Reactions of a Germacyclopropabenzene with Elemental Chalcogens: Syntheses and Structures of a Series of Stable 2*H*-Benzo[*c*][1,2]chalcogenagermetes

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Thermal reactions of a stable germacyclopropabenzene, Tbt(Dip)GeC_6H_4 (Tbt = 2,4,6-tris-[bis(trimethylsilyl)methyl]phenyl, Dip = 2,6-diisopropylphenyl), with elemental chalcogens in C_6D_6 at 130 °C resulted in the formation of novel Ge-containing four-membered heterocycles, 2*H*-benzo[*c*][1,2]chalcogenagermete derivatives. This is the first example of a ring expansion reaction of cyclopropabenzene derivatives using elemental chalcogen, while several types of ring-opening reactions have been explored for cyclopropabenzene so far. In addition, the 2*H*-benzo[*c*][1,2]telluragermete is the first stable compound as a tellurete derivative. Structures of the chalcogenagermetes obtained here were elucidated by X-ray crystallographic analysis, and the experimentally obtained structural parameters were supported by theoretical calculations. The skeletons of chalcogenagermetes have very little strain in their four-membered rings annelated with a benzene ring.

Introduction

Structures and properties of cyclopropabenzene derivatives have fascinated many organic chemists so far, because the balance of the aromatic character of the arene moiety and the angular strain in the three-membered ring results in their unique properties.[1] On the other hand, many studies on attempted synthesis of a heteracyclopropabenzene, which has a heteroatom as the bridging atom of its cyclopropabenzene skeleton instead of a carbon atom, have been reported.[2] However, no stable examples of heteracyclopropabenzenes have been known until our research project, because they might undergo polymerization or isomerization immediately due to their extremely high reactivities and/or inherent instability.[2] Recently, we have succeeded in the synthesis of the first stable silacyclopropabenzene (**1**)[3,4] and germacyclopropabenzene (**2**),[5] heavier element analogues of a cyclopropabenzene derivative, and reported their structures and physical properties. The key point to our success is the development of a synthetic method under mild conditions, i.e., the reaction of a dilithiometallane[6] having effective steric protection groups, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt) and 2,6-diisopropylphenyl (denoted as Dip), with 1,2-dibromobenzene at −78 °C. Furthermore, a similar synthetic approach led us to the isolation of the first stable bis(silacyclopropa)benzene derivatives.[4,7] Experimental and theoretical studies on the structural features of these metallacyclopropabenzenes of heavier group 14 elements revealed that they have less strain than cyclopropabenzenes most likely due to the longer and softer metal−carbon bonds than carbon−carbon bonds. That is, it can be concluded that a three-membered ring containing a heavier group 14 element can undergo annelation with a benzene ring with much less perturbation than the case of hydrocarbon systems. At the next stage, we became interested in the chemical properties of metallacyclopropabenzenes. While a great number of papers on the reactivity of cyclopropabenzene have appeared so far,[1] most of them are the addition reactions leading to the ring opening and ring expansion of its three-membered ring to release the strain energy. In most cases, the reagents added were found to attack the electron-rich π-bond or the strained σ-bond of the three-membered ring. By contrast, **1** and **2** do not react with MeOH, MesCNO, and mCPBA at all. Very recently, we have found the novel reactivity of germacyclopropabenzene **2** toward group 6 metal hexacarbonyl complexes [M(CO)$_6$] (M = Cr, Mo, W), leading to the

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[1] (a) Halton, B. *Chem. Rev.* **1989**, *89*, 1161−1185. (b) Halton, B. *Chem. Rev.* **2003**, *103*, 1327−1369. (c) Soncini, A.; Havenith, R. W. A.; Fowler, P. W.; Jenneskens, L. W.; Steiner, E. *J. Org. Chem.* **2002**, *67*, 4753−4758. (d) Bachrach, S. M. *J. Organomet. Chem.* **2002**, *643*, 39−46. (e) Naka, A.; Yoshizawa, K.; Kang, S.; Yamabe, T.; Ishikawa, M. *Organometallics* **1998**, *17*, 5830−5835. (f) Kyushin, S.; Kitahara, T.; Matsumoto, H. *Chem. Lett.* **1998**, 471−472. (g) EckertMaksic, M.; Glasovac, Z.; Hodoscek, M.; Lesar, A.; Maksic, Z. B. *J. Organomet. Chem.* **1996**, *524*, 107−114.

[2] (a) Thétaz, C.; Wentrup, C. *J. Am. Chem. Soc.* **1976**, *98*, 1258−1259. (b) Torres, M.; Clement, A.; Bertie, J. E.; Gunning, H. E.; Strausz, O. P. *J. Org. Chem.* **1978**, *43*, 2490−2493. (c) Cadogan, J. I. G.; Sharp, J. T.; Trattles, M. J. *J. Chem. Soc., Chem. Commun.* **1974**, 900−901. (d) Schulz, R.; Schweig, A. *Tetrahedron Lett.* **1984**, *25*, 2337−2340. (e) Steinfeld, J. I. *Spectrochim. Acta* **1990**, *46*, 589−596. (f) White, R. C.; Scoby, J.; Roberts, T. D. *Tetrahedron Lett.* **1979**, *20*, 2785−2788. (g) Kaiser, R. I.; Bettinger, H. G. *Angew. Chem., Int. Ed.* **2002**, *41*, 2350−2352.

[3] Hatano, K.; Tokitoh, N.; Takagi, N.; Nagase, S. *J. Am. Chem. Soc.* **2000**, *122*, 4829−4830.

[4] Tajima, T.; Hatano, K.; Sasaki, T.; Sasamori, T.; Takeda, N.; Tokitoh, N.; Takagi, N.; Nagase, S. *J. Organomet. Chem.* **2003**, *686*, 118−126.

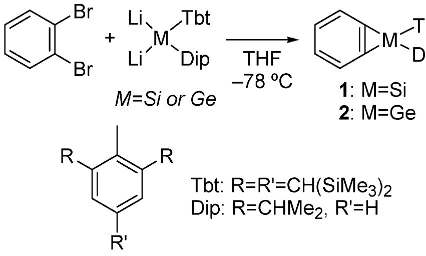
[5] Tokitoh, N.; Hatano, K.; Sasaki, T.; Sasamori, T.; Takeda, N.; Takagi, N.; Nagase, S. *Organometallics* **2002**, *21*, 4309−4311.

[6] (a) Tokitoh, N.; Hatano, K.; Sadahiro, T.; Okazaki, R. *Chem. Lett.* **1999**, *28*, 931−932. (b) Tokitoh, N.; Sadahiro, T.; Hatano, K.; Sasaki, T.; Takeda, N.; Okazaki, R. *Chem. Lett.* **2002**, *31*, 34−35.

[7] Tajima, T.; Hatano, K.; Sasaki, T.; Sasamori, T.; Takeda, N.; Tokitoh, N. *Chem. Lett.* **2003**, *32*, 220−221.

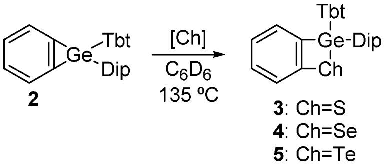
10.1021/om049216q CCC: \$30.25

Scheme 1



formation of cyclic germoxycarbene metal complexes.[8] In this paper, we present the reactions of germacyclopropabenzene **2** with elemental chalcogens, such as sulfur, selenium, and tellurium. In all cases, insertion reactions of a chalcogen atom into the three-membered ring of the germacyclopropabenzene occurred to give the corresponding chalcogenagermete derivatives. The isolated novel four-membered heterocycles, 2*H*-benzo[*c*]-[1,2]chalcogenagermetes, have been structurally characterized by X-ray crystallographic analysis.

Scheme 2



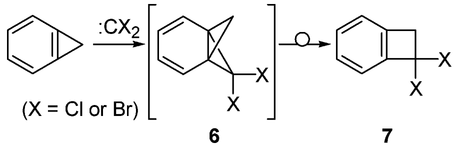
Results and Discussion

Reactions of Germacyclopropabenzene with Elemental Chalcogens. Heating of a C_6D_6 solution of germacyclopropabenzene **2** with an excess amount of elemental sulfur (S_8, 16 equiv as S) at 135 °C for 4.5 days in a sealed tube afforded the corresponding 2*H*-benzo[*c*][1,2]thiagermete **3** exclusively in 63% isolated yield. In this reaction, no other identifiable products were observed, as judged by ^{1}H NMR spectra of the crude reaction products. Therefore, it was conceivable that **3** may not undergo an over-sulfurization reaction leading to the formation of five- or six-membered cyclic compounds under these conditions. On the other hand, silacyclopropabenzene **1** was quite inert toward elemental sulfur under the same conditions. The lack of reactivity of **1** toward S_8 compared with **2** is most likely interpreted in terms of the difference of steric congestion around the metallacyclopropene skeleton due to the shorter Si−C bond lengths than Ge−C bond lengths. Indeed, **2** is gradually hydrolyzed, leading to Tbt(Dip)-Ge(Ph)OH through column chromatographic separation on silica gel, though **1** is very inert toward hydrolysis under the same conditions.[3−5]

Successful isolation of **3** naturally prompted us to examine the chalcogenation reactions of **2** with heavier elemental chalcogens, i.e., selenium and tellurium, in the hope of obtaining the heavier 2*H*-benzo[*c*][1,2]-chalcogenagermetes as stable compounds. When **2** was treated with an excess amount of elemental selenium (5 equiv) or elemental tellurium (5 equiv) under the same conditions as those for the sulfurization reaction of **2** (in a C_6D_6 sealed tube, at 135 °C, for a few days), the corresponding 2*H*-benzo[*c*][1,2]chalcogenagermete derivatives **4** and **5** were obtained as a sole product, respectively. It should be noted again that **4** and **5** showed no over-chalcogenation products under these conditions. The selenization and tellurization products were stable enough to be purified by HPLC and column chromatography on silica gel. The structures of **3**, **4**, and **5** were fully supported by ^{1}H and ^{13}C NMR spectra, mass spectra (FAB), elemental analyses, and X-ray crystallographic analysis (vide infra). In the multinuclear NMR spectroscopic analyses, **4** and **5** showed one characteristic singlet signal at 352.0 ppm (^{77}Se NMR of **4** in C_6D_6) and 612.3 ppm (^{125}Te NMR of **5** in C_6D_6), respectively.

Previous reports on the reactivities of cyclopropabenzenes indicate that the cyclopropabenzenes have two active sites in their three-membered rings, that is, the annelated C═C double bond and the strained C−C single bond.[1] For typical examples, several types of addition reactions and insertion reactions on the two active sites of cyclopropabenzene have been reported for the reactions with electron-deficient dienes[9] and transition metal (Ni, Pd, and so on) complexes.[10] On the other hand, an interesting result was reported in the reaction of cyclopropabenzene with dichloro- or dibromocarbene,[11] where the corresponding ring-expanded cyclobutabenzene **7** was afforded in a quantitative yield possibly via an initial [1+2] cycloaddition leading to **6** followed by its ready isomerization involving re-aromatization of the fused ring (Scheme 3). Considering the reactivity of cyclopropabenzenes,[1] it can be considered that the germacyclopropabenzene **2** should have two active sites, the strained Ge−C bond and the C═C bond in the three-membered ring systems. That is, addition of elemental chalcogens toward germacyclopropabenzene **2** might take place not only at the Ge−C bond but also at the C═C bond in the fused three-membered ring, leading to two types of products, type I and type II, respectively (Chart 1). Since only type I products were obtained in the chalcogenation reactions of **2**, it can be simply concluded that the Ge−C bond of **2** might be more reactive toward elemental chalcogens than its C═C bond. However, it is also conceivable that the reaction

Scheme 3



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(8) Tajima, T.; Sasaki, T.; Sasamori, T.; Takeda, N.; Tokitoh, N. *Chem. Commun.* **2004**, 402−403.

(9) (a) Neidlein, R.; Kohl, M.; Kramer, W. *Helv. Chim. Acta* **1989**, *72*, 1311−1318. (b) Brinker, U. H.; Wuster, H. *Tetrahedron Lett.* **1991**, *32*, 593−596. (c) Saracoglu, N.; Durucasu, I.; Balci, M. *Tetrahedron* **1995**, *51*, 10979−10986. (d) Halton, B.; Russell, S. G. G. *Aust. J. Chem.* **1990**, *43*, 2099−2105. (e) Saito, K.; Ishihara, H.; Kagabu, S. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 4141−4142.

(10) (a) Stang, P. J.; Song, L.; Halton, B. *J. Organomet. Chem.* **1990**, *388*, 215−220. (b) Krüger, C.; Laakmann, K.; Schroth, G.; Schwager, H.; Wilke, G. *Chem. Ber.* **1987**, *120*, 471−475. (c) Schwager, H.; Krüger, C.; Neidlein, R.; Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 65−67. (d) Schwager, H.; Benn, R.; Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 67−68. (e) Benn, R.; Schwager, H.; Wilke, G. *J. Organomet. Chem.* **1986**, *316*, 229−231. (f) Neidlein, R.; Rufinska, A.; Schwager, H.; Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 640−642.

(11) (a) Kagabu, S.; Saito, K. *Tetrahedron Lett.* **1988**, *29*, 675−676. (b) Durucasu, I.; Saraçoglu, N.; Balci, M. *Tetrahedron Lett.* **1991**, *32*, 7097−7098.

Chart 1

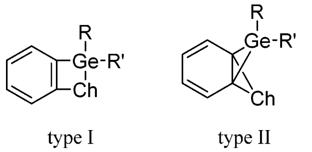
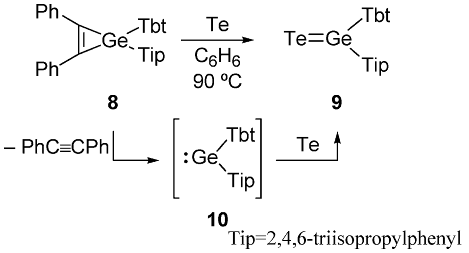


Table 1. Calculated Relative Energies[a] of Model Compounds (R = R′ = H) for Type I and Type II

kcal/mol	type I	type II
Ch = S	0.0 (0.0)	77.4 (78.0)
Ch = Se	0.0 (0.0)	75.0 (75.7)
Ch = Te	0.0 (0.0)	69.8

[a] At the B3LYP/TZ(2d) level for Ge, Lanl2DZdp for S, Se, Te, 6-311(2d,p) for C, H [values in parentheses are at the B3LYP/6-311G(2d,p) level].

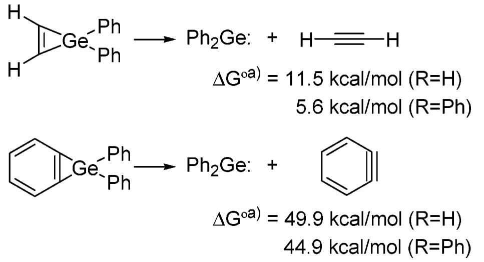
Scheme 4



products, chalcogenagermetes, may not be necessarily kinetic products. The reason only the product of type I was obtained here might be the large difference of the thermodynamic stability between type I and type II. This was supported by calculated thermodynamic energies of model compounds shown in Table 1. That is, a formal [1+2] cycloaddition of a chalcogen atom to the C═C double bond affords the type II compound, which might undergo immediate isomerization to give the type I product under these reaction conditions as well as the reaction of cyclopropabenzene with dichlorocarbene. Thus, the mechanisms of chalcogenation reactions of **2** are unclear at present. Investigation of the reaction mechanisms of heavier cyclopropabenzenes with elemental chalcogens is attractive and currently in progress.

It should also be noted that the reactivity of the germacyclopropabenzene differs from that of germacyclopropenes (germirenes). Thermal reaction of an overcrowded germirene **8**, which was prepared as a stable crystalline compound by the reaction of germylene Tbt(Tip)Ge: (Tip = 2,4,6-triisopropylphenyl) with diphenylacetylene, with elemental tellurium reportedly affords the stable germanetellone **9**, Tbt(Tip)Ge═Te (Scheme 4).[12] The key step in this reaction is the generation of germylene **10**, which was allowed to react with elemental tellurium to give germanetellone **9**, via the thermal cycloreversion of germacyclopropene **8**. That is, no telluragermete derivative was obtained in the tellurization reaction of **8** because the germirene more easily undergoes thermal retro-cycloaddition reaction to give the corresponding germylene than the germacyclopropabenzene. Indeed, theoretical calculations [B3LYP/6-311G(2d,p)] showed that the generation of a germylene (Ph_2Ge:) from 1,1-diphenylgermacyclopropene is much less endothermic than that from 1,1-diphenylgermacyclopropabenzene (Scheme 5).

Scheme 5



[a] Calculated free energies (298 K, 1.0 atm) at the B3LYP/6-311G(2d,p) level.

Crystal Structures of the 2*H*-Benzo[*c*][1,2]-chalcogenagermetes. The molecular structures of diaryl-substituted 2*H*-benzo[*c*][1,2]chalcogenagermetes **3**, **4**, and **5** were revealed by X-ray crystallographic analysis (Table 2). In Figures 1, 2, and 3 are shown the ORTEP drawings of **3**, **4**, and **5**, respectively. Although an inevitable disorder of its benzothiagermete moiety was observed in the case of **3** in every data collection and analyses with a number of different single crystals at low temperature (−170 °C), the molecular structure of **3** was solved adequately (Figure 4).

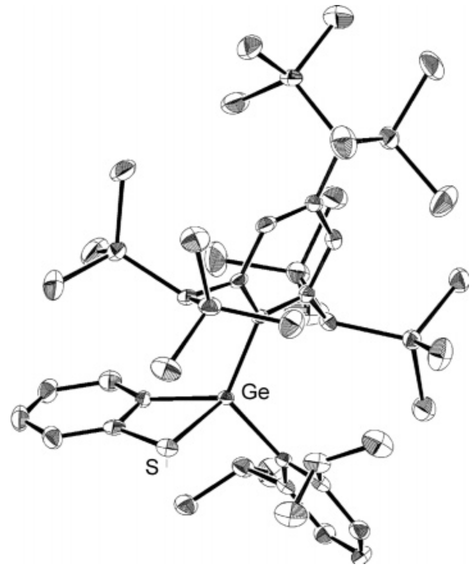


Figure 1. ORTEP drawing of the major part of **3** with thermal ellipsoid plots (50% probability). Hydrogen atoms were omitted for clarity.

Selected bond lengths and angles of **3**, **4**, and **5** are summarized in Table 3. One can see that their benzochalcogenagermete rings in the solid state are completely planar within the limits of error. In addition, the disordered moieties in benzothiagermete **3** lie on the same plane. In all cases, the observed bond lengths and bond angles in the benzene rings are 1.367−1.412 Å and 117.0−122.7°, respectively. It is obvious that the structural parameters of the benzene rings of **3**, **4**, and **5** are close to those of an unperturbed benzene; that is, almost no bond alternation was observed for **3**, **4**, and **5** as well as the parent cyclobutabenzene.[13] Since benzochalco-

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[12] Tokitoh, N.; Matsumoto, T.; Okazaki, R. *J. Am. Chem. Soc.* **1997**, *119*, 2337−2338.

[13] Boese, R.; Bläser, D. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 304−305.

Table 2. Crystal Data for 3, 4, and 5

	3	**4**	**5**
formula	$C_{45}H_{80}GeSSi_6$	$C_{45}H_{80}GeSeSi_6$	$C_{45}H_{80}GeSi_6Te$
fw	894.28	941.18	989.82
color	colorless	pale-yellow	orange
habit	prismatic	prismatic	prismatic
dimensions/mm	0.30 × 0.20 × 0.02	0.15 × 0.10 × 0.03	0.25 × 0.25 × 0.05
temp/°C	−170	−170	−170
cryst syst	triclinic	triclinic	monoclinic
space group	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)	$P2_1/n$ (#14)
a/Å	10.125(3)	11.874(4)	13.8849(14)
b/Å	11.941(3)	12.500(5)	18.3366(13)
c/Å	22.971(7)	19.770(6)	20.7964(15)
α/deg	76.768(11)	77.426(17)	90
β/deg	83.650(12)	88.937(16)	93.7513(10)
γ/deg	72.101(9)	65.979(5)	90
V/Å^3	2570.3(13)	2607.8(16)	5283.5(8)
Z	2	2	4
no. of data/params	8857/509	9156/500	9304/500
R_1 $[I>2\sigma(I)]$	0.0522	0.0670	0.0479
wR_2 (all data)	0.1004	0.1502	0.1097
GOF	1.115	0.930	0.964

genagermetes **3**, **4**, and **5** have inherently longer Ge−Ch bonds (Ch = S, Se, Te) than C−C bond, the inner bond angles around the juncture carbon atoms of their chalcogenagermete rings (α_3 and α_4) are all wider than those of highly strained, parent cyclobutabenzene (93.5°),[13] which is largely deviated from the ideal bond angle of an sp^2 carbon atom (120°). On the other hand, remarkably narrow inner bond angles are found around both germanium and chalcogen atoms. Interestingly, the angles of Ge−Ch−C of **3**−**5** showed a marked decrease on going from sulfur (**3**) to tellurium (**5**), while no regular fluctuation was observed for the angles around the germanium atom.

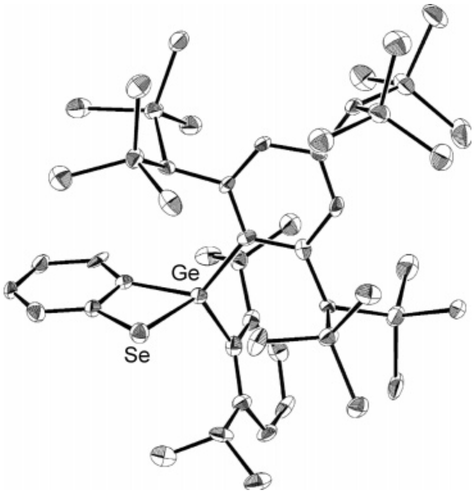


Figure 2. ORTEP drawing of **4** with thermal ellipsoid plots (50% probability). Hydrogen atoms were omitted for clarity.

The theoretical calculations indicate that the extreme bulkiness of the combination of Tbt and Dip groups results in very little perturbation to the chalcogenagermete rings, since the computed values for model compounds **11a**−**c**, **12a**−**c**, and **13a**−**c** (Scheme 6), which have much less hindered substituents such as H, Me, and Ph on the germanium atom, are very close to the observed parameters for **3**, **4**, and **5**. The optimized structural parameters for **11c**, **12c**, and **13c** were shown in Table 3 as representatives. In addition, the structural optimization for the real molecule of **3** (Figure 5 and Table 3) provided us with helpful evidence to justify our treatment of the inevitable disorder of **3** in the X-ray crystallographic analysis as judged by the good agreement of calculated values with experimentally observed ones.

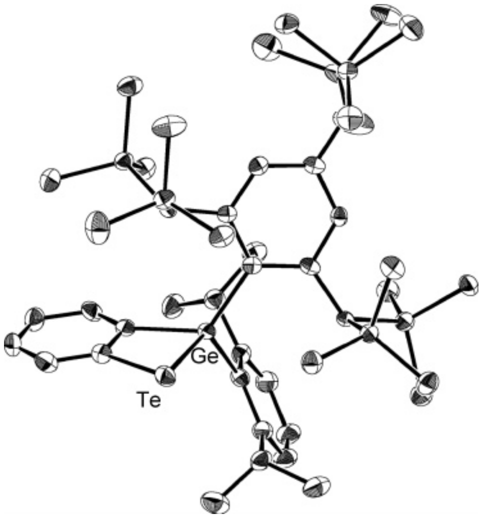


Figure 3. ORTEP drawing of **5** with thermal ellipsoid plots (50% probability). Hydrogen atoms were omitted for clarity.

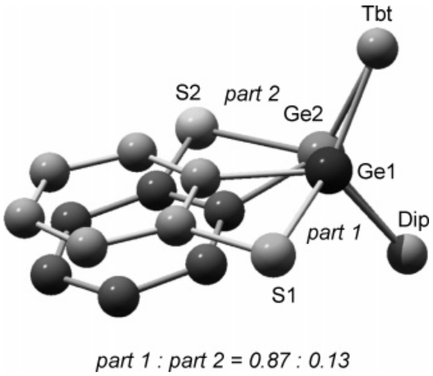


Figure 4. Ball-and-stick models of the disordered molecules of benzothiagermetes **3**.

Conclusion

In this paper, we reported novel reactivity of an overcrowded germacyclopropabenzene **2** with elemental

Table 3. Observed and Theoretically Optimized [B3LYP/TZ(2d) for Ge, Lanl2DZdp for S, Se, Te, 6-311G(2d,p) for C and H] Structural Parameters (Å, deg) of 3, 4, 5, 11c, 12c, and 13c

	3 (obsd)	**4** (obsd)	**5** (obsd)	**3** (calcd)	**11c** (Ch = S) (calcd)	**12c** (Ch = Se) (calcd)	**13c** (Ch =Te) (calcd)
R, R′	Tbt, Dip	Tbt, Dip	Tbt, Dip	Tbt, Dip	Ph, Ph	Ph, Ph	Ph, Ph
d_1	1.970(4)	1.971(6)	1.999(4)	1.973	1.957	1.961	1.966
d_2	2.3284(18)	2.4280(12)	2.6293(6)	2.376	2.320	2.452	2.648
d_3	1.783(4)	1.904(7)	2.130(5)	1.783	1.813	1.954	2.147
d_4	1.386(5)	1.412(9)	1.405(7)	1.410	1.404	1.404	1.406
d_5	1.393(5)	1.393(9)	1.367(7)	1.397	1.387	1.387	1.388
d_6	1.384(6)	1.397(9)	1.400(7)	1.397	1.395	1.395	1.395
d_7	1.376(6)	1.386(9)	1.379(7)	1.398	1.393	1.392	1.391
d_8	1.395(6)	1.405(9)	1.404(6)	1.400	1.396	1.395	1.395
d_9	1.385(5)	1.385(9)	1.369(7)	1.394	1.386	1.388	1.390
α_1	74.21(12)	76.05(19)	76.41(14)	74.16	76.1	76.8	77.4
α_2	76.46(13)	73.3(2)	69.18(13)	75.78	75.5	72.1	67.7
α_3	110.2(3)	110.2(4)	108.8(3)	111.13	110.4	110.0	109.6
α_4	99.0(2)	100.1(4)	105.5(3)	98.93	97.9	101.1	105.3
α_5	119.2(3)	119.6(6)	118.5(4)	119.25	120.0	119.8	119.6
α_6	122.7(3)	121.0(6)	122.0(5)	121.49	121.3	121.3	120.9
α_7	117.0(4)	118.2(6)	118.3(5)	118.39	118.0	118.2	118.7
α_8	121.4(4)	121.6(6)	121.3(5)	120.76	121.3	121.1	120.9
α_9	121.0(4)	119.7(6)	118.7(5)	120.39	120.2	120.2	120.1
α_{10}	118.8(4)	119.9(6)	121.2(5)	119.72	119.2	119.4	119.7
$\Sigma\alpha_{1-4}$[a]	359.9	359.7	359.9	360.0	359.9	360.0	360.0
$\Sigma\alpha_{5-10}$[b]	720.1	720.0	720.0	720.0	720.0	720.0	719.9

[a] The sum of interior angles of the chalcogenagermete ring. [b] The sum of interior angles of the benzene ring.

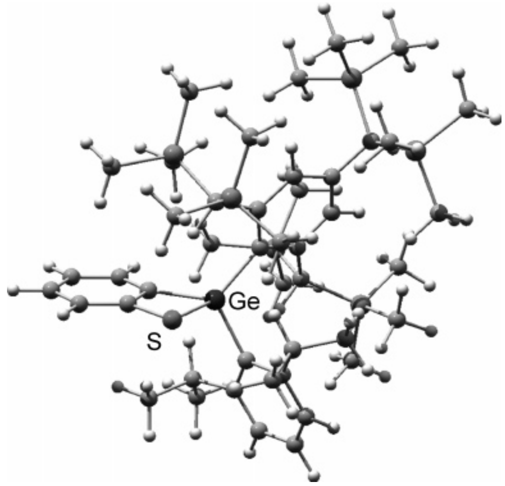
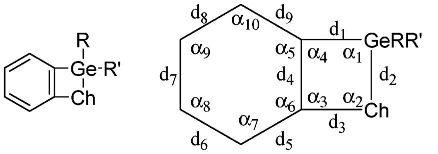


Figure 5. Theoretically optimized structure of **3** at the B3LYP/6-31G(d) level.

Scheme 6



3: Ch=S, R=Tbt, R'=Dip
4: Ch=S, R=Tbt, R'=Dip
5: Ch=S, R=Tbt, R'=Dip
11: Ch=S **a**: R=R'=H
12: Ch=Se **b**: R=R'=Me
13: Ch=Te **c**: R=R'=Ph

chalcogens (S, Se, Te) leading to the synthesis and isolation of a series of 2*H*-benzo[*c*][1,2]chalcogenagermete derivatives **3**, **4**, and **5**. X-ray structural analysis and theoretical calculations revealed the intrinsic structural features of 2*H*-benzo[*c*][1,2]chalcogenagermetes, i.e., completely planar skeletons with an unstrained benzene ring. It was evidenced here that the germacyclopropabenzene could be a good precursor for the synthesis of unprecedented small-ring compounds such as 2*H*-benzo[*c*][1,2]chalcogenagermetes. Small-ring compounds containing a heavier element fused with a benzene moiety should be attractive research targets because of their unique properties. Further investigation of the physical and chemical properties of 2*H*-benzo[*c*][1,2]chalcogenagermetes obtained here is currently in progress.

Experimental Section

General Procedures. All experiments were performed under an argon atmosphere unless otherwise noted. All solvents were dried by standard methods and freshly distilled prior to use. ^{1}H NMR (400 or 300 MHz) and ^{13}C NMR (100 or 75 MHz) spectra were measured in C_6D_6 with a JEOL JNM AL-400 or JEOL JNM AL-300 spectrometer. A signal due to C_6D_5H (7.15 ppm) was used as references in ^{1}H NMR and that due to C_6D_6 (128 ppm) was used in ^{13}C NMR. Multiplicity of signals in the ^{13}C NMR spectra was determined by DEPT technique. ^{77}Se NMR (57 MHz) and ^{125}Te NMR (94 MHz) spectra were measured in C_6D_6 with a JEOL AL-300 spectrometer using diphenyldiselenide (460 ppm) and diphenylditelluride (450 ppm) as an external standard, respectively. High- and low-resolution mass spectral data were obtained on a JEOL JMS-700 spectrometer. HPLC (high-performance liquid chromatography) was performed on an LC-908 or LC-918 (Japan Analytical Industry Co., Ltd.) equipped with JAIGEL 1H and 2H columns (eluent: toluene). Preparative thin-layer chromatography (PTLC) and flash column chromatography (FCC) were performed with Merck Kieselgel 60 PF254 and Merck silica gel 60, respectively. All melting points were determined on a Yanaco micro melting point apparatus and are uncorrected. Elemental analyses were carried out at the Microanalytical Laboratory of the Institute for Chemical Research, Kyoto University. Germacyclopropabenzene **2** was prepared according to the reported procedures.[5]

Reaction of 1-(2,6-Diisopropylphenyl)-1-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1-germacyclopropabenzene 2 with Elemental Sulfur. A benzene-d_6 solution (0.6 mL) of germacyclopropabenzene **2** (30 mg, 0.035 mmol) and elemental sulfur (S_8, 18 mg, 16 equiv as S) was degassed and sealed in an NMR tube. After heating the solution at 135 °C for 120 h, the signals of **2** disappeared and the signals that correspond to 2*H*-benzo[*c*][1,2]thiagermete **3** were observed as those for a main product in the ^{1}H NMR spectrum. The reaction mixture was separated by HPLC (toluene) and PTLC (hexane) to give 2-(2,6-diisopropylphenyl)-2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2*H*-benzo[*c*][1,2]thiagermete (**3**, 20 mg, 0.022 mmol, 63%). **3**: colorless crystals, mp 203.1−203.8 °C; ^{1}H NMR (400 MHz, 338 K, C_6D_6) δ 0.07 (s, 18H, TMS), 0.17 (s, 18H, TMS), 0.24 (s, 18H, TMS), 1.10 (br, 6H, CH_3 of Dip), 1.30 (d, 6H, $^3J_{HH}$ = 6.5 Hz, CH_3 of Dip), 1.48 (s, 1H, *p*-CH of Tbt), 2.60 (brs, 1H, *o*-CH of Tbt), 3.10 (brs, 1H, *o*-CH of Tbt), 3.50 (sept, 2H, $^3J_{HH}$ = 6.5 Hz, CH of Dip), 6.5−6.8 (br, 2H, *m*-arom-CH of Tbt), 6.9−7.0 (m, 3H, arom ring), 7.10 (d, 2H, $^3J_{HH}$ = 7.5 Hz, *m*-arom-CH of Dip), 7.19 (*t*, 1H, $^3J_{HH}$ = 7.5 Hz, *p*-arom-CH of Dip), 7.50 (d, 1H, $^3J_{HH}$ = 7.5 Hz, arom ring); ^{13}C NMR (100 MHz, 338 K, C_6D_6) δ 1.50 (q), 1.56 (q), 2.36 (q), 2.46 (q), 2.78 (q), 26.1 (q), 29.1 (q), 31.5 (d), 36.1 (d), 124.3 (d), 124.8 (d×2), 125.3 (d), 130.4 (d), 131.3 (d), 132.0 (d), 132.5 (s), 140.4 (s), 140.7 (s), 145.3 (s), 148.9 (s), 150.5 (s), signals due to *ortho*-benzyl, *ortho*- and *meta*-aromatic carbon atoms of the Tbt group were not observed. Anal. Calcd for $C_{45}H_{80}GeSSi_6$: C, 60.44; H, 9.02. Found: C, 60.63; H, 9.21.

Reaction of 1-(2,6-Diisopropylphenyl)-1-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1-germacyclopropabenzene 2 with Elemental Selenium. A benzene-*d*$_6$ suspension (0.6 mL) of germacyclopropabenzene **2** (50 mg, 0.058 mmol) and elemental selenium (gray Se, 23 mg, 5 equiv as Se) was degassed and sealed in an NMR tube. After heating the solution at 135 °C for 216 h, the signals of **2** disappeared and the signals that correspond to 2*H*-benzo[*c*][1,2]selenagermete **4** were observed as those for a main product in the ^{1}H NMR spectrum. The reaction mixture was separated by PTLC (hexane) to give 2-(2,6-diisopropylphenyl)-2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2*H*-benzo[*c*][1,2]selenagermete (**4**, 31 mg, 0.033 mmol, 56%). **4**: pale yellow crystals, mp 203.5−204.0 °C; ^{1}H NMR (400 MHz, 343 K, C_6D_6) δ 0.08 (s, 18H, TMS), 0.17 (s, 18H, TMS), 0.23 (s, 18H, TMS), 1.14 (d, 6H, $^3J_{HH}$ = 6.3 Hz, CH_3 of Dip), 1.27 (d, 6H, $^3J_{HH}$ = 6.3 Hz, CH_3 of Dip), 1.48 (s, 1H, *p*-CH of Tbt), 2.65 (brs, 1H, *o*-CH of Tbt), 3.11 (brs, 1H, *o*-CH of Tbt), 3.61 (sept, 2H, $^3J_{HH}$ = 6.3 Hz, CH of Dip), 6.64 (brs, 2H, *m*-arom-CH of Tbt), 6.97 (m, 2H, arom ring), 7.04 (dd, 1H, $^3J_{HH}$ = 6.0 Hz, $^4J_{HH}$ = 2.7 Hz, arom ring), 7.10 (d, 2H, $^3J_{HH}$ = 8.4 Hz, *m*-arom-CH of Dip), 7.19 (t, 1H, $^3J_{HH}$ = 8.4 Hz, *p*-arom-CH of Dip), 7.42 (dd, 1H, $^3J_{HH}$ = 5.3 Hz, $^4J_{HH}$ = 3.2 Hz, arom ring); ^{13}C NMR (100 MHz, 338 K, C_6D_6) δ 1.51 (q), 2.44 (q), 2.65 (q), 26.7 (q), 29.0 (q), 31.4 (d), 36.1 (d), 124.0 (d), 124.8 (d), 124.9 (d), 128.1 (d), 129.4 (d), 129.8 (s), 130.3 (d), 131.2 (d), 132.0 (s), 133.2 (d), 140.1 (s), 142.2 (s), 145.0 (s), 151.3 (s), 152.3 (s), 153.7 (s); ^{77}Se NMR (57 MHz, 343 K, C_6D_6) δ 352.0; high-resolution MS (FAB) *m/z* calcd for $C_{45}H_{80}{}^{74}Ge^{78}SeSi_6$ 942.3268 ([M]$^+$), found 942.3260 ([M]$^+$). Anal. Calcd for $C_{45}H_{80}GeSeSi_6$: C, 57.43; H, 8.57. Found: C, 57.58; H, 8.59.

Reaction of 1-(2,6-Diisopropylphenyl)-1-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1-germacyclopropabenzene 2 with Elemental Tellurium. A benzene-*d*$_6$ solution (0.6 mL) of germacyclopropabenzene **2** (50 mg, 0.058 mmol) and elemental tellurium (37 mg, 5 equiv as Te) was degassed and sealed in an NMR tube. After heating the solution at 135 °C for 336 h, the signals of **2** disappeared and the signals that correspond to 2*H*-benzo[*c*][1,2]telluragermete **5** were observed as those for a main product in the ^{1}H NMR spectrum. The reaction mixture was separated by HPLC (toluene) and FCC (hexane) to give 2-(2,6-diisopropylphenyl)-2-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-2*H*-benzo[*c*][1,2]telluragermete (**5**, 31 mg, 0.032 mmol, 54%). **5**: orange crystals, mp 168.0−169.0 °C; ^{1}H NMR (300 MHz, 343 K, C_6D_6) δ 0.06 (s, 18H, TMS), 0.16 (s, 9H, TMS), 0.17 (s, 9H, TMS), 0.24 (s, 18H, TMS), 1.14 (d, 6H, $^3J_{HH}$ = 6.8 Hz, CH_3 of Dip), 1.23 (d, 6H, $^3J_{HH}$ = 6.8 Hz, CH_3 of Dip), 1.47 (s, 1H, *p*-CH of Tbt), 2.76 (brs, 1H, *o*-CH of Tbt), 3.22 (brs, 1H, *o*-CH of Tbt), 3.67 (sept, 2H, $^3J_{HH}$ = 6.8 Hz, CH of Dip), 6.64 (brs, 2H, *m*-arom-CH of Tbt), 6.94 (ddd, 1H, $^3J_{HH}$ = 7.5 Hz, 7.5 Hz, $^4J_{HH}$ = 1.5 Hz, arom ring), 7.02 (ddd, 1H, $^3J_{HH}$ = 7.5 Hz, 7.5 Hz, $^4J_{HH}$ = 1.5 Hz, arom ring), 7.07 (dd, 1H, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.5 Hz, arom ring), 7.10 (d, 2H, $^3J_{HH}$ = 5.9 Hz, *m*-arom-CH of Dip), 7.18 (t, 1H, $^3J_{HH}$ = 5.9 Hz, *p*-arom-CH of Dip), 7.42 (dd, 1H, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.5 Hz, arom ring); ^{13}C NMR (75 MHz, 323 K, C_6D_6) δ 1.17 (q), 1.18 (q), 2.24 (q), 2.65 (q), 25.5 (q), 29.0 (q), 29.7 (q), 31.1 (d), 36.0 (d), 123.8 (d), 124.8 (d), 125.8 (d), 129.3 (d), 130.2 (d), 130.6 (s), 130.8 (d), 133.3 (d), 136.0 (d), 139.6 (s), 140.0 (s), 144.6 (s), 150.6 (s), 154.1 (s), 162.4 (s); ^{125}Te NMR (94 MHz, 343 K, C_6D_6) δ 612.3; high-resolution MS (FAB) *m/z* calcd for $C_{45}H_{80}{}^{74}GeSi_6{}^{128}Te$ 990.3150 ([M]$^+$), found 990.3140 ([M]$^+$). Anal. Calcd for $C_{45}H_{80}GeSi_6Te$: C, 54.60; H, 8.15. Found: C, 54.78; H, 8.40.

X-ray Crystallographic Analyses of 3, 4, and 5. Crystal data of **3**, **4**, and **5** are summarized in Table 2. The intensity data were collected on a Rigaku/MSC Mercury CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71070 Å) at −170 °C to $2\theta_{max}$ = 50°. The structures were solved by a direct method (SIR-97[14] for **3** and **5**, SHELXS-97[15] for **4**) and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-97[15]). All hydrogen atoms were placed using AFIX instructions, while all the other atoms were refined anisotropically unless otherwise noted.

Single crystals of **3** suitable for X-ray analysis were obtained by slow recrystallization from hexane at room temperature. A colorless, prismatic crystal of **3** was mounted on a glass fiber. The benzothiagermete moiety was disordered, and their occupancies were refined (0.87:0.13). The hexagonal skeleton of the benzene ring in the minor part of the disordered thiagermete moiety was restrained using AFIX instructions and refined isotropically. Single crystals of **4** suitable for X-ray analysis were obtained by slow recrystallization from acetone at room temperature. A pale yellow, prismatic crystal of **4** was mounted on a glass fiber. Single crystals of **5** suitable for X-ray analysis were obtained by slow recrystallization from acetone at room temperature. An orange, prismatic crystal of **5** was mounted on a glass fiber.

Theoretical Calculations. All calculations were conducted using the Gaussian 98 series of electronic structure programs.[16] The geometries were optimized with density functional theory at the B3LYP level.[17] It was confirmed by frequency calculations that the optimized structures have minimum energies. The basis sets used in the calculations were described each time in the text (Tables or Schemes). The basis sets of TZ(2d) for Ge mean the triple-ζ basis sets ([3s3p]) augmented by two sets of d polarization functions (d exponents 0.382 and 0.108) with effective core potential.[18] The Lanl2DZdp basis sets for S, Se, and Te were obtained from the Extensible Computational Chemistry Environment Basis Set Database (http://www.emsl.pnl.gov/forms/basisform.html), as developed

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(14) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115−119.

(15) Sheldrick, G. *SHELX-97*, Program for Crystal Structure Solution and the Refinement of Crystal Structures; Institüt für Anorganische Chemie der Universität: Tammanstrasse 4, D-3400 Göttingen, Germany, 1997.

(16) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; J. A. Montgomery, J.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*; Gaussian, Inc.: Pittsburgh, PA, 1998.

(17) (a) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *B37*, 785. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652. (c) Becke, A. D. *Phys. Rev.* **1988**, *A38*, 3098−3100.

(18) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284−298.

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Supporting Information Available: Theoretically optimized coordinates of **3**, **11a**–**c**, **12a**–**c**, and **13a**–**c** in PDF format. X-ray crystallographic files of **3**, **4**, and **5** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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