

Reactions of $\text{LiE}(\text{SiMe}_3)_3$, $\text{E} = \text{Si, Ge}$: X-ray Crystal Structure of the Cyclotetrastannane $[\text{ClSnSi}(\text{SiMe}_3)_3]_4$

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Reaction of $\text{SnCl}_2 \cdot \text{dioxane}$ with 2 equiv of $\text{Li}(\text{THF})_3\text{Si}(\text{SiMe}_3)_3$ in hexane afforded the cyclotetrastannane $[(\text{Me}_3\text{Si})_3\text{SiSnCl}]_4$ in reasonable yield. From pentane, the product crystallized as a red-orange disolvate in the $P\bar{1}$ space group (triclinic) with $a = 14.735(2) \text{ \AA}$, $b = 14.976(2) \text{ \AA}$, $c = 24.066(3) \text{ \AA}$, $\alpha = 76.94^\circ$, $\beta = 76.19^\circ$, $\gamma = 62.11^\circ$, $V = 4517.5 \text{ \AA}^3$, and $Z = 2$. The Sn_4 ring consisted of a slightly distorted, nonplanar (fold angle = 18.9°) rectangle with Sn–Sn distances of 2.8054(6), 2.8111(6), 2.9122(6), and 2.9146(6) \AA . The pentane molecules were disordered. Selected mono- and dihalogermanes were treated with 1 equiv of $\text{Li}(\text{THF})_3\text{Si}(\text{SiMe}_3)_3$ or $\text{Li}(\text{THF})_{2.5}\text{Ge}(\text{SiMe}_3)_3$, affording $(\text{Me}_3\text{Si})_3\text{EGe}(\text{CF}_3)_3$ ($\text{E} = \text{Si, Ge}$) and $(\text{Me}_3\text{Si})_3\text{GeGeR}_3$ ($\text{R} = \text{Cl, CH}_3, \text{C}_6\text{H}_5$). Besides the monosubstitution product, the reaction of GeCl_4 with 1 equiv of $\text{Li}(\text{THF})_{2.5}\text{Ge}(\text{SiMe}_3)_3$ also gave a small amount of the linear tetragermane $(\text{Me}_3\text{Si})_3\text{GeGeCl}_2\text{GeCl}_2\text{Ge}(\text{SiMe}_3)_3$. Good yields of the analogous phenyl derivative, $(\text{Me}_3\text{Si})_3\text{GeGePh}_2\text{GePh}_2\text{Ge}(\text{SiMe}_3)_3$, were obtained by treating Ph_2GeCl_2 with 2 equiv of the lithium–germyl reagent.

Introduction

The silyl and germlyl reagents, $(\text{THF})_3\text{LiSi}(\text{SiMe}_3)_3$ (**1a**) and $(\text{THF})_{2.5}\text{LiGe}(\text{SiMe}_3)_3$ (**1b**) react with metal halides to give a rich variety of products. Among the group 14 metals, for example, SnCl_4 yields mono- and disubstituted silyl/germyl products, $((\text{Me}_3\text{Si})_3\text{E})_n\text{SnCl}_{4-n}$ ($\text{E} = \text{Si}, n = 1, 2$; $\text{E} = \text{Ge}, n = 2$),¹ whereas GeCl_4 with **1a** initially gives the digermane $(\text{Me}_3\text{Si})_3\text{SiGeCl}_2\text{—GeCl}_2\text{Si}(\text{SiMe}_3)_3$ and subsequently yields the heteroleptic cyclotetragermane $[(\text{Me}_3\text{Si})_3\text{SiGeCl}]_4 \cdot \text{C}_6\text{H}_6$.² With PbCl_2 , **1a** and **1b** cause reduction to Pb accompanied by the coupled products $(\text{Me}_3\text{Si})_3\text{E—E}(\text{SiMe}_3)_3$ ($\text{E} = \text{Si}$ and Ge , respectively).³ Reaction of **1b** with $\text{GeCl}_2 \cdot \text{dioxane}$ leads to both a cyclotrigermane $((\text{Me}_3\text{Si})_2\text{Ge})_3$ and the cyclotetragermane $[(\text{Me}_3\text{Si})_3\text{GeGeCl}]_4 \cdot 2\text{Ge}(\text{SiMe}_3)_4$.⁴ With **1a**, the same halide gave the disilagermirane, $(\text{Me}_3\text{Si})_2\text{Ge}(\text{Si}(\text{SiMe}_3)_2)_2$.⁵ The utility of these reagents in forming small rings was recently extended to tin when it was shown that in hexane **1b** reacts with SnCl_2 to give the cyclotetrastannane $[(\text{Me}_3\text{Si})_3\text{GeSnCl}]_4 \cdot 2\text{Ge}(\text{SiMe}_3)_4$, along with $[(\text{Me}_3\text{Si})_3\text{Ge}]_2\text{SnCl}_2$.⁶ The cocrystallization of $\text{E}(\text{SiMe}_3)_4$ ($\text{E} = \text{Si, Ge}$) with the Ge_4 and Sn_4 products caused extensive disorder in their crystal structures; thus we sought a method of preparing the silyl derivative, $[(\text{Me}_3\text{Si})_3\text{SiSnCl}]_4$, without cocrystallized $\text{Si}(\text{SiMe}_3)_4$ to permit an improved structure determination. Reactions of $(\text{CF}_3)_3\text{GeI}$ and of selected organogermanium(IV) chlorides with **1a** and **1b** in hexane leading to monosubstituted mono- and digermanes will also be described.

Experimental Section

Materials. Tris(trifluoromethyl)germanium iodide was obtained from Aldrich. Tetrahydrofuran (THF) was distilled over LiAlH_4 under argon. Pentane and hexane were distilled over sodium just before use. The reagents $(\text{THF})_3\text{LiSi}(\text{SiMe}_3)_3$ (**1a**) and $(\text{THF})_{2.5}\text{LiGe}(\text{SiMe}_3)_3$ (**1b**) were prepared according to literature methods.⁷ Elemental analyses were by Atlantic Microlabs. All manipulations were conducted under argon dried with P_4O_{10} . ¹⁹F NMR spectra were recorded on a Varian QE300 in C_6D_6 with reference to external CF_3COOH . ¹H and ¹³C NMR and IR spectra were recorded as described earlier.⁸

$\text{SnCl}_2 \cdot \text{Dioxane}$ Reactions in Hexane. Tetrachlorotetrakis(trimethylsilyl)silylcyclotetrastannane Cocrystallized with Tetrakis(trimethylsilyl)silane, $[(\text{Me}_3\text{Si})_3\text{SiSnCl}]_4 \cdot 2\text{Si}(\text{SiMe}_3)_4$ (2a**).** A suspension of $\text{SnCl}_2 \cdot \text{dioxane}$ (614 mg, 2.21 mmol) in 20 mL of hexane was cooled to -78°C , and 100 mL of a hexane solution of **1a** (2084 mg, 4.425 mmol) was slowly added to it. The brick red reaction mixture was stirred at -78°C for 8 h, allowed to warm to ambient temperature, and stirred 18 h, giving a dark red-brown solution with a fine precipitate. Hexane was removed in vacuo, and the residue was extracted with 30 mL of pentane. The red brown filtrate was held at -10°C , producing 982 mg (78.9% yield) of red tetrahedral crystals of **2a**. In a sealed capillary under argon, crystals of **2a** darkened at 140°C and melted at 145°C . ¹H NMR (C_6D_6): δ 0.262 [$\text{Si}(\text{SiMe}_3)_4$], 0.517 [$-\text{Si}(\text{SiMe}_3)_3$]. ¹³C NMR (C_6D_6): δ 2.864 [$\text{Si}(\text{SiMe}_3)_4$], 4.067 [$-\text{Si}(\text{SiMe}_3)_3$]. ¹¹⁹Sn NMR (C_6D_6): δ 192.4 (¹ $J_{\text{Sn—Si}} = 2711 \text{ Hz}$, ² $J_{\text{Sn—Si}} = 2602 \text{ Hz}$ (area ratio = 2:1)). Anal. Calcd for $\text{C}_{30}\text{H}_{90}\text{Cl}_2\text{Sn}_2\text{Si}_{13}$: C, 32.04; H, 8.07. Found: C, 30.82;⁹ H, 8.03.

Tetrachlorotetrakis(trimethylsilyl)silylcyclotetrastannane Cocrystallized with C_5H_{12} , $[(\text{Me}_3\text{Si})_3\text{SiSnCl}]_4 \cdot 2\text{C}_5\text{H}_{12}$ (2b**).** A hexane (60 mL) suspension of $\text{SnCl}_2 \cdot \text{dioxane}$ (2347 mg, 8.45 mmol) and 150 mL of a hexane solution of **1a** (3980 mg, 8.45 mmol) were combined as described for **2a**. Workup in pentane and cooling to -10°C for 24 h afforded 1531 mg (45% yield) of red orange crystals of **2b**.

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- (9) The low % carbon may be due loss of $\text{Si}(\text{SiMe}_3)_4$ during purification and drying of the crystals.

Table 1. Crystal Data and Structure Refinement for **2b**

empirical formula	C ₃₆ H ₁₀₈ Cl ₄ Si ₁₆ Sn ₄ ·2C ₅ H ₁₂
fw	1751.5
cryst syst	triclinic
space group	P1
a, Å	14.735(2)
b, Å	14.976(2)
c, Å	24.066(3)
α, deg	76.94(1)
β, deg	76.19(1)
γ, deg	62.11(1)
vol, Å ³	4517.5(10)
Z	2
D _{calcd} , mg/m ³	1.288
temp, K	223(2)
wavelength, Å	0.710 73
abs coeff, μm ⁻¹	1.449
independent reflns	11702 (R _{int} = 0.0196)
goodness-of-fit on F ²	1.059
final R indices [I > 4σ(I)]	R ₁ ^a = 0.0269, R _w ^b = 0.0739
R indices (all data)	R ₁ = 0.0373, R _w = 0.0812

$${}^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad {}^b R_w = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}.$$

¹H NMR (C₆D₆): δ 0.515 (s) [Si(SiMe₃)₃]. ¹³C NMR (C₆D₆): δ 4.069 [Si(SiMe₃)₃]. Single crystals for X-ray structural study were obtained by recrystallizing from pentane at -10 °C. These were found to be stable for months in the presence of pentane at that temperature; however, they lost pentane in vacuo, forming a brick red powder. At room temperature in C₆D₆, **2b** decomposed within 2 h as evidenced by the appearance of new Si(SiMe₃)₃ NMR signals at ¹H NMR δ 0.211 (s) and ¹³C NMR -0.636.

X-ray Crystallography of 2b. Crystal data are presented in Table 1. Crystals of **2b** were orange blocks. The crystals were handled under mineral oil during the mounting procedure. Data were collected on a Siemens SMART CCD instrument. There were no unusual experimental difficulties. Full details can be found in the Supporting Information.

Tetrachlorotetrakis(tris(trimethylsilyl)germyl)cyclotetranane Adduct with Tetrakis(trimethylsilyl)germane, [(Me₃Si)₃-GeSnCl₄]₂Ge(SiMe₃)₄ (3). To a -78 °C hexane (25 mL) suspension of SnCl₂·dioxane (957 mg, 3.44 mmol) was added 120 mL of a hexane solution of **1b** (3304 mg, 6.89 mmol) dropwise. The reaction mixture was stirred at -78 °C for 8 h, allowed to warm to ambient temperature, and stirred another 16 h. Volatiles were removed in vacuo, the residue was extracted with 50 mL of pentane, and the brown filtrate was held at -10 °C for 7 days, producing 920 mg (42.4%) of blood red crystals of **3**. ¹H NMR (C₆D₆): δ 0.304 (lit.¹⁰ 0.297) [Ge(SiMe₃)₄]; 0.564 (lit.^{6a} 0.560) [-Ge(SiMe₃)₃]. ¹³C NMR (C₆D₆): δ 3.58 (lit.¹⁰ 3.45) [Ge(SiMe₃)₄]; 4.63 (lit.^{6a} 4.62) [-Ge(SiMe₃)₃].

Reaction of SnCl₂·Dioxane and 1a in THF. SnCl₂·dioxane (1630 mg, 5.9 mmol) and **1a** (5540 mg, 11.8 mmol) were combined as described for **2a** except that THF (75 mL) was used as the solvent. The clear, brown solution after extraction with pentane was held at -10 °C for 24 h affording very hygroscopic pale yellow crystals (¹H NMR (C₆D₆): δ 0.38, major, 0.40, 0.37, minor; ¹³C NMR (C₆D₆): δ 3.14, 3.29, 3.39) that decomposed on standing and were not characterized further. The residue after extraction with pentane was pyrophoric. Care should be taken in its disposal.

(a) [Tris(trimethylsilyl)silyl]tris(trifluoromethyl)germane, (Me₃-Si)₃SiGe(CF₃)₃ (4a). To a pentane (35 mL) solution of (CF₃)₃GeI (2161 mg, 5.32 mmol) at -78 °C was added dropwise 100 mL of a pentane solution of **1a** (2504 mg; 5.32 mmol) with vigorous stirring. After 8 h at -78 °C the mixture was warmed to room temperature and stirred another 16 h. Volatiles were removed in vacuo, the residue was extracted with pentane (50 mL) and filtered, and the filtrate was held at -10 °C overnight. An unidentified, C₆D₆-insoluble white product (262 mg) that later turned yellow-brown was filtered off. At -78 °C overnight, the pentane solution afforded white crystals of **4a** (1113 mg, 40%); mp 225 °C (sublimed/decomposed at 245 °C). ¹H NMR (C₆D₆):

δ 0.19. ¹³C NMR (C₆D₆): δ 1.62. ¹⁹F NMR (C₆D₆): δ -27.2. IR (AgBr, Nujol, cm⁻¹): 2755 (vw), 2695 (vw), 2275 (vw), 2210 (vw), 1915 (w), 1845 (w), 1705 (vw), 1405 (m), 1320 (w), 1260 (s), 1195 (m) (ν_{as}(CF₃) str.), 1115 (s, br), 1005 (m), 840 (s, br), 775 (m), 755 (m) (δ_s CF₃ def. E), 655 (s), 635 (sh), 555 (m) (δ_{as} CF₃ def. A₁), 475 (s), 460 (m), 440 (w), 350 (s). Anal. Calcd for C₁₂H₂₇F₉GeSi₄: C, 27.3; H, 5.16. Found: C, 27.24; H, 5.05.

[Tris(trimethylsilyl)germyl]tris(trifluoromethyl)germane, (Me₃Si)₃-GeGe(CF₃)₃ (4b). A pentane (90 mL) solution of **1b** (1960 mg, 4.09 mmol) was combined with 30 mL of a pentane solution of (CF₃)₃GeI (1665 mg, 4.09 mmol) as described for **4a**. Crystallization from pentane at -10 °C gave transparent crystals of **4b** (1180 mg, 50.6%); mp 272 °C (dec). ¹H NMR (C₆D₆): δ 0.22. ¹³C NMR (C₆D₆): δ 2.23. ¹⁹F NMR (C₆D₆): δ -26.8. IR (AgBr, Nujol, cm⁻¹): 2790 (sh), 2240 (vw), 1930 (w), 1860 (w), 1790 (w), 1730 (w), 1425 (m), 1325 (vw), 1380 (s), 1215 (m), 1180 (m) (ν_{as} CF₃ str.), 1120 (sh), 860 (vs), 795 (m), 765 (m) (δ_s CF₃ def. E), 670 (s), 585 (m) (δ_{as} CF₃ def. A₁), 455 (w), 360 (w). Anal. Calcd for C₁₂H₂₇F₉Ge₂Si₃: C, 25.2; H 4.76. Found: C, 25.3; H, 4.70.

[Tris(trimethylsilyl)germyl]trichlorogermane, (Me₃Si)₃GeGeCl₃ (5a). A pentane (90 mL) solution of **1b** (2700 mg, 5.6 mmol) was added dropwise to a -78 °C pentane (25 mL) solution of GeCl₄ (1200 mg, 5.59 mmol). After workup as described for **4a**, 40 mL of pentane extract was held at -78 °C overnight, giving 1370 mg (52.3%) of white crystals of **5a**; mp 217 °C (dec). ¹H NMR (C₆D₆): δ 0.276. ¹³C NMR (C₆D₆): δ 2.081. IR (AgBr, Nujol, cm⁻¹) 2605 (vw), 1920 (vw), 1850 (vw), 1720 (w), 1415 (m), 1330 (m), 1255 (vs), 990 (m), 860 (vs), 785 (w), 730 (s), 655 (s), 640 (sh), 450 (w), 415 (vs), 385 (m). Anal. Calcd for C₉H₂₇Cl₃Ge₂Si₃: C, 22.94; H, 5.77. Found: C, 23.04; H, 5.59. The pentane mother liquor was concentrated and stored at -10 °C for 2 days, forming transparent octahedral crystals of [(Me₃Si)₃GeGeCl₂]₂^{1b} (**5b**) [¹H NMR: δ 0.453 (lit.^{1b} 0.448); ¹³C NMR: δ 3.12 (lit.^{1b} 3.13)] along with some additional **5a**.

[Tris(trimethylsilyl)germyl]trimethylgermane, (Me₃Si)₃GeGeMe₃ (6). Following the procedure given for **5a**, Me₃GeCl (1000 mg, 6.5 mmol) was combined with **1b** (3200 mg, 6.60 mmol) in pentane. Workup and crystallization in pentane at -30 °C gave colorless needles of **6** cocrystallized with Ge(SiMe₃)₄; mp 140 °C (sublimes up to 270 °C). ¹H NMR (C₆D₆): δ 0.285 [-Ge(SiMe₃)₃], 0.295 [Ge(SiMe₃)₄], 0.435 [Me₃Ge-]. ¹³C NMR (C₆D₆): δ 2.97 [Me₃Ge-], 3.35 [-Ge(SiMe₃)₃], 3.41 [Ge(SiMe₃)₄]. We note that (Me₃Si)₃SiGeMe₃ (mp 135 °C) also exhibited extra NMR peaks assignable there to cocrystallized Si(SiMe₃)₄.¹¹

[Tris(trimethylsilyl)germyl]triphenylgermane, (Me₃Si)₃GeGePh₃ (7). A pentane solution (50 mL) of **1b** (1820 mg, 3.80 mmol) was added dropwise to a cold (-78 °C) pentane (25 mL) solution of Ph₃GeCl (1290 mg, 3.80 mmol). The mixture was stirred 6 h and then another 17 h at ambient temperature. Volatiles were removed in vacuo; the white residue was stirred with pentane (40 mL) and filtered. On cooling to -30 °C, the pentane solution afforded 1928 mg (87%) of white crystals of **7**; mp 97–99 °C. (On further heating, the melt boils at 178 °C.) ¹H NMR (C₆D₆): δ 0.25 [27H, -Ge(SiMe₃)₃], 7.08–7.15 (m), 7.63–7.69 (m) [15H, Ge-Ph]. ¹³C NMR (C₆D₆): δ 3.505 [-Ge(SiMe₃)₃], 128.8–128.9 (d), 130.6, 134.4, 135.9 [Ge-Ph]. Anal. Calcd for C₂₇H₄₂Ge₂Si₃: C, 54.41; H, 7.10. Found: C, 55.02; H, 6.79.

1,1,2-Tetraphenyl-1,2-bis[tris(trimethylsilyl)germyl]digermane, [(Me₃Si)₃GeGe(C₆H₅)₂]₂ (8). Pentane solutions of Ph₂GeCl₂ (1350 mg, 4.35 mmol) and **1b** (4346 mg, 9.06 mmol) were treated as described for **4a**. Cooling the pentane solution to -78 °C overnight resulted in 2100 mg (89%) of transparent crystals of **8**; mp 160 °C. ¹H NMR (C₆D₆): δ 0.304 [27H, -Ge(SiMe₃)₃], 7.13–7.15 (m), 7.82–7.84 (m) [10H, GePh₂]. ¹³C NMR (C₆D₆): δ 3.17 [-Ge(SiMe₃)₃], 128.5, 129.7, 133.8 [Ge-Ph]. IR (AgBr, Nujol, cm⁻¹): 3040 (w), 2690 (w), 1420 (sh), 1300 (m), 1250 (sh), 1240 (vs), 1185 (w), 1170 (w), 1090 (s), 1035 (m), 1005 (m), 845 (vs br), 745 (s), 710 (s), 635 (s), 625 (sh), 385 (vs), 425 (sh), 370 (m). Anal. Calcd for C₄₂H₇₄Ge₄Si₆: C, 48.59; H, 7.18. Found: C, 45.21; H, 6.80.

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Results and Discussion

Treatment of SnCl₂ with LiR (R = bulky alkyl, aryl, or other monohapto group) has led to a variety of products depending on the nature of R, the solvent, and conditions. The observation that SnCl₂ with 2 equiv of Li(THF)_{2.5}Ge(SiMe₃)₃ (**1b**) in hexane yielded red crystals of the heteroleptic cyclotetrastannane, [(Me₃-Si)₃GeSnCl]₄, an unreported type of product for such reactions,^{6a} led us to examine the reaction further and extend it using Li(THF)₃Si(SiMe₃)₃ (**1a**).¹² Combining SnCl₂·dioxane in 1:2 reactions with **1a** and **1b** gave silyl- and germyl-substituted cyclotetrastannanes in moderate yields. The red-orange products contained cocrystallized E(SiMe₃)₄ (E = Si or Ge) or solvent molecules.

The X-ray structure determination on [(Me₃Si)₃GeSnCl]₄·2Ge(SiMe₃)₄, **3**, had been complicated by extensive disorder in the cocrystallized Ge(SiMe₃)₄ molecules,^{6a} however, the presence of two and only two ¹¹⁹Sn–¹¹⁷Sn couplings with a ¹J²J intensity ratio of 2.0 confirmed that the product contained an Sn₄ ring.¹³ Reaction of SnCl₂ with 2 equiv of **1a** in hexane in the present work gave a 79% yield of red cyclotetrastannane [(Me₃Si)₃SiSnCl]₄·2Si(SiMe₃)₄, **2a**, identified by its NMR spectra.¹⁴ The ¹¹⁹Sn spectrum of **2a** consisted of a sharp center band and two pairs of satellites representing ¹J¹¹⁹Sn–¹¹⁷Sn (2711 Hz) and ²J¹¹⁹Sn–¹¹⁷Sn (2602 Hz) in a 2:1 area ratio indicative of a cyclotetrastannane ring.¹³ Seeking to avoid cocrystallized Si(SiMe₃)₄, we carried out 1:1 reactions of SnCl₂ with **1a** in hexane and then recrystallized from pentane, giving orange [(Me₃Si)₃SiSnCl]₄·2C₃H₁₂, **2b**, in 45% yield, identified by NMR spectra and an X-ray structure determination. Above –10 °C or under vacuum, **2b** loses pentane and changes color. The pentane solvate molecules were disordered in the crystal; however, the cyclotetrastannane itself was ordered and the structure determination gave well-defined structural parameters (Figure 1).

Compared to [(R₃E)₄Sn₄Cl₄] (E = Ge, R = SiMe₃), **3**, the structure of **2b** has a rectangular Sn₄ core (two Sn–Sn bonds about 2.81 Å and two about 2.91 Å) with the average being slightly longer than that in **3** and with a notably flatter ring (fold angle = 18.9° vs almost 30° in **3**). The Sn–Sn–Cl angles in **2b** are substantially below tetrahedral values, averaging about 99°, while the Sn–Sn–Si angles averaged about 128°, reflecting to some degree steric distortion induced by the bulky Si(SiMe₃)₃ groups. The absence of significantly elongated skeletal bonds and the near tetrahedral values for Cl–Sn–Si and Si–Si–Si angles in **2b** argue that steric crowding in the molecule is only moderate.

In **3**, the structure appeared to contain three conformations involving different rotations around trans pairs of Sn–GeR₃ axes,^{6a} but only one conformation, the staggered arrangement, was found in **2a**. In this arrangement, one methyl group is oriented across from two methyl groups above the Sn₄ ring, and the same conformation is found below the ring. (Figure 1). It appears that the shorter Sn–Si bonds in **2b** (compared to Sn–Ge in **3**) lead to more crowding around the Sn₄ ring, favoring only the least hindered conformation of the SiR₃ substituents. This condition is also consistent with the smaller ring fold angle in **2b**. The unit cell contains two molecules of **2b**.

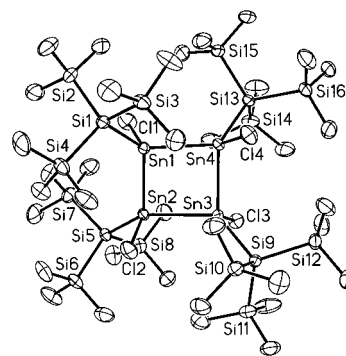
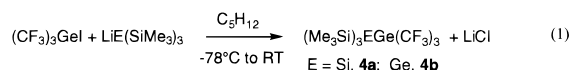


Figure 1. Molecular structure of **2b** showing the atom numbering scheme. The C₃H₁₂ solvate molecules were disordered and are not shown. Hydrogen atoms are omitted for the sake of clarity. Selected bond distances (Å) and angles (deg): Sn(1)–Sn(2) = 2.8054(6), Sn(2)–Sn(3) = 2.9146(6), Sn(3)–Sn(4) = 2.8111(6), Sn(1)–Sn(4) = 2.9122(6), Sn(1)–Cl(1) = 2.4234(14), Sn(2)–Cl(2) = 2.4005(13), Sn(1)–Si(1) = 2.6048(13), Sn(2)–Si(5) = 2.6576(12), Sn(3)–Si(9) = 2.6093(13), Sn(4)–Si(13) = 2.5877(12); Sn(2)–Sn(1)–Sn(4) = 90.373(16), Sn(1)–Sn(2)–Sn(3) = 88.203(16), Cl(1)–Sn(1)–Sn(2) = 96.28(4), Si(1)–Sn(1)–Sn(2) = 127.00(3), Si(5)–Sn(2)–Sn(3) = 130.23(3), Cl(1)–Sn(1)–Si(1) = 107.78(5), Si(4)–Si(1)–Si(2) = 109.13(7), the fold angle between planes defined by Sn(1)–Sn(2)–Sn(4) and Sn(2)–Sn(3)–Sn(4) = 18.9°.

When SnCl₂ was reacted with LiR containing the more sterically demanding –C(SiMe₃)₃¹⁵ and (2,6-Mes)₂C₆H₃ (Mes = 2,4,6-Me₃C₆H₂)¹⁶ R groups, the products were chlorine-bridged RSnCl dimers instead of the cyclotetramer structures with Sn–Sn bonds found in **2b** and **3**. It appears that those extremely bulky groups sterically block cyclooligomer formation, thereby favoring less crowded chlorine-bridged dimers with three-coordinate tin.

Reactions of selected germanium halides and organohalide derivatives with **1a** and **1b** reagents in 1:1 and 1:2 molar ratios in pentane have also been carried out. Discussion of the results is organized, according to the structures of the products, into 1:1 reactions of GeCl₄ with **1a** and of R₃GeX (R, X = CF₃, I; CH₃, Cl; C₆H₅, Cl) with **1b** and 1:2 reactions of Ph₂GeCl₂ with **1b**. The observation⁴ of a linear relationship between ¹H δ of new (Me₃Si)₃Ge–X and known (Me₃Si)₃Si–X compounds assisted initial product identification.¹⁷

Synthesis of R₃GeE(SiMe₃)₃ Derivatives. Treatment of GeCl₄ and R₃GeCl starting materials with the **1a** and **1b** reagents in pentane led mainly to single substitution reactions. Tris-(trifluoromethyl)germanium iodide reacts with **1a** and **1b** in pentane according to eq 1 giving moderate yields of **4a** and **4b**



which are thermally stable and more resistant to atmospheric exposure than the corresponding trimethylgermanium derivatives. GeCl₄ with 1 equiv of **1b** gave the monosubstituted trichlorogermanium(IV) product **5a** in 52% yield (eq 2). Unexpectedly, the product mixture also contained the linear

(12) Unsolvated M¹Si(SiMe₃)₃ reagents are more reactive than **1a** and have been used in the first successful preparation of Sn(Si(SiMe₃)₃)₂. Klinkhammer, K. W. *Chem. Eur. J.* **1997**, *3*, 1418.

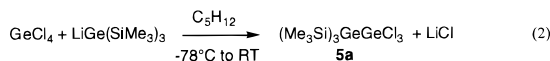
(13) Tsumuraya, T.; Batcheller, S.; Masamune, S. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 902.

(14) The carbon analysis for **2a** was consistently low, owing, we think, to silicon carbide formation during analysis.

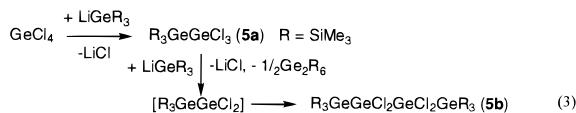
(15) Eaborn, C.; Hitchcock, P. B.; Smith, J. D.; Sözerli, S. E. *Organometallics* **1997**, *16*, 5653–5658.

(16) Simons, R. S.; Pu, L.; Olmstead, M. M.; Power, P. P. *Organometallics* **1997**, *16*, 1920–1925.

(17) For 16 characterized compounds, δ ¹H Ge–SiMe₃ = 0.974(δ ¹H Si–SiMe₃) + 0.0459 with a standard deviation of the fit of 9.39 × 10^{–3}. A linear relationship was also found for ¹³C chemical shifts. The ¹H shifts of the new compounds reported here match the calculated δ ¹H values reasonably well with the phenyl–germyl derivatives showing the greatest deviation (0.04 ppm).



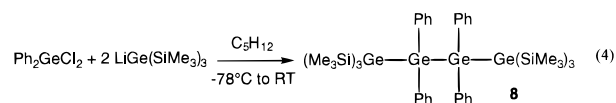
tetragermane $(\text{Me}_3\text{Si})_3\text{GeGeCl}_2\text{GeCl}_2\text{Ge}(\text{SiMe}_3)_3$, **5b**, identified by comparing its NMR spectra with published values.^{1b} Analogous $\text{R}_3\text{SiGeX}_2\text{GeX}_2\text{SiR}_3$ ($\text{R} = \text{SiMe}_3$; $\text{X} = \text{halide, alkyl, or aryl}$) products have been obtained from reactions of GeCl_4 or R_2GeCl_2 derivatives with **1a** but only in 1:2 reactions.² Since **1b** is a moderately strong reducing agent, the origin of **5b** in this reaction may be the reduction of **5a** by local excess of **1b** (eq 3). Support for this mode of formation of **5b** comes from



the presence of the NMR signals of Ge_2R_6 in the reaction mixture and the finding (vide infra) that with 2 equiv of **1b**, Ph_2GeCl_2 gives $\text{R}_3\text{GeGePh}_2\text{GePh}_2\text{GeR}_3$ as the major product (89%). In 1:1 reactions with **1b**, triorganogermanium chlorides formed $(\text{Me}_3\text{Si})_3\text{GeGeMe}_3$, **6**, and $(\text{Me}_3\text{Si})_3\text{GeGePh}_3$, **7**, which can be regarded as unsymmetrically substituted digermanes. These exhibited good thermal stability with **7** showing no apparent decomposition up to its boiling point (178 °C) in a sealed capillary. NMR spectra of **6** revealed the presence of $(\text{Me}_3\text{Si})_4\text{Ge}$ that cocrystallized with the product.

Synthesis of a Tetragermane Derivative. Reactions of GeCl_4 with 2 equiv of **1a**² or **1b**^{1b} did not produce the expected

$(\text{R}_3\text{E})_2\text{GeCl}_2$ ($\text{R} = \text{SiMe}_3$, $\text{E} = \text{Si, Ge}$) products but instead gave $\text{R}_3\text{SiGeCl}_2\text{GeCl}_2\text{SiR}_3$ and $\text{R}_3\text{GeGeCl}_2\text{GeCl}_2\text{GeR}_3$, respectively, along with other products. We have supposed that *either* disubstituted germanes, $(\text{R}_3\text{E})_2\text{GeCl}_2$, are unstable due to steric strain between the bulky R_3E groups² or that the effect of the second equivalent of **1a** or **1b**, instead of substituting for Cl, is to reduce the R_3EGeCl_3 intermediate, as proposed for the 1:1 GeCl_4 –**1b** reaction above (eq 3), eventually forming $\text{R}_3\text{EGeCl}_2\text{GeCl}_2\text{ER}_3$ in either case. In this work, the 1:2 reaction of Ph_2GeCl_2 with **1b** (eq 4) gave a high yield of the linear tetragermane, **8**, identified by its NMR spectra. This result closely parallels those of reactions carried out with **1a** earlier.



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Supporting Information Available: An X-ray crystallographic file, in CIF format, for the cyclotetrastannane **2b** is available free of charge via the Internet at <http://pubs.acs.org>.

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