me_3Si)_3Si]_2SnCl_2$ was found to be unusually large, but a smaller Ge–Sn–Ge angle would be expected in **III** due the longer Sn–Ge bond. Reaction of $SnCl_4$ with 2 equiv of $(THF)_{2.5}LiGe(SiMe_3)_3$ gave **III** as a mildly hygroscopic solid in higher yield (85%) than was found for its Si analogue (40%).[5] Elemental analysis and NMR spectra were consistent with the proposed formula, and an X-ray structure determination showed that its molecular structure (Figure 2) was only slightly less distorted from tetrahedral coordination around Sn than that of $[(Me_3Si)_3Si]_2SnCl_2$.[5] The crystallographic data and atomic coordinates for **III** are listed in Tables 4 and 5, respectively. The ∠Ge–Sn–Ge value was 142.1(1)° (Table 6) compared to 142.5(1)° in its $Si(SiMe_3)$ analogue,[5] and ∠Cl–Sn–Cl was 98.8(1)° compared to 99.1(1)°. Although **III** was essentially isomorphous with the

Table 5. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for III

	x	y	z	U(eq)[a]
Sn	2723(1)	3965(1)	8774(1)	49(1)
Cl(1)	1303(1)	3622(3)	8654(1)	92(1)
Cl(2)	3023(2)	1814(2)	8965(1)	100(1)
Ge(1)	3404(1)	3966(1)	8268(1)	52(1)
Si(2)	3775(2)	1689(3)	8186(1)	65(1)
Si(3)	2401(1)	433(3)	7931(1)	69(1)
Si(4)	4605(1)	5369(3)	8262(1)	69(1)
Ge(5)	2655(1)	5345(1)	9244(1)	51(1)
Si(6)	1346(1)	4774(3)	9452(1)	68(1)
Si(7)	3769(2)	4646(3)	9544(1)	70(1)
Si(8)	2723(1)	7653(2)	9123(1)	63(1)
C(1)	4637(5)	1218(8)	8430(2)	99(4)
C(2)	2847(4)	580(8)	8238(2)	78(4)
C(3)	4145(5)	1522(9)	7812(2)	103(4)
C(4)	2972(5)	4962(11)	7593(2)	114(5)
C(5)	1561(5)	3486(9)	7868(2)	103(5)
C(6)	1906(5)	6342(9)	8037(2)	100(5)
C(7)	4316(5)	7158(8)	8210(2)	104(5)
C(8)	5181(5)	5210(9)	8606(2)	118(5)
C(9)	5308(5)	4846(10)	7977(2)	123(5)
C(10)	475(4)	5679(9)	9267(2)	102(5)
C(11)	1152(5)	2932(8)	9448(2)	82(4)
C(12)	1399(5)	5351(9)	9830(2)	107(5)
C(13)	3876(5)	5929(9)	9823(2)	107(5)
C(14)	3524(5)	3034(9)	9719(2)	112(5)
C(15)	4759(4)	4511(9)	9353(2)	92(4)
C(16)	3805(4)	8131(8)	9036(2)	104(5)
C(17)	2031(5)	7992(9)	8819(2)	106(5)
C(18)	2348(5)	8663(8)	9430(2)	104(5)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 6. Selected Bond Lengths (Å) and Angles (deg) for III

Sn–Cl(1)	2.382(2)	Sn–Cl(2)	2.389(2)
Si(3)–C(5)	1.866(9)	Sn–Ge(1)	2.636(1)
Sn–Ge(5)	2.626(1)	Ge(1)–Si(2)	2.394(3)
Ge(1)–Si(3)	2.397(2)	Ge(1)–Si(4)	2.393(3)
Ge(5)–Si(6)	2.398(2)	Ge(5)–Si(7)	2.394(3)
Ge(5)–Si(8)	2.388(3)	Si–C(av)	1.866
Cl(1)–Sn–Cl(2)	98.8(1)	Cl(1)–Sn–Ge(1)	100.6(1)
Cl(2)–Sn–Ge(1)	105.1(1)	Cl(1)–Sn–Ge(5)	103.7(1)
Cl(2)–Sn–Ge(5)	99.4(1)	Ge(1)–Sn–Ge(5)	142.1(1)
Se–Ge(1)–Si(2)	104.6(1)	Sn–Ge(1)–Si(3)	109.0(1)
Si(2)–Ge(1)–Si(3)	111.5(1)	Sn–Ge(1)–Si(4)	110.3(1)
Si(2)–Ge(1)–Si(4)	111.0(1)	Si(3)–Ge(1)–Si(4)	110.4(1)
Ge(1)–Si(2)–C(1)	109.0(3)	Ge(1)–Si(2)–C(2)	110.2(3)
Ge(1)–Si(2)–C(3)	108.6(3)	Ge(1)–Si(3)–C(4)	106.3(3)
Ge(1)–Si(3)–C(S)	112.3(3)	Ge(1)–Si(4)–C(7)	111.4(3)
Ge(1)–Si(3)–C(6)	112.6(3)	Ge(1)–Si(4)–C(8)	109.8(3)
Ge(1)–Si(4)–C(9)	109.8(3)	Sn–Ge(5)–Si(6)	105.1(1)
Sn–Ge(5)–Si(7)	108.5(1)	Si(6)–Ge(5)–Si(7)	110.1(1)
Sn–Ge(5)–Si(8)	107.8(1)	Si(6)–Ge(5)–Si(8)	111.8(1)
Si(7)–Ge(5)–Si(8)	113.1(1)	Ge(5)–Si(6)–C(10)	110.3(3)
Ge(5)–Si(6)–C(11)	112.2(3)	Ge(5)–Si(6)–C(12)	106.1(3)
Ge(5)–Si(7)–C(13)	106.8(3)	Ge(5)–Si(7)–C(14)	111.1(3)
Ge(5)–Si(7)–C(15)	112.3(3)	Ge(5)–Si(8)–C(16)	110.4(3)
Ge(5)–Si(8)–C(17)	109.7(3)	Ge(5)–Si(8)–C(18)	108.9(3)
C–Si–C (avg)	109.1		
Ge(5)–Sn–Ge(1)–Si(2)	139.7	Sn–Ge(5)–Si(7)–C(14)	–77.9
Cl(1)–Sn–Ge(1)–Si(3)	28.3	Sn–Ge(5)–Si(7)–C(15)	45.6
Cl(1)–Sn–Ge(1)–Si(4)	149.6	Si(6)–Ge(5)–Si(7)–C(13)	–80.7
Cl(2)–Sn–Ge(1)–Si(2)	11.2	Si(6)–Ge(5)–Si(7)–C(14)	36.7
Cl(2)–Sn–Ge(1)–Si(3)	130.5	Si(6)–Ge(5)–Si(7)–C(15)	160.2
Cl(1)–Sn–Ge(1)–Si(2)	–91.0		

---

(22) Bulten, E. J. *MTP Int. Rev. Sci., Inorg. Chem., Ser. 2* **1975**, *4*, 241.

(23) *Organometallic Compounds of Germanium, Tin and Lead*; Harrison, P. G., Ed.; Chapman and Hall: London, 1985.

(24) Gyanne, M. J. S.; Lappert, M. F.; Riley, P. I.; Riviere, P.; Riviere-Baudet, M. *J. Organomet. Chem.* **1980**, *202*, 5.

(25) Mallela, S. P.; Geanangel, R. A. *Inorg. Chem.* **1993**, *32*, 5623.

(26) By comparison with an authentic sample of $(Me_3Si)_3GeH$.

silyl derivative, the average Sn–Cl distance was found to be 2.386(2) Å as compared to 2.433(3) Å in the silyl. The Sn–Ge distances in **III** average 2.631(1) Å, which is longer than that in $Me_3GeSnPh_3$ (2.599(3) Å)[27] but shorter than in $Ph_3GeSnMe_3$ (2.652(2) Å).[27] (Pannell et al. attributed the considerable difference in the Sn–Ge bond lengths in $Me_3GeSnPh_3$ and $Ph_3GeSnMe_3$ to electronic effects since steric factors should be similar in the isomeric pair.[27]) We conclude that the steric influence of the $-Ge(SiMe_3)_3$ group is not materially different from that of $-Si(SiMe_3)_3$ with a Sn(IV) central atom. The cone angle of $Sn-Ge(SiMe_3)_3$ was calculated using atomic coordinates of **III** (Table 5) as described in ref 3. The value obtained, 168(9)°, was indistinguishable from that for $Sn-Si(SiMe_3)_3$, 168(5)°, supporting the above conclusion.

Other Derivatives and Reactions. The reaction of $LaCl_3$ with 3 equiv of $(THF)_3LiSi(SiMe_3)_3$ gave a high yield of a very hygroscopic, white solid product the analytical results and NMR spectra of which were reasonably consistent with the formula $(THF)La[Si(SiMe_3)_3]_2Cl$. Efforts to make $La[Si(SiMe_3)_3]_3$ were not successful.

Attempts to introduce more than two $Si(SiMe_3)_3$ groups into a Sn(IV) molecule were carried out by reacting $SnCl_4$ with 4 equiv of $(THF)_3LiSi(SiMe_3)_3$ and by treating $((Me_3Si)_3Si)_2SnCl_2$ with 2 equiv of the same reagent, but both gave only unreacted starting materials, $Si(SiMe_3)_4$, and small amounts of $HSi(SiMe_3)_3$ and $(Me_3Si)_3SiSi(SiMe_3)_3$.

The reaction of **II** with 2 equiv of $(THF)_{2.5}LiGe(SiMe_3)_3$ led only to recovery of starting materials along with some $(Me_3Si)_4Ge$. Attempted reduction of **II** with either Li or $LiAlH_4$ gave unreacted starting materials, some $(Me_3Si)_3Ge-Ge(SiMe_3)_3$, and a minor, unidentified product. A similar reaction employing $LiAlH_4$, after 5 days at room temperature, afforded some unreacted **II**, significant amounts of $(Me_3Si)_4Ge$ and $(Me_3Si)_3Ge-Ge(SiMe_3)_3$, minor amounts of $(Me_3Si)_3GeH$, and several unidentified products. In no case have we been able to introduce more than two $Si(SiMe_3)_3$ or $Ge(SiMe_3)_3$ groups on the same central atom.

Acknowledgment. The authors gratefully acknowledge the support of this investigation by the Robert A. Welch Foundation under Grant E-1105 and the University of Houston Limited Grant in Aid Program. We are also grateful to J. Korp for carrying out the X-ray structure determinations and for helpful discussions of the results and to Dr. Bessy Fan of Shell Development Co. for obtaining field desorption mass spectra.

Supplementary Material Available: For **I** and **III**, tables listing full data collection and processing parameters, full bond lengths and angles, torsion angles, anisotropic displacement parameters, and H atom coordinates (10 pages). Ordering information is given on any current masthead page.

---

[27] Pannell, K. H.; Parkanyi, L.; Sharma, H.; Cervantes-Lee, F. *Inorg. Chem.* **1992**, *31*, 522.