

Preparation and Structural Characterization of New Derivatives of Digermene Bearing Tris(trimethylsilyl)silyl Substituents

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The reaction of GeCl_4 with 2 equiv of $(\text{THF})_3\text{LiSi}(\text{SiMe}_3)_3$ affords the unusual digermene derivative $[(\text{Me}_3\text{Si})_3\text{SiGeCl}_2]_2$ instead of the expected disubstituted monogermene dichloride. In addition to characterization by elemental analyses and NMR spectra (^1H , ^{13}C , and ^{29}Si), the molecular formula of the digermene was determined by field desorption mass spectra, which indicated the presence of a Ge-Ge bond in the structure. An X-ray crystal structure determination revealed extensive disorder in the solid-state arrangement; the structure of the digermanium core was determined by holding the geometry of the $\text{Si}(\text{Si}(\text{CH}_3)_3)_3$ groups fixed. Crystals of $[(\text{Me}_3\text{Si})_3\text{SiGeCl}_2]_2$ were cubic, $\text{Pa}\bar{3}$, with $a = 16.103(2) \text{ \AA}$, $V = 4176 \text{ \AA}^3$, and $Z = 4$. Also prepared were two organo derivatives $[(\text{Me}_3\text{Si})_3\text{SeGeR}_2]_2$ ($\text{R} = \text{CH}_3, \text{C}_6\text{H}_5$) that, according to their NMR spectra, appear to have the same digermene structure. All the digermene products are unreactive toward atmospheric moisture.

Introduction

The effects of the very bulky tris(trimethylsilyl)silyl group on the properties of main-group compounds have been only sparingly investigated.^{1,2} Indications of increased thermal stability in $[(\text{Me}_3\text{Si})_3\text{Si}]_2\text{M}$ ($\text{M} = \text{Zn}, \text{Cd}, \text{Hg}$) compounds, compared to analogous trimethylsilyl derivatives,³ offered some promise of similar results with main-group metals and metalloids. Our interest in the potential of bulky substituents to stabilize unusual structures, such as the recently reported digermene $\text{Ar}_2\text{Ge}=\text{GeAr}_2$, where $\text{Ar} = 2,6$ -diethylphenyl,⁴ led us to prepare several tin(IV) derivatives bearing one or two $(\text{Me}_3\text{Si})_3\text{Si}$ substituents.² A structure determination on $[(\text{Me}_3\text{Si})_3\text{Si}]_2\text{SnCl}_2$ revealed a significant distortion of the tetrahedral geometry around tin involving a Si-Sn-Si bond angle of exceptional size (142°), suggesting that the bulk of the $\text{Si}(\text{SiMe}_3)_3$ substituent is sufficient to cause pronounced steric strain even with a central atom as large as tin. Molloy and co-workers⁵ have also recently reported that the presence of two tris(trimethylsilyl)methyl, $(\text{Me}_3\text{Si})_3\text{C}$, substituents on tin also will cause severe steric crowding. In order to further gauge the effect of such substitution, the synthesis of the germanium derivative $[(\text{Me}_3\text{Si})_3\text{Si}]_2\text{GeCl}_2$, where the strain should be greater than in the tin derivative, was attempted. We wish to report here the results of that investigation.

Experimental Section

Materials. Dimethylgermanium dichloride was obtained from Strem products, while germanium tetrachloride and diphenylgermanium dichloride came from Alfa. After their purity was checked by using ^1H NMR spectroscopy, all germanium compounds were degassed at -196°C and stored under argon. The lithium silyl $(\text{THF})_3\text{LiSi}(\text{SiMe}_3)_3$ was prepared according to the published procedure⁶ with the minor modification of using halide-free methyl lithium.

Procedures. All manipulations were conducted by using Schlenk techniques⁷ under an atmosphere of argon unless otherwise noted. Hygroscopic solids were handled in a Vacuum Atmospheres glovebox under dry nitrogen. Diethyl ether and tetrahydrofuran (THF) were distilled from LiAlH_4 under dry nitrogen. Benzene was distilled from CaH_2 ; pentane and hexane were distilled off sodium just before use. If not used immediately, solvents were degassed and stored under argon.

Elemental analyses were performed by Atlantic Microlabs and by Galbraith Laboratories. NMR spectra were obtained by using a General Electric QE-300 spectrometer, except for ^{29}Si spectra which were ob-

Table I. Comparison of Parent Ion Isotopic Abundances with Theoretical Values for $\text{C}_{18}\text{H}_{54}\text{Cl}_4\text{Si}_8\text{Ge}_2$ (I)

mass	% abundance ^a	theory for I	mass	% abundance ^a	theory for I
774 ^b		4	782	48	100
775	10	3	783	67	63
776	40	18	784	35	86
777	10	11	785	45	45
778	45	47	786	30	48
779	40	31	787	20	20
780	100	81	788	22	16
781	47	56	790 ^c	12	3

^a From plot of spectrum. Estimated error $\pm 5\%$.
^b $^{12}\text{C}_{18}\text{H}_{54}\text{Cl}_4\text{Si}_8\text{Ge}_2$. ^c $^{13}\text{C}_{18}\text{H}_{54}\text{Cl}_4\text{Si}_8\text{Ge}_2$.

tained at 59.6 MHz in decoupled mode on a General Electric/Nicolet NT-300 widebore instrument equipped with a Libra data station based on a Macintosh II computer and an array processor. Mass spectra were obtained by using a JEOL HX110HF double-focusing mass spectrometer in the field desorption mode. The cathode voltage was held at 1 kV, and the 10- μm silicon emitter was heated and held at 30 mA.

1,1,2,2-Tetrachloro-1,2-bis((trimethylsilyl)silyl)digermene, $[(\text{Me}_3\text{Si})_3\text{SiGeCl}_2]_2$ (I). To a cold (-78°C) hexane solution (100 mL) of $(\text{THF})_3\text{LiSi}(\text{Si}(\text{CH}_3)_3)_3$ (2756.1 mg, 5.85 mmol) was added dropwise a solution of GeCl_4 (627.2 mg, 2.925 mmol) in 30 mL of hexane while vigorous stirring was maintained. The reaction mixture was stirred for 7 h at -78°C , then allowed to warm to ambient temperature, and stirred for another 14 h. Hexane was then removed in vacuo, and the residue was stirred with 50 mL of dry benzene for 2 h. The solution was then filtered, the benzene was removed from the filtrate in vacuo, and the residue was extracted with pentane ($2 \times 25 \text{ mL}$). After concentration and storage overnight near 0°C , the pentane solution afforded clear, colorless octahedral crystals. The crystals were separated by filtration, washed twice with small volumes of pentane, and dried in vacuo (1122.9 mg, 49%); mp 195°C dec. Anal. Calcd for $\text{C}_{18}\text{H}_{54}\text{Cl}_4\text{Si}_8\text{Ge}_2$: C, 27.6; H, 6.96; Cl, 18.1. Found: C, 27.7; H, 7.00; Cl, 18.1. NMR (C_6D_6): ^1H δ 0.42; ^{13}C δ 2.61; ^{29}Si δ -7.36 [$-\text{Si}(\text{SiMe}_3)_3$], -92.5 [$-\text{Si}(\text{SiMe}_3)_3$]. IR (cm^{-1}): 2600 (m), 1935 (w), 1870 (w), 1400 (sh), 1310 (m), 1235 (vs), 820 (br, vs), 745 (m), 685 (s), 665 (m), 615 (s), 470 (w), 445 (m), 415 (m), 370 (vs), 360 (vs). Mass spectra of I in CH_2Cl_2 solution exhibited a parent ion isotopic envelope with peaks observed from m/e 774 to 790, resembling that expected for the formula $\text{C}_{18}\text{H}_{54}\text{Cl}_4\text{Ge}_2\text{Si}_8$ (Table I). Spectral parameters were very sensitive to instrument conditions, and samples held in CH_2Cl_2 solution longer than 30 min showed evidence of decomposition.

1,1,2,2-Tetramethyl-1,2-bis((trimethylsilyl)silyl)digermene, $[(\text{Me}_3\text{Si})_3\text{SiGe}(\text{CH}_3)_2]_2$ (II). The procedure described for I was employed by starting with $(\text{CH}_3)_2\text{GeCl}_2$ (634.0 mg, 3.65 mmol) and $(\text{THF})_3\text{LiSi}(\text{Si}(\text{CH}_3)_3)_3$ (3446.0 mg, 7.30 mmol) in hexane. The product obtained was very soluble in pentane, so crystallization was carried out in a benzene/ethanol mixture (1:1 by volume) at approximately 0°C for 48 h. The colorless platelike crystals were washed with ethanol and dried in vacuo (1020 mg, 40%); mp 195°C (sharp). Anal. Calcd for $\text{C}_{22}\text{H}_{66}\text{Ge}_2\text{Si}_8$: C, 37.7; H, 9.49. Found: C, 38.0; H, 9.41. NMR (C_6D_6): ^1H δ 0.35 [$-\text{Si}(\text{SiMe}_3)_3$], 0.74 [Ge-Me]; ^{13}C δ 4.05 [$-\text{Si}(\text{SiMe}_3)_3$], 5.93 [Ge-Me]; ^{29}Si δ 0.50 [$-\text{Si}(\text{SiMe}_3)_3$], -99.3 [$-\text{Si}(\text{SiMe}_3)_3$]. IR (Nujol, cm^{-1}): 2590 (m), 1920 (w), 1860 (w), 1305 (m),

- Arif, A. M.; Cowley, A. H.; Elkins, T. M. *J. Organomet. Chem.* **1987**, 325, C11.
- Mallela, S. P.; Geanangel, R. A. *Inorg. Chem.* **1990**, 29, 3525.
- Arnold, J.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *Inorg. Chem.* **1987**, 26, 2106.
- (a) Snow, J. T.; Murkami, S.; Masamune, S.; Williams, D. J. *Tetrahedron Lett.* **1984**, 25, 4191. (b) Masamune, S.; Hanzawa, Y.; Williams, D. J. *J. Am. Chem. Soc.* **1982**, 104, 6136.
- Brown, P.; Mahon, M. F.; Molloy, K. C. *J. Chem. Soc., Dalton Trans.* **1990**, 2643.
- Gutekunst, G.; Brook, A. G. *J. Organomet. Chem.* **1982**, 225, 1.
- Shriver, D. F.; Drezdon, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley: New York, 1986.

Table II. Crystallographic Data for $[(\text{C}_6\text{H}_5)_3\text{Si}]_3\text{SiGeCl}_2$ (I)

$\text{C}_{18}\text{H}_{54}\text{Cl}_4\text{Si}_8\text{Ge}_2$	$P\bar{a}3$ (cubic)
fw = 782.42	$T = 22^\circ\text{C}$
$a = 16.103$ (2) Å	$\lambda = 0.71073$ Å
$V = 4176$ Å ³	$\rho = 1.24$ g cm ⁻³
$Z = 4$	$\mu = 19.1$ cm ⁻¹
$R = \frac{\sum F_o - F_c }{\sum F_o } = 0.073$	$R_w = \frac{[\sum w(F_o - F_c)^2 / \sum w F_o ^2]^{1/2}}{\sum w F_o ^2} = 0.035$

1225 (vs), 820 (br, vs), 765 (sh), 670 (s), 610 (s), 560 (s), 545 (s), 450 (m), 440 (m), 415 (m), (2870 (vb, m) as neat solid).

1,1,2,2-Tetraphenyl-1,2-bis(trimethylsilyl)silyl digermane, $[(\text{Me}_3\text{Si})_3\text{SiGe}(\text{C}_6\text{H}_5)_2]_2$ (III). The procedure described for I was repeated with $(\text{C}_6\text{H}_5)_2\text{GeCl}_2$ (1071.3 mg, 3.60 mmol) and $(\text{THF})_3\text{LiSi}(\text{Si}(\text{CH}_3)_3)_3$ (3389.6 mg, 7.20 mmol) in diethyl ether. The solvent was removed in vacuo, and the residue was extracted with pentane (50 mL). After the pentane was stripped off, the solid obtained was dissolved in a benzene/ethanol mixture (1:1), and the product crystallized at approximately 0°C after 48 h. After filtration, the crystals were washed with ethanol and dried under dynamic vacuum (1220 mg, 32.2%); mp 340°C dec. Anal. Calcd for $\text{C}_{42}\text{H}_{74}\text{Ge}_2\text{Si}_8$: C, 53.2; H, 7.86. Found: C, 52.8; H, 7.79. NMR (C_6D_6): ^1H δ 0.22 [-Si(SiMe₃)₃], 7.11 (m), 7.70 (d) [Ge-Ph]; ^{13}C δ 3.33 [-Si(SiMe₃)₃], 128.7, 131.9, 136.5, 136.7 [Ge-Ph]; ^{29}Si δ 0.10 [-Si(SiMe₃)₃], -125.8 [-Si(SiMe₃)₃]. IR (Nujol, cm⁻¹): 2660 (m), 1930 (w), 1865 (w), 1395 (sh), 1305 (m), 1240 (vs), 1080 (m), 1020 (m), 803 (br, vs), 745 (m), 685 (s), 620 (s), 465 (sh), 455 (s).

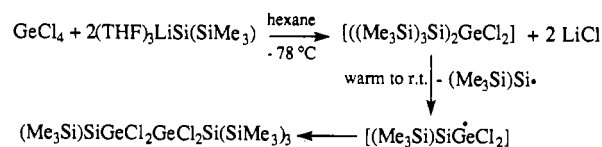
X-ray Structure Determination of I. A clear colorless octahedron having approximate dimensions $0.3 \times 0.3 \times 0.3$ mm was mounted in a random orientation on a Nicolet R3m/V automated diffractometer. The radiation used was Mo K α monochromatized by a highly ordered graphite crystal. Final cell constants, as well as other information pertinent to data collection and refinement, are listed in Table II. The Laue symmetry was determined to be $m\bar{3}$, and from the systematic absences noted the space group was shown unambiguously to be $P\bar{a}3$. Intensities were measured by 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 variation. 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° .

Since there are only four molecules in the unit cell, each one must lie about a $\bar{3}$ site. This implies extensive disorder and explains the relative paucity of observed data from such a large sample crystal. The structure was solved by interpretation of the Patterson map, which revealed the position of the Ge atom. Approximate positions for the remaining non-hydrogen atoms were located in subsequent difference Fourier syntheses. Technically, the asymmetric unit consists of one-sixth molecule situated about a $\bar{3}$ site, but due to the extreme nature of the disorder involved, it was not possible to refine the trimethylsilyl atoms individually. And since there are several different orientations of these groups to the common silicon (Si(1)) it was decided to refine three separate trimethylsilyl rigid bodies, each having one-third occupancy. Only the Ge and Si atoms were refined anisotropically, with all remaining atoms being treated isotropically. Hydrogen atoms were added in ideal calculated positions as part of the rigid bodies. Several slightly different orientations of the chlorine positions were found, and all were refined with partial occupancies determined by initially fixing a common temperature factor. In the final refinement the population factors used for Cl(1), Cl(2), Cl(1)', Cl(2)', and Cl(3)' were 0.17, 0.16, 0.14, 0.10, and 0.09, respectively. The total population of 0.66 is as expected for two atoms in general positions involved in a 3-fold disorder. After all shift/esd ratios were less than 0.2, convergence was reached at the agreement factors listed in Table II. 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 0.3 e/Å. All calculations were made by using Nicolet's SHELXTL PLUS (1987) series of crystallographic programs.

Results and Discussion

The pronounced steric bulk of the tris(trimethylsilyl)silyl group was made evident by the recently reported structure of $[(\text{Me}_3\text{Si})_3\text{Si}]_2\text{SnCl}_2$, which exhibits an unusually large Si-Sn-Si bond angle of 142° .² The considerable distortion of the molecule was attributed to steric interaction between the two $(\text{Me}_3\text{Si})_3\text{Si}$ groups although little perturbation was observed of the Si-C frameworks of the silyl substituents in the context of structures such as $(\text{Me}_3\text{Si})_3\text{Si}_2\text{Hg}$ where the $(\text{Me}_3\text{Si})_3\text{Si}$ should be unhindered. The steric requirements of the group are such that, as

Scheme I

**Table III.** Selected Bond Lengths (Å) and Angles (deg) in the Structure of I

Ge-Cl(1)	2.288 (28)	Ge-Cl(2)	2.158 (30)
Ge-Si(1)	2.514 (44)	Ge-Ge'	2.421 (13)
Si(1)-Si(2)	2.619 (40)	Si(1)-Si(3)	2.028 (39)
Si(1)-Si(4)	2.450 (52)		
Cl(1)-Ge-Cl(2)	99.7 (14)	Cl(1)-Ge-Si(1)	112.7 (12)
Cl(2)-Ge-Si(1)	112.5 (16)	Cl(1)-Ge-Ge'	103.9 (10)
Cl(2)-Ge-Ge'	103.4 (10)	Si(1)-Ge-Ge'	122.1 (9)
Ge-Si(1)-Si(2)	89.0 (15)	Ge-Si(1)-Si(3)	120.1 (20)
Si(2)-Si(1)-Si(3)	107.7 (16)	Ge-Si(1)-Si(4)	106.4 (13)
Si(2)-Si(1)-Si(4)	104.9 (14)	Si(3)-Si(1)-Si(4)	122.5 (23)

yet, no examples of structures with more than two such groups attached to a single atom have been reported and the majority of those with two groups are linear MR_2 types, i.e., where $\text{M} = \text{Zn}, \text{Cd}, \text{Hg}$,¹ where unfavorable steric interactions are obviated.

In view of the large degree of strain suggested by the structure of the tin derivative, it was of interest to determine whether the analogous germanium analogue could be prepared. Since the covalent radius of Ge is about 13% smaller than that of Sn,⁸ the steric crowding around the central atom should be greater for germanium, perhaps leading to even more severe distortion of the structure. The synthesis of $[(\text{Me}_3\text{Si})_3\text{Si}]_2\text{GeCl}_2$ was attempted according to the first step of Scheme I, but the reaction did not proceed as expected instead, giving a white solid (I) with elemental analyses corresponding to the empirical formula $(\text{Me}_3\text{Si})_3\text{SiGeCl}_2$. The implication of a trivalent germanium led us to determine the molecular formula of the product using mass spectroscopy. Neither conventional (heated solids probe) nor FAB techniques gave satisfactory mass spectra; better results were obtained by using the field desorption technique, but spectral characteristics were found to be strongly dependent on both the instrumental parameters and the length of time the sample was held in CH_2Cl_2 solution before spectra were obtained. Under optimal conditions the full isotopic envelope corresponding to the dimer $(\text{Me}_3\text{Si})_3\text{SiGeCl}_2\text{GeCl}_2\text{Si}(\text{SiMe}_3)_3$ (m/e 774-790) was observed. Relative abundances of the peaks were in reasonable agreement with the calculated values (Table I). Other envelopes were observed near m/e 767, 747, 717, 675, 640, 603, and 525, representing fragments arising from the loss of methyl groups, chlorines, and silyl fragments in various sensible combinations. The presence of a germanium-germanium link in the parent species was shown by the appearance of an envelope centered near m/e 391, representing the $(\text{Me}_3\text{Si})_3\text{SiGeCl}_2$ monomer. This indication from mass spectra of the formation of the unexpected Ge-Ge-bonded dimeric species led us to confirm the structure via an X-ray structure determination.

Description of the Structure of I. Clear, colorless crystals of I were grown from pentane at about 0°C . Crystal and data collection parameters are summarized in Table II; geometric parameters are presented in Table III. The existence of extensive disorder in the $P\bar{a}3$ space group of I prevented completion of a fully rigorous structure determination including the trimethylsilyl groups. Under more usual circumstances, the structure determination would probably not have been pursued further because of the disorder but, owing to the importance of verifying the unusual and unexpected configuration of I, it was decided to extract whatever information was possible from the collected data. In order to do so, the Me_3Si groups were treated as rigid bodies with geometries defined according to those in $[(\text{Me}_3\text{Si})_3\text{Si}]_2\text{SnCl}_2$,² allowing the anisotropic refinement of the remaining silicons and

(8) Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper & Row: New York, 1983.

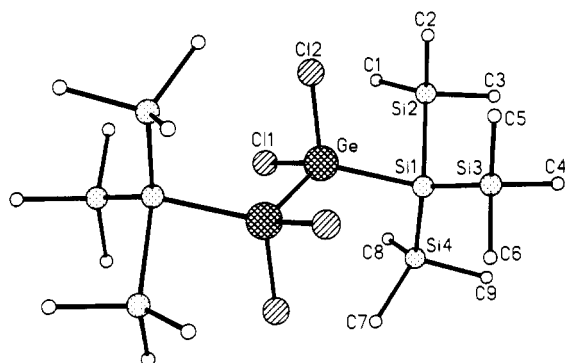


Figure 1. A rendering of the molecular structure of I (hydrogens omitted) as derived from a highly disordered model.

the other atoms. Figure 1 shows the heavy-atom molecular structure derived for I. The results confirm the mass spectroscopic indication of a Ge-Ge-bonded dimeric arrangement in I.

While the approach necessitated by the structural disorder caused large uncertainties in the bond lengths and bond angles (Table III), the values reported are in good agreement with literature values where these are available. For example, the Ge-Ge bond length, 2.421 (13) Å, is in accord with the literature value of 2.41 Å and the Ge-Cl bond lengths, 2.288 (28) and 2.158 (30) Å, lie near the literature value of 2.1 Å.⁸ The observed Ge-Si separation of 2.514 (44) Å is somewhat longer than the sum of the Ge and Si covalent radii,⁸ 2.40 Å, but we are not aware of any published values for this separation determined by diffraction with which it could be compared. The fact that observed bond distances tend to be larger than the literature values could be due to steric strain in the molecule caused by the presence of the Si(SiMe₃)₃ substituents, as is suggested by the space-filling model of the structure. The large Ge-Ge-Si bond angle (122°) also seems indicative of some strain in the structure.

We conclude from the structure of I that the expected dichlorobis(tris(trimethylsilyl)silyl)germane product may be unstable under ambient conditions due to crowding, perhaps suffering cleavage of a Ge-Si bond (Scheme I) giving the dichloro(tris(trimethylsilyl)silyl)germyl radical, coupling of which could lead to the observed product. Several other possible routes exist for the formation of I, but the available evidence does not permit a choice. This unexpected behavior was also found to extend to the reaction of the lithium silyl reagent with two R₂GeCl₂ species.

Whereas the reaction of 2 equiv of (THF)₃LiSi(SiMe₃)₃ with R₂SnCl₂ (R = CH₃, *n*-C₄H₁₀) gave the disubstituted monostannanes [(Me₃Si)₃Si]₂SnR₂,² the same reaction with R₂GeCl₂ (R = CH₃, C₆H₅) produces digermans, [(Me₃Si)₃SiGeR₂]₂, where R = CH₃ (II) and C₆H₅ (III). The ¹H, ¹³C, and ²⁹Si NMR results are consistent with Ge-Ge-bonded structures for II and III analogous to that of I. This similar behavior seems to support the proposition that it is the steric strain introduced by incorporation of the second Si(SiMe₃)₃ group which causes the instability of the [(Me₃Si)₃Si]₂GeR₂ structures.⁹ The reasonable yields of I-III obtained suggest that the reaction is fairly clean and might serve as a useful way to prepare digermane derivatives. All three isolated products are unreactive toward atmospheric moisture and dissolve readily in a range of organic solvents including pentane, dichloromethane, benzene, and THF.

The reaction of SnCl₄ with 1 equiv of (THF)₃LiSi(SiMe₃)₃ was previously shown to produce the monosilyl-substituted stannane, (Me₃Si)₃SiSnCl₃, as a THF solvate; however the same reaction using GeCl₄ gave only an unidentified yellow solid (mp 136 °C), which was found to be insoluble in most solvents. The infrared spectrum of the solid suggested that THF cleavage had occurred during the reaction.

In conclusion, the reactions of GeCl₄ and of R₂GeCl₂ (R = CH₃, C₆H₅) with 2 equiv of (THF)₃LiSi(SiMe₃)₃ do not yield the expected bis(tris(trimethylsilyl)silyl)germane derivatives; instead they produce 1,2-bis(tris(trimethylsilyl)silyl)digermans, probably as the result of severe steric interactions making the monogermane product unstable. The digermans are air- and moisture-stable solids.

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Supplementary Material Available: Tables SI-SVII, listing data collection and processing parameters, atomic coordinates and equivalent isotropic displacement parameters, bond lengths, bond angles, anisotropic displacement parameters, and hydrogen atomic coordinates and isotropic displacement parameters (3 pages); a table of observed and calculated structure factors (4 pages). Ordering information is given on any current masthead page.

(9) Preliminary studies of the reaction of SiCl₄ with 2 equiv of (THF)₃LiSi(SiMe₃)₃ suggest that a reaction similar to that of GeCl₄ is occurring. Further studies of the reaction are underway.