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Synthesis and Structure of Novel Germanium-Containing Cyclic Polysulfides

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Novel germanium-containing cyclic polysulfides 1,2,3,4,5-tetrathiagermolanes **5** (Tbt(Ar)-GeS_4; Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl; Ar = mesityl, 2,6-diethylphenyl, 2,4,6-triisopropylphenyl) have been synthesized, and the molecular structure of Tbt(Mes)GeS_4 was determined by X-ray crystallographic analysis. Reaction of the tetrathiagermolanes **5** with diphenyldiazomethane gave 1,2,3,5-tetrathia-4-germacyclohexanes **10**, 1,2,4,5-tetrathia-3-germacyclohexanes **11**, and 1,2,4-trithia-3-germacyclopentanes **12**. The structure of 1,2,3,5-tetrathia-4-germacyclohexane **10a** was determined by X-ray structural analysis.

Introduction

In recent years, there has been much interest in the chemistry of polysulfido complexes containing transition metals because of their structural features, synthetic utility, and biological activities.[1] There have been reported syntheses and structures of some cyclic polysulfides such as Cp_2TiS_5,[2] Cp_2VS_5,[3] Cp_2MoS_4,[4] Cp_2WS_4,[5] $Cp^*_2TiS_3$,[6] and $Cp^*_2ZrS_3$[6] (Cp = C_5H_5, Cp* = C_5Me_5), which can be used as versatile sources to prepare the sulfur rings of predetermined size. On the other hand, polysulfides containing group 14 elements such as Si, Ge, and Sn had not been investigated when we started the present study. Recently we preliminarily reported the synthesis of the first 1,2,3,4,5-tetrathiametallolanes $RR'MS_4$ (M = Si, Ge, Sn)[7,8] having an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt).[9] Immediately after our communication[7] Steudel independently reported the synthesis of the same type of polysulfides Ph_2MS_4 (M = Si, Ge).[10] In this paper we delineate a detailed account of the synthesis of kinetically stabilized 1,2,3,4,5-tetrathiagermolanes and their reactions, which gave some novel cyclic polysulfides.[11]

Results and Discussion

Synthesis of Diarylgermanes. The trichlorogermane $TbtGeCl_3$ (**1**) was synthesized from tetrachlorogermane and TbtLi, which was prepared by treatment of TbtBr with *t*-BuLi in THF. Another aryl group was introduced by nucleophilic reaction with Grignard reagents, giving the bromochlorogermanes Tbt(Ar)GeBrCl (**2**) instead of the expected Tbt(Ar)$GeCl_2$.[12] The formation of **2** can be rationalized in terms of rapid chlorine−bromine exchange in $TbtGeCl_3$ or Tbt(Ar)$GeCl_2$ by bromide ion derived from either ArMgBr or LiBr generated in the preparation of TbtLi from TbtBr. In these reactions no trisubstituted halogermane Tbt$(Ar)_2$GeX was formed even upon addition of excess Grignard reagents (ArMgBr), in contrast to similar reactions using tin compounds.[8] This is most likely because of bond lengths around the Ge atom being shorter than those around the Sn atom, which renders **2** more congested than the corresponding Sn compound and hence prohibits the attack of a second Grignard reagent (Scheme 1).

[⊗] Abstract published in *Advance ACS Abstracts*, December 15, 1994.

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[6] Bird, P. H.; McCall, J. M.; Shaver, A.; Siriwardane, U. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 384.

[7] Tokitoh, N.; Suzuki, H.; Matsumoto, T.; Matsuhashi, Y.; Okazaki, R.; Goto, M. *J. Am. Chem. Soc.* **1991**, *113*, 7047.

[8] Matsuhashi, Y.; Tokitoh, N.; Okazaki, R. *Organometallics* **1993**, *12*, 1351.

[9] Although the 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl group has been denoted as Tb in our previous papers, we change this acronym to Tbt in order to avoid confusion with the symbol of an element (terbium). (a) Okazaki, R.; Unno, M.; Inamoto, N. *Chem. Lett.* **1987**, 2293. (b) Okazaki, R.; Unno, M.; Inamoto, N.; Yamamoto, G. *Chem. Lett.* **1989**, 493. (c) Okazaki, R.; Unno, M.; Inamoto, N. *Chem. Lett.* **1989**, 791.

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[12] The structure of **2** was established by mass spectroscopy and elemental analysis.

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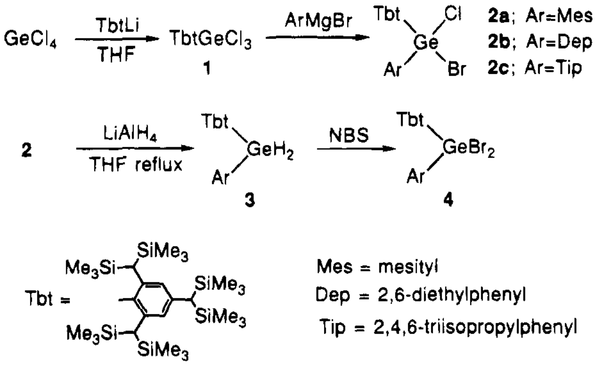
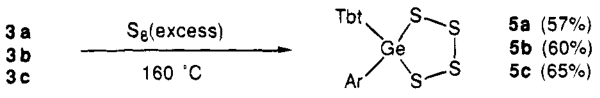
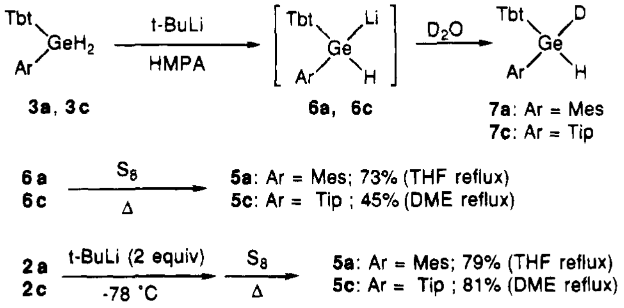
Scheme 1



Scheme 2



Scheme 3



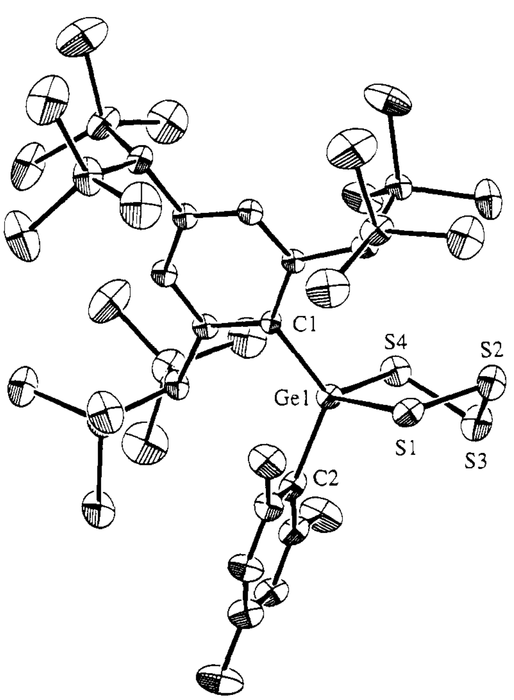


Figure 1. ORTEP drawing of 1,2,3,4,5-tetrathiagermolane **5a**. Selected bond lengths (Å) and angles (deg): Ge(1)–S(1), 2.320(2); S(1)–S(2), 2.046(3); S(2)–S(3), 2.052(5); S(3)–S(4), 2.048(3); S(4)–Ge(1), 2.257(2); Ge(1)–C(1), 1.960(6); Ge(1)–C(2), 1.996(8); S(1)–Ge(1)–S(4), 98.4(1); Ge(1)–S(1)–S(2), 102.2(2); S(1)–S(2)–S(3), 100.4(2); S(2)–S(3)–S(4), 98.3(2); S(3)–S(4)–Ge(1), 99.7(2); C(1)–Ge(1)–S(1), 119.4(2); C(1)–Ge(1)–S(4), 104.2(2); C(2)–Ge(1)–S(1), 96.0(2); C(2)–Ge(1)–S(4), 118.2(2); C(1)–Ge(1)–C(2), 119.4(3).

Treatment of **2** with $LiAlH_4$ gave dihydrogermanes **3** in good yields. Dibromogermanes **4** could be obtained by bromination of **3** using 2 equiv of *N*-bromosuccinimide.

Synthesis of Tetrathiagermolanes. Hydrogermanes are known to be sulfurized by elemental sulfur at elevated temperatures.[13] Reaction of a mixture of diarylgermanes **3** and elemental sulfur at 160 °C gave 1,2,3,4,5-tetrathiagermolanes **5** as pale yellow crystals in good yields with concomitant generation of gaseous hydrogen sulfide. Compounds **5** are novel cyclic polysulfides containing a germanium atom (Scheme 2).

Recently Steudel et al. reported the synthesis of the same type of polysulfide, Ph_2GeS_4, by the reaction of $Cp_2TiS_2GePh_2$ with S_2Cl_2.[10] While Ph_2GeS_4 is unstable to decompose above −20 °C, tetrathiagermolanes **5** are remarkably stable under ambient conditions because of sterically bulky groups on germanium. Their thermal stability is also shown in their high decomposition points (**5a**, 171–173 °C; **5b**, 222–224 °C; **5c**, 211–212 °C).

Some years ago, Satgé and his co-workers reported the preparation of (diarylgermyl)lithiums Ar_2GeHLi (Ar = Ph, Mes) by treatment of Ar_2GeH_2 with *t*-BuLi in THF.[14] Although lithiation of diarylgermane **3a**, bearing bulkier groups, did not proceed under their conditions, addition of HMPA was found to be effective for the lithiation of **3a**. In the case of **3c**, a high concentration of **3c** and HMPA was necessary. The formation of germyllithium **6** was confirmed by quenching with deuterated water (Scheme 3).

Germyllithium **6a**, thus prepared in situ, was allowed to react with elemental sulfur in refluxing THF to give **5a** in high yield. In the synthesis of **5c**, bearing bulkier groups, DME was used as solvent instead of THF, because a higher temperature was necessary for the reaction to proceed.

Tetrathiagermolanes **5** were also synthesized via treatment of dihalogermanes **2** with *t*-BuLi, followed by addition of elemental sulfur.

Structure of 1,2,3,4,5-Tetrathiagermolanes 5. Compounds **5** showed satisfactory spectral and analytical data. The molecular structure of **5a** was definitively determined by X-ray crystallographic analysis, and an ORTEP drawing is shown in Figure 1. Of particular note is the preferred distorted half-chair conformation of nearly envelope type in the GeS_4 five-membered ring. The distances between the two germanium–sulfur bonds are different (2.32 and 2.26 Å), whereas there is no distinct alternation in S–S bond lengths of the sulfur chain.

It should be noted that all of the reactions gave only five-membered polysulfides selectively, as in the case of polysulfides containing Si or Sn (**8** and **9**).[7,8] As was discussed in a previous paper concerning tetrathiastannolanes,[8] the isolation of only five-membered-ring compounds is probably due to the steric repulsion between the bulky Tbt and Ar (Mes, Dep or Tip) groups substituted on the Ge atom. It enlarges the bond angle of C–Ge–C and hence narrows the angle S–Ge–S, thus

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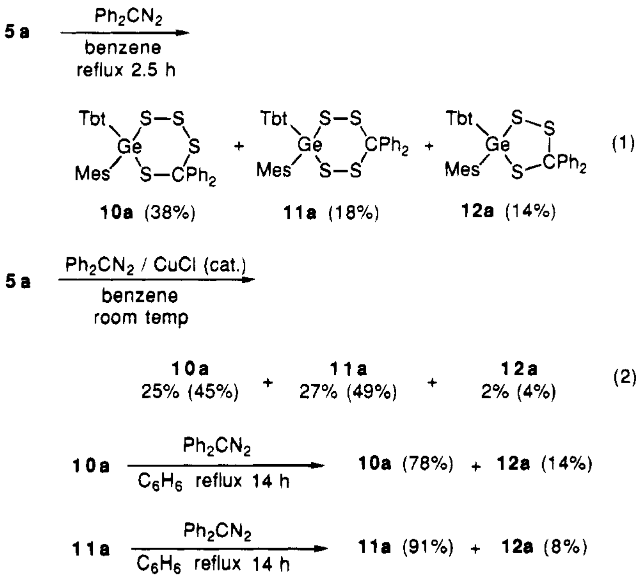
(13) For example, see: Vyazankin, N. S.; Bochkarev, M. N.; Sanina, L. P. *Zh. Obshch. Khim.* **1966**, *36*, 166.

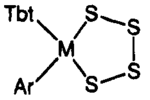
(14) Castel, A.; Riviere, P.; Satgé, J.; Ko, H. Y. *Organometallics* **1990**, *9*, 205.

Scheme 4[a]



[a] Values in parentheses denote conversion yields.

favoring the selective formation of the five-membered ring.



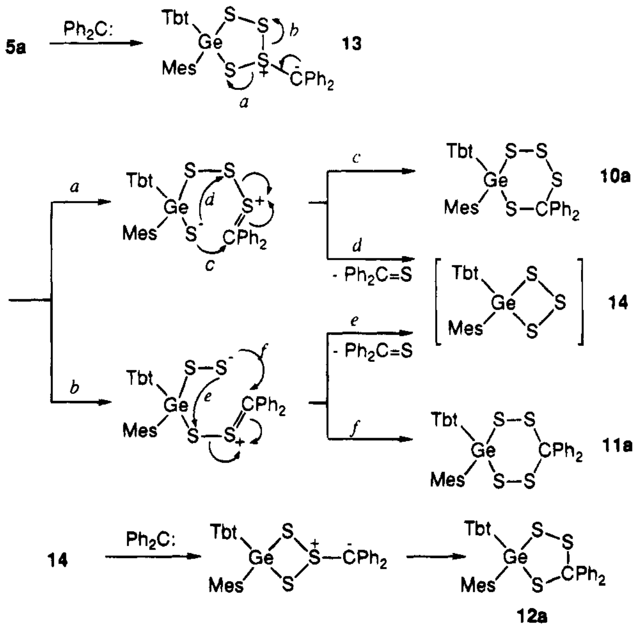
8; M = Si
9; M = Sn

Reactions of Tetrathiagermolanes 5 with Diphenyldiazomethane.[11] Novel polysulfides **5** have two types of S-S bonds in their five-membered-ring systems. We became interested in the reactions of **5** with diphenyldiazomethane, because they would not only provide information on the reactivity of these S–S bonds but also lead to the formation of new germanium-containing heterocycles. When **5a** was treated with a large excess of diphenyldiazomethane in refluxing benzene for 2.5 h, two isomeric products, i.e. 1,2,3,5-tetrathia-4-germacyclohexane **10a** and 1,2,4,5-tetrathia-3-germacyclohexane **11a** were isolated in 38 and 18% yields, respectively, along with 1,2,4-trithia-3-germacyclopentane **12a** (14%) (Scheme 4). The structures of the two isomers **10a** and **11a** were determined by their chemical reactivity and an X-ray structural analysis of **10a** (vide infra).

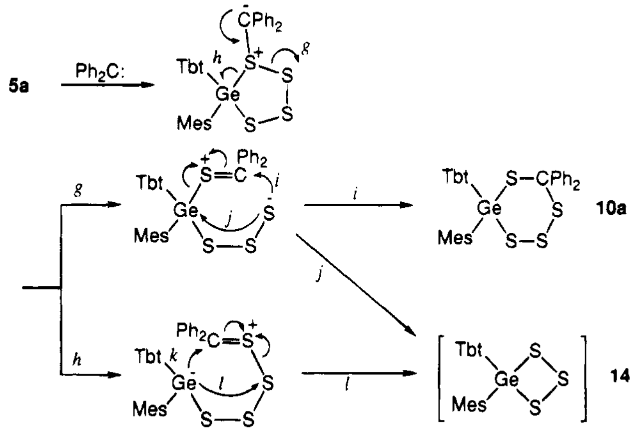
Diazomethanes are known to generate the corresponding carbene in the presence of catalytic amount of Cu salts.[15] Reaction of **5a** with diphenyldiazomethane in benzene in the presence of CuCl at room temperature proceeded very slowly to give **10a** and **11a** in a 1:1 ratio along with a small amount of **12a** and the recovered starting material **5a**.

To clarify the mechanism, reactions of isolated **10a** and **11a** with diphenyldiazomethane were carried out in refluxing benzene. No reaction took place for **10a** even after 4 h (longer than the reaction time in reaction 1 of Scheme 4), whereas refluxing for 14 h resulted in 14% of **12a** with 78% recovery of **10a**. Similar results were obtained for **11a** (Scheme 5). These results show that **12a** is generated directly from the reaction of **5a** and diphenyldiazomethane.

Scheme 5



Scheme 6



A plausible mechanism is shown in Scheme 5. In reaction 2 of Scheme 4, an electrophilic attack occurs on the sulfur atom at the kinetically favorable 2-position, followed by ring expansion of the intermediary sulfonium ylide **13** (paths *c* and *f* of Scheme 5) to give **10a** and **11a**. Trithiagermacyclopentane **12a** is probably produced by further reaction of diphenylcarbene with trithiagermacyclobutane **14** formed via path *d* or *e*. This mechanism can account for the 1:1 ratio of **10a** and **11a**, because there seems to be neither kinetic nor thermodynamic preference between paths *a* and *b*.

On the other hand, a reaction at higher temperature (reaction 1 of Scheme 4) would make possible an attack also on the sulfur atom at the 1-position (Scheme 6), thus enhancing the yield of **10a** (reaction 1). Path *k* is thought to be impossible because of unfavorable steric hindrance.

Reaction of **5c**, bearing a bulkier Tip group on germanium, gave only the two isomeric six-membered-ring compounds **10c** and **11c** (Scheme 7). However, trithiagermacyclopentane **12c** could be synthesized by desulfurization of **10c** with hexamethylphosphorous triamide. We previously reported a similar reaction with

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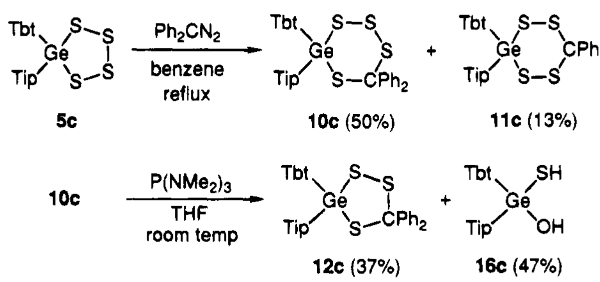
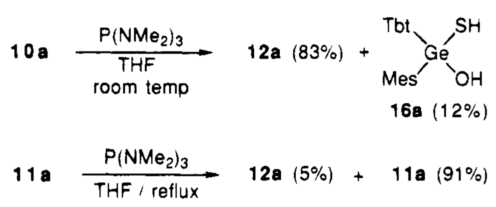
[15] Helquist, P. In *Comprehensive Organic Synthesis;* Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, U.K., 1991; Vol. 4, pp 951–998, and references cited therein.

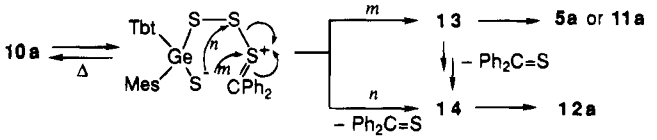
Scheme 7



Scheme 8



Scheme 9



diphenyldiazomethane using the tin analog **9** (Ar = Tip), where three products corresponding to **10-12** were obtained.[16] The formation of a trithiastannacyclopentane derivative in the reaction of **9** is considered to result from the reduced congestion around the tin atom which favors an electrophilic attack on the sulfur at the 1-position, leading to a trithiastannacyclobutane, a possible precursor of the trithiastannacyclopentane.

Structures of 10 and 11. (1) Desulfurization Reactions. Although there are three possible isomers for a $GeCS_4$ ring system, i.e., **10**, **11**, and 1,2,3,4-tetrathia-5-germacyclohexane, the last isomer is reasonably excluded as a reaction product of **5** with diphenyldiazomethane because of its severe steric congestion. In order to determine the structure of **10** and **11**, they were subjected to a desulfurization reaction. Reaction of **10a** with hexamethylphosphorous triamide in THF at room temperature gave **12a** in 83% yield, whereas a similar reaction of **11a** in refluxing THF afforded **12a** only in 5% yield with 91% of **11a** being recovered (Scheme 8). This fact clearly indicates that **10a** has a 1,2,3,5-tetrathia-4-germacyclohexane skeleton, because in this structure sulfur at the 2-position is exposed to an attack by the phosphorus reagent while both sulfurs in **11** are sterically protected.

Interesting thermal isomerization was observed for **10a** in $CDCl_3$ at 100 °C to give the isomer **11a** (37%) along with the two types of ring-contraction products **5a** (17%) and **12a** (9%) and recovered **10a** (37%). A possible mechanism is shown in Scheme 9. The first step would be a heterolytic cleavage of the Ge–S bond due to steric repulsion between aryl groups on Ge and C atoms. Path *m* would give the sulfonium ylide **13**, which would further react as shown in Scheme 6. Path *n* would give intermediate **14**, which eventually affords **12a**. Neither thermal decomposition nor isomerization was observed below 80 °C.

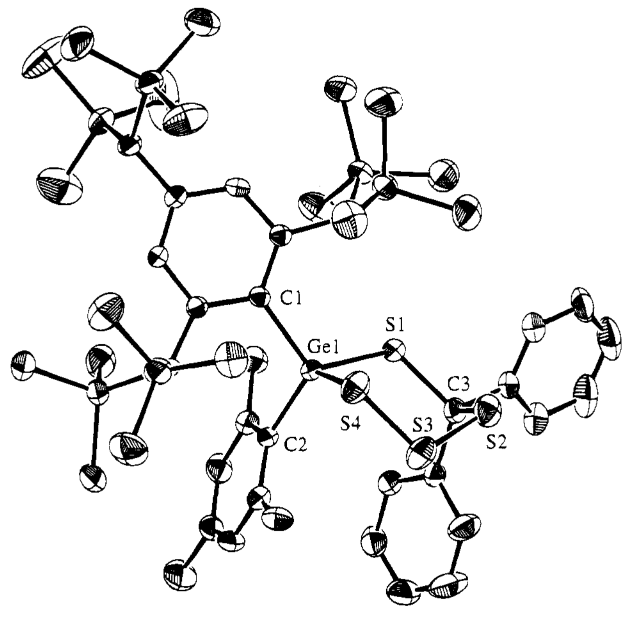


Figure 2. ORTEP drawing of 1,2,3,5-tetrathia-4-germacyclohexane **10a**. Selected bond lengths (Å) and angles (deg): Ge(1)–S(1), 2.290(2); S(1)–C(3), 1.864(6); C(3)–S(2), 1.851(6); S(2)–S(3), 2.012(3); S(3)–S(4), 2.045(3); S(4)–Ge(1), 2.251(2); Ge(1)–C(1), 1.997(5); Ge(1)–C(2), 1.977(6); C(1)–Ge(1)–C(2), 113.7(2); C(1)–Ge(1)–S(1), 114.1(2); C(1)–Ge(1)–S(4), 102.0(2); C(2)–Ge(1)–S(1), 103.3(2); C(2)–Ge(1)–S(4), 121.0(2); Ge(1)–S(1)–C(3), 111.8(2); S(1)–C(3)–S(2), 110.9(3); C(3)–S(2)–S(3), 103.3(2); S(2)–S(3)–S(4),106.5(1); S(3)–S(4)–Ge(1), 104.3(1); S(1)–C(3)–C(4), 103.6(4); S(1)–C(3)–C(5), 114.0(4); S(2)–C(3)–C(4), 102.9(4); S(2)–C(3)–C(5),111.9(4); C(4)–C(3)–C(5), 112.8(5).

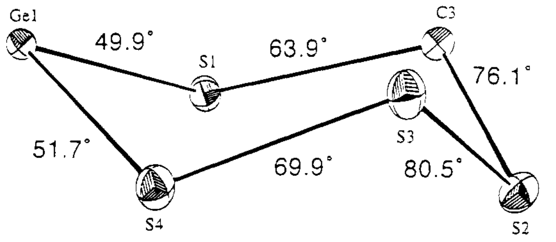


Figure 3. Torsion angles of **10a**.

(2) X-ray Structural Analysis. To distinguish **10a** from **11a**, the molecular structure of **10a** was definitively determined by X-ray crystallographic analysis, as shown in Figure 2. The molecular geometry of **10a** is of great interest as the first example of tetrathiagermacyclohexane. As in the case of known examples of saturated six-membered rings containing sulfurs such as 1,3,5-trithiacyclohexane,[17] 1,2,3,4-tetrathiacyclohexane,[18] and cyclohexathiane,[19] **10a** adopts a chair conformation. Torsional angles shown in Figure 3 indicate that the germanium atom-containing moiety is significantly flatter than the carbon-containing moiety, though **10a** shows an average torsional angle of 65.3°, which is comparable to that of 1,3,5-trithiacyclohexane (ca. 64°).[17]

Concluding Remarks

We have succeeded in the syntheses of novel cyclic polysulfides containing germanium, such as Tbt(Ar)-

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[16] Matsuhashi, Y.; Tokitoh, N.; Okazaki, R.; Goto, M. *Organometallics* **1993**, *12*, 2573.

[17] Valle, G.; Carazzolo, G.; Mammi, M. *Ric. Sci., Parte 2: Sez. A* **1965**, *8*, 1469; *Chem. Abstr.* **1966**, *65*, 1514.

[18] Fehér, F.; Klaeren, A.; Linke, K.-H. *Acta Crystallogr., Sect. B* **1972**, *28*, 534.

[19] Donohue, J.; Caron, A.; Goldish, E. *J. Am. Chem. Soc.* **1961**, *83*, 3748.

GeS_4 (**5**), Tbt(Ar)GeS_4CPh_2 (two isomers) (**10** and **11**), and Tbt(Ar)GeS_3CPh_2 (**12**), by taking advantage of the bulky groups Tbt and Ar (Mes, Dep, Tip), and two of the polysulfides have been crystallographically analyzed. It is noteworthy that our tetrathiagermolanes **5** are much more stable than the recently reported Ph_2GeS_4,[10] indicating the importance of the bulky group Tbt in stabilizing the tetrathiagermolane skeleton, which is otherwise highly susceptible to hydrolysis. The polysulfides synthesized in the present work are considered to be useful precursors of novel low-coordinated germanium species which are of much current interest. We have preliminarily reported the synthesis of the first stable diarylgermanethione, Tbt(Tip)Ge=S, by desulfurization of Tbt(Tip)GeS_4.[20] Further investigation along this line is now under way.

Experimental Section

General Procedure. All melting points were uncorrected. All solvents used in the reactions were purified by the reported methods. THF was purified by distillation from benzophenone ketyl before use. All reactions were carried out under an argon atmosphere unless otherwise noted. Preparative gel permeation liquid chromatography (GPLC) was performed by LC-908 with JAI gel 1H and 2H columns (Japan Analytical Industry) with chloroform as solvent. Dry column chromatography (DCC) was performed with ISN silica DCC 60A. Preparative thin-layer chromatography was carried out with Merck Kieselgel 60 PF254 (Art. No. 7747). The ^1H NMR (500 MHz) and ^{13}C NMR spectra (125 MHz) were measured in $CDCl_3$ with a Bruker AM-500 spectrometer using $CHCl_3$ as internal standard.

Preparation of {2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl}bromochloro(mesityl)germane (2a). To a solution of 1-bromo-2,4,6-tris[bis(trimethylsilyl)methyl]benzene[9a] (TbtBr; 10.0 g, 15.9 mmol) in THF (150 mL) was added *t*-BuLi (1.61 M in pentane, 22 mL, 35 mmol) at −78 °C. After the mixture was stirred for 10 min, $GeCl_4$ (1.9 mL, 17.4 mmol) was added at −78 °C. The reaction mixture was warmed to room temperature within 10 h to give a solution of $TbtGeCl_3$, to which MesMgBr (0.9 M in THF, 34 mL, 31 mmol) prepared from Mg and MesBr was added at room temperature. After this solution was stirred for 10 h, a few drops of aqueous NH_4Cl was added and almost all of the THF was removed under reduced pressure. Chloroform and diluted HCl were added to the residue, which was extracted by $CHCl_3$ several times. The organic layer was dried over $MgSO_4$, and the solvent was removed under reduced pressure. The white solid thus obtained was dissolved into CH_2Cl_2, and to the solution was added approximately the same volume of ethanol to afford a precipitate of Tbt(Mes)GeBrCl (**2a**; 9.5 g, 70%) as white crystals by the evaporation of CH_2Cl_2 at room temperature under reduced pressure. **2a**: white crystals; mp 225–227 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ −0.02 (s, 9H), 0.009 (s, 9H), 0.014 (s, 9H), 0.05 (s, 9H), 0.06 (s, 18H), 1.35 (s, 1H), 2.26 (s, 3H), 2.57 (br s, 1H), 2.61 (s, 6H), 2.73 (br s, 1H), 6.30 (br s, 1H), 6.44 (br s, 1H), 6.84 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 0.81 (q), 0.87 (q), 1.03 (q), 1.30 (q), 1.32 (q), 1.57 (q), 20.91 (q), 25.49 (q), 27.49 (d), 27.64 (d), 30.81 (d), 123.44 (d), 128.43 (d), 130.25 (s), 130.55 (d), 137.59 (s), 140.69 (s), 141.44 (s), 146.63 (s), 150.40 (s), 150.77 (s); high-resolution FAB-MS observed *m/z* 858.2031, calcd for $C_{36}H_{70}{}^{79}Br^{35}Cl^{74}GeSi_6$ 858.2177.

Preparation of {2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl}bromochloro(2,6-diethylphenyl)germane (2b). Compound **2b** was synthesized by the same procedure as that for **2a**, except that the reaction with DepMgBr (Dep = 2,6-diethylphenyl) was performed under reflux. TbtBr (5.0 g, 7.9 mmol), $GeCl_4$ (0.9 mL, 8.7 mmol), and DepMgBr (1.1 M in THF, 12 mL, 13 mmol) gave Tbt(Dep)GeBrCl (**2b**; 4.5 g, 65%). **2b**: white crystals; mp 215–216 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ −0.05 (s, 9H), −0.005 (s, 9H), 0.003 (s, 9H), 0.02 (s, 9H), 0.05 (s, 18H), 1.31 (t, *J* = 7.3 Hz, 6H), 1.34 (s, 1H), 2.58 (br s, 1H), 2.73 (br s, 1H), 2.93 (br s, 2H), 3.01 (br s, 2H), 6.28 (s, 1H), 6.42 (s, 1H), 7.10 (d, *J* = 7.7 Hz, 2H), 7.32 (t, *J* = 7.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 0.80 (q), 0.89 (q), 1.03 (q), 1.32 (q), 1.41 (q), 1.65 (q), 16.22 (q), 27.30 (d), 27.55 (d), 29.99 (t), 30.74 (d), 123.42 (d), 127.82 (d), 128.44 (d), 130.93 (d), 131.10 (s), 140.32 (s), 146.48 (s), 147.64 (s), 150.00 (s), 150.38 (s); high-resolution FAB-MS observed *m/z* 872.2130; calcd for $C_{37}H_{72}{}^{79}Br^{35}Cl^{74}GeSi_6$ 872.2334. Anal. Found: C, 54.93; H, 9.42; Br, 9.03; Cl, 4.01. Calcd for $C_{37}H_{72}BrClGeSi_6$: C, 50.88; H, 8.31; Br, 9.15; Cl, 4.06.

Preparation of {2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl}bromochloro(2,4,6-triisopropylphenyl)germane (2c). Compound **2c** was synthesized by the same procedure as that for **2a**, except that the reaction with TipMgBr was performed under reflux. The use of TbtBr (5.0 g, 8.0 mmol), $GeCl_4$ (0.9 mL, 8.7 mmol), and TipMgBr (1.8 M in THF, 8.5 mL, 15 mmol) gave Tbt(Tip)GeBrCl (**2c**; 5.0 g, 66%). **2c**: white crystals; mp 232–233 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ −0.07 (s, 9H), −0.02 (s, 9H), 0.045 (s, 9H), 0.048 (s, 9H), 0.08 (s, 9H), 0.10 (s, 9H), 1.04 (br s, 3H), 1.16 (br s, 3H), 1.20 (d, *J* = 6.9 Hz, 6H), 1.28 (d, *J* = 6.9 Hz, 6H), 1.33 (s, 1H), 2.49 (br s, 1H), 2.63 (br s, 1H), 2.84 (sept, *J* = 6.9 Hz, 1H), 3.28 (br s, 1H), 4.09 (br s, 1H), 6.31 (br s, 1H), 6.43 (br s, 1H), 7.03 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 0.82 (q), 0.87 (q), 0.96 (q), 1.55 (q), 1.85 (q), 2.12 (q), 22.70 (q × 2), 23.73 (q), 23.77 (q), 24.50 (q × 2), 26.67 (d), 26.97 (d), 27.47 (d), 28.13 (d), 30.72 (d), 34.28 (d), 122.66 (d), 123.39 (d), 123.84 (d), 128.96 (d), 131.49 (s), 136.31 (s), 145.83 (s), 149.44 (s), 149.92 (s), 151.59 (s), 152.50 (s); high-resolution FAB-MS observed *m/z* 942.3298, calcd for $C_{42}H_{82}{}^{79}Br^{35}Cl^{74}GeSi_6$ 942.3116.

Preparation of {2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl}(mesityl)germane (3a). To a THF solution (20 mL) of **2a** (298 mg, 0.347 mmol) was added $LiAlH_4$ (29 mg, 0.73 mmol) at 0 °C, and the mixture was refluxed for 10 h. After quenching by aqueous NH_4Cl, the organic layer was washed with diluted HCl. The water layer was extracted with $CHCl_3$ several times. The organic layer was dried over $MgSO_4$, and all of the solvent was removed under reduced pressure. The residue was dissolved into CH_2Cl_2, and approximately the same volume of ethanol was added to give precipitates of **3a** (185 mg, 72%) as white crystals by the evaporation of CH_2Cl_2 at room temperature under reduced pressure. **3a**: mp 162–163 °C dec; ^1H NMR ($CDCl_3$, 500 MHz) δ −0.04 (s, 18H), 0.00 (s,18H), 0.05 (s, 18H), 1.31 (s, 1H), 2.01 (s, 1H), 2.22 (s, 1H), 2.26 (s, 3H), 2.42 (s, 6H), 5.14 (s, 2H), 6.29 (s, 1H), 6.44 (s, 1H), 6.83 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 0.59 (q), 0.79 (q), 0.93 (q), 21.01 (q), 24.69 (q), 28.93 (d × 2), 30.27 (d), 122.26 (d), 127.08 (d), 128.14 (s), 128.44 (d), 133.00 (s), 138.51 (s), 143.24 (s), 143.29 (s), 150.28 (s), 150.38 (s); IR (KBr) 2070 cm^{-1} (Ge–H); high-resolution EI-MS observed *m/z* 746.3484; calcd for $C_{36}H_{72}{}^{74}GeSi_6$ 746.3454. Anal. Found: C, 54.93; H, 9.42. Calcd for $C_{36}H_{72}GeSi_6 \cdot 2H_2O$: C, 55.28; H, 9.79.

Preparation of {2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl}(2,6-diethylphenyl)germane (3b). Using the same procedure as that for **3a**, **3b** (3.7 g, 96%) was obtained from **2b** (4.5 g, 5.2 mmol). **3b**: white crystals; mp 189–190 °C dec; ^1H NMR ($CDCl_3$, 500 MHz) δ −0.07 (s, 18H), 0.02 (s, 18H), 0.04 (s, 18H), 1.23 (t, *J* = 7.3 Hz, 6H), 1.29 (s, 1H), 1.99 (s, 1H), 2.19 (s, 1H), 2.76 (q, *J* = 7.3 Hz, 4H), 5.13 (s, 2H), 6.27 (s, 1H), 6.42 (s, 1H), 7.05 (d, *J* = 7.7 Hz, 2H), 7.25 (t, *J* = 7.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 0.56 (q), 0.77 (q), 0.89 (q), 16.14 (q), 28.90 (d), 29.01 (d), 30.25 (d), 30.92 (t), 122.20 (d), 125.84 (d), 127.06 (d), 128.53 (s), 129.26 (d), 135.82 (s), 143.31 (s), 149.56 (s), 150.20 (s), 150.31 (s); IR (KBr) 2058 cm^{-1} (Ge–H). Anal. Found: C, 58.46; H, 9.53. Calcd for $C_{37}H_{74}GeSi_6$: C, 58.46; H, 9.81.

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[20] Tokitoh, N.; Matsumoto, T.; Manmaru, K.; Okazaki, R. *J. Am. Chem. Soc.* **1993**, *115*, 8855.

Preparation of {2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl}(2,4,6-triisopropylphenyl)germane (3c). Using the same procedure as that for **3a**, **3c** (277 mg, 99%) was obtained from **2c** (315 mg, 0.334 mmol). **3c**: white crystals; mp 162−164 °C dec; ^{1}H NMR (CDCl$_3$, 500 MHz) δ −0.08 (s, 18H), 0.00 (s, 18H), 0.03 (s, 18H), 1.21 (d, J = 6.9 Hz, 6H), 1.23 (d, J = 6.9 Hz, 12H), 1.27 (s, 1H), 1.96 (br s, 1H), 2.24 (br s, 1H), 2.84 (sept, J = 6.9 Hz, 1H), 3.22 (sept, J = 6.9 Hz, 2H), 5.16 (s, 2H), 6.25 (s, 1H), 6.43 (s, 1H), 7.00 (s, 2H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 0.78 (q), 1.09 (q), 23.98 (q), 24.67 (q), 28.84 (d), 28.93 (d), 30.22 (d), 33.80 (d), 34.41 (d), 120.66 (d), 122.32 (d), 127.24 (d), 129.77 (s), 132.17 (s), 142.97 (s), 149.69 (s), 149.93 (s), 150.01 (s), 153.83 (s); IR (KBr) 2065 cm^{-1} (Ge−H). Anal. Found: C, 58.70; H, 9.84. Calcd for $C_{42}H_{84}GeSi_6 \cdot 1.5H_2O$: C, 58.84; H, 10.23.

Preparation of {2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl}dibromo(mesityl)germane (4a). To a benzene solution (100 mL) of diarylgermane **3a** (6.6 g, 8.8 mmol) was added *N*-bromosuccinimide (3.6 g, 20 mmol) at room temperature. While the solution was stirred, *N*-bromosuccinimide (0.33 g, 1.9 mmol) was added to it over a period of 10 h, until all of the **3a** was consumed. The crude reaction mixture was chromatographed with column chromatography (SiO$_2$/benzene) to give a fraction containing **4a**, which was dissolved into CHCl$_3$ and reprecipitated as mentioned for **2a**. **4a** (7.3 g, 91%): white crystals; mp 225−227 °C; ^{1}H NMR (CDCl$_3$, 500 MHz) δ −0.001 (s, 18H), 0.04 (s, 18H), 0.06 (s, 18H), 1.34 (s, 1H), 2.26 (s, 3H), 2.63 (br s, 1H), 2.64 (s, 6H), 2.81 (br s, 1H), 6.29 (br s, 1H), 6.43 (br s, 1H), 6.82 (s, 2H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 0.84 (q), 1.30 (q), 1.58 (q), 20.88 (q), 25.71 (q), 27.42 (d), 27.57 (d), 30.78 (d), 123.48 (d), 128.48 (d), 130.06 (s), 130.61 (d), 137.62 (s), 140.59 (s), 141.27 (s), 146.56 (s), 150.24 (s), 150.65 (s). Anal. Found: C, 47.67; H, 7.84; Br, 18.05. Calcd for $C_{36}H_{70}Br_2GeSi_6$: C, 47.83; H, 7.80; Br, 17.68.

Preparation of {2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl}dibromo(2,4,6-triisopropylphenyl)germane (4c). Using the same procedure as that for **4a**, **4c** (8.8 g, 88%) was obtained from **3c** (8.4 g, 10 mmol). **4c**: white crystals; mp 232−233 °C; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 0.02 (br s, 18H), 0.04 (br s, 18H), 0.05 (s, 18H), 1.15 (br s, 6H), 1.20 (d, J = 6.9 Hz, 6H), 1.28 (br s, 6H), 1.33 (s, 1H), 2.13 (br s, 1H), 2.29 (br s, 1H), 2.84 (sept, J = 6.9 Hz, 1H), 3.78 (sept, J = 6.9 Hz, 2H), 6.32 (br s, 1H), 6.44 (br s, 1H), 7.02 (s, 2H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 0.85 (q), 1.93 (q), 2.20 (q), 23.64 (q), 23.72 (q), 27.01 (d), 27.49 (d), 30.70 (d), 32.92 (d), 34.24 (d), 123.38 (d), 123.88 (d), 128.97 (d), 131.66 (s), 136.05 (s), 145.78 (s), 149.40 (s), 149.98 (s), 151.46 (s), 152.29 (s). Anal. Found: C, 50.78; H, 8.42; Br, 16.59. Calcd for $C_{42}H_{82}Br_2GeSi_6$: C, 51.05; H, 8.37; Br, 16.17.

Synthesis of 5-{2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl}-5-mesityl-1,2,3,4,5-tetrathiagermolane (5a). Method 1. Diarylgermane **3a** (1.13 g, 1.15 mmol) was mixed with S$_8$ (4.1 g, 16 mmol as S$_8$) and heated to 160 °C for 10 min. Most of the excess sulfur was removed by recrystallization from chloroform. The residue was separated with DCC (SiO$_2$/hexane) and GPLC. The solid material thus obtained was dissolved into CH$_2$Cl$_2$, to which was added approximately the same volume of ethanol. Evaporation of CH$_2$Cl$_2$ at room temperature under reduced pressure gave **5a** (0.75 g, 57%) as pale yellow crystals.

Method 2. To a THF solution (10 mL) of **3a** (177 mg, 0.237 mmol) was added at −78 °C *t*-BuLi (1.54 M in pentane, 0.24 mL, 0.38 mmol) and then hexamethylphosphoric triamide (0.20 mL, 1.2 mmol). The solution was warmed to −25 °C over 2 h, and to it was added a THF (10 mL) suspension of elemental sulfur (0.12 g, 0.47 mmol as S$_8$). The mixture was warmed to room temperature and then refluxed for 10 h. Solvent was removed under reduced pressure, and the residue was separated as was mentioned in method 1, to afford **5a** (150.8 mg, 73%).

Method 3. To a THF solution (15 mL) of bromochlorogermane **2a** (241 mg, 0.296 mmol) was added at −78 °C *t*-BuLi (1.54 M in pentane, 0.39 mL, 0.59 mmol). The solution was stirred for 5 min at −78 °C, and to it was added a THF (10 mL) suspension of elemental sulfur (0.15 g, 0.60 mmol as S$_8$). The mixture was warmed to room temperature over 2 h and then refluxed for 10 h. The solvent was removed under reduced pressure, and the residue was separated as was mentioned in method 1 to give **5a** (204.1 mg, 79%). **5a**: pale yellow crystals; mp 171−173 °C dec; ^{1}H NMR (CDCl$_3$, 500 MHz) δ −0.022 (br s, 18H), −0.018 (br s, 18H), 0.06 (s, 18H), 1.35 (s, 1H), 1.97 (s, 1H), 2.04 (s, 1H), 2.21 (s, 3H), 2.51 (s, 6H), 6.34 (s, 1H), 6.46 (s, 1H), 6.80 (s, 2H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 0.82 (q), 1.30 (q), 1.59 (q), 20.86 (q), 25.70 (q), 28.48 (d), 28.87 (d), 30.79 (d), 123.18 (d), 128.32 (d), 128.68 (s), 130.13 (d), 139.43 (s), 139.82 (s), 140.74 (s), 146.25 (s), 151.72 (s), 151.88 (s); UV (CHCl$_3$) λ_{max} 273 (sh, ϵ 9800), 318 (sh, 3000) nm. Anal. Found: C, 49.42; H, 7.82; S, 14.30. Calcd for $C_{36}H_{70}GeS_4Si_6$: C, 49.56; H, 8.09; S, 14.71.

Synthesis of 5-{2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl}-5-(2,6-diethylphenyl)-1,2,3,4,5-tetrathiagermolane (5b). Diarylgermane **3b** (252 mg, 0.332 mmol) was mixed with S$_8$ (2.0 g, 7.8 mmol as S$_8$) and heated to 160 °C for 1 h. Most of the excess sulfur was removed by recrystallization from chloroform. The residue was separated with DCC (SiO$_2$/hexane) follwed by GPLC. The solid material thus obtained was recrystallized from ethanol to afford **5b** (206 mg, 70%) as pale yellow crystals. **5b**: mp 222−224 °C dec; ^{1}H NMR (CDCl$_3$, 500 MHz) δ −0.02 (s, 18H), −0.01 (s, 18H), 0.05 (s, 18H), 1.24 (t, J = 7.3 Hz, 6H), 1.34 (s, 1H), 1.97 (s, 1H), 2.01 (s, 1H), 2.99 (q, J = 7.3 Hz, 4H), 6.33 (s, 1H), 6.46 (s, 1H), 7.10 (d, J = 7.7 Hz, 2H), 7.28 (t, J = 7.7 Hz, 1H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 0.84 (q), 1.39 (q), 1.68 (q), 14.58 (q), 28.37 (d), 28.76 (d), 30.77 (d), 31.08 (t), 123.18 (d), 126.45 (d), 128.45 (d), 129.97 (s + d), 142.34 (s), 146.13 (s), 146.43 (s), 151.31 (s), 151.57 (s). Anal. Found: C, 50.11; H, 8.03; S, 14.19. Calcd for $C_{37}H_{72}GeS_4Si_6$: C, 50.13; H, 8.19; S, 14.47.

Synthesis of 5-{2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl}-5-(2,4,6-triisopropylphenyl)-1,2,3,4,5-tetrathiagermolane (5c). Method 1. Diarylgermane **3c** (515 mg, 0.620 mmol) was mixed with S$_8$ (2.0 g, 8.0 mmol as S$_8$) and heated to 160 °C for 30 min. Most of the excess sulfur was removed by recrystallization from chloroform. The residue was separated with DCC (SiO$_2$/hexane) and GPLC. The solid material thus obtained was recrystallized from ethanol to afford **5c** (386 mg, 65%) as pale yellow crystals.

Method 2. To a DME (3 mL) solution of **3c** (625 mg, 0.753 mmol) were added at −78 °C *t*-BuLi (1.61 M in pentane, 1.40 mL, 2.25 mmol) and hexamethylphosphoric triamide (0.66 mL, 3.8 mmol). The solution was warmed to −12 °C over 3 h, and elemental sulfur (0.58 g, 2.27 mmol as S$_8$) was added. After the mixture was warmed to room temperature, DME (10 mL) was added, and this solution was refluxed for 10 h. Solvent was removed under reduced pressure, and the residue was separated as was mentioned in method 1, giving **5c** (324 mg, 45%).

Method 3. To a DME (15 mL) solution of bromochlorogermane **2c** (205 mg, 0.229 mmol) was added *t*-BuLi (1.61 M in pentane, 0.28 mL, 0.46 mmol) at −78 °C. The solution was stirred for 5 min at −78 °C, and then elemental sulfur (160 mg, 46 mmol as S$_8$) was added. The mixture was warmed to room temperature over 2 h and refluxed for 10 h. Solvent was removed under reduced pressure, and the residue was separated as was mentioned in method 1 to give **5c** (177 mg, 81%). **5c**: pale yellow crystals; mp 211−212 °C dec; ^{1}H NMR (CDCl$_3$, 500 MHz, 340 K) δ 0.03 (s, 36H), 0.07 (s, 18H), 1.16 (d, J = 6.9 Hz, 12H), 1.21 (d, J = 6.9 Hz, 6H), 1.35 (s, 1H), 2.07 (br s, 2H), 2.83 (sept, J = 6.9Hz, 1H), 3.78 (br s, 2H), 6.41 (br s, 2H), 7.03 (s, 2H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 1.01 (q), 2.33 (q), 23.73 (q), 24.39 (q), 28.74 (d), 30.96 (d), 34.27 (d), 35.79 (d), 123.41 (d), 123.63 (d), 129.27 (d), 132.74 (s), 137.40 (s), 145.57 (s), 150.67 (s), 151.19 (s), 151.71 (s), 152.55 (s). Anal. Found: C, 52.68; H, 8.48; S, 12.96. Calcd for $C_{42}H_{82}GeS_4Si_6$: C, 52.73; H, 8.64; S, 13.40.

Reaction of 1,2,3,4,5-Tetrathiagermolane 5a with Diphenyldiazomethane. To a benzene solution (15 mL) of **5a** (252 mg, 0.289 mmol) was added diphenyldiazomethane (530 mg, 2.9 mmol), and the purple mixture was refluxed for 2.5 h. Solvent was removed under reduced pressure, and tetraphenylethylene and tetraphenylazine were removed from the residue with HPLC. Separation with DCC and PTLC (SiO_2 with 5/1 hexane/CH_2Cl_2) gave 4-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-4-mesityl-1,2,3,5-tetrathia-4-germacyclohexane (**10a**; 113 mg, 38%), 3-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-3-mesityl-1,2,4,5-tetrathia-3-germacyclohexane (**11a**; 54.5 mg, 18%), and 3-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-3-mesityl-1,2,4-trithia-3-germacyclopentane (**12a**; 39.5 mg, 14%). **10a**: white crystals; mp 208–209 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ −0.04 (br s, 18H), 0.04 (s, 9H), 0.05 (s, 9H), 0.07 (s, 9H), 0.09 (s, 9H), 1.30 (s, 1H), 2.26 (s, 3H), 2.41 (s, 3H), 2.60 (s, 3H), 6.26 (br s, 1H), 6.39 (br s, 1H), 6.55 (s, 1H), 6.65 (s, 1H), 6.84–7.29 (m, 10H), the two o-benzyl protons of the Tbt group appeared at δ 2.48 as a broad singlet at 370 K; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 0.80 (q), 0.94 (q), 1.14 (q), 1.49 (q), 1.87 (q), 2.08 (q), 20.82 (q), 22.69 (q), 25.48 (q), 28.30 (d), 28.79 (d), 30.38 (d), 74.21 (s), 123.36 (d), 126.16 (d), 127.21 (d), 127.99 (d), 128.29 (d), 128.31 (d), 128.44 (d), 129.67 (d), 130.35 (d), 130.47 (d), 132.56 (s), 137.70 (s), 139.27 (s), 139.51 (s), 142.31 (s), 142.44 (s), 145.23 (s), 146.97 (s), 150.51 (s), 150.80 (s). Anal. Found: C, 56.36; H, 7.65; S, 11.88. Calcd for $C_{49}H_{80}GeS_4Si_6$: C, 56.66; H, 7.76; S, 12.35. **11a**: white crystals; mp 278–279 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ −0.19 (br s, 18H), 0.02 (br s, 36H), 1.30 (s, 1H), 2.18 (br s, 1H), 2.20 (s, 3H), 2.23 (br s, 1H), 2.51 (br s, 6H), 6.32 (br s, 1H), 6.41 (br s, 1H), 6.75 (s, 2H), 7.22–7.54 (m, 10H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 0.82 (q), 1.12 (br q), 1.47 (br q), 20.85 (q), 25.89 (q), 29.39 (d), 29.45 (d), 30.64 (d), 75.72 (s), 122.96 (d), 127.82 (d), 128.14 (d), 128.18 (d), 128.22 (d × 2), 128.29 (d), 128.33 (d), 130.12 (d), 133.16 (s), 137.96 (s), 139.18 (s), 141.56 (s), 141.59 (s), 141.93 (s), 145.35 (s), 150.92 (s), 151.01 (s). Anal. Found: C, 56.38; H, 7.55; S, 12.50. Calcd for $C_{49}H_{80}GeS_4Si_6$: C, 56.66; H, 7.76; S, 12.35. **12a**: white crystals; mp 203.5–205 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ −0.09 (s, 18H), −0.06 (s, 18H), 0.03 (s, 18H), 1.31 (s, 1H), 2.20 (s, 3H), 2.37 (s, 2H), 2.44 (s, 6H), 6.31 (br s, 1H), 6.42 (br s, 1H), 6.69 (s, 2H), 7.03–7.64 (m, 10H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 0.83 (q), 0.86 (q), 1.13 (q), 1.37 (q), 1.38 (q), 20.82 (q), 25.05 (q), 28.61 (d), 29.23 (d), 30.60 (d), 82.56 (s), 123.18 (d), 127.20 (d), 127.25 (d), 127.51 (d), 127.92 (d), 128.36 (d), 128.63 (d), 129.24 (d), 129.58 (d), 131.60 (s), 138.82 (s), 139.11 (s), 141.66 (s), 143.48 (s), 143.98 (s), 146.99 (s), 151.02 (s), 151.11 (s). Anal. Found: C, 58.23; H, 7.88; S, 9.44. Calcd for $C_{49}H_{80}GeS_3Si_6$: C, 58.47; H, 8.01; S, 9.56.

Reaction of 1,2,3,4,5-Tetrathiagermolane 5a with Diphenyldiazomethane in the Presence of CuCl. To a benzene solution (8 mL) of **5a** (309 mg, 0.354 mmol) with a catalytic amount of CuCl was added diphenyldiazomethane (65 mg, 36 mmol) at 0 °C, and the mixture was stirred for 1 h at room temperature. Since **5a** still remained, an excess of diphenyldiazomethane was added and the solution was stirred for 1 h. After the solvent was evaporated under reduced pressure, tetraphenylethylene and tetraphenylazine were removed from the residue with HPLC. Separation with DCC and PTLC (SiO_2 with 5/1 hexane/CH_2Cl_2) gave **10a** (93 mg, 25%), **11a** (101 mg, 27%), and **12a** (8 mg, 2%) with recovery of **5a** (138 mg, 45%).

Reaction of 1,2,3,5-Tetrathia-4-germacyclohexane 10a with Diphenyldiazomethane. To a benzene solution (3 mL) of **10a** (50.8 mg, 0.042 mmol) was added diphenyldiazomethane (190 mg, 24 mmol), and the purple mixture was refluxed for 14 h. Workup similar to that above gave **12a** (6.8 mg, 14%) with recovery of **10a** (39.6 mg, 78%).

Reaction of 1,2,4,5-Tetrathia-3-germacyclohexane 11a with Diphenyldiazomethane. To a benzene solution (3 mL) of **11a** (43.5 mg, 0.042 mmol) was added diphenyldiazomethane (180 mg, 22 mmol), and the purple mixture was refluxed for 14 h. Workup similar to that above gave **12a** (3.3 mg, 8%) with recovery of **10a** (39.5 mg, 91%).

Reaction of 1,2,3,4,5-Tetrathiagermolane 5c with Diphenyldiazomethane. To a benzene solution (15 mL) of **5c** (116 mg, 0.121 mmol) was added diphenyldiazomethane (230 mg, 1.20 mmol), and the purple mixture was refluxed for 10 h. Workup similar to that above gave 4-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-4-(2,4,6-triisopropylphenyl)-1,2,3,5-tetrathia-4-germacyclohexane (**10c**; 67.6 mg, 50%) and 3-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-3-(2,4,6-triisopropylphenyl)-1,2,4,5-tetrathia-3-germacyclohexane (**11c**; 16.8 mg, 13%). **10c**: white crystals; mp 210–210.5 °C; ^{1}H NMR ($CDCl_3$, 500 MHz, 340 K) δ −0.26 (br s, 9H), 0.04 (br s, 18H), 0.06 (br s, 9H), 0.08 (s, 9H), 0.30 (br s, 9H), 0.60 (br s, 3H), 0.81 (d, J = 7 Hz, 3H), 1.03 (d, J = 7 Hz, 3H), 1.24 (s, 1H), 1.31 (d, J = 7 Hz, 6H), 1.36 (br s, 3H), 1.82 (br s, 1H), 2.91 (sept, J = 7 Hz, 1H), 2.97 (br s, 1H), 4.13 (br s, 1H), 4.32 (br s, 1H), 6.38 (br s, 1H), 6.47 (br s, 1H), 6.82 (br s, 2H), 6.93 (s, 1H), 7.01 (m, 1H), 7.11 (s, 1H), 7.16–7.29 (m, 7H). Anal. Found: C, 58.97; H, 8.23; S, 11.80. Calcd for $C_{55}H_{92}GeS_4Si_6$: C, 58.83; H, 8.26; S, 11.43. **11c**: white crystals; mp 160–164 °C dec; ^{1}H NMR ($CDCl_3$, 500 MHz) δ −0.10 (br s, 9H), −0.07 (br s, 9H), −0.03 (br s, 9H), 0.03 (s, 18H), 0.04 (br s, 9H), 1.01 (br s, 3H), 1.09 (br s, 3H), 1.14 (br s, 3H), 1.18 (d, J = 6.9 Hz, 6H), 1.24 (br s, 3H), 1.29 (s, 1H), 2.21 (br s, 1H), 2.38 (br s, 1H), 2.80 (sept, J = 6.9 Hz, 1H), 2.95 (br s, 1H), 3.85 (br s, 1H), 6.31 (br s, 1H), 6.45 (br s, 1H), 6.94 (br s, 1H), 7.02 (br s, 1H), 7.22–7.59 (m, 10H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 0.94 (q), 2.09 (q), 2.25 (q), 2.39 (q), 23.72 (q), 24.81 (q), 28.10 (q), 28.76 (q), 29.53 (d), 30.54 (d), 33.97 (d), 34.12 (d), 36.15 (d), 76.34 (s), 123.40 (d × 2), 123.68 (d), 127.99 (d), 128.08 (d × 2), 128.17 (d), 128.21 (d), 128.32 (d), 128.98 (d), 135.34 (s), 135.89 (s), 141.47 (s), 141.53 (s), 144.62 (s), 150.12 (s), 150.26 (s), 150.94 (s), 152.83 (s), 153.57 (s). Anal. Found: C, 58.92; H, 8.53; S, 11.21. Calcd for $C_{55}H_{92}GeS_4Si_6$: C, 58.83; H, 8.26; S, 11.43.

Synthesis of 1,2,4-Trithia-3-germacyclopentane 12c. To a THF solution (40 mL) of **10c** (750 mg, 0.668 mmol) was added at −78 °C hexamethylphosphorous triamide (0.38 mL, 2.0 mmol). After the solution was warmed to room temperature over 10 h, the solvent was removed under reduced pressure. Separation with DCC (SiO_2 with 25/1 hexane/CH_2Cl_2) afforded 3-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-3-(2,4,6-triisopropylphenyl)-1,2,4-trithia-3-germacyclopentane (**12c**; 272 mg, 37%) and {2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}hydroxy(2,4,6-triisopropylphenyl)mercaptogermane (**16c**; 278 mg, 47%). **12c**: white crystals; mp 160–165 °C dec; ^{1}H NMR ($CDCl_3$, 500 MHz) δ −0.17 (s, 18H), 0.055 (s, 9H), 0.062 (s, 9H), 0.09 (s, 9H), 0.13 (s, 9H), 0.50 (br s, 3H), 0.93 (br s, 3H), 1.09 (br s, 3H), 1.19 (br s, 3H), 1.19 (d, J = 6.9 Hz, 6H), 1.32 (s, 1H), 2.14 (br s, 1H), 2.46 (br s, 1H), 2.81 (sept, J = 6.9 Hz, 1H), 3.71 (br s, 1H), 3.99 (br s, 1H), 6.31 (br s, 1H), 6.47 (br s, 1H), 6.95 (s, 2H), 7.12–7.73 (m, 10H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 0.90 (q), 1.12 (q), 1.97 (q), 2.25 (q), 2.31 (q × 2), 23.64 (q), 23.83 (q), 24.71 (q), 25.10 (q), 25.80 (q), 27.28 (q), 28.56 (d), 29.05 (d), 30.46 (d), 32.44 (d), 34.08 (d), 35.07 (d), 83.16 (s), 123.53 (d), 123.71 (d), 126.94 (d), 127.14 (d), 128.06 (d), 128.07 (d), 128.15 (d), 128.74 (d × 2), 129.23 (d), 134.11 (s), 137.66 (s), 144.52 (s), 144.74 (s), 145.01 (s), 149.64 (s), 150.40 (s), 151.17 (s), 151.42 (s), 153.59 (s). Anal. Found: C, 59.19; H, 8.50; S, 8.81. Calcd for $C_{55}H_{92}GeS_3Si_6$: C, 60.57; H, 8.50; S, 8.82. **16c**: white crystals; mp 160–165 °C dec; ^{1}H NMR ($CDCl_3$, 500 MHz) δ −0.12 (s, 9H), −0.05 (s, 9H), 0.05 (s, 9H), 0.06 (s, 9H), 0.11 (s, 9H), 0.15 (s, 9H), 1.01 (br s, 3H), 1.05 (s, 1H, Ge–SH), 1.15 (d, J = 6.9 Hz, 6H), 1.25 (br s, 3H), 1.32 (s, 1H), 1.33 (br s, 6H), 1.71 (s, 1H, Ge–OH), 2.48 (br s, 1H), 2.65 (br s, 1H), 2.85 (sept, J = 6.9 Hz, 1H), 2.96 (br s, 1H), 4.43 (br s, 1H), 6.30 (br s, 1H), 6.43 (br s, 1H), 7.02 (s, 2H), 7.12–7.73 (m, 10H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 0.81 (q), 1.00 (q), 1.20 (q), 1.44 (q), 1.66 (q), 1.94 (q), 22.35 (q × 2), 23.63 (q), 23.89 (q), 24.72 (q × 2), 26.70 (d), 27.19 (d), 27.50 (d), 28.23 (d), 30.53 (d), 34.34 (d), 121.66 (d), 122.84 (d), 123.38 (d), 128.46 (d), 132.09 (s), 137.27

(s), 144.72 (s), 149.48 (s), 149.74 (s), 150.81 (s), 152.80 (s), 152.94 (s). Anal. Found: C, 57.50; H, 9.44; S, 4.09. Calcd for $C_{42}H_{84}GeOSSi_6$: C, 57.43; H, 9.64; S, 3.65.

Desulfurization of 1,2,3,5-tetrathia-4-germacyclohexane 10a. To a THF solution (10 mL) of **10a** (115 mg, 0.111 mmol) was added at −78 °C hexamethylphosphorous triamide (85 mL, 0.45 mmol). After the solution was warmed to room temperature over 10 h, the solvent was removed under reduced pressure. Separation with DCC (SiO_2 with 10/1 hexane/CH_2Cl_2) afforded **12a** (92.6 mg, 83%) and {2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}hydroxy(mercapto)(mesityl)germane (**16a**; (10.6 mg, 12%). **16a**: white crystals; mp 131−135 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ −0.11 (s, 9H), −0.06 (s, 9H), 0.04 (s, 18H), 0.06 (s, 18H), 0.91 (s, 1H, Ge−SH), 1.31 (s, 1H), 1.50 (s, 1H, Ge−OH), 2.23 (s, 3H), 2.36 (br s, 1H), 2.50 (br s, 1H), 2.52 (s, 6H), 6.27 (br s, 1H), 6.40 (br s, 1H), 6.79 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 0.75 (q), 0.85 (q), 1.26 (q), 1.54 (q), 20.92 (d), 24.52 (q), 27.60 (d), 27.62 (d), 30.50 (q), 122.99 (d), 127.93 (d), 129.70 (d), 130.98 (s), 138.30 (s), 139.72 (s), 141.94 (s), 145.29 (s), 150.01 (s), 150.25 (s). Anal. Found: C, 53.25; H, 8.82; S, 3.94. Calcd for $C_{36}H_{72}GeOSSi_6 \cdot H_2O$: C, 53.23; H, 9.18; S, 3.95.

Thiomethylation of 16a. To a mixture of **16a** (95.0 mg, 0.12 mmol) and sodium hydride (60% in mineral oil, 25 mg, 0.60 mmol) in THF (12 mL) was added methyl iodide at room temperature for 3 h. Insoluble salts were removed by filteration under argon, and the solvent was removed under reduced pressure. The residue was separated by PTLC (SiO_2 with 3/1 hexane/CH_2Cl_2) to afford {2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}hydroxy(mesityl)(methylthio)germane (**17a**; (87.4 mg, 90%). **17a**: white crystals; mp 202−205 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ −0.15 (s, 9H), −0.09 (s, 9H), 0.037 (s, 9H), 0.040 (s, 9H), 0.08 (s, 9H), 0.10 (s, 9H), 1.31 (s, 1H), 1.84 (s, 3H), 2.19 (s, 1H), 2.23 (s, 3H), 2.24 (s, 1H), 2.52 (br s, 6H), 6.27 (br s, 1H), 6.40 (br s, 1H), 6.78 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 0.39 (q), 0.73 (q), 0.78 (q), 0.88 (q), 1.41 (q), 1.69 (q), 11.55 (q), 20.96 (d), 24.16 (q), 27.96 (d), 28.37 (d), 30.46 (q), 122.82 (d), 127.80 (d), 129.43 (d), 131.89 (s), 133.01 (s), 139.42 (s), 143.31 (s), 145.02 (s), 149.84 (s), 150.01 (s). Anal. Found: C, 55.11; H, 9.00; S, 4.45. Calcd for $C_{37}H_{74}GeOSSi_6$: C, 54.98; H, 9.23; S, 3.97.

Desulfurization of 1,2,4,5-Tetrathia-3-germacyclohexane 11a. A THF solution (5 mL) of **11a** (23.0 mg, 0.022 mmol) and hexamethylphosphorous triamide (4.3 mL, 0.023 mmol) was refluxed for 10 h. The solvent was removed under reduced pressure, and the residue was chromatographed with DCC (SiO_2 with 10/1 hexane/CH_2Cl_2) to afford **12a** (1.6 mg, 5%) with recovery of **11a** (21.7 mg, 91%).

Thermal Reaction of 1,2,3,5-Tetrathia-4-germacyclohexane 10a. A $CDCl_3$ solution (0.5 mL) of **10a** (38.6 mg, 0.0368 mmol) was sealed in a 5 mm i.d. NMR tube and heated to 100 °C for 40 h while being monitored by ^1H NMR. The solvent was removed, and the residue was separated with PTLC (SiO_2 with 10/1 hexane/CH_2Cl_2) to afford **10a** (14.9 mg, 37%), **11a** (14.8 mg, 37%), **5a** (5.8 mg, 17%), and **12a** (4.2 mg, 9%).

Crystal and Experimental Data for 5a and 10a. 5a: $C_{36}H_{70}S_4Si_6Ge \cdot CHCl_3$, fw = 989.64, crystal size (mm) 0.2 × 0.2 × 0.5, monoclinic, space group $P2_1/n$, $a = 12.299(2)$ Å, $b = 13.069(2)$ Å, $c = 33.612(5)$ Å, $\beta = 91.58(1)°$, $V = 5401(2)$ Å^3, $Z = 4$, $D_c = 1.221$ g cm^{-3}, $R = 0.089$ ($R_w = 0.093$), $w = 1/\{A|F_o|2 + B|F_o| + C\}$, $A = 1086.4$, $B = -985.5$, $C = 227.1$. Data were collected through a capillary glass tube with Cu Kα radiation ($\lambda = 1.5418$ Å) on an Enraf-Nonius CAD-4 diifractometer; $\mu = 49.95$ cm^{-1}. A total of 5609 unique reflections ($|F_o| > 3\sigma|F_o|$) were observed ($2° < 2\theta < 120°$). Empirical absorption correction was not applied due to the noticeable decay of reflections. The structure was solved by direct methods (MULTAN 78)[21] using the program system UNICS III.[22] All hydrogen atoms were located by calculation. Refinement was performed by full-matrix least-squares method (anisotropic thermal parameters for non-hydrogen atoms), where the positions and thermal parameters for hydrogen atoms were not refined. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.[7]

10a: $C_{49}H_{80}GeS_4Si_6$, fw = 1038.51, crystal size (mm) 0.2 × 0.3 × 0.4, triclinic, $a = 13.329(2)$ Å, $b = 20.803(3)$ Å, $c = 12.325(2)$ Å, $\alpha = 105.37(1)°$, $\beta = 116.93(1)°$, $\gamma = 77.31(1)°$, $V = 2918.0(8)$ Å^3, $Z = 2$, space group $P\bar{1}$, $D_c = 1.182$ g cm^{-3}, $\mu = 8.05$ cm^{-1}. The intensity data ($2\theta \le 55°$) were collected on a Rigaku AFC5R diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,69$ Å), and the structure was solved by direct methods.[23] All calculations were performed using the TEXSAN[24] crystallographic software package of Molecular Structure Corp. The non-hydrogen atoms were refined anisotropically, and all the hydrogen atoms were located by calculation. The final cycle of full-matrix least-squares refinement was based on 3881 observed reflections ($I > 3\sigma(I)$) and 541 variable parameters with R (R_w) = 0.039 (0.044). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.[11]

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Supplementary Material Available: Tables giving crystallographic data, atomic coordinates, temperature factors, and bond lengths and angles, for **5a** and **10a** and a table of torsion angles for **10a** (31 pages). Ordering information is given on any current masthead page.

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