

The First Kinetically Stabilized Germanethiones and Germaneselones: Syntheses, Structures, and Reactivities

Tsuyoshi Matsumoto,[†] Norihiro Tokitoh,^{*,‡} and Renji Okazaki^{*,§}

Contribution from the Department of Chemistry, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

Received April 12, 1999

Abstract: The first kinetically stabilized germanethiones (germanium–sulfur double-bond species) and germaneselones (germanium–selenium double-bond species) were synthesized. Dechalcogenation of the novel 1,2,3,4,5-tetrachalcogenagermolane Tbt(Tip)GeX₄ (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, Tip = 2,4,6-triisopropylphenyl, X = S or Se) with 3 molar equiv of triphenylphosphine gave diaryl-substituted germanethione Tbt(Tip)Ge=S **1a** and germaneselonone Tbt(Tip)Ge=Se **2a** as orange–yellow crystals and red crystals, respectively, which were unstable in air but thermally quite stable. Chalcogenation of germylene Tbt(Dis)Ge: resulted in the isolation of the corresponding germanethione Tbt(Dis)Ge=S **1b** and germaneselonone Tbt(Dis)Ge=Se **2b** (Dis = bis(trimethylsilyl)methyl). The molecular structures of germanethione **1a** and germaneselones **2a,b** determined by X-ray crystallographic analysis indicate that they have trigonal planar geometries around the germanium atom and a remarkably shorter Ge–S (2.049(3) Å for **1a**) or Ge–Se bond lengths (2.180(2) Å for **2a** and 2.173(3) Å for **2b**), compared with that of typical single bonds. The double-bond characters are also reflected in their spectral data such as UV/vis (**1a**, 450 nm; **1b**, 432 nm; **2a**, 519 nm; **2b**, 492 nm), Raman (**1a**, 521 cm⁻¹; **1b**, 512 cm⁻¹; **2a**, 381 cm⁻¹; **2b**, 386 cm⁻¹), and ⁷⁷Se NMR (**2a**, 941 ppm; **2b**, 872 ppm). The germanethiones and germaneselones underwent [2 + 2] (with phenyl isothiocyanate), [3 + 2] (with mesitonitrile oxide), and [4 + 2] cycloadditions (with 1,3-dienes) to give the corresponding adducts in high yields. The regioselectivities of the [4 + 2] cycloadditions were examined using unsymmetrical dienes such as isoprene and interpreted in terms of the interaction between LUMO of the Ge=X unit and HOMO of the diene part.

Introduction

Over the past few decades, it had been commonly considered that double bonds between heavier main-group elements would not be stable for their weak π -bonds, which was the so-called “double-bond rule”. In the 1960s, however, the double-bond species between the heavier groups 14 and 15 elements came to be proposed via trapping experiments, and the isolation of compounds with Si=C,¹ Si=Si,² and P=P³ bonds was achieved in 1981. After this breakthrough, remarkable progress has been made in the chemistry of multiply bonded compounds of heavier main group elements.

Among them are double-bond species between groups 14 and 16 elements, that is, congeners of a carbonyl compound, which are of current interest. Although many reports have also been published for transient germanium–chalcogen double-bond species,⁴ the examples of stable species are rare. Three Ge–S^{5–7} and two Ge–Se double-bond compounds^{6,7} have been isolated, but all of them were stabilized by intramolecular coordination of nitrogen ligands. We preliminarily reported the

first isolation of kinetically stabilized germanethione Tbt(Tip)Ge=S **1a**^{8a} and germaneselonone Tbt(Tip)Ge=Se **2a**,^{8b} along with some other analogues of double-bond species between group 14 and group 16 elements,^{8c,9,10} by taking advantage of a very effective steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt¹¹).

This paper describes the detailed account of the isolation, molecular structure, physical properties, and reactivities of the diarylgermanethione **1a** and diarylgermaneselonone **2a** as well as new germanethione Tbt(Dis)Ge=S **1b** and germaneselonone Tbt(Dis)Ge=Se **2b**, having Dis group [Dis; bis(trimethylsilyl)methyl]. The syntheses of **1b** and **2b** are expected to enable us

(4) For reviews: (a) Barrau, J.; Escudié, J.; Satgé, J. *Chem. Rev.* **1990**, *90*, 283. (b) Satgé, J. *Adv. Organomet. Chem.* **1982**, *21*, 241. (c) Rivière, P.; Rivière-Baudet, M.; Satgé, J. *Comprehensive Organometallic Chemistry*; Pergamon Press: New York, 1982; Vol. 2, Chapter 2. (d) Power, P. P. *J. Chem. Soc., Dalton. Trans.* **1998**, 2939.

(5) (a) Veith, M.; Becker, S.; Huch, V. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1237. (b) Veith, M.; Detemple, A.; Huch, V. *Chem. Ber.* **1991**, *124*, 1135. (c) Veith, M.; Detemple, A. *Phosphorus, Sulfur Silicon Relat. Elem.* **1992**, *65*, 17.

(6) (a) Kuchta, M. C.; Parkin, G. *J. Chem. Soc., Chem. Commun.* **1994**, 1351. (b) *idem, ibid.* **1996**, 1669.

(7) Ossig, G.; Meller, A.; Brönneke, C.; Müller, O.; Schäfer, M.; Herbst-Irmer, R. *Organometallics* **1997**, *16*, 2116.

(8) (a) Tokitoh, N.; Matsumoto, T.; Manmaru, K.; Okazaki, R. *J. Am. Chem. Soc.* **1993**, *115*, 8855. (b) Matsumoto, T.; Tokitoh, N.; Okazaki, R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2316. (c) Tokitoh, N.; Matsumoto, T.; Okazaki, R. *J. Am. Chem. Soc.* **1997**, *119*, 2337.

(9) (a) Suzuki, H.; Tokitoh, N.; Nagase, S.; Okazaki, R.; *J. Am. Chem. Soc.* **1994**, *116*, 11578. (b) Suzuki, H.; Tokitoh, N.; Okazaki, R.; Nagase, S.; Goto, M. *J. Am. Chem. Soc.* **1998**, *120*, 11096.

(10) (a) Tokitoh, N.; Saito, M.; Okazaki, R. *J. Am. Chem. Soc.* **1993**, *115*, 2065. (b) Saito, M.; Tokitoh, N.; Okazaki, R. *J. Organomet. Chem.* **1995**, *499*, 43. (c) *idem, Organometallics* **1996**, *15*, 4531. (d) *idem, J. Am. Chem. Soc.* **1997**, *119*, 11124.

[†] Present address: Department of Chemistry, Graduate School of Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8602, Japan.

[‡] Present address: Institute for Fundamental Research of Organic Chemistry, Kyusyu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan.

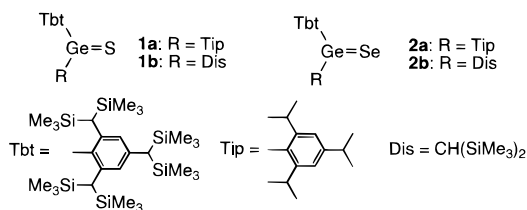
[§] Present address: Department of Chemical and Biological Sciences, Faculty of Science, Japan Women's University, Mejirodai, Bunkyo-ku, Tokyo 112-8681, Japan.

(1) Brook, A. G.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K. *J. Chem. Soc., Chem. Commun.* **1981**, 191.

(2) West, R.; Fink, M. J.; Michl, J. *Science (Washington, D.C.)* **1981**, *214*, 1343.

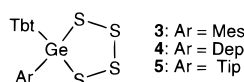
(3) Yoshifuji, M.; Shima, I.; Inamoto, N.; Hirotsu, K.; Higuchi, T. *J. Am. Chem. Soc.* **1981**, *103*, 4587.

to study a possible effect of an aryl group on the properties of those double-bond species.



Results and Discussion

Synthesis of Diaryl-Substituted Germanethione, Tbt(Tip)-Ge=S (1a). We previously reported the synthesis of novel cyclic polysulfides containing Ge atom, 1,2,3,4,5-tetrathiagermolanes Tbt(Ar)GeS₄ [**3**, Ar = 2,4,6-trimethylphenyl (Mes); **4**, Ar = 2,6-diethylphenyl (Dep); **5**, Ar = 2,4,6-triisopropylphenyl (Tip)], which are a useful precursor for the germanethione.¹²



The desulfurization of tetrathiagermolane **3** with 3 equiv of hexamethylphosphorous triamide at -78°C gave hydroxy-(mercapto)germane **6** and *cis*-1,3,2,4-dithiadigermetane **7**. This indicates the generation of germanethione Tbt(Mes)Ge=S **8** because the formation of **6** and **7** is reasonably explained in terms of reaction with water and head-to-tail dimerization of **8**, respectively.¹³ The desulfurization with hexamethylphosphorus triamide in a sealed tube in THF at 90°C afforded the dimer **7** exclusively. Even in the presence of 2,3-dimethyl-1,3-butadiene as a trapping reagent, only the dimer **7** was obtained, indicating the very fast self-dimerization of **8** (Scheme 1).^{14,15}

By contrast, the desulfurization of the tetrathiagermolane **5**, having a much bulkier Tip group, exclusively gave hydroxy-(mercapto)germane Tbt(Tip)Ge(OH)(SH) **9** regardless of the reaction conditions after usual workup without any precaution toward water, suggesting the generation of monomeric germanethione Tbt(Tip)Ge=S **1a**. When the desulfurization of **5** by 3 equiv of triphenylphosphine in hexane in a glovebox filled with pure argon, germanethione **1a** was quantitatively yielded as orange–yellow crystals after filtration of triphenylphosphine sulfide, which was formed quantitatively and totally insoluble in hexane (Scheme 2). The molecular structure was confirmed by spectral data and X-ray structural analysis (*vide supra*). Germanethione **1a** is very sensitive toward moisture, but

(11) Although 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl group had been denoted as Tbt in our previous papers, we changed this acronym to Tbt in order to avoid confusion with a 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.

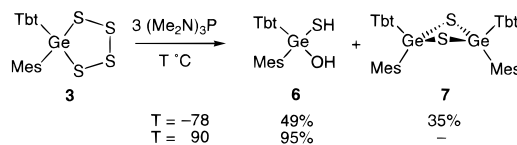
(12) (a) Tokitoh, N.; Suzuki, H.; Matsumoto, T.; Matsushashi, Y.; Okazaki, R.; Goto, M. *J. Am. Chem. Soc.* **1991**, 113, 7047. (b) Matsumoto, T.; Tokitoh, N.; Okazaki, R.; Goto, M. *Organometallics* **1995**, 14, 1008.

(13) The molecular structure of **7** was determined by X-ray structural analysis, which revealed the extremely congested *cis* configuration of four bulky aryl groups with unprecedentedly large fold angles of the central rhombic dithiadigermetane ring. Tokitoh, N.; Matsumoto, T.; Ichida, H.; Okazaki, R. *Tetrahedron Lett.* **1991**, 32, 6877.

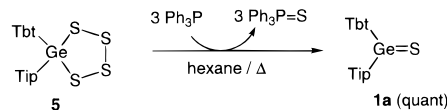
(14) The same result was also obtained in the case of Tbt(Dep)GeS₄ **4** bearing a bulkier group Dep on germanium, the corresponding 1,3,2,4-dithiadigermetane being formed.

(15) Ando and co-workers reported that dimesitylgermanethione underwent dimerization to give 1,3,2,4-dithiadigermetane without any formation of [4 + 2] adduct, even when the germanethione was generated in the presence of 2,3-dimethyl-1,3-butadiene; see Tsumuraya, T.; Sato, S.; Ando, W. *Organometallics* **1988**, 7, 2015.

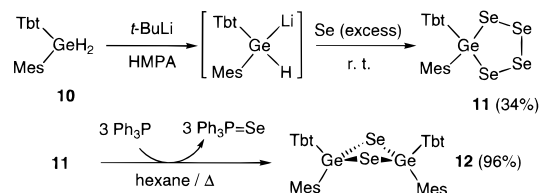
Scheme 1



Scheme 2



Scheme 3



thermally very stable. It melted at $163\text{--}165^\circ\text{C}$ without decomposition, no change being observed even after heating of its hexane solution at 160°C for 3 days in a sealed tube.

Synthesis of Diaryl-Substituted Germaneselenone, Tbt(Tip)-Ge=Se (2a).¹⁶ Although a cyclic polyselenide containing Ge atom is considered to be a proper starting material for the synthesis of germaneselenone as in the case of germanethione, no selenated product was obtained by the direct thermal selenation of diarylgermane Tbt(Mes)GeH₂ **10** with elemental selenium even in refluxing *o*-dichlorobenzene in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene as an activator of the selenation.¹⁶ However, we succeeded in the isolation of the first 1,2,3,4,5-tetraselenagermolane **11** (Scheme 3) by the reaction of elemental selenium with a germyllithium generated from dihydrogermane **10** with *tert*-butyllithium in THF at -20°C in the presence of cosolvent, hexamethylphosphoramide (HMPA), and its structure was revealed by X-ray crystallographic analysis.¹⁷ Deselenation of **11** with triphenylphosphine at 90°C gave 1,3,2,4-diselenadigermetane **12**, a dimer of the corresponding germaneselenone Tbt(Mes)Ge=Se, despite the presence of excess 2,3-dimethyl-1,3-butadiene as was observed in the desulfurization of Tbt(Mes)GeS₄ **3**. The molecular structure of **12** is shown in Figure 1 along with selected bond lengths and angles. Figure 1b shows that the folding of the four-membered ring releases the steric hindrance effectively as is observed also in 1,3,2,4-dithiadigermetane **7**.¹³ Dihedral angle between Se(1)–Ge(1)–Se(1*) plane and Se(1)–Ge(1*)–Se(1*) plane is 43.8° for **12**, whereas the corresponding angle is 37.8° for **7**.

The synthesis of Tbt(Tip)GeSe₄ **13** bearing a bulkier Tip group was achieved by treatment of the corresponding germyllithium with elemental selenium, but the yield was only 7% (13% conversion yield), probably because of the lower reactivity of the sterically hindered germyllithium and the instability of **13** under the basic reaction conditions unlike the corresponding tetrathiagermolanes. We then used diarylgermylene Tbt(Tip)-Ge: **14** as a precursor for the desired tetraselenagermolane, because a germylene is known to be highly reactive.¹⁸ Although

(16) The activation of elemental selenium with amines has been reported; see (a) Tokitoh, N.; Hayakawa, H.; Goto, M.; Ando, W. *Tetrahedron Lett.* **1988**, 29, 1935. (b) Chenard, B. L.; Miller, T. J. *J. Org. Chem.* **1984**, 49, 1221. (c) Yoshida, H.; Kabe, Y.; Ando, W. *Organometallics* **1991**, 10, 27.

(17) A preliminary communication: Tokitoh, N.; Matsumoto, T.; Okazaki, R. *Tetrahedron Lett.* **1992**, 33, 2531.

(18) Neumann, W. P. *Chem. Rev.* **1991**, 91, 311, and references therein.

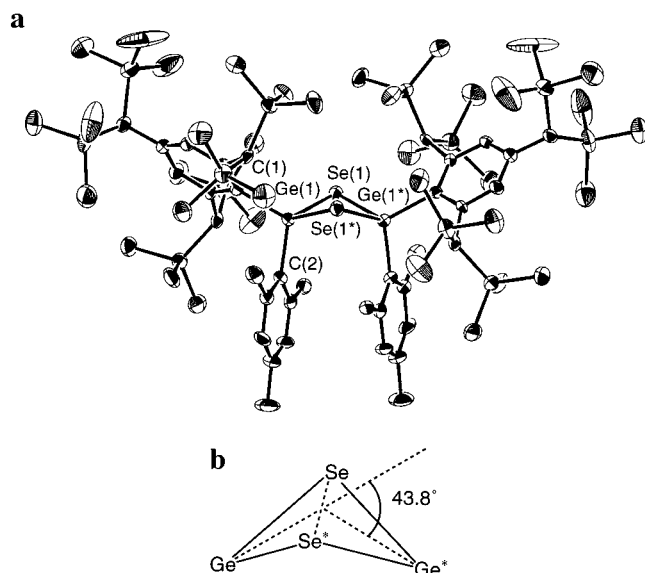


Figure 1. (a) ORTEP drawing of **12** with thermal ellipsoid plot (30% probability). Selected bond lengths (Å) and angles (deg): Ge(1)–Se(1) 2.397(1), Ge(1)–Se(1*) 2.433(1), Ge(1)–C(1) 2.013(7), Ge(1)–C(2) 1.994(7), Ge(1)–Se(1)–Ge(1*) 83.54(4), Se(1)–Ge(1)–Se(1*) 88.23(4), C(1)–Ge(1)–Se(1) 114.3(2), C(1)–Ge(1)–Se(1*) 118.8(2), C(2)–Ge(1)–Se(1) 112.9(2), C(2)–Ge(1)–Se(1*) 107.6(2), C(1)–Ge(1)–C(2) 112.7(3). (b) Dihedral angle of **12**.

we previously reported the generation of **14** by the reaction of GeI_2 with TbtLi and TipLi ,¹⁹ the yield was low. We then took advantage of reductive debromination of dibromogermene $\text{Tbt}(\text{Tip})\text{GeBr}_2$ **15** by lithium naphthalenide for the synthesis of **14**.²⁰ Treatment of **15** with 2 equiv of lithium naphthalenide in THF at -78°C afforded a blue solution ($\lambda_{\text{max}} = 581\text{ nm}$) of an expected germylene **14**. This absorption maximum is similar, although relatively red shifted, to those reported for other diorganogermynes which are attributed to an $n\text{-p}$ transition.^{21,22} The large groups substituted on germanium atom expand the bond angle of R-Ge-R and hence make the difference between n and p energy levels smaller, resulting in the red shift of $n\text{-p}$ transition. The generation of germylene **14** was also confirmed by a trapping reaction with 2,3-dimethyl-1,3-butadiene to give germacyclopentene **16** in 68% yield (Scheme 4).

The reaction of **14** with an excess amount of elemental selenium resulted in the successful isolation of the expected 1,2,3,4,5-tetraselenagermolane **13** in a reasonable yield as orange crystals. Here it should be noted that any selenation reaction (see also the formation of **20** in Scheme 6) gave only five-

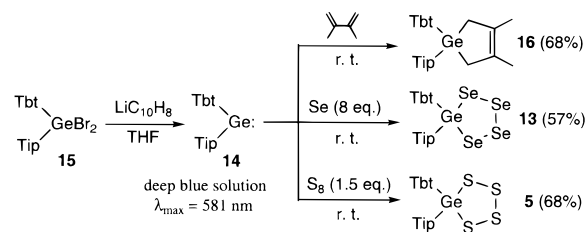
(19) (a) Tokitoh, N.; Manmaru, K.; Okazaki, R. *Organometallics* **1994**, *13*, 167. (b) Tokitoh, N.; Manmaru, K.; Okazaki, R. *Nippon Kagaku Kaishi* **1994**, 240.

(20) Masamune and co-workers reported the reductive coupling of dichlorodiarylgermenes with lithium naphthalenide to give a cyclotrimerane from dichloro[bis(2,6-diethylphenyl)]germane and a digermene (germanium–germanium double-bond species) from dichloro[bis(2,6-diisopropylphenyl)]germane. (a) Masamune, S.; Hanzawa, Y.; Williams, D. J. *J. Am. Chem. Soc.* **1982**, *104*, 6136. (b) Snow, J. T.; Murakami, S.; Masamune, S.; Williams, D. J. *Tetrahedron Lett.* **1984**, *25*, 4191. (c) Park, J.; Batcheller, S. A.; Masamune, S. *J. Organomet. Chem.* **1989**, *367*, 39. (d) Tsumuraya, T.; Batcheller, S. A.; Masamune, S. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 902.

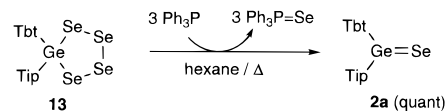
(21) Some recent examples, see (a) Jutzi, P.; Schmidt, H.; Neumann, B.; Stammmer, H. G. *Organometallics* **1996**, *15*, 741. (b) Simons, R. S.; Pu, L.; Olmstead, M. M.; Power, P. P. *Organometallics* **1997**, *16*, 1920. (c) Jutzi, P.; Becker, A.; Stammmer, H. G.; Neumann, B. *Organometallics* **1991**, *10*, 1647.

(22) (a) Ando, W.; Itoh, H.; Tsumuraya, T.; Yoshida, H. *Organometallics* **1988**, *7*, 1880. (b) Ando, W.; Itoh, H.; Tsumuraya, T. *Organometallics* **1989**, *8*, 2759, and references therein.

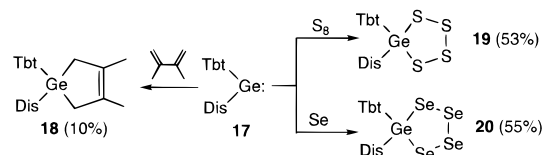
Scheme 4



Scheme 5



Scheme 6



membered polyselenide selectively, as in the case of the polysulfides **3**, **4** and **5**.¹² As was discussed in the previous paper,^{13b} the isolation of only five-membered-ring compounds is probably owing to the steric repulsion between the bulky Tbt and Ar (Mes or Tip) groups on Ge atom which enlarges the bond angle of C-Ge-C and hence narrows the angle S-Ge-S or Se-Ge-Se .

The germylene **14** also reacted with elemental sulfur to give 1,2,3,4,5-tetrathiagermolane **5** in 68% yield.

Unlike **11**, the deselenation of **13** with triphenylphosphine resulted in the quantitative isolation of the first stable germaneselenone **2a** as red crystals (Scheme 5). Dimerization of **2a** was not observed even in refluxing hexane, despite the longer bond distance of Ge=Se than that of Ge=S . Germaneselenone **2a** is the first example of a kinetically stabilized germaneselenone; it is extremely sensitive to moisture but thermally very stable like **1a**.

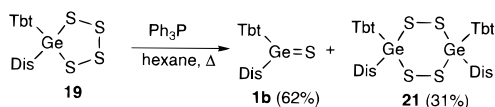
Synthesis of Cyclic Polysulfide and Polyselenide bearing Tbt and Dis. To synthesize $\text{Tbt}(\text{Dis})\text{Ge=X}$, having a bulky alkyl group Dis instead of Tip , we examined the syntheses of cyclic polychalcogenides containing Ge atom. Germylene $\text{Tbt}(\text{Dis})\text{Ge:}$ **17** was generated by reductive debromination of dibromogermene $\text{Tbt}(\text{Dis})\text{GeBr}_2$ with 2 equiv of lithium naphthalenide and confirmed by its UV–vis spectrum ($\lambda_{\text{max}} = 535\text{ nm}$ in THF) and the formation of a trapping product with 2,3-dimethyl-1,3-butadiene, albeit in low yield probably because of steric congestion (Scheme 6).

Germylene **17** was allowed to react with an excess amount of elemental sulfur and selenium to afford the five-membered 1,2,3,4,5-tetrathiagermolane **19** and 1,2,3,4,5-tetraselenagermolane **20**, respectively.²³

Synthesis of Alkyl,aryl-Disubstituted $\text{Tbt}(\text{Dis})\text{Ge=X}$ ($\text{X} = \text{S}, \text{Se}$). Desulfurization of tetrathiagermolane **19** was carried out using 3 equiv of triphenylphosphine in a manner similar to that for diarylgermanethione **1a** to afford germanethione **1b** as yellow crystals (Scheme 7). The yield was, however, only 62%,

(23) Although the final level has not yet been reached due to the low quality of the single crystal used, the molecular structure of $\text{Tbt}(\text{Dis})\text{GeSe}_4$ (**20**) was preliminarily determined by X-ray crystallographic analysis, whose configuration of the tetraselenolane ring and the geometry around the Ge atom were almost similar to those of $\text{Tbt}(\text{Mes})\text{GeSe}_4$ (**11**);¹⁷ Matsumoto, T. Doctor Thesis, The University of Tokyo, 1994.

Scheme 7



Scheme 8

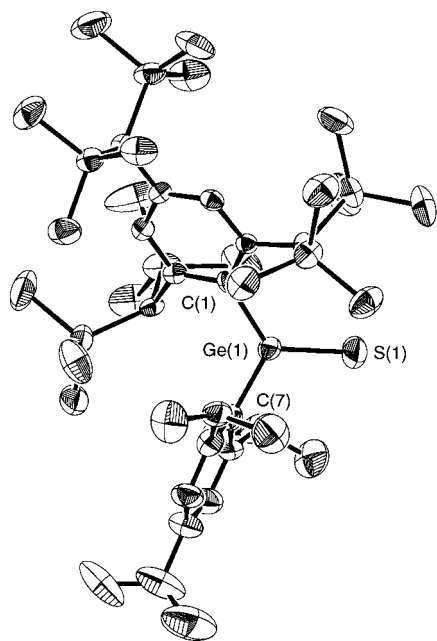
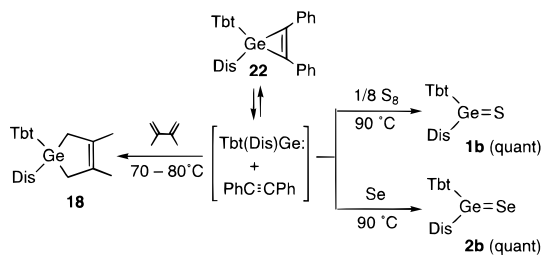


Figure 2. ORTEP drawing of $\text{Tbt}(\text{Tip})\text{Ge}=\text{S}$ **1a** with thermal ellipsoid plot (30% probability).

owing to the formation of unexpected tetrathiadigermacyclohexane **21** as a white solid totally insoluble in common organic solvents.²⁴

To obtain the germanethione in higher yield, we used germirene (germacyclopropene) **22** as the germylene precursor. We previously reported that the germirene **22**, prepared from germylene **17** and diphenylacetylene as a stable solid, regenerated the germylene **17** via cycloreversion on heating to 80°C .²⁵ Thermolysis of the germirene **22** in the presence of $1/8$ equiv of S_8 in C_6D_6 quantitatively gave germanethione **1b**, which was isolated as yellow crystals in a glovebox filled with argon (Scheme 8).

Similarly, germaneselenone $\text{Tbt}(\text{Dis})\text{Ge}=\text{Se}$ **2b** was synthesized quantitatively and isolated as orange-red crystals.

Crystal Structures of Germanethione 1a and Germaneselenones 2a, 2b. The molecular structures of **1a** and **2a, 2b** were determined by X-ray crystallographic analysis. The ORTEP drawings (Figures 2, 3, and 4) show that the germanium-chalcogen units are effectively protected by bulky groups. The

(24) The yield of the germanethione was estimated by the yield of hydroxy(mercapto)germane $\text{Tbt}(\text{Dis})\text{Ge}(\text{SH})(\text{OH})$, which was formed by the addition of water. See Experimental Section.

(25) Tokitoh, N.; Kishikawa, K.; Matsumoto, T.; Okazaki, R. *Chem. Lett.* **1995**, 827.

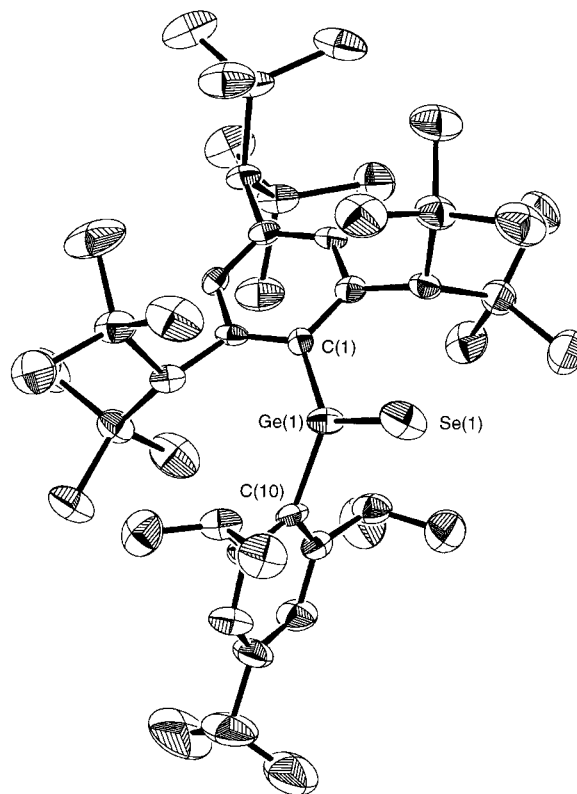


Figure 3. ORTEP drawing of $\text{Tbt}(\text{Tip})\text{Ge}=\text{Se}$ **2a** with thermal ellipsoid plot (30% probability).

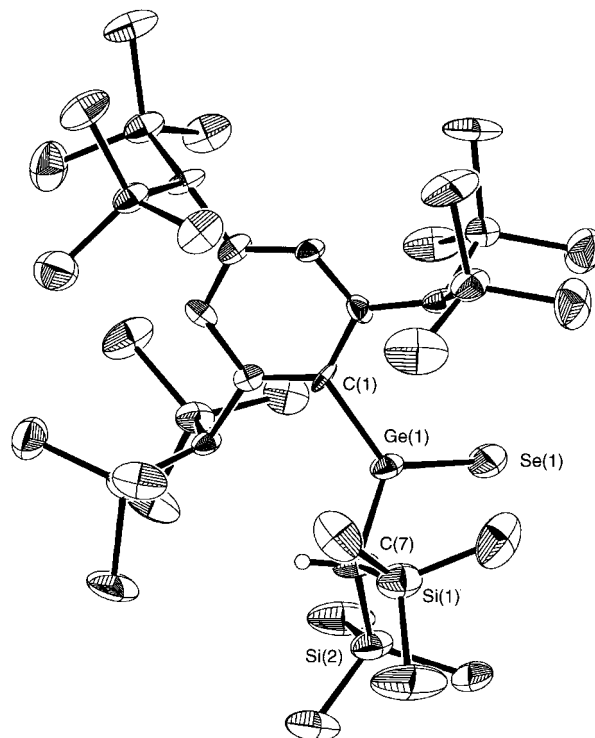


Figure 4. ORTEP drawing of $\text{Tbt}(\text{Dis})\text{Ge}=\text{Se}$ **2b** with thermal ellipsoid plot (30% probability).

shortest intermolecular distance between Ge and S in **1a** is 5.91 \AA , which is much longer than the sum of van der Waals radii (3.90 \AA), indicating the absence of intermolecular interaction even in the solid state. This is also the case with the germaneselenones, in which the intermolecular Ge-Se distances are 5.69 and 8.13 \AA for **2a** and **2b**, respectively.²⁶ The selected bond lengths and bond angles are summarized in Table 1.

Table 1. Selected Bond Lengths (Å) and Angles (deg) of Germanethione **1a** and Germaneselenones **2a**, **2b**

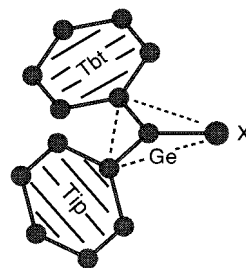
Tbt(Tip)Ge=S 1a		Tbt(Tip)Ge=Se 2a		Tbt(Dis)Ge=Se 2b	
bond lengths (Å)					
Ge(1)–S(1)	2.049(3)	Ge(1)–Se(1)	2.180(2)	Ge(1)–Se(1)	2.173(3)
Ge(1)–C(1)	1.953(9)	Ge(1)–C(1)	1.932(9)	Ge(1)–C(1)	1.99(1)
Ge(1)–C(7)	1.91(1)	Ge(1)–C(10)	1.945(9)	Ge(1)–C(7)	1.92(2)
bond angles (deg)					
S(1)–Ge(1)–C(1)	124.8(3)	Se(1)–Ge(1)–C(1)	126.4(3)	Se(1)–Ge(1)–C(1)	122.5(4)
S(1)–Ge(1)–C(7)	116.2(3)	Se(1)–Ge(1)–C(10)	113.8(3)	Se(1)–Ge(1)–C(7)	117.8(4)
C(1)–Ge(1)–C(7)	118.4(4)	C(1)–Ge(1)–C(10)	119.1(4)	C(1)–Ge(1)–C(7)	119.7(6)

In the germanethione **1a**, the intramolecular Ge–S distance is 2.049(3) Å, which is 9% shorter than typical Ge–S single bond lengths (2.21 ± 0.04 Å)²⁷ and in good agreement with the calculated one (2.042 Å for H₂Ge=S).²⁸ The geometry around the germanium atom is trigonal planar, the sum of the angles being 359.6°. These facts clearly show that the germanium–sulfur bond in **1a** has a double-bond character. The bond lengths of base-stabilized germathioureas are reported to be longer [2.063(3) and 2.110(2) Å]^{5,6} than that of germanethione **1a**.

Similar structural properties were observed for the germaneselenones. Their trigonal planar geometry is shown in the sum of the bond angles around the germanium atom (359.3° for **2a** and 360.0° for **2b**). The Ge–Se bond distances of **2a** [2.180(2) Å] and **2b** [2.173(3) Å] are reduced by 9% compared with those reported for typical germanium–selenium single bonds²⁹ and shorter than those of the reported germaselenourea [2.247(1) and 2.2472(7)].^{6,7} The calculated Ge=Se bond length for H₂Ge=Se is 2.174 Å,²⁸ which agrees well with these results.

The dihedral angles observed for **1a** and **2a** are shown in Table 2. Two aryl groups are arranged almost perpendicular to each other. The large groups on the ortho position of the aromatic rings hinder the aryl groups from situating on the germathiocarbonyl π plane, indicating the absence of significant conjugative interaction between the two aryl groups and the Ge=X double bond in the solid state. In the case of Tbt(Dis)-Ge=Se **2b**, the dihedral angle between the π -plane of Ge=Se and the aryl ring is 56°, being considerably larger than that for **1a** (39°) and **2a** (38°).

Physical Properties. (1) Electronic Spectra. The absorption maxima of the n- π^* transition are summarized in Table 3. In hexane the absorption maxima due to the n- π^* transition of Ge=Se bond in **2a** appears at 519 nm (ϵ 140), being red-shifted compared to germanethione **1a** (450 nm, ϵ 100) as is observed for the corresponding carbon analogues (thioketone vs sele-

Table 2. Dihedral Angles of Germanethione **1a** and Germaneselenone **2a**

plane	plane	angles (deg)	
		1a (X = S)	2a (X = Se)
Tbt	π (Ge=X)	39	38
Tip	π (Ge=X)	70	72
Tbt	Tip	89	89

Table 3. UV–Vis Spectra of Germanethiones **1a,b** and Germaneselenones **2a,b**

solvent	λ_{\max}/nm			
	1a	1b	2a	2b
hexane	450	432	519	492
benzene	444	427	513	486
Et ₂ O	451			
THF	444		510	

noketone).³⁰ One can see that the absorption maxima show only slight solvent dependency, suggesting no coordination of the solvent toward the Ge=X bond. Small red shifts in λ_{\max} (n- π^*) on going from Tbt(Tip)Ge=X to Tbt(Dis)Ge=X ($\Delta\lambda$ = 18 nm for germanethiones and 27 nm for germaneselenones) indicate a minor contribution from conjugation between the aryl group and the Ge=X bond in solution.

(2) Raman Spectra. Raman shifts attributed to the stretching of the Ge=S groups were observed at 521 (for **1a**) and 512 cm⁻¹ (for **1b**). This suggests a fair degree of double-bond character in this polar bond since the stretching vibrations of Ge–S single bonds normally appear near 410 cm⁻¹.³¹ Nefedov and co-workers reported the IR spectrum for dimethylgermanethione in an argon matrix at 17–18 K and assigned an absorption at 518 cm⁻¹ to the stretching of the Ge=S bond.³² Their result is in good agreement with those for **1a** and **1b** observed here. In the germaneselenones were observed the Raman shifts at 381 (**2a**) and 386 cm⁻¹ (**2b**), that is, at a lower field compared to the germanethiones. These observed values are in

(26) The sum of van der Waals radii of Ge and Se is 4.0 Å.

(27) A search of the Cambridge Crystallographic Database indicates the following metrical data for Ge–S bond interactions (given in the order of mean, range, and number of observations in distribution): $d(\text{Ge}–\text{S}) = 2.26$ Å, 2.06–2.84 Å, 145. The bond lengths of organogermane sulfide are reported to vary within a range of 2.21 ± 0.04 Å. For example, see: (a) Benno, R. H.; Frichie, C. J. *J. Chem. Soc., Dalton Trans.* **1973**, 543. (b) Jutzi, P.; Steiner, W.; König, E.; Huttner, G.; Frank, A.; Schubert, U. *Chem. Ber.* **1978**, *111*, 606. (c) Chadha, R. K.; Drake, J. E.; Sarkar, A. B. *Inorg. Chem.* **1987**, *26*, 2885. (d) Ando, W.; Kadowaki, T.; Kabe, Y.; Ishii, M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 59. For a review, see (e) Baines, K. M.; Stibbs, W. G. *Coord. Chem. Rev.* **1995**, *145*, 157.

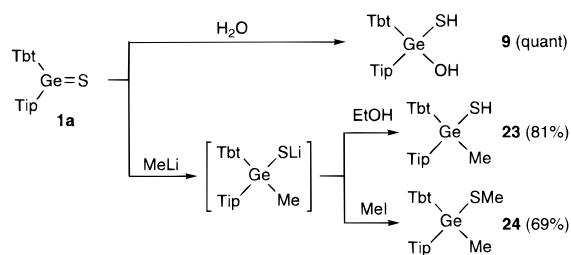
(28) Calculated with B3LYP/TZ(d, p); see ref 9b.

(29) A search of the Cambridge Crystallographic Database indicates the following metrical data for Ge–Se bond interactions (given in the order of mean, range, and number of observations in distribution): $d(\text{Ge}–\text{Se}) = 2.37$ Å, 2.31–2.77 Å, 38. The bond lengths of organogermane selenides are reported to vary from 2.337 to 2.421 Å. For example, see: (a) Weidenbruch, M.; Ritschl, A.; Peters, K.; Schnering, H. G. *J. Organomet. Chem.* **1992**, *438*, 39. (b) Dräger, M.; Häberle, K. *ibid.* **1985**, *280*, 183. (c) Ross, V. L.; Dräger, M. *Z. Anorg. Allg. Chem.* **1981**, *472*, 109, and references cited therein. See also ref 27e.

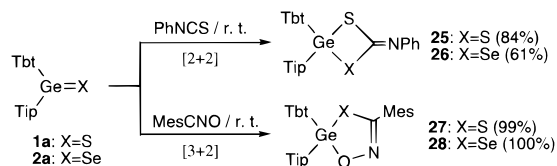
(30) (a) For thioketones: Duus, F. In *Comprehensive Organic Chemistry*; Barton, D. H. R., Ollis, W. D., Eds.; Pergamon Press: Oxford, U.K., 1979; Vol. 3, p 373. (b) For selenoketones: Guziac, F. S., Jr. In *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Ed.; John Wiley & Sons: New York, 1987; Vol. 2, p 215, and references therein.

(31) (a) Cradock, S. J. *J. Chem. Soc. A* **1968**, 1426. (b) Goldfarb, T. D.; Sujishi, S. *J. Am. Chem. Soc.* **1964**, *86*, 1679. (c) Schumann, H.; Schmidt, M. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 1007. (d) Vyazankin, N. S.; Bochkarev, M. N.; Sanina, L. P.; Egorochkin, A. N.; Khorshv, S. Ya. *Zh. Obshch. Khim.* **1967**, *37*, 2576 (Russ), 2451 (Engl).

Scheme 9



Scheme 10



keeping with the calculated values (B3LYP/TZ(d,p) level), that is, 542 cm^{-1} for $\text{H}_2\text{Ge}=\text{S}$ and 379 cm^{-1} for $\text{H}_2\text{Ge}=\text{Se}$.^{9b}

(3) **⁷⁷Se NMR of the Germaneselenones.** It is reported that the ⁷⁷Se chemical shift of $(\text{H}_3\text{Ge})_2\text{Se}$, having Ge–Se single bonds, is –612 ppm (relative to $(\text{H}_3\text{C})_2\text{Se}$).³³ By contrast, ⁷⁷Se NMR of the germaneselenones shows a signal at a much lower field (941 ppm for **2a** and 872 ppm for **2b**), which is characteristic of doubly bonded selenium atoms.³⁴ One can see that Tbt(Tip)Ge=Se **2a** resonates at a lower field than Tbt(Dis)Ge=Se **2b**, which agrees with the trend observed in the electronic spectra,³⁵ although the difference is quite small.

Reactions of Germanethiones and Germaneselenones. Germanethione **1a** was allowed to react with water to give hydroxy-(mercaptop)germane **9**. Exposure of **1a** to air also immediately afforded **9** quantitatively, indicating the high reactivity of the Ge=S bond to water. No adduct was obtained in the reaction with methyl iodide at ambient temperature. This is in contrast to the results reported for thermodynamically stabilized germanium–sulfur compounds.^{5–7} The addition of methyl lithium gave **23** or **24** after quenching with ethanol or methyl iodide, respectively, reflecting the polarization of the Ge=S bond like $\text{Ge}^{\delta+}=\text{S}^{\delta-}$ in contrast to thiocarbonyl compounds, in which thiophilic reactions were observed (Scheme 9).³⁶

The double-bond character of the Ge=X bond (X = S, Se) in **1** and **2** manifested itself in the cycloaddition reactions with various 2π and 4π systems. For example, phenyl isothiocyanate reacted smoothly with **1a** and **2a** at room temperature to afford [2 + 2] cycloadduct **25** and **26** in 84% and 61%, respectively (Scheme 10). These are the first examples of imino-substituted

(32) The IR spectrum of the matrix-isolated dimethylgermanethione generated by gas-phase pyrolysis of $(\text{Me}_2\text{GeS})_3$ was reported by Michl and co-workers to be 605 cm^{-1} for the Ge=S stretching. However, immediately after their report, the assignment was revised to be 518 cm^{-1} by Nefedov et al. The observed frequencies and their relative intensities are in good agreement with those calculated at the ab initio Hartree–Fock level. See (a) Barrau, J.; Balaji, V.; Michl, J. *Organometallics* **1989**, *8*, 2034. (b) Khabashesku, V. N.; Boganov, S. E.; Zuev, P. S.; Nefedov, O. M. *J. Organomet. Chem.* **1991**, *402*, 161.

(33) McFarlane, H. C. E.; McFarlane, W. In *Multinuclear NMR*; Mason, J., Ed.; Plenum Press: New York, 1987; p 417, and references therein.

(34) The ⁷⁷Se chemical shifts of most of dialkyl selenoketones are in the range between 1600 and 2200 ppm. See (a) Wong, T. C.; Guziec, F. S. Jr.; Moustakis, C. A. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1471. (b) Cullen, E. R.; Guziec, F. S., Jr.; Murphy, C. J.; Wong, T. C.; Andersen, K. K. *J. Am. Chem. Soc.* **1981**, *103*, 7055. (c) Okazaki, R.; Ishii, A.; Inamoto, N. *J. Chem. Soc., Chem. Commun.* **1983**, 1429.

(35) In NMR the shielding constant is correlated to ΔE^{-1} (ΔE = an average electron excitation energy), see (a) Pople, J. A. *Mol. Phys.* **1963**, *7*, 301. (b) Karplus, M.; Pople, J. A. *J. Chem. Phys.* **1963**, *38*, 2803.

Table 4. [4 + 2] Cycloaddition Reactions of Germanethione **1a** with Dienes

entry	diene (equiv)	solvent	temp/°C	product (yield)
1	(10)	hexane	90	29 (84%)
2	(10)	hexane	90	30 (70%)
3	(10)	hexane	150	30 (36%) + 31 (8%)
4	(15)	THF	90	30 (76%) + 31 (8%)
5	(20)	hexane	50	32 (89%)
6	(20)	hexane	90	33 (50%)
7	Ph--Ph (5)	hexane	r. t. – 150	no reaction
8	(10)	hexane	r. t. – 150	no reaction

1,3,2-dichalcogenagermetane, and the molecular structure of **25** was determined by single-crystal X-ray diffraction.³⁷

In the reactions of **1a** and **2a** with mesitonitrile oxide, a 1,3-dipolar reagent, [3 + 2] cycloaddition proceeded to afford oxachalcogenazagermole **27** and **28**, respectively. The regiochemistry of this [3 + 2] cycloaddition was tentatively assigned on the basis of the mass spectra of the cycloadducts. In the mass spectrum of the adduct **27** were observed the fragments corresponding to the mesitylisothiocyanate and germanone Tbt(Tip)Ge=O, which would be expected only from the assigned structure. The regiochemistry observed here is interpreted in terms of the orbital interactions between germanethione LUMO and nitrile oxide HOMO, which will be discussed below in [4 + 2] cycloaddition reactions.

Dienes reacted with germanethiones and germaneselenones to give [4 + 2] cycloadducts. The results for the reactions of the germanethione **1a** are summarized in Table 4. The yields of the corresponding adducts are moderate to good, except in the case of 1,4-disubstituted dienes where no reaction took place. These are the first examples of Diels–Alder reaction of germanium–chalcogen double-bond species. The desulfurization of Tbt(Mes)GeS₄ in the presence of an excess amount of 2,3-dimethyl-1,3-butadiene gave only the dimer **7**, no corresponding [4 + 2] cycloadduct being formed.¹⁵

Regiochemistry of the Diels–Alder reactions was examined using unsymmetrically substituted dienes (entries 2–6). Reaction with isoprene at 90 °C gave two regioisomers in the ratio of 9:1. Similar selectivity and reaction rate were observed also in THF (entry 4). The observed regioselectivity is consistent with the frontier molecular orbital interpretation based on the PM3 calculation concerning the [4 + 2] cycloaddition reaction between dimethylgermanethione and isoprene.³⁸ The energies and coefficients of the frontier orbitals in this model reaction are shown in Figure 5. The calculation shows that the predominant transition state interaction involves the germathio-carbonyl LUMO and the diene HOMO and that the favorable

(36) The reactions of thiocarbonyl compounds with organometallic compounds were reported to proceed via single electron transfer. Whether the nucleophiles attack on a carbon or sulfur atom depends on the spin density on each atom of the generated anion radical $[\text{R}_2\text{C}=\text{S}]^{\cdot-}$, which is affected by the substituents R. See (a) Duus, F. In *Comprehensive Organic Chemistry*; Barton, D. H. R., Ollis, W. D., Eds.; Pergamon Press: Oxford, U.K., 1979; Vol. 3, p 373. (b) Ohno, A.; Nakamura, K.; Uohama, M.; Oka, S.; Yamabe, T.; Nagata, S. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 3718.

(37) Tokitoh, N.; Kishikawa, K.; Manmaru, K.; Okazaki, R. *Heterocycles* **1997**, *44* 149.

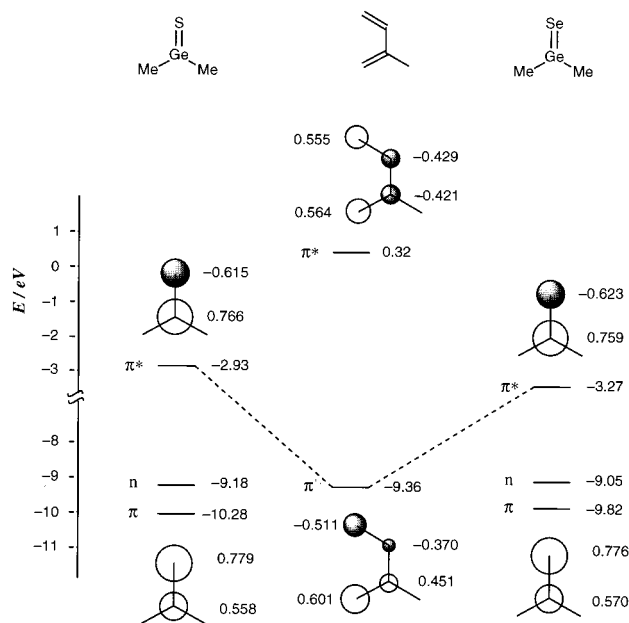


Figure 5. The energies (eV) and coefficients of the frontier orbitals involved in the [4 + 2] cycloaddition reactions of dimethylgermanethione and dimethylgermaneselonone with isoprene.

regioisomer would be compound **30**, judging from the coefficients on the pertinent molecular orbitals. Regiochemistry observed here and its interpretation are similar to those already reported for the cycloaddition of thioaldehydes.³⁹


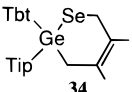

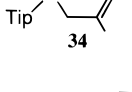

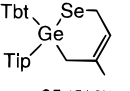
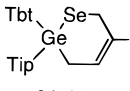
It is noteworthy that only one isomer was obtained with 2-methyl-1,3-pentadiene and 2,4-dimethyl-1,3-pentadiene (entries 5 and 6). These high regioselectivities are explicable in terms of steric effect as well as the favorable orbital overlap. This interpretation is supported by the fact that the reaction with 1,4-disubstituted dienes did not give a corresponding adduct (entries 7 and 8).

In entry 3, the regioselectivity was lost when the reaction was carried out at 150 °C. Furthermore, heating of **30** in hexane at 150 °C afforded **30** and **31** in the ratio of 1:1. These results clearly show that retro Diels–Alder reaction proceeded at about 150 °C. Examination of the CPK model indicates that there seems to be no difference between **30** and **31** in the steric interaction of the methyl group in the diene moiety with the two aryl groups on the Ge atom. A slight difference in the orbital coefficients of the 1 and 4 positions of isoprene HOMO is also consistent with the fact that the regioselectivity is lost in the reaction at higher temperature.

The occurrence of the retro Diels–Alder reaction was also shown when compound **32** was heated at 150 °C; the color of the solution changed from colorless to orange–yellow most likely due to **1a** regenerated, and in the presence of an excess amount of 2,3-dimethyl-1,3-butadiene, the corresponding adduct **29** was formed.

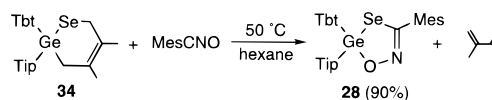
Diels–Alder reactions with dienes were also examined for germaneselonone **2a**. The results are summarized in Table 5. When germaneselonone **2a** was allowed to react with 10 equiv of 2,3-dimethyl-1,3-butadiene, the reaction proceeded at room temperature very slowly and the yield of [4 + 2] cycloadduct **34**

Table 5. [4 + 2] Cycloaddition Reactions of Germaneselonone **2a** with Dienes^a

entry	dienes (equiv)	products (yield)
1	 (10 eq.)	 (22%)
2	 (40 eq.)	 (84%)
3	 (40 eq.)	 (51%) +  (35%)

^a In hexane at room temperature.

Scheme 11



was low (entry 1), but the use of large excess of the dimethylbutadiene (40 equiv) increased the yield up to 84% (entry 2). The reactions proceeded under milder conditions than those for germanethione **1a** (~50–90 °C).

Regiochemistry of the Diels–Alder reaction of germaneselonone **2a** was also examined in the reaction with isoprene, which afforded two regioisomers **35** and **36** in 51% and 35% yields, respectively (entry 3). A more favorable regioisomer was the same as in the case of germanethione **1a**. This tendency was also similar to that in Diels–Alder reactions reported for selenoaldehydes.⁴⁰ It is noteworthy that the selectivity was lower than that observed for germanethione **1a**. The low selectivity is probably explicable in terms of the smaller activation energies in Diels–Alder and retro Diels–Alder reactions of germaneselonone **2a** than those of germanethione **1a**, which is in keeping with the results obtained by the PM3 calculation (Figure 5). The calculation shows that the predominant transition state interaction is again that between the germaneselenocarbonyl LUMO and the diene HOMO and that the HOMO–LUMO gap is smaller for the reaction with dimethylgermaneselonone, thus accelerating the Diels–Alder reaction for a germaneselonone compared to that for a germanethione. The difference in the LUMO coefficients between germanium and selenium atoms is slightly smaller than that for dimethylgermanethione, which would be partly responsible for the lower selectivity in the reaction with a germaneselonone. The occurrence of the [4 + 2] cycloreversion to **2a** was indicated by color change from colorless to red upon heating of a hexane solution of the adduct **34** at 50 °C. It was chemically confirmed by a trapping reaction with mesitronitrile oxide to afford **28** in 90% (Scheme 11).





Germanethione **1b** also gave cycloadducts with some dienes, as summarized in Table 6. Since the reaction was slower than that of Tbt(Tip)Ge=S **1a**, much more of a diene (50 equiv) was added in other entries. In the reaction with isoprene only one isomer **38** was obtained (entry 3) and the regiochemistry was opposite of that of germanethione **1a**. These results indicate larger steric congestion around germanium atom in **1b** with Tbt and Dis groups than **1a** with Tbt and Tip groups. In addition, the regioselectivity is not changed in the reaction at 150 °C, under whose conditions the retro Diels–Alder reaction should occur as in the thermolysis of the [4 + 2] cycloadduct of germanethione **1a**. When a colorless hexane solution of the isoprene adduct **38** was heated to 150 °C, the solution turned

(38) PM3 calculations were conducted using standard methods as implemented in the MOPAC 6.0 semiempirical molecular orbital package. For the geometry of Me₂Ge=S, the distance between Ge and S was fixed to 2.049 Å, which is the observed value for **1a**. Stewart, J. J. P. *QCPE Bull.* **1989**, 9, 10.

(39) (a) Vedejs, E.; Perry, D. A. *J. Am. Chem. Soc.* **1983**, *105*, 6999. (b) Rao, V. P.; Chandrasekhar, J.; Ramamurthy, V. *J. Chem. Soc., Perkin Trans. 2* **1988**, 647.

(40) (a) Meinke, P. T.; Krafft, G. A. *Tetrahedron Lett.* **1987**, 5121. (b) Idem *J. Am. Chem. Soc.* **1988**, *110*, 8671. (c) Idem *ibid.* **1988**, *110*, 8679.

Table 6. [4 + 2] Cycloaddition Reactions of Germanethione **1b** with Dienes

entry	diene (equiv)	time / h	temp / °C	product (yield)
1	 (10 eq.)	20	90	Tbt-Ge-S-phenyl (33%)
2	 (50 eq.)	70	90	Dis-Ge-S-phenyl-37 (50%)
3	 (50 eq.)	10	90	Tbt-Ge-S-phenyl (62%)
4	 (50 eq.)	10	150	Dis-Ge-S-phenyl-38 (67%)

yellow, indicating the formation of **1b**. When the solution was cooled to 90 °C, the color was slowly diminished, indicating the occurrence of a cycloaddition reaction. This color change was reversible. These facts suggest that the selectivity observed in the Diels–Alder reaction with isoprene is thermodynamically controlled owing to the steric hindrance.

Conclusion

The dechalcogenation of the novel 1,2,3,4,5-tetrathia- and tetraselenagermolanes Tbt(Tip)GeX₄ with triphenyl phosphine resulted in the successful isolation of the first kinetically stabilized germanethione Tbt(Tip)Ge=S **1a** and germanesolone Tbt(Tip)Ge=Se **2a**. A germanium–chalcogen double-bond species having an alkyl group, Tbt(Dis)Ge=X (**1b**, **2b**), was also synthesized by the reaction of germylene [Tbt(Dis)Ge:] with 1 molar equiv of chalcogens. Although one might think that **1** and **2** have rather exotic substituents such as Tbt and Dis, the results obtained in this study show that they have intrinsic physical and chemical properties. For example, the bond lengths of Ge=S and Ge=Se determined by X-ray diffraction are quite close to the calculated values for H₂Ge=S and H₂Ge=Se. The Raman shifts for the stretching of the Ge=S bond (521 cm⁻¹ for **1a** and 512 cm⁻¹ for **1b**) are very similar to the values of 518 cm⁻¹ observed for Me₂Ge=S and 542 cm⁻¹ calculated for H₂Ge=S. Furthermore, **1** and **2** are highly reactive with regard to the addition and cycloaddition reactions, despite the presence of very bulky substituents, thus enabling us to know the intrinsic reactivity of germanethione and germanesolone.

There is not so much difference between Tbt(Tip)Ge=X and Tbt(Dis)Ge=X (X = S, Se) in terms of their structural and spectral properties, but the difference in the chemical reactivities is obvious. In the former compounds, the dimerization is prevented by the intermolecular repulsion of the aryl groups, which interferes in an approach to another Tbt(Tip)Ge=X molecule. On the contrary, in the latter compounds, not only such an effect but also the Dis group itself directly inhibits an intermolecular attack onto the germanium atom, thus lowering the chemical reactivity.

Experimental Section

General Procedure. All melting points are 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 (GLPC) 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 (PTLC) was carried out with Merck Kieselgel 60 PF254 (Art. No. 7747). The ¹H NMR (500 MHz) and ¹³C NMR spectra (125 MHz) were measured in CDCl₃ or C₆D₆ with a Bruker AM-500 spectrometer using CHCl₃ or C₆H₆ as the internal standard. The ⁷⁷Se NMR spectra (51.5 MHz) were measured with a JEOL EX-270 spectrometer using Me₂Se as the external standard. High-

resolution mass spectral data were obtained on a JEOL SX-102 mass spectrometer. Electronic spectra were recorded on a JASCO Ubest-50 UV/vis spectrometer. Elemental analyses were performed by the Microanalytical Laboratory of the Department of Chemistry, Faculty of Science, The University of Tokyo.

Desulfurization of 5-[2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl]-5-mesityl-1,2,3,4,5-tetrathiagermolane (3). (1) To a THF solution (20 mL) of **3**¹² (311 mg, 0.357 mmol) was added hexamethylphosphorous triamide (0.194 mL, 1.07 mmol) at -78 °C. After the solution was warmed to room temperature over 10 h, the solvent was removed under reduced pressure and the residue was chromatographed by DCC (SiO₂ with 10:1 hexane/CH₂Cl₂) to afford {2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}(hydroxy)(mercapto)(mesityl)germane (**6**; 121 mg, 49%) and 2,4-bis{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2,4-dimesityl-1,3,2,4-dithiadigermatane (**7**; 84.7 mg, 35%). **6**: white crystals; mp 131–135 °C; ¹H NMR (CDCl₃, 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); ¹³C NMR (CDCl₃, 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 C₃₆H₇₂GeOSSi₆·H₂O: C, 53.23; H, 9.18; S, 3.95. **7**: white crystals; mp >300 °C; It was impossible to assign the NMR data owing to the complexity resulting from the steric congestion. The final structure was determined by X-ray structural analysis. Anal. found C, 55.42; H, 8.83; S, 4.26. Calcd for C₈₄H₁₆₄S₂Si₁₂Ge₂: C, 55.71; H, 9.09; S, 4.13. (2) To a THF solution (0.6 mL) of **3** (117 mg, 0.134 mmol) was added hexamethylphosphorous triamide (88 μL, 0.40 mmol) at room temperature in a 5 mm i.d. Pyrex tube. After five freeze–pump–thaw cycles, the tube was evacuated and sealed. Heating the solution at 90 °C for 1 day afforded **7** (98.4 mg, 95%).

Desulfurization of 5-[2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl]-5-(2,6-diethylphenyl)-1,2,3,4,5-tetrathiagermolane (4). In an 8 mm i.d. Pyrex glass tube was placed a hexane (1.5 mL) solution of **4** (72.9 mg, 0.0823 mmol) and triphenylphosphine (65.0 mg, 0.248 mmol). After five freeze–pump–thaw cycles, the tube was evacuated and sealed. The mixture was heated at 90 °C for 1 min to give a yellow solution. The mixture was heated at 100 °C for 1 h, during which time the yellow color disappeared. After removal of the solvent, the residue was separated by GLPC to give 2,4-bis(2,6-diethylphenyl)-2,4-bis{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1,3,2,4-dithiadigermatane (56.3 mg, 87%) as white crystals with mp >300 °C (CH₂Cl₂/EtOH). It was impossible to assign the NMR data owing to the complexity resulting from the steric congestion. Anal. found: C, 55.57; H, 9.27; S, 4.85. Calcd for C₇₄H₁₄₄Ge₂S₂Si₁₂·H₂O: C, 55.60; H, 9.21; S, 4.01.

Desulfurization of 5-[2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl]-5-(2,4,6-triisopropylphenyl)-1,2,3,4,5-tetrathiagermolane (5). To a THF solution (1 mL) of **5** (136 mg, 0.142 mmol) was added hexamethylphosphorous triamide (93 μL, 0.42 mmol) at -78 °C. After the solution was warmed to room temperature over 10 h, the solvent was removed under reduced pressure and the residue was chromatographed by DCC (SiO₂ with hexane) to afford {2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}(hydroxy)(2,4,6-triisopropylphenyl)(mercapto)germane (**9**; 107 mg, 95%). **9**: white crystals; mp 160–165 °C dec (CH₂Cl₂/*i*-PrOH); ¹H NMR (CDCl₃, 500 MHz, 300 K) 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); ¹³C NMR (CDCl₃, 125 MHz, 300 K) 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 C₄₂H₈₄GeOSSi₆: C, 57.43; H, 9.64; S, 3.65.

Isolation of {2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl}(2,4,6-triisopropylphenyl)germanethione (1a). To a mixture of **5** (800 mg,

Table 7. Experimental Crystallographic Data for **1a**, **2a**, **2b**, and **12**

	1a	2a	2b	12
empirical formula	C ₄₂ H ₈₂ GeSSi ₆	C ₄₂ H ₈₂ GeSeSi ₆	C ₃₄ H ₇₈ GeSeSi ₈	C ₇₂ H ₁₄₀ Ge ₂ Se ₂ Si ₁₂
formula weight	860.27	907.17	863.22	1646.02
crystal size, mm	0.40 × 0.10 × 0.50	0.50 × 0.60 × 0.10	0.40 × 0.30 × 0.30	0.50 × 0.30 × 0.30
temp, K	294	296	296	298
crystal system	triclinic	triclinic	triclinic	monoclinic
space group	P $\bar{1}$	P $\bar{1}$	P $\bar{1}$	C2/c
unit cell dimensions				
A, Å	13.508(4)	13.507(2)	12.696(3)	20.974(6)
B, Å	20.722(8)	20.662(5)	22.117(6)	15.243(5)
C, Å	9.740(3)	9.468(2)	9.525(3)	30.197(3)
α , deg	96.96(3)	96.35(2)	92.16(2)	
β , deg	90.01(3)	89.49(2)	109.48(2)	102.41(1)
γ , deg	81.87(3)	98.49(2)	86.89(2)	
V, Å ³	2679(3)	2597(1)	2517(1)	9428(4)
Z	2	2	2	4
density (calcd), g cm ⁻³	1.066	1.160	1.139	1.159
scan type	2 θ - ω	2 θ - ω	2 θ - ω	2 θ - ω
no. of obsd reflns	3454	3395	2185	5062
data-to-param ratio	7.66	7.53	5.50	12.75
largest diff peak, e Å ⁻³	0.69	0.76	0.55	0.78
largest diff hole, e Å ⁻³	-0.56	-0.54	-0.43	-0.95
R, %	0.065	0.058	0.050	0.051
R _w , %	0.076	0.062	0.060	0.038
goodness of fit	2.60	2.27	1.44	3.97

0.837 mmol) and triphenylphosphine (658 mg, 2.51 mmol) was added hexane (5 mL), and the solution was refluxed for 2 h. After filtration of triphenylphosphine sulfide under argon, the residual bright yellow solution was concentrated in a glovebox filled with argon to give orange–yellow crystals, which contained 96% of **5** (728 mg, 100%) and 4% of triphenylphosphine sulfide (52 mg). **1a**: orange–yellow crystals; mp 163–165 °C (hexane); ¹H NMR (C₆D₆, 500 MHz, 300 K) δ 0.15 (s, 18H), 0.16 (s, 18H), 0.26 (br s, 18H), 1.19 (d, J = 6.9 Hz, 6H), 1.35 (br d, J = 6.9 Hz, 6H), 1.48 (d, J = 6.9 Hz, 6H), 2.74 (sept, J = 6.9 Hz, 1H), 3.18 (br s, 1H), 3.29 (br s, 1H), 3.30 (sept, J = 6.9 Hz, 1H), 3.65 (br s, 1H), 6.52 (br s, 1H), 6.70 (br s, 1H), 7.07 (s, 2H); ¹³C NMR (C₆D₆, 125 MHz, 300 K) δ 1.08 (q), 1.28 (q), 1.61 (q), 22.32 (q), 24.11 (q × 2), 27.68 (q), 29.56 (d), 29.60 (d), 31.74 (d), 34.83 (d), 37.52 (d), 122.30 (d × 2), 123.89 (d), 128.98 (d), 142.25 (s), 147.50 (s), 147.62 (s), 149.98 (s), 150.99 (s), 151.27 (s × 2), 152.30 (s). FT-Raman (solid, excitation; Nd:YAG laser 1064 nm) 521 cm⁻¹. High-resolution FAB-MS: observed m/z 861.4042 ([M + H]⁺); calcd for C₄₂H₈₃⁷⁴GeSSi₆ 861.4043.

Synthesis of 5-{2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl}-5-mesityl-1,2,3,4,5-tetraselenagermolane (11). To a THF solution (20 mL) of {2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}(mesityl)germane (**10**; 328 mg, 0.439 mmol) was added at -78 °C *t*-BuLi (1.60 M in pentane, 0.36 mL, 0.58 mmol) and then hexamethylphosphoric triamide (0.30 mL, 1.9 mmol). The solution was warmed to -25 °C over 2 h and to it was added elemental selenium (0.30 g, 3.9 mmol). The mixture was warmed to room temperature over 2 h. The solvent was removed under reduced pressure, and the residue was separated by flush column chromatography (SiO₂ with hexane at -10 °C) and GLPC to afford **11** (169 mg, 34%). **11**: orange crystals; mp 209 °C dec (CH₂Cl₂/EtOH); ¹H NMR (CDCl₃, 500 MHz, 300 K) δ -0.01 (br s, 36H), 0.06 (s, 18H), 1.33 (s, 1H), 2.07 (br s, 1H), 2.13 (br s, 1H), 2.19 (s, 3H), 2.55 (s, 6H), 6.34 (br s, 1H), 6.46 (br s, 1H), 6.76 (s, 2H); ¹³C NMR (CDCl₃, 125 MHz, 300 K) δ 0.83 (q), 1.62 (q), 1.91 (q), 20.82 (q), 26.10 (d), 28.73 (d), 28.91 (d), 30.71 (q), 123.25 (d), 128.46 (d), 130.19 (d), 131.60 (s), 139.34 (s), 140.49 (s), 141.42 (s), 145.74 (s), 151.51 (s), 151.61 (s); ⁷⁷Se NMR (toluene-*d*₈, 17 MHz, 300 K) δ 443.2, 785.1. Anal. found: C, 40.51; H, 6.49; Se, 29.49. Calcd for C₃₆H₇₀GeSe₄Si₆: C, 40.79; H, 6.65; Se, 29.79.

Desulfurization of 1,2,3,4,5-Tetraselenagermolane 11. To a mixture of **11** (31.8 mg, 0.030 mmol) and triphenylphosphine (24.0 mg, 0.090 mmol) in a 5 mm i.d. Pyrex tube was added hexane (0.6 mL) and 2,3-dimethyl-1,3-butadiene (0.1 mL, 0.88 mmol). After five freeze–pump–thaw cycles, the tube was evacuated and sealed. The solution was heated at 90 °C for 1 h. After removal of the solvent, the crude reaction products were chromatographed by DCC (SiO₂ with hexane) to afford 2,4-dimesityl-2,4-bis{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1,3,2,4-diselenadigermetane (**12**; 23.8 mg, 96%) (Table 7).

12: white crystals; mp > 300 °C (CH₂Cl₂/EtOH). It was impossible to assign the NMR data owing to the complexity resulting from the steric congestion. The final structure was determined by X-ray structural analysis. Anal. found C, 52.29; H, 8.33; Se, 9.08. Calcd for C₈₄H₁₆₄-Se₂Si₁₂Ge₂: C, 52.53; H, 8.57; Se, 9.59. High-resolution FAB-MS: observed m/z 1646.5045 (M⁺); calcd for C₇₂H₁₄₀⁷⁴Ge₂⁷⁸Se⁸⁰SeSi₁₂, 1646.4948.

Synthesis of 5-{2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl}-5-(2,4,6-triisopropylphenyl)-1,2,3,4,5-tetraselenagermolane (13). To a THF solution (20 mL) of {2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-(2,4,6-triisopropylphenyl)germane (213 mg, 0.256 mmol) was added at -78 °C *t*-BuLi (1.60 M in pentane, 0.32 mL, 0.51 mmol) and then hexamethylphosphoric triamide (0.23 mL, 1.4 mmol). The solution was warmed to -20 °C over 3 h and to it was added elemental selenium (0.20 g, 2.5 mmol). The mixture was warmed to room temperature over 20 min. Solvent was removed under reduced pressure, and the residue was separated by flush column chromatography (SiO₂ with hexane at -40 °C) and GLPC to afford **13** (21.5 mg, 7%) along with the recovery of the starting material (95.4 mg, 45%). **13**: orange crystals; mp 215–218 °C dec (CH₂Cl₂/EtOH); ¹H NMR (CDCl₃, 500 MHz, 340 K) δ 0.05 (br s, 36H), 0.73 (s, 18H), 1.13 (br d, J = 6.9 Hz, 12H), 1.21 (d, J = 6.9 Hz, 6H), 1.36 (s, 1H), 2.17 (br s, 2H), 2.82 (sept, J = 6.9 Hz, 1H), 3.96 (br s, 2H), 6.44 (br s, 2H), 7.01 (s, 2H); ¹³C NMR (CDCl₃, 125 MHz, 340 K) δ 1.03 (q), 2.71 (br q), 23.69 (q), 24.76 (q), 28.19 (d), 31.02 (d), 34.22 (d), 35.68 (d), 123.60 (d), 129.30 (d), 135.48 (s), 139.07 (s), 145.14 (s), 150.33 (s), 151.17 (s), 152.50 (s); ⁷⁷Se NMR (CDCl₃, 51.5 MHz, 300 K) δ 411.1, 471.8, 730.2, 841.3. Anal. found: C, 43.78; H, 7.00; Se, 27.73. Calcd for C₄₂H₈₂GeSe₄Si₆: C, 44.09; H, 7.22; Se, 27.61.

Trapping of {2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl}(2,4,6-triisopropylphenyl)germylene (14) with 2,3-Dimethyl-1,3-butadiene. To a solution of dibromogermane **15**^{11b} (101 mg, 0.102 mmol) in THF (5 mL) was added lithium naphthalenide (0.38 M in THF, 0.53 mL, 0.20 mmol) at -78 °C. The mixture was warmed to room temperature over 1 h to give a blue solution of **14**, to which was added 2,3-dimethyl-1,3-butadiene (0.1 mL, 0.88 mmol), and the solution was stirred for 1 h. After removal of the solvent, the residue was chromatographed by DCC (SiO₂ with hexane) to afford 1-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2,5-dihydro-1-(2,4,6-triisopropyl-phenyl)-3,4-dimethylgermylene (**16**; 57.3 mg, 68%).^{18a}

Synthesis of 1,2,3,4,5-Tetraselenagermolane 13 from Germylene 14. To a solution of dibromogermane **15** (267 mg, 0.245 mmol) in THF (9 mL) was added lithium naphthalenide (0.47 M in THF, 1.3 mL, 0.61 mmol) at -60 °C, and the solution was warmed to room temperature over 1.5 h to give a blue solution of **14**. After cooling to -20 °C, elemental selenium (160 mg, 2.0 mmol) was added to this solution and it was stirred for 2.5 h, during which time it was warmed

to room temperature. After removal of the solvent, the residue was roughly purified by short column chromatography (SiO₂ with CH₂Cl₂) and then by GLPC and flush column chromatography (SiO₂ with hexane). The orange solid thus obtained was reprecipitated from CH₂Cl₂/hexane to afford **13** (160 mg, 57%).

Synthesis of 1,2,3,4,5-Tetrathiagermolane 5 from Germylene 14. To a solution of dibromogermene **15** (1.26 g, 1.28 mmol) in THF (40 mL) was added lithium naphthalenide (0.74 M in THF, 4.1 mL, 3.0 mmol) at -50 °C, and the solution was warmed to room temperature over 3 h to give a blue solution of **14**. To this solution was added elemental sulfur (390 mg, 1.5 mmol as S₈), and the solution was stirred for 5 h. After removal of the solvent, the residue was roughly purified by short column chromatography (SiO₂ with CH₂Cl₂) and GLPC. The yellow solid thus obtained was reprecipitated from CH₂Cl₂/hexane to afford **5** (829 mg, 68%).

Synthesis of {2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl}{2,4,6-triisopropylphenyl}germanesolone (2a). To a mixture of **13** (500 mg, 0.437 mmol) and triphenylphosphine (340 mg, 1.30 mmol) was added hexane (3 mL), and the solution was refluxed for 2 h. After filtration of triphenylphosphine selenide under argon, the residual red solution was concentrated in a glovebox filled with argon to give red crystals, which contained 99% of **2a** (392 mg, 100%) and 1% of triphenylphosphine selenide (8 mg). **2a**: red crystals, mp 191–194 °C; ¹H NMR (C₆D₆, 500 MHz, 300 K) δ 0.15 (s, 18H), 0.18 (s, 18H), 0.25 (s, 18H), 1.19 (d, *J* = 6.9 Hz, 6H), 1.34 (d, *J* = 6.9 Hz, 6H), 1.46 (d, *J* = 6.9 Hz, 6H), 1.49 (s, 1H), 2.73 (sept, *J* = 6.9 Hz, 1H), 3.40 (br s, 1H), 3.41 (sept, *J* = 6.9 Hz, 2H), 3.79 (br s, 1H), 6.51 (br s, 1H), 6.68 (brs, 1H), 7.05 (s, 2H); ¹³C NMR (C₆D₆, 125 MHz, 300 K) δ 1.11 (q), 1.37 (q), 1.67 (q), 22.28 (q), 24.09 (q × 2), 27.39 (d), 29.08 (br d × 2), 31.83 (d), 34.83 (d), 36.52 (d), 122.64 (d × 2), 124.38 (d), 128.29 (d), 144.04 (s), 147.42 (s), 149.58 (s), 150.06 (s), 150.43 (s), 151.01 (s × 2), 152.08 (s); ⁷⁷Se NMR (C₆D₆, 51.5 MHz, 300 K) δ 940.6. FT-Raman (solid, excitation; Nd: YAG laser 1064 nm) 382 cm⁻¹. High-resolution FAB-MS: observed *m/z* 908.3455 ([M + H]⁺). Calcd for C₄₂H₈₃⁷⁴-GeSeSi₆: 908.3409.

Preparation of {2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl}-dibromo[bis(trimethylsilyl)methyl]germane. (1) Synthesis of {2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}[bis(trimethylsilyl)methyl]-dihalogermene. To a solution of 1-bromo-2,4,6-tris[bis(trimethylsilyl)methyl]benzene¹¹ (TbtBr, 5.0 g, 7.92 mmol) in THF (80 mL) was added *t*-BuLi (1.62 M in pentane, 10.5 mL, 17.0 mmol) at -78 °C. After the reaction solution was stirred for 10 min, GeCl₄ (0.95 mL, 8.3 mmol) was added to it at -78 °C. The reaction mixture was warmed to room temperature over 10 h to give a solution of TbtGeCl₃, to which DisMgCl, prepared from bis(trimethylsilyl)chlorosilane (DisCl; 3.5 mL, 16.0 mmol) and magnesium (580 mg, 24 mmol) in THF, was added at room temperature. After the solution was refluxed for 10 h, a few drops of aqueous NH₄Cl was added and almost all THF was removed under reduced pressure. Chloroform and diluted HCl were added to the residue, and the aqueous layer was extracted by CHCl₃ several times. The organic layer was dried over MgSO₄, and the solvent was removed under reduced pressure. The white solid thus obtained was dissolved into CH₂Cl₂, and to the solution was added approximately the same volume of ethanol. Evaporation of CH₂Cl₂ at room temperature under reduced pressure afforded precipitates of {2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}[bis(trimethylsilyl)methyl]dihalogermene (4.26 g) as a mixture of dichlorogermene, bromochlorogermene, and dibromogermene as judged by mass spectrometry and elemental analysis.

(2) Synthesis of {2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}[bis(trimethylsilyl)methyl]germane. The mixture of the dihalogermenes obtained above was dissolved in THF (100 mL), and LiAlH₄ (380 mg, 10.0 mmol) was added to it at 0 °C. After being warmed to room temperature, the mixture was refluxed for 10 h. After being quenched by aqueous NH₄Cl, the organic layer was washed by dilute HCl. The water layer was extracted with CHCl₃ several times. The organic layer was dried over MgSO₄, and all of the solvent was removed under reduced pressure. The residue was dissolved in CH₂Cl₂, and approximately the same volume of ethanol was added to it. Evaporation of CH₂Cl₂ at room temperature under reduced pressure afforded precipitates of {2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}[bis(trimethylsilyl)methyl]germane (Tbt(Dis)GeH₂, 3.44 g, 55% from TbtBr) as

white crystals. Tbt(Dis)GeH₂: white crystals; mp 180–182 °C (CH₂-Cl₂/EtOH); ¹H NMR (CDCl₃, 500 MHz, 300 K) δ -0.20 (t, *J* = 3.2 Hz, 1H), 0.03 (s, 18H), 0.06 (s, 18H), 0.07 (s, 18H), 0.15 (s, 18H), 1.28 (s, 1H), 1.94 (s, 1H), 2.18 (s, 1H), 4.55 (d, *J* = 3.2 Hz, 2H, Ge-H), 6.23 (s, 1H), 6.39 (s, 1H); ¹³C NMR (CDCl₃, 125 MHz, 300 K) δ 0.07 (d), 0.85 (q), 1.05 (q), 1.32 (q), 1.99 (q), 28.73 (d), 28.79 (d), 30.26 (d), 122.53 (d), 127.36 (d), 129.57 (s), 143.11 (s), 149.63 (s), 149.78 (s). Anal. found: C, 50.06; H, 10.46. Calcd for C₃₄H₈₀GeSi₈·2H₂O: C, 49.66; H, 10.30.

(3) Bromination of Tbt(Dis)GeH₂. To a benzene solution (100 mL) of Tbt(Dis)GeH₂ (3.44 g, 4.38 mmol) obtained as above was added *N*-bromosuccinimide (1.7 g, 9.6 mmol) at room temperature, and the solution was stirred for 10 h. The crude reaction mixture was chromatographed over SiO₂ with benzene. The white solid thus obtained was dissolved into CH₂Cl₂, and to the solution was added approximately the same volume of ethanol. Evaporation of CH₂Cl₂ at room temperature under reduced pressure afforded precipitates of Tbt(Dis)GeBr₂ (3.3 g, 80%). White crystals; mp 199–201 °C (CH₂Cl₂/EtOH); ¹H NMR (CDCl₃, 500 MHz, 300 K) δ 0.05 (s, 18H), 0.12 (s, 18H), 0.14 (s, 18H), 0.32 (s, 18H), 1.32 (s, 1H), 1.37 (s, 1H), 2.63 (s, 1H), 3.03 (s, 1H), 6.27 (s, 1H), 6.39 (s, 1H); ¹³C NMR (CDCl₃, 125 MHz, 300 K) δ 0.95 (q), 1.90 (q), 2.03 (q), 3.77 (q), 22.71 (d), 27.00 (d), 27.27 (d), 30.69 (d), 123.98 (d), 128.86 (d), 130.04 (s), 146.12 (s), 149.79 (s), 150.57 (s). Anal. found: C, 43.01; H, 8.24; Br, 16.87. Calcd for C₃₄H₇₈-Br₂GeSi₈: C, 43.25; H, 8.33; Br, 16.93. High-resolution FAB-MS: observed *m/z* 944.1930 (M⁺); calcd for C₃₄H₇₈⁷⁹Br⁸¹Br⁷⁴GeSi₈ 944.1816.

Trapping of {2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl}[bis(trimethylsilyl)methyl]germylene (17) with 2,3-Dimethyl-1,3-butadiene. To a solution of the Tbt(Dis)GeBr₂ (73.9 mg, 0.0783 mmol) in THF (3 mL) was added lithium naphthalenide (0.50 M in THF, 0.37 mL, 0.19 mmol) at -55 °C, and the mixture was warmed to room temperature over 1.5 h. To the resulting purple solution of **17** was added 2,3-dimethyl-1,3-butadiene (0.1 mL, 0.88 mmol), and the solution was stirred for 1 h. After removal of the solvent, the residue was purified by GLPC and DCC (SiO₂ with hexane) to afford 1-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2,5-dihydro-1-[bis(trimethylsilyl)methyl]-3,4-dimethylgermole (**18**) (10%). White crystals; mp 174–176 °C (CH₂Cl₂/EtOH); ¹H NMR (CDCl₃, 500 MHz, 300 K) δ 0.00 (s, 18H), 0.03 (s, 18H), 0.05 (s, 18H), 0.10 (s, 18H), 0.21 (s, 1H), 1.25 (s, 1H), 1.71 (s, 6H), 1.90 (s, 1H), 1.97 (d, *J* = 16.1 Hz, 2H), 1.99 (s, 1H), 2.06 (d, *J* = 16.1 Hz, 2H), 6.21 (s, 1H), 6.34 (s, 1H); ¹³C NMR (CDCl₃, 125 MHz, 300 K) δ 0.38 (q), 0.94 (q), 1.62 (q), 1.83 (q), 3.71 (q), 5.38 (d), 19.44 (q), 27.74 (d), 29.69 (d), 29.91 (d), 33.71 (t), 122.72 (d), 128.15 (d), 131.32 (d), 133.38 (d), 142.35 (s), 142.61 (s), 149.75 (s), 150.16 (s). Anal. found: C, 55.14; H, 10.44. Calcd for C₄₀H₈₈-GeSi₈: C, 55.45; H, 10.24. High-resolution FAB-MS: observed *m/z* 867.4466 ([M+H]⁺); calcd for C₄₀H₈₉⁷⁴GeSi₈ 867.4330.

Synthesis of 5-{2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl}-5-[bis(trimethylsilyl)methyl]-1,2,3,4,5-tetrathiagermolane (19). To a solution of Tbt(Dis)GeBr₂ (155 mg, 0.164 mmol) in THF (6 mL) was added lithium naphthalenide (0.50 M in THF, 0.78 mL, 0.39 mmol) at -55 °C, and the solution was warmed to room temperature over 2.5 h to give a purple solution of germylene **17**. To this solution was added elemental sulfur (50 mg, 0.20 mmol as S₈), and the solution was stirred for 0.5 h. After removal of the solvent, the residue was roughly purified by short column chromatography (SiO₂ with CH₂Cl₂) and GLPC. The yellow solid thus obtained was purified by DCC (SiO₂ with hexane) and reprecipitated from CH₂Cl₂/EtOH to afford **19** (78.7 mg, 53%). **19**: pale yellow crystals; mp 206–210 °C dec (CH₂Cl₂/EtOH); ¹H NMR (CDCl₃, 500 MHz, 300 K) δ 0.05 (s, 18H), 0.11 (s, 36H), 0.23 (s, 18H), 1.06 (s, 1H), 1.32 (s, 1H), 2.20 (s, 1H), 2.21 (s, 1H), 6.26 (s, 1H), 6.41 (s, 1H); ¹³C NMR (CDCl₃, 125 MHz, 300 K) δ 0.99 (q), 1.93 (q), 2.23 (q), 4.49 (q), 18.30 (d), 28.69 (d), 28.78 (d), 30.51 (d), 123.42 (d), 128.87 (d), 132.06 (s), 145.31 (s), 150.32 (s), 150.91 (s). Anal. found: C, 43.58; H, 9.11; S, 13.30. Calcd for C₃₄H₇₈GeS₄Si₈·H₂O: C, 43.88; H, 8.67; S, 13.78.

Synthesis of 5-{2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl}-5-[bis(trimethylsilyl)methyl]-1,2,3,4,5-tetraselenagermolane (20). To a solution of Tbt(Dis)GeBr₂ (213 mg, 0.225 mmol) in THF (8 mL) was added lithium naphthalenide (0.63 M in THF, 0.90 mL, 0.57 mmol) at -60 °C, and the solution was warmed to room temperature over 1.5

h to give a purple solution of germylene **17**. To the resulting purple solution was added elemental selenium (100 mg, 1.3 mmol), and the solution was stirred for 1 h. After removal of the solvent, the residue was roughly purified by short column chromatography (SiO₂ with hexane) and GLPC. The orange solid thus obtained was purified by DCC (SiO₂ with hexane) and reprecipitated from CH₂Cl₂/EtOH to afford **20** (137 mg, 55%). **20**: orange crystals; mp 194–198 °C (CH₂Cl₂/EtOH); ¹H NMR (CDCl₃, 500 MHz, 300 K) δ 0.05 (s, 18H), 0.12 (s, 36H), 0.24 (s, 18H), 1.31 (s, 1H), 1.34 (s, 1H), 2.25 (s, 1H), 2.26 (s, 1H), 6.27 (br s, 1H), 6.41 (br s, 1H); ¹³C NMR (CDCl₃, 125 MHz, 300 K) δ 1.04 (q), 2.22 (q), 2.52 (q), 4.86 (q), 20.04 (d), 28.85 (d), 28.89 (d), 30.48 (d), 123.51 (d), 129.11 (d), 134.22 (s), 144.91 (s), 150.16 (s), 150.76 (s); ⁷⁷Se NMR (CDCl₃, 95.2 MHz, 300 K) δ 405.6, 776.0. Anal. found: C, 36.55; H, 6.89. Calcd for C₃₄H₇₈GeSe₄Si₈: C, 36.81; H, 7.18.

Sulfurization of Tetrathiagermolane 19: Synthesis of {2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl}[bis(trimethylsilyl)methyl]germanethione (1b). To a mixture of **19** (289 mg, 0.317 mmol) and triphenylphosphine (249 mg, 0.950 mmol) was added hexane (4 mL), and the solution was refluxed for 3 h. After filtration of the precipitates, the residual bright yellow solution was concentrated in a glovebox filled with argon to give yellow crystals, which contained 94% of **1b** (166 mg, 62%), 5% of triphenylphosphine (24.1 mg), and 1% of triphenylphosphine sulfide (5.6 mg). The yields were determined after the hydrolysis of germanethione **1b**, which gave the corresponding adduct quantitatively. The white precipitates initially filtered-off were dissolved into chloroform, and the insoluble white solid was separated by filtration to give triphenylphosphine sulfide (246 mg, 88% from triphenylphosphine) from the filtrate and 3,6-bis[bis(trimethylsilyl)methyl]-3,6-bis-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1,2,4,5-tetrathia-3,6-digermycyclohexane (**21**; 82.5 mg, 31%) from the insoluble substances. **1b**: yellow crystals; mp 190–193 °C (hexane); ¹H NMR (C₆D₆, 500 MHz, 300 K) δ 0.14 (s, 9H), 0.27 (br s, 18H), 0.31 (br s, 18H), 0.40 (s, 18H), 1.48 (s, 1H), 2.05 (s, 1H), 2.63 (br s, 1H), 2.73 (br s, 1H), 6.52 (s, 1H), 6.67 (s, 1H); ¹³C NMR (C₆D₆, 125 MHz, 300 K) δ 0.95 (q), 1.57 (q), 1.91 (q), 3.92 (q), 31.35 (d), 31.50 (d), 31.81 (d), 40.70 (d), 123.09 (d), 129.50 (d), 143.41 (s), 147.14 (s), 148.39 (s), 148.96 (s). FT-Raman (solid, excitation; Nd: YAG laser 1064 nm) 512 cm⁻¹. High-resolution FAB-MS: observed *m/z* 817.3217 ([M + H]⁺); calcd for C₃₄H₇₉⁷⁴GeSSi₈ 817.3268. **21**: white crystals; mp > 300 °C (CHCl₃); ¹H NMR (CDCl₃, 500 MHz, 300 K) δ -0.02 (s, 9H), 0.00 (s, 9H), 0.04 (s, 9H), 0.09 (s, 9H), 0.21 (s, 36H), 0.61 (s, 1H), 1.34 (s, 1H), 2.91 (s, 1H), 3.01 (s, 1H), 6.37 (s, 1H), 6.54 (s, 1H). It was impossible to measure the ¹³C NMR owing to its insolubility. Anal. found: C, 47.05; H, 9.58; S, 7.85. Calcd for C₆₈H₁₅₆Ge₂S₄Si₁₂·2H₂O: C, 47.13; H, 9.30; S, 7.40.

Hydrolysis of Germanethione 1b. One drop of water was added to a yellow solution of germanethione **1b** (20.0 mg, 0.025 mmol) in hexane (1 mL). The yellow color immediately disappeared. Separation by PTLC (SiO₂ with 20:1 hexane/CH₂Cl₂) gave {2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}(hydroxy)(mercapto)[bis(trimethylsilyl)methyl]germane Tbt(Dis)Ge(SH)(OH) (20.4 mg, 100%). White crystals; mp 175–180 °C (CH₂Cl₂/EtOH); ¹H NMR (CDCl₃, 500 MHz, 300 K) δ 0.04 (s, 9H), 0.05 (s, 9H), 0.10 (s, 9H), 0.11 (s, 9H), 0.12 (s, 9H), 0.248 (s, 9H), 0.253 (s, 9H), 0.61 (s, 1H), 0.94 (s, 1H, SH), 1.31 (s, 1H), 1.56 (br s, 1H, OH), 2.45 (s, 1H), 2.68 (s, 1H), 6.27 (s, 1H), 6.38 (s, 1H); ¹³C NMR (CDCl₃, 125 MHz, 300 K) δ 0.87 (q), 0.92 (q), 1.54 (q), 1.71 (q × 2), 1.94 (q), 3.608 (q), 3.614 (q), 15.33 (d), 27.03 (d), 27.18 (d), 30.44 (d), 123.52 (d), 128.55 (d), 128.70 (s), 144.96 (d), 149.80 (d), 150.29 (d). Anal. Found: C, 48.02; H, 9.67. Calcd for C₃₄H₈₀GeOSSi₈·H₂O: C, 47.91; H, 9.70. High-resolution FAB-MS: observed *m/z* 834.3331 ([M + H]⁺); calcd for C₃₄H₈₀⁷⁴GeOSSi₈ 834.3296.

Reaction of Germylene 17 with Diphenylacetylene. To a solution of Tbt(Dis)GeBr₂ (824 mg, 0.873 mmol) in THF (30 mL) was added lithium naphthalenide (0.63 M in THF, 3.3 mL, 2.1 mmol) at -55 °C, and the mixture was warmed to room temperature over 1.5 h. To the resulting purple solution of germylene **17** was added diphenylacetylene (200 mg, 1.1 mmol), and the solution was stirred for 10 h. After removal of the solvent, the residue was chromatographed by GLPC and DCC (SiO₂ with hexane) to afford 2,3-diphenyl-1-{2,4,6-tris[bis(trimethyl-

silyl)methyl]phenyl}-1-[bis(trimethylsilyl)methyl]germyrene (**22**; 378 mg, 45%). **22**: white crystals; mp 153–156 °C (CH₂Cl₂/EtOH); ¹H NMR (CDCl₃, 500 MHz, 300 K) δ -0.02 (s, 18H), -0.01 (s, 18H), 0.04 (s, 18H), 0.12 (s, 18H), 0.37 (s, 1H), 1.29 (s, 1H), 2.21 (s, 1H), 2.28 (s, 1H), 6.26 (s, 1H), 6.40 (s, 1H), 7.19–7.22 (m, 2H), 7.27–7.31 (m, 4H), 7.53–7.55 (m, 4H); ¹³C NMR (CDCl₃, 125 MHz, 300 K) δ 0.97 (q), 1.61 (q), 1.89 (q), 3.51 (q), 9.35 (d), 28.88 (d), 29.03 (d), 30.27 (d), 122.71 (d), 127.11 (d), 128.10 (d), 128.14 (d), 129.09 (d), 133.34 (s), 135.37 (s), 143.32 (s), 150.15 (s), 150.38 (s), 155.21 (s). Anal. found: C, 56.93; H, 9.14. Calcd for C₄₈H₈₈GeSi₈·3H₂O: C, 56.71; H, 9.32.

Thermal Reaction of 22 in the Presence of 2,3-Dimethyl-1,3-butadiene. In a 5 mm i.d. NMR tube was placed a benzene-*d*₆ (1.0 mL) solution of **22** (24.4 mg, 0.0253 mmol) and 2,3-dimethyl-1,3-butadiene (0.02 mL, 0.18 mmol). After five freeze–pump–thaw cycles, the tube was evacuated and sealed. The solution was heated at 70 °C for 3.5 h. ¹H NMR of the reaction mixture measured at this stage indicated that the starting material remained. After being heated at 80 °C for 20 h, the solvent was removed under reduced pressure and the crude reaction products were chromatographed by PTLC (SiO₂ with hexane) to afford **18** (15.7 mg, 71%) together with diphenylacetylene (4.4 mg, 97%).

Synthesis of {2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl}[bis(trimethylsilyl)methyl]germanethione (1b). In a 5 mm i.d. NMR tube was placed a benzene-*d*₆ (0.8 mL) solution of **22** (23.0 mg, 0.0239 mmol) and elemental sulfur (0.8 mg, 0.003 mmol as S₈). After five freeze–pump–thaw cycles, the tube was evacuated and sealed. The solution was heated at 90 °C for 7 days to afford a yellow solution. The quantitative generation of germanethione **1b** and diphenylacetylene was observed by ¹H NMR. The solvent was removed in a glovebox filled with argon to afford **1b** together with diphenylacetylene.

Synthesis of {2,4,6-Tris[bis(trimethylsilyl)methyl]phenyl}[bis(trimethylsilyl)methyl]germaneselonone (2b). In a 5 mm i.d. NMR tube was placed a benzene-*d*₆ (0.8 mL) solution of **22** (30.9 mg, 0.0321 mmol) and elemental selenium (2.6 mg, 0.033 mmol). After five freeze–pump–thaw cycles, the tube was evacuated and sealed. The solution was heated at 90 °C for 7 days to afford an orange–red solution. The quantitative generation of germaneselonone **2b** and diphenylacetylene was observed by ¹H NMR. The solvent was removed in a glovebox filled with argon to afford **2b** together with diphenylacetylene. **2b**: red orange crystals; mp 195–198 °C; ¹H NMR (C₆D₆, 500 MHz, 300 K) δ 0.14 (s, 18H), 0.28 (br s, 18H), 0.31 (br s, 18H), 0.40 (s, 18H), 1.48 (s, 1H), 2.35 (s, 1H), 2.84 (s, 1H), 6.50 (s, 1H), 6.65 (s, 1H); ¹³C NMR (C₆D₆, 125 MHz, 300 K) δ 0.97 (q), 1.70 (q), 2.00 (q), 3.98 (q), 30.58 (d), 31.27 (d), 31.55 (d), 44.13 (d), 123.52 (d), 129.49 (d), 145.15 (s), 146.92 (s), 147.88 (s), 148.32 (s); ⁷⁷Se NMR (C₆D₆, 51.5 MHz, 300 K) δ 872.7. FT-Raman (solid, excitation; Nd: YAG laser 1064 nm) 386 cm⁻¹. High-resolution FAB-MS: observed *m/z* 865.2625 ([M+H]⁺); calcd for C₃₄H₇₈⁷⁴GeSeSi₈ 865.2713.

Hydrolysis of Germanethione 1a. One drop of water was added to a yellow solution of germanethione **1a** (21.0 mg, 0.024 mmol) in hexane (1 mL). The yellow color immediately disappeared. Separation with PTLC (SiO₂ with 10:1 hexane/CH₂Cl₂) gave **9** (21.4 mg, 100%).

Reaction of Germanethione 1a with Methylolithium. (1) To a mixture of **5** (108 mg, 0.113 mmol) and triphenylphosphine (89.0 mg, 0.340 mmol) was added hexane (0.5 mL), and the solution was refluxed for 2 h to afford a yellow solution of germanethione **1a**. Methylolithium (0.95 M in ether, 0.20 mL, 0.19 mmol) was added dropwise to this solution at -65 °C. The color of the solution disappeared at -20 °C, and then ethanol (0.01 mL, 0.2 mmol) was added to this solution. After the solution was warmed to room temperature, the solvent was removed under reduced pressure and the residue was chromatographed by DCC (SiO₂ with hexane) to afford {2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}(2,4,6-triisopropylphenyl)(mercapto)(methyl)germane (**23**; 68.6 mg, 81%). **23**: white crystals, mp 212–213 °C (CH₂Cl₂/EtOH); ¹H NMR (CDCl₃, 500 MHz, 340 K) δ -0.01 (s, 18H), 0.06 (s, 18H), 0.07 (s, 18H), 0.42 (s, 1H, SH), 1.14 (br s, 6H), 1.21 (d, *J* = 6.9 Hz, 6H), 1.24 (d, *J* = 6.9 Hz, 6H), 1.31 (s, 1H), 1.38 (s, 3H, GeMe), 2.39 (br s, 1H), 2.53 (br s, 1H), 2.83 (sept, *J* = 6.9 Hz, 1H), 3.42 (br s, 2H), 6.37 (br s, 2H), 7.00 (br s, 2H); ¹³C NMR (CDCl₃, 125 MHz, 300 K) δ 0.87 (q), 0.93 (q), 1.89 (q), 1.93 (q), 2.16 (q), 2.23 (q), 17.27 (q,

GeMe), 23.42 (q), 23.83 (q), 24.56 (q), 27.68 (d), 28.20 (d), 30.18 (d), 32.77 (d), 33.37 (d), 34.19 (d), 121.66 (d), 123.44 (d × 2), 128.58 (d), 132.52 (s), 137.59 (s), 143.44 (s), 149.70 (s), 149.76 (s), 150.23 (s), 152.11 (s), 154.05 (s). Anal. found: C, 58.52; H, 9.48; S, 3.72. Calcd for C₄₃H₈₆GeSSi₆: C, 58.93; H, 9.89; S, 3.66. (2) To a mixture of **5** (161 mg, 0.168 mmol) and triphenylphosphine (132 mg, 0.504 mmol) was added hexane (1.2 mL), and the solution was refluxed for 2 h to afford a yellow solution of germanethione **1a**. Methylolithium (1.0 M in ether, 0.30 mL, 0.30 mmol) was added dropwise to this solution at -65 °C, which was warmed gradually. The color of the solution disappeared at -20 °C, and methyl iodide (0.05 mL, 0.8 mmol) was added to the solution. After it was warmed to room temperature, the solvent was removed under reduced pressure and the residue was chromatographed by DCC (SiO₂ with hexane) to afford {2,4,6-tris[tris(trimethylsilyl)methyl]phenyl}(2,4,6-triisopropylphenyl)(methyl)-(methylthio)germane (**24**; 123 mg, 69%). **24**: white crystals, mp 178–179 °C (CH₂Cl₂/EtOH); ¹H NMR (CDCl₃, 500 MHz, 300 K) δ -0.15 (br s, 9H), -0.04 (br s, 9H), 0.03 (s, 9H), 0.04 (s, 9H), 0.07 (br s, 9H), 0.13 (br s, 9H), 0.83 (d, *J* = 6.9 Hz, 3H), 1.18 (d, *J* = 6.9 Hz, 3H), 1.19 (d, *J* = 6.9 Hz, 6H), 1.23 (d, *J* = 6.9 Hz, 3H), 1.27 (s, 1H), 1.30 (s, 3H, GeMe), 1.36 (d, *J* = 6.9 Hz, 3H), 1.78 (s, 3H, SMe), 2.20 (br s, 1H), 2.38 (br s, 1H), 2.81 (sept, *J* = 6.9 Hz, 1H), 3.26 (sept, *J* = 6.9 Hz, 1H), 3.37 (sept, *J* = 6.9 Hz, 1H), 6.28 (s, 1H), 6.39 (s, 1H), 6.97 (s, 1H); ¹³C NMR (CDCl₃, 125 MHz, 300 K) δ 0.85 (q), 1.07 (q), 1.80 (q), 1.85 (q), 2.03 (q), 2.16 (q), 11.72 (q), 12.52 (q), 23.79 (q), 23.89 (q), 25.55 (q), 26.48 (d), 27.22 (d), 30.15 (d), 31.67 (d), 33.84 (d), 34.12 (d), 121.47 (d), 123.52 (d), 124.00 (d), 128.64 (d), 133.38 (s), 134.16 (s), 143.01 (s), 149.69 (s), 149.93 (s), 153.61 (s), 154.83 (s). Anal. found: C, 59.07; H, 10.08; S, 3.77. Calcd for C₄₃H₈₆GeSSi₆: C, 59.35; H, 9.96; S, 3.60.

Reaction of Germanethione 1a with Phenyl Isothiocyanate. To a mixture of **5** (74.0 mg, 0.0774 mmol) and triphenylphosphine (60.8 mg, 0.232 mmol) was added hexane (1.0 mL), and the solution was refluxed for 1.5 h to afford a yellow solution of germanethione **1a**. Phenyl isothiocyanate (0.02 mL, 0.170 mmol) was added to the solution, which was stirred for 10 h. After removal of the solvent, the crude reaction products were chromatographed by DCC (SiO₂ with 3:1 hexane/CH₂Cl₂) to afford 2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2-(2,4,6-triisopropylphenyl)-4-phenylimino-1,3,2-dithiagermetane (**25**; 64.8 mg, 84%). **25**: white crystals; mp 150–153 °C dec (CH₂Cl₂/EtOH); ¹H NMR (CDCl₃, 500 MHz, 300 K) δ -0.05 (s, 9H), -0.03 (s, 9H), 0.03 (s, 9H), 0.05 (s, 9H), 0.09 (s, 9H), 1.16 (br s, 3H), 1.20 (br s, 6H), 1.22 (d, *J* = 6.9 Hz, 6H), 1.32 (br s, 3H), 1.33 (s, 1H), 2.43 (br s, 1H), 2.87 (sept, *J* = 6.9 Hz, 1H), 3.08 (br s, 3H), 6.33 (s, 1H), 6.51 (s, 1H), 6.92 (s, 1H), 6.93 (s, 1H), 7.04–7.29 (m, 5H); ¹³C NMR (CDCl₃, 125 MHz, 300 K) δ 0.90 (q), 1.58 (q), 1.62 (q), 1.72 (q), 23.12 (br q), 23.58 (q), 28.18 (d), 28.24 (d), 30.82 (d), 34.35 (d), 35.73 (d), 35.85 (d), 121.20 (d), 122.96 (d), 123.81 (d), 124.13 (d), 128.80 (d), 129.03 (d), 129.60 (s), 137.36 (s), 146.16 (s), 149.03 (s), 151.12 (s), 151.68 (s), 151.91 (s), 153.16 (s). Anal. found: C, 58.64; H, 8.51; N, 1.46; S, 6.39. Calcd for C₄₇H₈₇GeNS₂Si₆·0.5H₂O: C, 58.59; H, 8.83; N, 1.39; S, 6.39.

Reaction of Germanesolone 2a with Phenyl Isothiocyanate. To a mixture of **13** (59.6 mg, 0.0521 mmol) and triphenylphosphine (40.0 mg, 0.153 mmol) was added hexane (0.5 mL), and the solution was refluxed for 1.5 h to afford a red solution of germanesolone **2a**. Phenyl isothiocyanate (0.1 mL, 0.84 mmol) was added to the solution, which was stirred for 1.5 h. After removal of the solvent, the crude reaction products were chromatographed by GPLC to afford 2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2-(2,4,6-triisopropylphenyl)-4-phenylimino-1,3,2-thiaselenagermetane (**26**; 33.1 mg, 61%). **26**: white crystals; mp 199–203 °C dec (CH₂Cl₂/EtOH); ¹H NMR (CDCl₃, 500 MHz, 300 K) δ -0.06 (s, 9H), -0.03 (s, 9H), 0.04 (s, 9H), 0.047 (s, 9H), 0.051 (s, 9H), 0.11 (s, 9H), 1.12 (br s, 3H), 1.20 (br s, 3H), 1.22 (d, *J* = 6.9 Hz, 6H), 1.28 (br s, 6H), 1.33 (s, 1H), 2.45 (br s, 1H), 2.87 (sept, *J* = 6.9 Hz, 1H), 2.99 (br s, 1H), 3.18 (br s, 1H), 3.30 (br s, 1H), 6.33 (s, 1H), 6.51 (s, 1H), 6.90–6.92 (m, 2H), 7.03 (s, 2H), 7.08–7.10 (m, 1H), 7.28–7.30 (m, 2H); ¹³C NMR (CDCl₃, 125 MHz, 300 K) δ 0.87 (q), 0.95 (q), 1.60 (q), 1.67 (q), 1.76 (q × 2), 22.96 (q), 23.54 (q), 23.84 (q), 23.89 (q), 27.76 (q), 28.06 (q), 28.20 (d), 28.50 (d), 30.76 (d), 34.34 (d), 35.57 (d), 35.84 (d), 120.67 (d), 122.96 (d), 123.10 (d), 123.82

(d), 124.56 (d), 125.74 (d), 129.00 (d), 129.31 (s), 137.42 (s), 143.77 (s), 145.91 (s), 150.44 (s), 150.86 (s), 150.98 (s), 151.51 (s), 151.63 (s), 151.87 (s); ⁷⁷Se NMR (CDCl₃, 51.5 MHz, 300 K) δ -16.2. High-resolution FAB-MS: observed *m/z* 1044.3621 ([M + H]⁺); calcd for C₄₉H₈₈⁷⁴GeNSSeSi₆ 1044.3631.

Reaction of Germanethione 1a with Mesitronitrile Oxide. To a mixture of **5** (228 mg, 0.239 mmol) and triphenylphosphine (188 mg, 0.718 mmol) was added hexane (1.0 mL), and the solution was refluxed for 2 h to afford a yellow solution of germanethione **1a**. Mesitronitrile oxide (60 mg, 0.63 mmol) was added to the solution at room temperature and the mixture was stirred for 10 h. After removal of the solvent, the crude reaction products were chromatographed by GPLC to afford 2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2-(2,4,6-triisopropylphenyl)-4-mesityl-1,3,5,2-oxathiazagermole (**27**; 243 mg, 99%). **27**: white crystals; mp 213–215 °C (CH₂Cl₂/EtOH); ¹H NMR (CDCl₃, 500 MHz, 300 K) δ 0.01 (s, 9H), 0.03 (s, 18H), 0.04 (s, 9H), 0.06 (s, 9H), 0.08 (s, 9H), 1.20 (d, *J* = 6.9 Hz, 6H), 1.21 (d, *J* = 6.9 Hz, 6H), 1.22 (d, *J* = 6.9 Hz, 6H), 1.36 (s, 1H), 2.16 (s, 6H), 2.25 (s, 3H), 2.31 (s, 1H), 2.52 (s, 1H), 2.85 (sept, *J* = 6.9 Hz, 1H), 3.15 (br s, 1H), 3.35 (br s, 1H), 6.38 (s, 1H), 6.51 (s, 1H), 6.62 (s, 2H), 7.00 (s, 2H); ¹³C NMR (CDCl₃, 125 MHz, 300 K) δ 1.10 (q), 1.36 (q), 1.45 (q), 1.53 (q), 1.82 (q), 20.62 (q), 21.05 (q), 23.77 (q), 23.85 (q), 28.51 (d), 28.73 (d), 30.87 (d), 31.58 (d), 34.23 (d), 122.80 (d), 124.02 (d), 128.50 (d), 129.33 (d), 129.43 (s), 130.24 (s), 137.07 (s), 137.14 (s), 138.43 (s), 145.84 (s), 150.91 (s), 151.34 (s), 151.20 (s), 151.98 (s), 153.18 (s). Anal. found: C, 60.38; H, 9.12; N, 1.33; S, 3.36. Calcd for C₅₂H₉₃GeNOSSi₆·0.5H₂O: C, 60.60; H, 9.19; N, 1.36; S, 3.11.

Reaction of Germanesolone 2a with Mesitronitrile Oxide. To a mixture of **13** (60.0 mg, 0.0524 mmol) and triphenylphosphine (41.0 mg, 0.156 mmol) was added hexane (0.5 mL), and the solution was refluxed for 1.5 h to afford a red solution of germanesolone **2a**. Mesitronitrile oxide (10 mg, 0.062 mmol) was added to the solution at room temperature, and the mixture was stirred for 5 min. After removal of the solvent, the crude reaction products were chromatographed by GPLC and wet column chromatography (SiO₂ with CH₂Cl₂) to afford 2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2-(2,4,6-triisopropylphenyl)-4-mesityl-1,3,5,2-oxaselenazagermole (**28**; 57.0 mg, 100%). **28**: white crystals; mp 237–239 °C (CH₂Cl₂/EtOH); ¹H NMR (CDCl₃, 500 MHz, 300 K) δ 0.00 (s, 18H), 0.06 (s, 9H), 0.067 (s, 9H), 0.069 (s, 9H), 0.082 (s, 9H), 1.18 (br s, 6H), 1.22 (d, *J* = 6.9 Hz, 6H), 1.29 (br s, 6H), 1.36 (s, 1H), 2.19 (s, 6H), 2.25 (s, 3H), 2.36 (s, 1H), 2.46 (s, 1H), 2.85 (sept, *J* = 6.9 Hz, 1H), 3.22 (br s, 1H), 3.43 (br s, 1H), 6.38 (s, 1H), 6.50 (s, 1H), 6.82 (s, 2H), 7.01 (s, 2H); ¹³C NMR (CDCl₃, 125 MHz, 300 K) δ 1.09 (q), 1.17 (q), 1.39 (q), 1.54 (q), 1.69 (q), 1.93 (q), 20.70 (q), 20.87 (q), 23.67 (q), 23.73 (q), 23.89 (q), 28.12 (d), 28.27 (d), 28.47 (d), 30.84 (d), 34.21 (d), 34.67 (d), 122.87 (br d), 124.13 (d), 128.48 (d), 129.51 (d), 130.56 (s), 131.37 (s), 136.90 (s), 137.11 (s), 138.43 (s), 145.60 (s), 148.79 (s), 150.77 (s), 151.20 (s), 151.32 (s), 152.31 (s), 153.16 (s); ⁷⁷Se NMR (CDCl₃, 51.5 MHz, 300 K) δ 212.4. Anal. found: C, 58.55; H, 8.94; N, 1.44; Se, 7.58. Calcd for C₅₂H₉₃GeNOSeSi₆: C, 58.75; H, 8.77; N, 1.31; Se, 7.39.

Reaction of Germanethione 1a with 2,3-Dimethyl-1,3-butadiene. To a mixture of **5** (69.2 mg, 0.0724 mmol) and triphenylphosphine (56.9 mg, 0.217 mmol) in a 5 mm i.d. Pyrex glass tube was added 2,3-dimethyl-1,3-butadiene (0.08 mL, 0.72 mmol) and hexane (0.8 mL) at room temperature. After five freeze–pump–thaw cycles, the tube was evacuated and sealed. The solution was heated at 90 °C for 10 h, during which time the yellow color disappeared. After removal of the solvent, the crude reaction products were chromatographed by DCC (SiO₂ with hexane) to afford 2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2-(2,4,6-triisopropylphenyl)-4,5-dimethyl-1-thia-2-germacyclohex-4-ene (**29**; 57.1 mg, 84%) together with **9** (7.0 mg, 11%). **29**: white crystals; mp 164–168 °C dec (CH₂Cl₂/EtOH); ¹H NMR (CDCl₃, 500 MHz, 340 K) δ -0.02 (br s, 18H), 0.06 (s, 9H), 0.07 (s, 9H), 0.12 (br s, 18H), 1.06 (br d, *J* = 6.9 Hz, 6H), 1.18 (d, *J* = 6.9 Hz, 6H), 1.22 (br s, 6H), 1.32 (s, 1H), 1.39 (br s, 3H), 1.80 (s, 3H), 2.13 (br s, 2H), 2.28 (d, *J* = 12.2 Hz, 1H), 2.55 (d, *J* = 12.2 Hz, 1H), 2.79 (sept, *J* = 6.9 Hz, 1H), 3.03 (br s, 1H), 3.16 (d, *J* = 13.4 Hz, 1H), 3.30 (d, *J* = 13.4 Hz, 1H), 4.26 (br s, 1H), 6.39 (br s, 2H), 6.92 (s, 2H); ¹³C NMR (CDCl₃, 125 MHz, 340 K) δ 1.01 (q), 1.21 (q), 2.16 (q), 2.47 (q), 20.31 (q), 20.96 (q), 23.77 (q), 23.81 (q), 25.59 (q), 26.42 (d), 26.88 (d),

28.51 (q), 30.47 (d), 31.44 (d), 33.26 (t), 33.49 (t), 33.75 (d), 34.14 (d), 122.72 (d), 122.75 (s), 122.96 (s), 123.16 (d), 128.77 (d), 129.04 (s), 129.81 (d), 135.87 (s), 136.26 (s), 143.16 (s), 149.33 (s), 149.96 (s), 152.76 (s), 155.125 (s). Anal. found: C, 60.38; H, 9.56; S, 3.81. Calcd for $C_{48}H_{92}GeSSi_6 \cdot 0.5H_2O$: C, 60.59; H, 9.85; S, 3.37.

Reaction of Germanethione 1a with Isoprene at 90 °C. To a mixture of **5** (102 mg, 0.107 mmol) and triphenylphosphine (84.0 mg, 0.321 mmol) in a 5 mm i.d. Pyrex glass tube was added isoprene (0.11 mL, 1.1 mmol) and hexane (0.8 mL) at room temperature. After five freeze-pump-thaw cycles, the tube was evacuated and sealed. The solution was heated at 90 °C for 10 h, during which time the yellow color disappeared. After removal of the solvent, the crude reaction products were chromatographed by DCC (SiO_2 with hexane) to afford 2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2-(2,4,6-triisopropylphenyl)-4-methyl-1-thia-2-germacyclohex-4-ene (**30**; 69.7 mg, 70%) and 2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2-(2,4,6-triisopropylphenyl)-5-methyl-1-thia-2-germacyclohex-4-ene (**31**; 7.5 mg, 8%) together with **9** (11.1 mg, 13%). **30**: white crystals; mp 166–169 °C dec ($CH_2Cl_2/EtOH$); 1H NMR ($CDCl_3$, 500 MHz, 300 K) δ -0.09 (br s, 18H), 0.03 (s, 9H), 0.05 (s, 9H), 0.06 (s, 9H), 0.13 (br s, 9H), 0.92 (br s, 3H), 1.10 (d, $J = 6.9$ Hz, 3H), 1.15 (s, 3H), 1.16 (d, $J = 6.9$ Hz, 6H), 1.28 (s, 1H), 1.33 (br s, 3H), 1.94 (br s, 1H), 2.12 (br s, 1H), 2.17 (d, $J = 11.9$ Hz, 1H), 2.48 (d, $J = 11.9$ Hz, 1H), 3.15 (dd, $J_1 = 13.5$ Hz, $J_2 = 5.2$ Hz, 1H), 3.37 (dd, 1H, $J_1 = 13.5$ Hz, $J_2 = 7.7$ Hz), 4.59 (br s, 1H), 5.74 (m, 1H), 6.29 (s, 1H), 6.40 (s, 1H), 6.67 (s, 1H), 6.92 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz, 300 K) δ 0.91 (q), 1.15 (q), 1.82 (q), 2.01 (q \times 2), 2.37 (q), 23.81 (q), 23.87 (q), 25.24 (q), 25.63 (q), 26.17 (d), 26.24 (t), 28.02 (d), 28.09 (d), 30.15 (d), 31.43 (t), 33.57 (d), 34.05 (d), 122.48 (d), 122.76 (d), 123.28 (d), 123.36 (d), 128.67 (d), 135.01 (s), 137.63 (s), 143.11 (s), 149.25 (s), 149.36 (s), 150.16 (s), 152.40 (s), 155.32 (s), 155.37 (s). Anal. found: C, 60.41; H, 9.45; S, 3.23. Calcd for $C_{47}H_{90}GeSSi_6$: C, 60.80; H, 9.77; S, 3.45. High-resolution FAB-MS: observed m/z 929.4764 ($[M + H]^+$); calcd for $C_{47}H_{91}^{74}GeSSi_6$ 929.4669. **31**: white crystals; mp 177–180 °C dec ($CH_2Cl_2/EtOH$); 1H NMR ($CDCl_3$, 500 MHz, 335 K) δ 0.02 (s, 18H), 0.04 (s, 18H), 0.052 (s, 9H), 0.054 (s, 9H), 1.13 (d, $J = 6.9$ Hz, 12H), 1.20 (d, $J = 6.9$ Hz, 6H), 1.30 (s, 1H), 1.87 (s, 3H), 2.24 (br s, 2H), 2.25–2.42 (m, 2H), 2.80 (sept, $J = 6.9$ Hz, 1H), 3.11 (br s, 1H), 3.14 (s, 2H), 4.12 (br s, 1H), 5.69 (m, 1H), 6.39 (br s, 2H), 6.96 (br s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz, 300 K) δ 0.93 (q), 0.95 (q), 1.96 (q), 2.21 (q \times 2), 2.42 (q), 23.78 (q), 23.81 (q), 23.98 (q), 24.43 (q), 24.65 (d), 25.69 (t), 27.73 (d), 27.96 (d), 29.78 (t), 30.14 (d), 33.75 (d), 34.10 (d), 122.45 (d), 123.08 (d), 123.20 (d), 128.67 (d), 128.80 (d), 134.42 (s), 137.21 (s), 137.58 (s), 143.04 (s), 148.96 (s), 149.81 (s), 150.30 (s), 151.97 (s), 153.86 (s). Anal. found: C, 60.57; H, 9.56; S, 3.41. Calcd for $C_{47}H_{90}GeSSi_6$: C, 60.80; H, 9.77; S, 3.45. High-resolution FAB-MS: observed m/z 929.4659 ($[M + H]^+$); calcd for $C_{47}H_{90}^{74}GeSSi_6$ 929.4669.

Reaction of Germanethione 1a with Isoprene at 150 °C. A solution of **1a** obtained from **5** (93.2 mg, 0.0975 mmol) in a manner similar to the above reaction at 90 °C was heated with isoprene (0.11 mL, 1.1 mmol) at 150 °C for 10 h and gradually cooled to room temperature over 5 h. The products were **30** (32.1 mg, 36%) and **31** (32.7 mg, 36%) together with **9** (11.1 mg, 13%).

Reaction of Germanethione 1a with Isoprene at 90 °C in THF. Similarly, a THF solution (0.5 mL) of **1a**, obtained from **5** (40.4 mg, 0.0423 mmol), was heated with isoprene (0.08 mL, 0.63 mmol) at 80 °C for 10 h, during which time the yellow color disappeared. The products were **30** (26.6 mg, 76%) and **31** (2.9 mg, 8%).

Reaction of Germanethione 1a with 2-Methyl-1,3-pentadiene. A similar reaction using **5** (83.7 mg, 0.0876 mmol), triphenylphosphine (68.8 mg, 0.263 mmol), and 2-methyl-1,3-pentadiene (0.20 mL, 1.8 mmol) in hexane (0.8 mL) at 50 °C for 10 h afforded 2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2-(2,4,6-triisopropylphenyl)-4,6-dimethyl-1-thia-2-germacyclohex-4-ene (**32**; 73.6 mg, 89%) together with **9** (5.2 mg, 7%). **32**: white crystals; mp 163–165 °C dec ($CH_2Cl_2/EtOH$); 1H NMR ($CDCl_3$, 500 MHz, 340 K) δ -0.07 (s, 9H), 0.058 (s, 9H), 0.062 (s, 9H), 0.08 (s, 9H), 0.13 (s, 18H), 0.95 (br s, 3H), 1.11 (br s, 3H), 1.17 (d, $J = 6.9$ Hz, 6H), 1.21 (d, $J = 6.9$ Hz, 3H), 1.23 (s, 3H), 1.317 (s, 1H), 1.323 (d, $J = 6.9$ Hz, 3H), 1.54 (d, $J = 6.9$ Hz, 3H), 2.10 (br s, 2H), 2.15 (d, $J = 10.5$ Hz, 1H), 2.55 (d, $J = 10.5$ Hz,

1H), 2.77 (sept, $J = 6.9$ Hz, 1H), 2.99 (br s, 1H), 3.47 (m, 1H), 4.63 (br s, 1H), 5.47 (m, 1H), 6.40 (br s, 2H), 6.89 (br s, 1H), 6.93 (br s, 1H). It was impossible to assign the ^{13}C NMR data owing to the complexity resulting from the steric congestion. Anal. found: C, 61.29; H, 9.52; S, 3.22. Calcd for $C_{48}H_{92}GeSSi_6$: C, 61.17; H, 9.84; S, 3.40. High-resolution FAB-MS: observed m/z 943.4796 ($[M + H]^+$); calcd for $C_{48}H_{93}^{74}GeSSi_6$ 943.4825.

Reaction of Germanethione 1a with 2,4-Dimethyl-1,3-pentadiene. The reaction using **5** (84.7 mg, 0.0886 mmol), triphenylphosphine (70.0 mg, 0.267 mmol), and 2,4-dimethyl-1,3-pentadiene (0.20 mL, 1.8 mmol) in hexane (0.8 mL) at 90 °C for 10 h gave 2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2-(2,4,6-triisopropylphenyl)-4,6,6-trimethyl-1-thia-2-germacyclohex-4-ene (**33**; 42.5 mg, 50%) together with **9** (20.2 mg, 26%). **33**: white crystals; mp 168–170 °C dec ($CH_2Cl_2/EtOH$); 1H NMR ($CDCl_3$, 500 MHz, 340 K) δ -0.06 (s, 18H), 0.06 (s, 9H), 0.07 (s, 9H), 0.14 (s, 9H), 0.18 (s, 9H), 0.87 (br s, 3H), 1.12 (br s, 3H), 1.179 (d, $J = 6.9$ Hz, 3H), 1.182 (d, $J = 6.9$ Hz, 3H), 1.24 (d, $J = 6.9$ Hz, 6H), 1.32 (s, 1H), 1.35 (s, 3H), 1.54 (s, 3H), 1.55 (br s, 3H), 2.12 (br s, 2H), 2.36 (d, $J = 11.4$ Hz, 1H), 2.47 (d, $J = 11.4$ Hz, 1H), 2.78 (sept, $J = 6.9$ Hz, 1H), 2.91 (br s, 1H), 4.59 (br s, 1H), 5.48 (s, 1H), 6.37 (br s, 2H), 6.88 (s, 1H), 6.96 (s, 1H). It was impossible to assign the ^{13}C NMR data owing to the complexity resulting from the steric congestion. Anal. found: C, 61.17; H, 9.77; S, 2.98. Calcd for $C_{49}H_{94}GeSSi_6$: C, 61.53; H, 9.91; S, 3.35. High-resolution FAB-MS: observed m/z 957.5008 ($[M + H]^+$); calcd for $C_{49}H_{95}^{74}GeSSi_6$ 957.4892.

Reaction of Germanethione 1a with 2,4-Hexadiene. The reaction of **5** (93.6 mg, 0.0980 mmol), triphenylphosphine (77.0 mg, 0.294 mmol), and 2,4-hexadiene (0.10 mL, 1.0 mmol) in hexane (0.8 mL) at 150 °C over 10 h afforded **9** (86.0 mg, 100%).

Reaction of Germanethione 1a with trans,trans-1,4-Diphenyl-1,3-butadiene. The reaction of **5** (59.2 mg, 0.0619 mmol), triphenylphosphine (49.0 mg, 0.187 mmol), and *trans,trans*-1,4-diphenyl-1,3-butadiene (64.0 mg, 0.311 mmol) in hexane (0.8 mL) at 130 °C for 10 h gave **9** (53.3 mg, 98%).

Thermal Reaction of the Diene Adduct 31 in the Presence of Isoprene. In a 5 mm i.d. Pyrex glass tube was placed a hexane (0.5 mL) solution of **31** (40.0 mg, 0.0431 mmol) and isoprene (0.10 mL, 0.1 mmol). After five freeze-pump-thaw cycles, the tube was evacuated and sealed. The solution was heated at 150 °C for 10 h. After removal of the solvent, the crude reaction products were chromatographed by DCC (SiO_2 with hexane) to afford **30** (16.2 mg, 41%), **31** (17.3 mg, 43%), and **9** (5.0 mg, 13%).

Thermal Reaction of Diene Adduct 32 in the Presence of 2,3-Dimethyl-1,3-butadiene. The reaction of **32** (30.8 mg, 0.0326 mmol) and 2,3-dimethyl-1,3-butadiene (0.14 mL, 0.98 mmol) at 150 °C for 10 h was similarly carried out to give **29** (22.0 mg, 71%) and **9** (3.6 mg, 13%).

Reaction of Germaneselon 2a with 10 and 40 equiv of 2,3-Dimethyl-1,3-butadiene. The reaction was carried out in a manner similar to that of **1a**. The reaction of **13** (54.7 mg, 0.0478 mmol), triphenylphosphine (37.0 mg, 0.141 mmol), and 2,3-dimethyl-1,3-butadiene (0.06 mL, 0.53 mmol) in hexane (0.8 mL) at 90 °C for 10 h, and then at room temperature for 10 h, afforded 2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2-(2,4,6-triisopropylphenyl)-4,5-dimethyl-1-selena-2-germacyclohex-4-ene (**34**; 10.5 mg, 22%). **34**: white crystals, mp 148–154 °C dec ($CH_2Cl_2/EtOH$); 1H NMR ($CDCl_3$, 500 MHz, 350 K) δ -0.02 (br s, 18H), 0.07 (s, 9H), 0.09 (s, 9H), 0.14 (s, 18H), 0.93 (br s, 3H), 1.05 (br s, 3H), 1.19 (d, $J = 6.9$ Hz, 6H), 1.21 (br s, 3H), 1.28 (br s, 6H), 1.32 (br s, 6H), 1.33 (s, 1H), 1.79 (s, 3H), 2.14 (br s, 2H), 2.29 (d, $J = 10.8$ Hz, 1H), 2.67 (d, $J = 10.8$ Hz, 1H), 2.79 (sept, $J = 6.9$ Hz, 1H), 3.07 (br s, 1H), 3.17 (d, $J = 11.8$ Hz, 1H), 3.29 (d, $J = 11.8$ Hz, 1H), 4.33 (br s, 1H), 6.40 (br s, 2H), 6.92 (s, 2H); ^{77}Se NMR ($CDCl_3$, 51.5 MHz, 300 K) δ 30.9, 32.6. It was impossible to assign the ^{13}C NMR because there were at least two conformers at room temperature and also **34** gradually decomposed at elevated temperature. Anal. found: C, 57.74; H, 9.02; Se, 8.33. Calcd for $C_{48}H_{92}GeSeSi_6$: C, 58.27; H, 9.37; S, 7.98.

Similarly, the reaction of **13** (68.3 mg, 0.0597 mmol), triphenylphosphine (47.0 mg, 0.180 mmol), and 2,3-dimethyl-1,3-butadiene (0.30 mL, 2.6 mmol) in hexane (0.7 mL) at 90 °C for 2 h and then at room temperature for 10 h gave **34** (49.4 mg, 84%).

Reaction of Germanesolone 2a with Isoprene. The reaction of isolated germanesolone **2a** (52.0 mg, 0.0573 mmol) and isoprene (0.23 mL, 2.3 mmol) in hexane (0.5 mL) at room temperature for 10 h afforded 2-[2,4,6-tris[bis(trimethylsilyl)methyl]phenyl]-2-(2,4,6-triisopropylphenyl)-4-methyl-1-selena-2-germacyclohex-4-ene (**35**; 28.5 mg, 51%) and 2-[2,4,6-tris[bis(trimethylsilyl)methyl]phenyl]-2-(2,4,6-triisopropylphenyl)-5-methyl-1-selena-2-germacyclohex-4-ene (**36**; 19.6 mg, 35%). **35**: white crystals; mp 126–130 °C dec (CH₂Cl₂/EtOH); ¹H NMR (CDCl₃, 500 MHz, 300 K) δ -0.01 (br s, 9H), 0.07 (s, 18H), 0.08 (s, 9H), 0.09 (s, 9H), 0.15 (s, 9H), 0.95 (br s, 3H), 1.11 (br s, 3H), 1.19 (d, *J* = 6.9 Hz, 6H), 1.23 (br s, 6H), 1.27 (s, 1H), 1.33 (s, 3H), 2.15 (br s, 2H), 2.26 (d, 1H, *J* = 11.4 Hz), 2.66 (d, 1H, *J* = 11.4 Hz), 2.79 (sept, *J* = 6.9 Hz, 1H), 3.16 (dd, *J*₁ = 12.1 Hz, *J*₂ = 5.2 Hz, 1H), 3.40 (dd, *J*₁ = 12.1 Hz, *J*₂ = 8.2 Hz, 1H), 4.56 (br s, 1H), 5.71 (m, 1H), 6.42 (br s, 2H), 6.92 (s, 2H). It was impossible to assign the ¹³C NMR data owing to the complexity resulting from the steric congestion. Anal. found: C, 57.46; H, 9.11. Calcd for C₄₇H₉₀GeSeSi₆: C, 57.88; H, 9.30. High-resolution FAB-MS: observed *m/z* 977.4230 ([M + H]⁺); calcd for C₄₉H₉₅⁷⁴GeSSi₆ 977.4114. **36**: white crystals; mp 147–150 °C dec (CH₂Cl₂/EtOH); ¹H NMR (CDCl₃, 500 MHz, 350 K) δ 0.07 (s, 18H), 0.08 (s, 18H), 0.09 (s, 18H), 1.11 (d, *J* = 6.9 Hz, 6H), 1.14 (br d, *J* = 6.9 Hz, 6H), 1.20 (d, *J* = 6.9 Hz, 6H), 1.32 (s, 1H), 1.88 (s, 3H), 2.27–2.33 (m, 1H), 2.37 (br s, 2H), 2.50–2.55 (m, 1H), 2.80 (sept, *J* = 6.9 Hz, 1H), 3.10 (d, *J* = 12.0 Hz, 1H), 3.17 (d, *J* = 12.0 Hz, 1H), 3.18 (br s, 1H), 3.96 (br s, 1H), 5.59 (m, 1H), 6.40 (br s, 2H), 6.96 (s, 2H). It was impossible to assign the ¹³C NMR data owing to the complexity resulting from the steric congestion. Anal. found: C, 57.70; H, 9.15. Calcd for C₄₇H₉₀GeSeSi₆: C, 57.88; H, 9.30. High-resolution FAB-MS: observed *m/z* 977.4203 ([M + H]⁺); calcd for C₄₇H₉₁⁷⁴Ge⁸⁰SeSi₆ 977.4114.

Thermal Reaction of Diene Adduct 34 in the Presence of Mesitronitrile Oxide. In a 5 mm i.d. Pyrex glass tube was placed a hexane (0.6 mL) solution of **34** (20.5 mg, 0.021 mmol) and mesitronitrile oxide (4.0 mg, 0.025 mmol). After five freeze–pump–thaw cycles, the tube was evacuated and sealed. The solution was heated at 50 °C for 2 h. After removal of the solvent, the crude reaction products were chromatographed by DCC (SiO₂ with 5:1 hexane/CH₂Cl₂) to afford **28** (19.9 mg, 90%).

Reaction of Germanethione 1b with excess 2,3-Dimethyl-1,3-butadiene. The reaction was carried out in a manner similar to that of **1a**. The reaction of **1b** (50.0 mg, 0.0548 mmol), triphenylphosphine (43.1 mg, 0.164 mmol), and 2,3-dimethyl-1,3-butadiene (0.06 mL, 0.53 mmol) in hexane (2.0 mL) at 90 °C for 20 h gave 2-[2,4,6-tris[bis(trimethylsilyl)methyl]phenyl]-4,5-dimethyl-2-[bis(trimethylsilyl)methyl]-1-thia-2-germacyclohex-4-ene (**37**; 16.2 mg, 33%). **37**: white crystals; mp 160–164 °C dec (CH₂Cl₂/EtOH); ¹H NMR (CDCl₃, 500 MHz, 300 K) δ 0.036 (s, 9H), 0.039 (s, 9H), 0.076 (s, 9H), 0.081 (s, 9H), 0.11 (s, 9H), 0.12 (s, 9H), 0.14 (s, 9H), 0.18 (s, 9H), 0.37 (s, 1H), 1.27 (s, 1H), 1.79 (s, 3H), 1.80 (s, 3H), 1.90 (d, *J* = 14.4 Hz, 1H), 2.34 (d, *J* = 14.4 Hz, 1H), 2.55 (s, 1H), 2.67 (s, 1H), 2.99 (d, *J* = 13.8 Hz, 1H), 3.12 (d, *J* = 13.8 Hz, 1H), 6.21 (s, 1H), 6.35 (s, 1H); ¹³C NMR (CDCl₃, 125 MHz, 300 K) δ 1.00 (q), 1.04 (q), 2.10 (q), 2.18 (q), 2.37 (q), 2.45 (q), 3.65 (q), 4.87 (q), 10.49 (d), 20.34 (q), 23.24 (q), 27.45 (d), 27.53 (d), 29.87 (t), 29.94 (d), 32.11 (t), 123.32 (d), 128.16 (s), 128.46 (s), 128.90 (d), 134.32 (s), 142.89 (s), 149.80 (s), 150.28 (s). Anal. found: C, 53.88; H, 10.04; S, 3.08. Calcd for C₄₀H₈₈GeSSi₈: C, 53.47; H, 9.87; S, 3.57. High-resolution FAB-MS: observed *m/z* 899.4158 ([M + H]⁺); calcd for C₄₀H₈₉⁷⁴GeSSi₈ 899.4051.

When a hexane solution (2.0 mL) of **19** (50.0 mg, 0.0548 mmol), triphenylphosphine (43.1 mg, 0.164 mmol), and 2,3-dimethyl-1,3-butadiene (0.30 mL, 0.26 mmol) was heated at 90 °C for 70 h, the product was **37** (24.5 mg, 50%).

Reaction of Germanethione 1b with Isoprene. (1) Reaction at 90 °C. In a 5 mm i.d. NMR tube was placed a benzene-*d*₆ (1.0 mL) solution of **22** (48.3 mg, 0.0502 mmol) and elemental sulfur (1.6 mg, 0.0063 mmol). After five freeze–pump–thaw cycles, the tube was evacuated and sealed. The solution was heated at 90 °C for 10 h to afford a yellow solution. The quantitative generation of germanethione **1b** and diphenylacetylene was observed by ¹H NMR. The sealed tube was opened in a glovebox, and the solvent was removed. The yellow solid thus obtained was dissolved in hexane (0.3 mL), and the solution

was placed in a 8 mm i.d. Pyrex glass tube. To this solution was added isoprene (0.3 mL, 3.0 mmol), and the solution was heated at 90 °C for 10 h. The solvent was removed under reduced pressure, and the residue was separated by DCC (SiO₂ with hexane) to give 2-[2,4,6-tris[bis(trimethylsilyl)methyl]phenyl]-5-methyl-2-[bis(trimethylsilyl)methyl]-1-thia-2-germa-cyclohex-4-ene (**38**; 27.5 mg, 62%) together with a quantitative amount of diphenylacetylene. **38**: white crystals; mp 166–169 °C dec (CH₂Cl₂/EtOH); ¹H NMR (CDCl₃, 500 MHz, 300 K) δ 0.036 (s, 9H), 0.039 (s, 9H), 0.08 (s, 9H), 0.10 (s, 18H), 0.125 (s, 9H), 0.134 (s, 9H), 0.18 (s, 9H), 0.40 (s, 1H), 1.28 (s, 1H), 1.85 (s, 3H), 2.06 (dd, *J*₁ = 13.8 Hz, *J*₂ = 6.9 Hz, 1H), 2.13 (dd, *J*₁ = 13.8 Hz, *J*₂ = 7.4 Hz, 1H), 2.37 (s, 1H), 2.44 (s, 1H), 3.07 (d, *J* = 13.7 Hz, 1H), 3.10 (d, 13.7 Hz, 1H), 5.64 (m, 1H), 6.19 (s, 1H), 6.35 (s, 1H); ¹³C NMR (CDCl₃, 125 MHz, 300 K) δ 1.00 (q), 1.04 (q), 1.99 (q), 2.14 (q), 2.37 (q), 2.41 (q), 4.22 (q), 4.95 (q), 10.84 (d), 23.51 (t), 24.51 (q), 27.58 (d), 27.97 (d), 29.68 (t), 29.98 (d), 122.90 (d), 123.11 (d), 128.80 (d), 134.05 (s), 136.34 (s), 143.14 (s), 149.66 (s), 150.10 (s). Anal. found: C, 52.55; H, 9.68. Calcd for C₃₉H₈₆GeSSi₈: C, 52.96; H, 9.80. High-resolution FAB-MS: observed *m/z* 885.3832 ([M + H]⁺); calcd for C₃₉H₈₇⁷⁴GeSSi₈ 885.3895.

(2) Reaction at 150 °C. A similar reaction at 150 °C for 10 h gave **38** (29.8 mg, 67%) and a quantitative amount of diphenylacetylene.

X-ray Data Collection. Single crystals of **1a**, **2a**, and **2b** were grown by the slow evaporation of its saturated solution in hexane at room temperature in a glovebox filled with argon, and single crystals of **12** were grown by the slow evaporation of its saturated solution in ethanol and dichloromethane at room temperature. The intensity data were collected on Rigaku AFC5R (for **1a**, **2b**) and AFC7R (for **2a**, **12**) diffractometers with graphite monochromated Mo Kα radiation (λ = 0.71069 Å). The structure was solved by direct methods with SHELXS-86⁴¹ and refined by the full matrix least-squares method. All of the nonhydrogen atoms were refined anisotropically. The final cycle of the least-squares refinement was based on 3454 observed reflections [*I* > 4σ(*I*)] and 451 variable parameters for **1a**, 3395 observed reflections [*I* > 3σ(*I*)] and 451 variable parameters for **2a**, 2185 observed reflections [*I* > 4σ(*I*)] and 397 variable parameters for **2b**, and 5062 observed reflections [*I* > 3σ(*I*)] and 397 variable parameters for **12**. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

Acknowledgment. This work was partially supported by a Grant-in-Aid for Scientific Research on Priority Area (No. 0536102) from the Ministry of Education, Science, Sports and Culture, Japan. T.M. is grateful to the Research Fellowship of the Japan Society for the Promotion of Science for Young Scientists. We acknowledge Dr. M. Minoura of Hiroshima University for molecular orbital calculations, Prof. Y. Furukawa of Waseda University, and Mr. K. Kawachi of JEOL Ltd. for the measurement of the FT-Raman spectra. We would also like to thank ASAI Germanium Research Institute, Shin-etsu Chemical Co., Ltd., and Tosoh Akzo Co., Ltd. for the generous gifts of tetrachlorogermane, chlorosilanes, and alkyllithiums, respectively.

Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **1a**, **2a**, **2b**, and **12** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA991147X

(41) Sheldrick, G. M. SHELX-86, Program for Crystal Structure Determination. University of Göttingen, Göttingen, Germany, 1986.