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New Small-Ring Cyclogermanes: Syntheses and X-ray Crystal Structures

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Reaction of $GeCl_2$·dioxane with 2 equiv of $Li(THF)_{2.5}Ge(SiMe_3)_3$ in hexane afforded moderate yields of two cyclopolygermanes. A cyclotrigermane, $(Ge(SiMe_3)_2)_3$, was characterized by NMR spectra, elemental analyses, and an X-ray crystal structure determination. It crystallized from pentane in the $R\bar{3}c$ space group (rhombohedral) with $a = 19.294(3)$ Å, $\alpha = 31.89(1)°$, $V = 1781$ Å^3, and $Z = 2$. The Ge_3 core consisted of an equilateral triangle with a Ge−Ge distance of 2.460(1) Å, the shortest so far measured in cyclotrigermanes. The second product was tentatively identified by its NMR spectra as a cyclotetragermane, $((Me_3Si)_3GeGeCl)_4$, and this was confirmed by elemental analyses and an X-ray structure determination on the yellow crystals formed from pentane. The product was found to crystallize as a complex with two molecules of $Ge(SiMe_3)_4$ in the $F2_3$ (cubic) space group with $a = 22.7731(3)$ Å, $V = 11\,810.5$ Å^3, and $Z = 8$. The Ge_4 core consisted of a nonplanar four-membered ring (fold angle = 18.7°) disordered over three positions related by 3-fold symmetry. In the assumed ordered structure, ring Ge−Ge distances averaged 2.503 Å. When the reaction was repeated with $GeCl_2$·dioxane and 2 equiv of $Li(THF)_3Si(SiMe_3)_3$, the known disilagermirane, $(Me_3Si)_2Ge(Si(SiMe_3)_2)_2$, was isolated (66% yield) along with a small yield of the known cyclotetragermane, $((Me_3Si)_3SiGeCl)_4$. Reaction of GeI_2 with $Li(THF)_{2.5}Ge(SiMe_3)_3$ gave only traces of the cyclotrigermane.

Introduction

Compounds with three- and four-membered rings involving group 14 elements have attracted considerable interest.[1,2] Cyclotrigermanes are useful photochemical precursors for germylenes and digermenes. Bulky ligands have served to stabilize such small cyclic systems by protecting reactive centers with an organic "layer" that also prevents dimerization reactions. Steric hindrance by bulky $-Si[C(CH_3)_3]_3$ groups help stabilize a free germanyl cation.[3] In some cases, silyl and germyl anionic reagents were employed in the synthesis of cyclotrigermanes,[4] however, Masmune and others[5] obtained cyclotrigermanes by reductive cyclization of dichlorodiorganogermanes with lithium naphthalide, while Ando and co-workers[6] used Mg−$MgBr_2$ for reductive coupling. Recently, the first mixed group 14, three-membered ring compounds were reported.[7] Using a different approach, we prepared a cyclotetragermane[8] and related structures[9] incorporating $-E(SiMe_3)_3$ (E = Si, Ge) groups. As a part of a comparative study of $Ge(SiMe_3)_3$ and $Si(SiMe_3)_3$ substituents, we now report the sytheses and structures of hexakis(trimethylsilyl)cyclotrigermane and tetrachlorotetrakis(tris(trimethylsilyl)germyl)cyclotetragermane.

Experimental Section

Materials. The germanium(II) chloride−dioxane complex was prepared as described in the literature,[10] and GeI_2 was purchased from Gelest and used as received. The lithium silyl and germyl reagents $Li(THF)_3Si(SiMe_3)_3$ (**1a**) and $Li(THF)_{2.5}Ge(SiMe_3)_3$ (**1b**) were prepared according to published procedures.[11,12] Hexane and pentane were distilled just prior to use from Na/benzophenone under argon. THF and ether were distilled from $LiAlH_4$ under argon.

Procedures. All synthetic reactions were conducted using Schlenk techniques under argon. Elemental analyses were performed by Atlantic Microlabs, Norcross, GA. NMR spectra were obtained and other manipulations and characterizations were carried out as described earlier.[13] Infrared spectra were recorded as Nujol mulls between AgBr windows.

Hexakis(trimethylsilyl)cyclotrigermane, $[Ge(SiMe_3)_2]_3$ (2). A suspension of $GeCl_2$·dioxane (1755 mg, 7.58 mmol) in hexane (30 mL) was cooled to −78 °C and treated with 170 mL of a hexane solution of **1b** (7274 mg, 15.17 mmol). The orange-yellow reaction mixture was stirred at −78 °C for 9 h and then allowed to warm to ambient temperature and stirred 15 h, giving a dark brown solution with a fine gray precipitate. Hexane was removed in vacuo, and the residue was stirred with pentane (100 mL) for 1 h. The brown pentane solution obtained after filteration was concentrated to about 50 mL and held at −78 °C for 6 h, affording 1026 mg of colorless, transparent, hexagonal slab crystals. Further concentration and recooling of the filtrate to −78 °C for 6 h gave 300 mg more product for a total yield of 1326 mg (26.6% based on germanium dichloride). The mother liquor was retained for further work-up. In a sealed capillary under argon, crystals of **2** decompose at 135 °C, becoming orange, and melt at 185 °C. Anal.

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Calcd for $C_{18}H_{54}Ge_3Si_6$: C, 32.9; H, 8.28. Found: C, 32.2; H, 8.10. NMR (C_6D_6): ^1H δ 0.466; $^{13}C\{^1H\}$ δ 5.06. IR (cm^{-1}): 2700 (vw), 1910 (vw), 1845 (vw), 1320 (m), 1260 (vs), 1035 (sh), 1080 (vs), 860 (vs), 1790 (w), 520 (s), 650 (m), 590 (sh), 450 (w), 390 (m).

Tetrachlorotetrakis(tris(trimethylsilyl)germyl)cyclotetragermane Adduct with Tetrakis(trimethylsilyl)germane, $[(Me_3Si)_3GeGeCl]_4{\cdot}2Ge(SiMe_3)_4$ (3). After crystallization of **2**, the brown pentane mother liquor was further concentrated and held at −10 °C for 3 days, affording **3** as bright yellow rectangular crystals (274 mg). The remaining solution was kept at −78 °C overnight and gave an additional 124 mg of yellow crystals for a total isolated yield of 18.0% based on starting germanium dichloride (24.5% based on the remaining germanium dichloride). In a sealed capillary under argon, crystals of **3** turned red at 125 °C, decomposed at 151 °C, and melted to a brown liquid at 171 °C. Anal. Calcd for $C_{30}H_{90}Cl_2Ge_5Si_{10}$: C, 30.9; H, 7.78. Found: C, 30.76; H, 7.38. NMR (C_6D_6): ^1H NMR δ 0.569 (27 H, $(Me_3Si)_3GeGeCl$), 0.298 (18 H, $Ge(SiMe_3)_4$); $^{13}C\{^1H\}$ NMR δ 5.27 ($(Me_3Si)_3GeGeCl$), 3.44 ($Ge(SiMe_3)_4$). IR (cm^{-1}): 2700 (vw), 1850 (vw), 1720 (w), 1320 (w), 1255 (vs), 1180 (vw), 1140 (vw), 1050 (w), 985 (m), 855 (vs), 790 (s), 725 (ms), 655 (s), 645 (sh), 370 (s). The mother liquor still exhibited several NMR signals: $^1H/^{13}C$ NMR (major) δ 0.291/3.48 ($Ge(SiMe_3)_4$), 0.278/3.54 ($HGe(SiMe_3)_3$), 0.270/3.57; (minor) 0.208/1.13, 0.368/4.40, 0.385/4.90 ($Ge_2(SiMe_3)_6$), 0.436 (m).

Reaction of $GeCl_2{\cdot}$dioxane with $(THF)_3LiSi(SiMe_3)_3$. $GeCl_2{\cdot}$dioxane (734.2 mg, 3.17 mmol) and **1a** (2986.2 mg, 6.34 mmol) were allowed to react in hexane as decribed for **2**, followed by work-up affording 1191 mg (66%) of disilagermirane, $(Me_3Si)_2Ge(Si(SiMe_3)_2)_2$ (**4**). NMR (C_6D_6): ^1H NMR δ 0.423 ($Si(SiMe_3)_2$), 0.452 ($Ge(SiMe_3)_2$) (lit.[7b] δ 0.43, 0.45); $^{13}C\{^1H\}$ NMR δ 4.51 ($Si(SiMe_3)_2$), 5.26 ($Ge(SiMe_3)_2$). After **4** was separated by crystallizations (3×), the mother liquor was concentrated and held at −10 °C for 14 days, yielding a small batch of yellow crystals identified as tetrachlorotetrakis(tris(trimethylsilyl)silyl)cyclotetragermane, $((Me_3Si)_3Si)GeCl)_4$.[8] NMR (C_6D_6): ^1H NMR δ 0.531; $^{13}C\{^1H\}$ NMR δ 4.89 (lit.[8] δ 0.533, 4.85).

Reaction of GeI_2 with $(THF)_{2.5}LiGe(SiMe_3)_3$. A hexane (50 mL) suspension of GeI_2 (1322.6 mg, 4.05 mmol) and 150 mL of a hexane solution of **1b** (3885 mg, 8.1 mmol) were combined and worked up in pentane as described for **2**. The resulting red-brown solution, held at −10 °C for 20 h, afforded 147.4 mg of a crude product mixture. NMR (C_6D_6) ^1H δ 0.461 (minor, **2**), 0.285 (trace, $HGe(SiMe_3)_3$), 0.296 (major, $Ge(SiMe_3)_4$), 0.391 (major, $Ge_2(SiMe_3)_6$). Repeating the GeI_2 reaction in diethyl ether gave comparable results with only a small amount of the cyclotrigermane product.

X-ray Structure Determination of 2. A colorless block having approximate dimensions of 0.25 × 0.50 × 0.60 mm was cut from a large hexagonal slab and mounted in a random orientation on a Nicolet R3m/V automatic diffractometer. The sample was held in a stream of dry nitrogen gas at −50 °C, and 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 symmetry was determined to be $\bar{3}m$, and from systematic absences, the space group was shown to be $R3c$ or $R\bar{3}c$. 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 every 2 h or every 100 data collected, and these showed no significant change. During data reduction, Lorentz and polarization corrections were applied, as well as a semiempirical absorption correction based on ψ scans of 10 reflections having χ values between 70 and 90°.

Table 1. Data Collection and Processing Parameters for **2** and **3**

	2	**3**
empirical formula	$C_{18}H_{54}Si_6Ge_3$	$C_{30}H_{90}Cl_2Ge_5Si_{10}$
fw	657.03	1165.77
space group	$R\bar{3}c$ (rhombohedral)	$F2_3$
a, Å	19.294(3)	$a = b = c = 22.7731(3)$
α, deg	31.89(1)	$\alpha = \beta = \gamma = 90$
V, Å^3	1781	11810.5(3)
Z	2	8
ρ_{calc}, g cm^{-3}	1.23	1.311
μ, cm^{-1}	26.9	28.28
T, °C	−50	−100(2)
λ, Å (Mo Kα)	0.710 73	0.710 73
collection range, deg	$4 < 2\theta < 50$	$1.55 < 2\theta < 24.95$
no. of total data collected	1262	25 664
no. of indep data, $I > 3\sigma(I)$	818	1759 ($R_{int} = 0.0336$)
no. of total variables	43	83
R^a	0.026	R1 = 0.0849 ($I > 2\theta(I) = 1561$)
$R_w{}^b$	0.027	wR2^c = 0.2208

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum_w(|F_o| - |F_c|^2/\sum_w|F_o|^2]^{1/2}$, $w = \sigma(F)^{-2}$. ^{c} $w = [s^2(F_o^2) + (AP)^2 + (BP)^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$, $A = 0.1344$, $B = 187.6490$.

Since the unitary structure factors displayed centric statistics, space group $R\bar{3}c$ was chosen from the outset. The structure was solved by the SHELXTL direct-methods program which revealed the positions of all of the atoms in the asymmetric unit, consisting of $^1/_6$ of a molecule situated about a crystallographic 3_2 site. In Schönflies notation, the molecule possesses D_3 symmetry. 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, with a single variable isotropic temperature factor for all of them. 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 0.25 e/Å^3. All calculations were made using Nicolet's SHELXTL PLUS (1987) series of crystallographic programs.

X-ray Structure Determination of 3. A crystal of **3** was attached to a glass fiber and mounted on the Siemens SMART system for a data collection at 173(2) K. An initial set of cell constants was calculated from reflections harvested from three sets of 20 frames. These initial sets of frames are oriented such that orthogonal wedges of reciprocal space were surveyed. This produces orientation matrices determined from 211 reflections. Final cell constants were calculated from a set of 4306 strong reflections from the actual data collection. Table 1 contains crystal and refinement information. The space group $F2_3$ was determined based on systematic absences and intensity statistics. A successful direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Several full-matrix least-squares/difference Fourier cycles were performed, which located the remainder of the non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters unless stated otherwise. All hydrogen atoms were placed in ideal positions and refined as riding atoms with group isotropic displacement parameters. Two molecules of $Ge(SiMe_3)_4$ were found in addition to the cyclotetragermane. The central Ge_4 core of the complex is disordered over three positions related by 3-fold symmetry. (Ge(1) is pulled off the crystallographic 3_1 axis.) It is this statistical disorder which likely results in the higher than expected residuals ($R_{int} = 0.0336$). The largest difference feature was located in the vicinity of Si(1). A second data set collected from a different sample did not yield a better result (R1 for that refinement was 10.36%). Because of the disorder, the fold angle and some bond distances and angles were determined by importing the atomic coordinates of the skeleton atoms of the assumed ordered structure of **3** into the CAChe program and measuring them graphically. Data collection and structure solution were conducted at the X-Ray Crystallographic Laboratory, 160 Kolthoff Hall, Chemistry Department, The University of Minnesota. All calculations were preformed using SGI INDY R4400-SC or Pentium computers using the SHELXTL V5.0 suite of programs.

Results and Discussion

Consideration of the size and electronic properties suggests that $-Si(SiMe_3)_3$ and $-Ge(Me_3)_3$ groups should exhibit similar effects on compounds in which they are substituents. The slightly larger Ge atom (radius of 122 vs 118 pm for Si[14]) should lead to a smaller cone angle[15] for $M-Ge(SiMe_3)_3$ compared to

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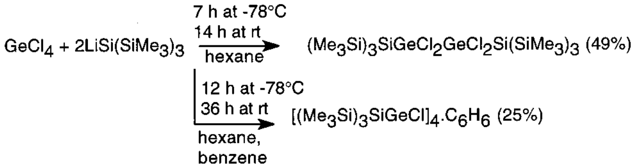
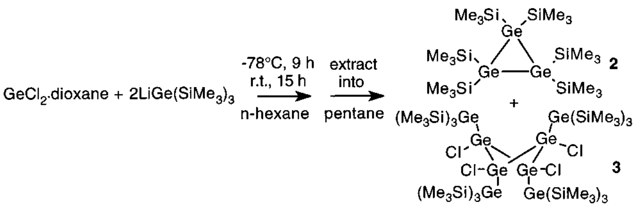
Scheme 1

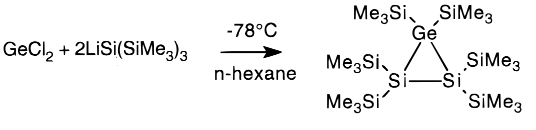


Scheme 2



$M{-}Si(SiMe_3)_3$ and perhaps to less steric strain for the former in crowded molecules. In $((Me_3Si)_3E)_2SnCl_2$ (E = Si, Ge), however, the Si−Sn−Si and Ge−Sn−Ge angles and the $-E(SiMe_3)_3$ cone angles are essentially the same.[8,16] The electronegativity of Ge slightly exceeds that of Si, indicative of a small difference in the inductive effects of the $E(SiMe_3)_3$ substituents. The Taft inductivity parameter, σ^*, of the $SiMe_3$ group is reported as −0.95,[17] consistent with moderate to strong electropositive behavior. This suggests that both $E(SiMe_3)_3$ groups should be notably electropositive, and theoretical studies indicate that this quality causes a marked relief of strain in small rings of group 14 atoms with $E(SiMe_3)_3$ substituents.[18] Both $LiE(SiMe_3)_3$ reagents behave as strong reducing agents. Often, substituting $LiGe(SiMe_3)_3$ for $LiSi(SiMe_3)_3$ causes no change in the course of reactions, but in some instances differences do occur, such as in the reaction shown in Scheme 1. Using **1a**, both digermane and cyclotetragermane products were isolated, as shown in Scheme 1; however, **1b** gave only the acyclic tetragermane $(Me_3Si)_3GeGeCl_2GeCl_2Ge(SiMe_3)_3$, analogous to the digermane in Scheme 1, despite our efforts to identify the expected tetragermylcyclotetragermane.[8]

The recent synthesis of the disilagermirane (**4**) shown in eq 1 represented an interesting case in which to compare the behavior of the lithium silyl and germyl reagents.[7b] The report by Heine and Stalke led us to the expectation of a cyclotrigermane product in an analogous reaction using **1b**. When that reaction was carried out under literature conditions, except that $GeCl_2{\cdot}dioxane$ was employed, the anticipated cyclotrigermane was isolated in 26% yield (Scheme 2). Further crystallization from the pentane extract of the reaction mixture residue also afforded the cyclotetragermane, **3**, described below. The formation of **2** in the reaction shown in Scheme 2, thus, parallels the previous results,[7b] but the simultaneous formation of a cyclotetragermane was not observed earlier. The mechanism of formation of the disilagermirane suggested by those investigators seems equally applicable to the formation of **2** (see Scheme 3). Although the yield of **2** was moderately low, partly owing to the simultaneous formation of **3**, the synthetic approach is somewhat cleaner than the reductive coupling reactions employing lithium napthalide or $Mg{-}MgBr_2$ previously used to prepare cyclotrimetallanes, $(R_2M)_3$ (M = Si, Ge, and Sn).[5−7] In an interesting variation on such reactions, silyl-substituted cyclotrigermenes were obtained by treating $GeCl_2{\cdot}dioxane$ with $t\text{-}Bu_3GeLi$ or $t\text{-}Bu_3SiNa$ in THF.[3]



4

(1)

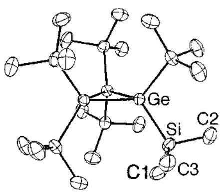
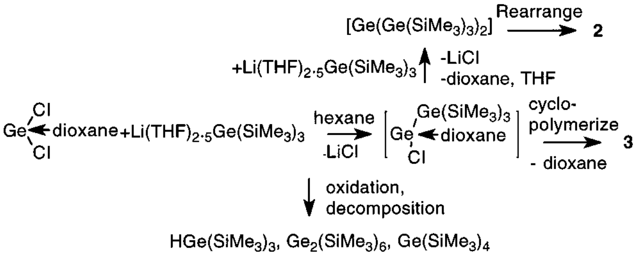


Figure 1. View of the molecular structure of **2** showing the labeling scheme. Hydrogens are omitted for clarity.

Scheme 3



The cyclotrigermane, **2**, crystallizes as very hygroscopic, transparent, hexagonal slabs that are stable in pentane solution for months but decompose to a liquid mixture within 1 week, even under argon at −10 °C. During the recording of its IR spectrum, **2** reacted with the AgBr windows. From an X-ray structure determination, **2** was found to be isomorphous with **4**, crystallizing in the $R\bar{3}c$ space group (Table 1). Each Ge in the symmetrical ring exhibits approximately tetrahedral geometry in the exocyclic bond angles (Figure 1). The Ge−Ge distance, 2.460(1) Å, is the shortest yet reported for cyclotrigermanes, except for the computed value of 2.45 Å for the parent, $(GeH_2)_3$.[19] Since Ge−Ge bond lengths are considered to increase with increasing steric congestion around the Ge_3 ring,[1f] the short Ge−Ge bonds suggest that the Ge coordination sphere in **2** is relatively uncrowded, probably owing to the longer Ge−Si bonds (2.388 Å, Table 2) compared to the Ge−C links (1.98−2.06 Å)[1f] in other structurally characterized cyclotrigermanes. The fact that the Ge−Si−C angles average close to the tetrahedral value (Table 2) is also consistent with minimal steric crowding around Ge in **2**.

As noted above, the investigators who prepared **4** from $GeCl_2$ and **1a** (eq 1) reported no other Ge-bearing products from the reaction.[7b] Unidentified NMR peaks in the product mixture of our similar reaction of $GeCl_2{\cdot}dioxane$ and **1b** led us to carry out further crystallizations from the concentrated pentane extract, which afforded a moderate yield of bright yellow crystals. The chemical shifts of the yellow compound, ^1H NMR δ 0.569 and ^{13}C NMR δ 5.27, supported a tentative identification of this product as a cyclotetragermane with $Ge(SiMe_3)_3$ and Cl substituents on each ring Ge.[20] Its identity was confirmed by an X-ray structure determination that showed a disordered $[(Me_3Si)_3GeGeCl]_4$ molecule accompanied in the lattice by two molecules of $Ge(SiMe_3)_4$ (Table 1). The Ge_4 core in **3** is

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[20] On the basis of NMR shifts for its $Si(SiMe_3)_3$ counterpart (Scheme 1), the $\Delta\delta$ relationship found for structurally characterized $Si(SiMe_3)_3$ and $Ge(SiMe_3)_3$ derivatives (ref 9b predicted ^1H NMR δ 0.563 ± 0.007 and ^{13}C NMR δ 5.41 ± 0.22 for **3**).

Table 2. Selected Bond Lengths and Angles for **2**

Bond Lengths (Å)			
Ge−Ge′	2.460(1)	Si−C(1)	1.874(4)
Ge−Si	2.388(4)	Si−C(2)	1.882(5)
Si−C(3)	1.879(4)		
Bond Angles (deg)			
Si−Ge−Ge′	120.7(1)	Si−Ge−Ge″	121.9(1)
Ge′−Ge−Ge″	60.0	Si−Ge−Si′	106.3(1)
Ge−Si−C(1)	115.7(3)	Ge−Si−C(2)	109.7(4)
C(1)−Si−C(2)	104.8(4)	Ge−Si−C(3)	107.8(4)
C(1)−Si−C(3)	110.3(5)	C(2)−Si−C(3)	108.3(2)
Torsion Angles (deg)			
Ge′−Ge−Si−C1	60.8	Si′−Ge−Si−C3	81.3
Ge′−Ge−Si−C2	179.1	Ge″−Ge′−Ge−Si	−111.5
Ge′−Ge−Si−C3	−63.2	Ge″−Ge′−Ge−Ge	0.0
Ge″−Ge−Si−C1	−10.8	Ge″−Ge′−Ge−Si′	109.6
Ge″−Ge−Si−C2	107.5	Ge′−Ge″−Ge−Si	109.6
Ge″−Ge−Si−C3	−134.8	Ge′−Ge″−Ge−Si′	−111.5
Si′−Ge−Si−C1	−154.8	Si′−Ge−Si−C2	−36.5

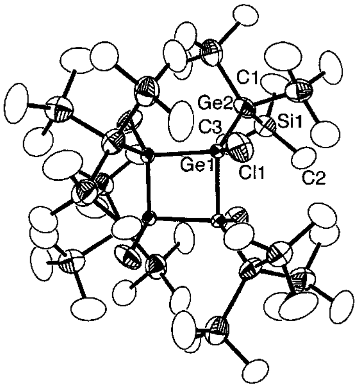

Figure 2. View of the (assumed ordered) molecular structure of **3** showing the labeling scheme. There are two molecules of $Ge(SiMe_3)_4$ that are not shown. Hydrogens are omitted for clarity.

Table 3. Selected Bond Lengths and Angles for **3**

Bond Lengths (Å)			
Ge(1)−Cl(1)	2.367(5)	Ge(1)−Ge(2)	2.589(3)
Ge(2)−Si(1)	2.404(4)	Ge(3)−Si(2)	2.392(7)
Ge(4)−Si(3)	2.378(6)	Si(1)−C(1)	1.92(2)
Si(1)−C(2)	1.881(14)	Si(1)−C(3)	1.870(14)
Bond Angles (deg)			
Si(1)−Ge(2)−Ge(1)	94.15(11)	Cl(1)−Ge(1)−Ge(2)	119.29(11)
C(3)−Si(1)−C(2)	104.5(8)	C(3)−Si(1)−C(1)	112.6(8)
C(2)−Si(1)−C(1)	114.7(8)	C(3)−Si(1)−Ge(2)	107.0(5)
C(2)−Si(1)−Ge(2)	110.5(5)	C(1)−Si(1)−Ge(2)	107.3(6)
C(5)−Si(3)−Ge(4)	110.6(5)	C(4)−Si(2)−Ge(3)	109.9(6)
Torsion Angles (deg)			
Cl(1)−Ge(1)−Ge(2)−Si(1)	17.61(14)		
Ge(1)−Ge(2)−Si(1)−C(3)	167.7(6)		
Ge(1)−Ge(2)−Si(1)−C(2)	54.5(6)		

disordered over three positions related by 3-fold symmetry (i.e., Ge(1) is pulled off the crystallographic 3_1 axis). This statistical disorder is the probable reason for the higher than expected residuals ($R_{int} = 0.0336$). A second data set collected from a different sample did not yield an improved result.

Figure 2 shows an ORTEP view of the assumed ordered structure of **3**. The structure of **3** closely resembles that of its tris(trimethylsilyl)silyl counterpart, $[(Me_3Si)_3SiGeCl]_4$, **5**.[8] The ring in **3** has Ge−Ge bond lengths (2.501 and 2.505 Å, Table 3) that average slightly shorter than those in **5** (2.509 and 2.558 Å), indicative of less steric crowding around the Ge_4 core in **3**. This difference is likely due at least in part to the greater Ge−Ge(exo) distance (2.589 Å) compared to Ge−Si (average 2.460 Å) in **5**, moving the bulky substituents further from the ring. The mean Ge−Ge−Si angle in **3** (111.4°) is nearly identical to the corresponding (Ge−Si−Si) angle in **5**, indicating that the small distortion of the $Ge(SiMe_3)_3$ and $Si(SiMe_3)_3$ substituents from the tetrahedral ideal is similar in the two molecules. The "fold" angles in **3** and **5** are 18.7° and 17.1°, respectively. The next closest analogue of **3**, $(t\text{-}BuGeCl)_4$, has shorter Ge−Ge bonds (average 2.463 Å) and a smaller fold angle (14.6°).[2b] Qualitatively, at least, there appears to be some lengthening of ring Ge−Ge distances with increasing steric bulk of the substituents in the Ge_4 rings similar to the behavior described for Ge_3 rings.[1f]

The formation of **3** in the reaction of $GeCl_2$·dioxane and **1b** led us to repeat the literature reaction[7b] using $GeCl_2$·dioxane, instead of $GeCl_2$, with 2 equiv of **1a** to determine whether any **5** formed. Besides a 66% (lit.[7b] 48%) yield of the reported disilagermirane (^{1}H NMR δ 0.432 ($Si(SiMe_3)_2$), 0.452 ($Ge(SiMe_3)_2$), lit.[7b] δ 0.43, 0.45), we isolated a small yield of yellow crystals identified by their NMR spectra (^{1}H NMR 0.531, ^{13}C NMR δ 4.89, lit.[8] δ 0.533, 4.85, respectively) as **5**. Since the reaction conditions closely followed those in the literature,[7b] it appears that the presence of dioxane may influence the course of the reaction, favoring the cyclotetragermane product. If so, it may have also favored the formation of **3** in the reaction in Scheme 2.

The variety of products identified from the reaction of $GeCl_2$·dioxane and **1b** suggests that multiple pathways are active (Scheme 3). Formation of **3** could reasonably be the result of monosubstitution of $GeCl_2$·dioxane by $Ge(SiMe_3)_3$ followed by cyclopolymerization and loss of dioxane. The origin of **2** may involve the formation of a disubstituted germylene intermediate that rearranges via $SiMe_3$ migration, perhaps due to steric strain, to yield **2**. We did not detect the putative germylene or any oligomer of it, although there were ^{1}H NMR peaks in the mother liquor that were not assigned. The presence of resonances for $HGe(SiMe_3)_3$, $Ge_2(SiMe_3)_6$, and $Ge(SiMe_3)_4$ is common for reactions where **1b** is oxidized, for example, by $PbCl_2$.[21]

In summary, the reaction of $GeCl_2$·dioxane with **1b** gives a cyclotrigermane, **2**, probably originating from rearrangement of a sterically crowded $Ge(GeR_3)_2$ intermediate, paralleling the behavior of $GeCl_2$ with **1a**, the SiR_3 counterpart of **1b**. Simultaneous formation of another product, the cyclotetragermane, **3**, appears to be associated with the use of $GeCl_2$·dioxane instead of $GeCl_2$ since **5**, the SiR_3 counterpart of **3**, was present when the literature **1a** reaction was repeated using $GeCl_2$·dioxane but not when the reaction was originally reported.

To study the influence of the halogen in GeX_2, reactions of GeI_2 with 2 equiv of **1b** in hexane and in ether were carried out. Only traces of **2** were found along with the oxidation products of **1b**. Reactions of $SnCl_2$ with **1a** and **1b** are currently being investigated.

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Supporting Information Available: Tables listing full data collection and processing parameters, atomic coordinates, bond distances and angles, anisotropic displacement parameters and H atom coordinates and ORTEP and packing diagrams for **2** and **3** (28 pages). Ordering information is given on any current masthead page. Observed and calculated structure factors are available from the corresponding authors.

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