

Reactions of 2-Germanaphthalene with Elemental Sulfur and Selenium: Synthesis of Novel Cyclic Polychalcogenides Containing a Germanium, Trichalcogenagermolanes

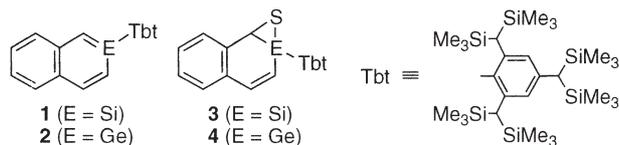
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Novel five-membered cyclic trichalcogenides containing a germanium atom were synthesized by the reactions of a kinetically stabilized 2-germanaphthalene with elemental sulfur and selenium, and the molecular structure of the triselenide was determined by X-ray crystallographic analysis.

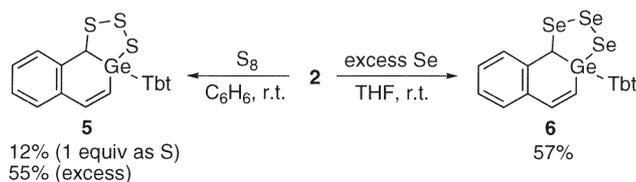
The chemistry of cyclic polychalcogenides has attracted much interest because of their unique structures, reactivities and biological activities.¹ Among them, however, cyclic polychalcogenides containing a germanium atom have been little known. Indeed, there have been only a few reports on tetrathiagermolanes,² a hexathiagermepane,³ and a tetraselenagermolane.⁴

Meanwhile, in recent years there has been much attention to metallaaromatic compounds of heavier group 14 elements,^{5,6} i.e., heavier congeners of aromatic hydrocarbons which occupy a great part of organic chemistry.⁷ We have recently succeeded in the synthesis of the first stable 2-silanaphthalene **1** by taking advantage of an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt),^{8a} and revealed that the reaction of **1** with elemental sulfur afforded the novel thiasilirane **3** or five-membered trisulfide depending on the stoichiometry of sulfur.^{8b} Very recently, 2-germanaphthalene **2** bearing a Tbt group, the first example of a stable neutral germaaromatic compound, was also synthesized and fully characterized by us.⁹ Herein, we present the reactions of **2** with elemental sulfur and selenium leading to the formation of novel Ge-containing cyclic trisulfide **5** and triselenide **6**, respectively. We also describe the X-ray crystallographic analysis of **6** and dechalcogenation of **5** and **6**.



To a benzene solution of **2** was added excess amount of sulfur at room temperature, and the reaction mixture was stirred for 48 h. After removal of the solvent, the crude products were separated by gel permeation liquid chromatography (eluent: CHCl₃) and subsequent preparative thin-layer chromatography (eluent: hexane) to afford a novel Ge-containing cyclic trisulfide, 1,2,3,4-trithiagermolane **5**¹⁰ as colorless crystals in 55% yield. The reaction of **2** with 1 equiv (as S atom) of elemental sulfur did not afford the corresponding Ge-containing three-membered ring product, i.e., thiagermirane **4**, but resulted in the formation of **1** in 12% yield. This result contrasted with the reaction of **1** with 1 equiv (as S atom) of elemental sulfur giving the corresponding thiasilirane **3**.^{8b} The selenium derivative, a novel Ge-containing cyclic triselenide **6**,¹¹ was also obtained as orange crystals in 57% yield when elemental selenium was used instead of elemental

sulfur in THF (Scheme 1).



Scheme 1.

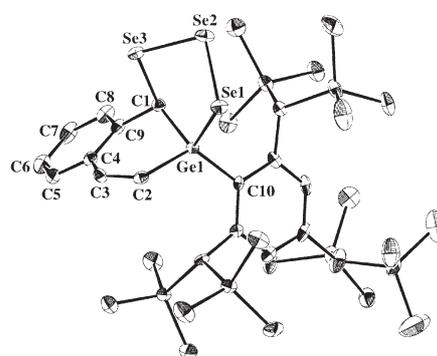


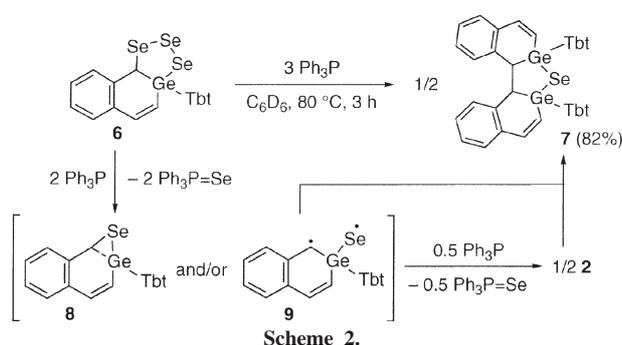
Figure 1. ORTEP drawing of **6** with thermal ellipsoids (50% probability). Selected bond lengths (Å) and angles (°): Ge(1)–Se(1) 2.402(1), Se(1)–Se(2) 2.350(1), Se(2)–Se(3) 2.325(1), Se(3)–C(1) 1.984(4), Ge(1)–C(1) 1.979(5); Ge(1)–Se(1)–Se(2) 93.72(4), Se(1)–Se(2)–Se(3) 98.54(3), Se(2)–Se(3)–C(1) 96.62(14).

We have revealed that the Ge–C(1) double bond of **2** has high reactivity towards a variety of addition reactions even though it is incorporated in the aromatic 2-germanaphthalene ring.¹² The reactivity of **2** with elemental chalcogens here observed is also another experimental demonstration for the high reactivity of the germene moiety.

The structures of cyclic trichalcogenides **5** and **6** were satisfactorily confirmed by mass spectrometry, elemental analysis, and NMR spectroscopy, and the molecular structure of **6** was finally determined by X-ray crystallographic analysis.¹³ In Figure 1 is shown the ORTEP drawing of **6** together with some selected bond lengths and angles. The CGeSe₃ ring of **6** adopts a distorted half-chair conformation where the Se(2) and Se(3) atoms lie at opposite sides of the plane containing C(1), Ge(1), and Se(1) atoms with irregular distances from the plane (0.56 Å for Se(2) and 0.75 Å for Se(3)). The Se–Se bond lengths (2.325(1), 2.350(1) Å), and the Se–Se–Se bond angle (98.54(3)°) of the CGeSe₃ ring are roughly similar to those of Tbt(Mes)GeSe₄⁴ (2.311(2)–2.327(4) Å for the Se–Se bond lengths, 96.94(8), and 96.03(8)° for the Se–Se–Se bond angles). In the ⁷⁷Se NMR spectrum of **6** (in CDCl₃), three signals were observed at 296, 531, and 717 ppm. On the basis of the chemical shifts of related polyselenides,^{4,14} these signals are assigned to the selenium atoms

of the α -, γ -, and β -positions to the germanium atom, respectively.

Trisulfide **5** is fairly stable toward air and moisture, and does not undergo any decomposition by the thermolysis at 100 °C in solution and even at 230 °C in the solid state. On the other hand, triselenide **6** gradually decomposed with liberation of red selenium on standing in a hexane or CHCl₃ solution for a few hours to give a complex mixture. Of particular note among the reactivities of **5** and **6** is that they gave quite different products on dechalcogenation reactions with triphenylphosphine. Desulfurization of **5** with 3 equiv. of Ph₃P in C₆D₆ at 80 °C for 24 h gave the 2-germanaphthalene **2** (76%) together with Ph₃P = S (91%) as judged by ¹H NMR. On the other hand, deselenation of **6** under similar reaction conditions for 3 h afforded a novel heterocycle, 1-selena-2,5-digermycyclopentane **7** (82%), as an inseparable mixture of the structural isomers together with Ph₃P = Se (80%) (Scheme 2).



The structure of **7** was confirmed by its ¹H and ⁷⁷Se NMR, high-resolution FAB-MS and elemental analysis.¹⁵ In the ¹H and ⁷⁷Se NMR spectra of **7**, two structural isomers were observed (major : minor = 4 : 3, δ_{Se} ; -451.2, -447.4). These two isomers are most likely assigned to **7a** and **7b** judging from the consistency with their ¹H NMR spectra and the calculated relative energies for the four isomeric structures **7a-d** (Figure 2). Although the formation mechanism of **7** is not clear at present, one might be able to postulate the intermediacy of extremely reactive selenagermirane derivative **8** and/or its ring opened biradical isomer **9** and their subsequent coupling reactions with the exhaustively deselenated product **2** (Scheme 2). The exclusive formation of the five-membered ring compounds **5** and **6** in the reactions of **2** may be due to the steric effect of Tbt group and/or the instability of the chalcogenagermirane skeletons. Further investigation on the reactivity of **2**, **5**, and **6** is currently in progress.

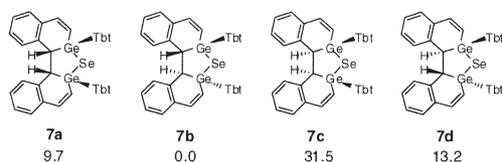


Figure 2. Calculated relative energies for the four isomers of **7** (kcal/mol, B3LYP/6-31G(d)).

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References and Notes

- a) R. Sato, T. Goto, and M. Saito, *Yuki Gosei Kagaku Kyokaiishi*, **48**, 797 (1990). b) B. S. Davidson, T. F. Molinski, L. R. Barrows, and C. M. Ireland, *J. Am. Chem. Soc.*, **113**, 4709 (1991). c) M. Litaudon and M. Guyot, *Tetrahedron Lett.*, **32**, 911 (1991). d) A. Ishii and J. Nakayama, *Rev. Heteroat. Chem.*, **19**, 1 (1998). e) R. Okazaki, *Phosphorus, Sulfur Silicon Relat. Elem.*, **168-169**, 41 (2001).
- a) N. Tokitoh, H. Suzuki, T. Matsumoto, Y. Matsuhashi, R. Okazaki, and M. Goto, *J. Am. Chem. Soc.*, **113**, 7047 (1991). b) N. Tokitoh, T. Matsumoto, and R. Okazaki, *Tetrahedron Lett.*, **32**, 6143 (1991). c) T. Matsumoto, N. Tokitoh, and R. Okazaki, *Organometallics*, **14**, 1008 (1995).
- T. Matsumoto, Y. Matsui, Y. Nakaya, and K. Tatsumi, *Chem. Lett.*, **2001**, 60.
- N. Tokitoh, T. Matsumoto, and R. Okazaki, *Tetrahedron Lett.*, **33**, 2531 (1992).
- For reviews of sila-aromatic compounds, see: a) G. Raabe and J. Michl, *Chem. Rev.*, **85**, 419 (1985). b) G. Raabe and J. Michl, in "The Chemistry of Organic Silicon Compounds," ed. by S. Patai and Z. Rappoport, Wiley, New York (1989), Chap. 17. c) A. G. Brook and M. A. Brook, *Adv. Organomet. Chem.*, **39**, 71 (1996). d) Y. Apeloig and M. Kami, in "The Chemistry of Organic Silicon Compounds," ed. by Z. Rappoport and Y. Apeloig, Wiley, New York (1998), Vol. 2.
- For reviews of germa-aromatic compounds, see: a) J. Barrau, J. Escudicé, and J. Satgé, *Chem. Rev.*, **90**, 283 (1990). b) V. Y. Lee, A. Sekiguchi, M. Ichinohe, and N. Fukaya, *J. Organomet. Chem.*, **611**, 228 (2000).
- V. J. Minkin, M. N. Glukhovtsev, Y. B. Simkin, in "Aromaticity and Antiaromaticity; Electronic and Structural Aspects," Wiley, New York (1994).
- a) N. Tokitoh, K. Wakita, R. Okazaki, S. Nagase, P. v. R. Schleyer, and H. Jiao, *J. Am. Chem. Soc.*, **119**, 6951 (1997). b) K. Wakita, N. Tokitoh, R. Okazaki, S. Nagase, P. v. R. Schleyer, and H. Jiao, *J. Am. Chem. Soc.*, **121**, 11336 (1999).
- N. Nakata, N. Takeda, and N. Tokitoh, *Organometallics*, **20**, 5507 (2001).
- 5**: mp 220–223 °C; ¹H NMR (300 MHz, CDCl₃) δ -0.10 (s, 9H), -0.06 (s, 9H), 0.02 (s, 18H), 0.05 (s, 9H), 0.09 (s, 9H), 1.32 (s, 1H), 2.12 (br s, 2H), 4.44 (s, 1H), 6.32 (br s, 1H), 6.36 (d, J = 12.9 Hz, 1H), 6.44 (br s, 1H), 7.14 (d, J = 12.9 Hz, 1H), 7.14–7.32 (m, 4H); ¹³C NMR (75 MHz, CDCl₃) δ 0.40 (q), 0.67 (q), 0.69 (q), 0.76 (q), 0.80 (q), 1.14 (q), 29.59 (d), 29.90 (d), 30.64 (d), 46.96 (d), 122.45 (d), 125.45 (s), 127.45 (s), 127.94 (d), 128.12 (d), 128.95 (d), 131.85 (d), 134.13 (d), 134.37 (d), 135.50 (s), 141.49 (d), 146.36 (s), 151.33 (s), 151.66 (s); FABMS m/z 836 [M⁺], 740 [(M-S₃)⁺]. Anal. Calcd for C₃₆H₆₆GeS₃Si₆: C, 51.71; H, 7.96%. Found: C, 51.63; H, 7.99%.
- 6**: mp 203–205 °C (decomp.); ¹H NMR (300 MHz, CDCl₃) δ -0.11 (s, 9H), -0.07 (s, 9H), 0.01 (s, 18H), 0.09 (s, 9H), 0.12 (s, 9H), 1.30 (s, 1H), 2.22 (s, 2H), 5.06 (s, 1H), 6.30 (br s, 1H), 6.37 (d, J = 12.9 Hz, 1H), 6.42 (br s, 1H), 7.06 (d, J = 12.9 Hz, 1H), 7.07–7.33 (m, 4H); ¹³C NMR (75 MHz, CDCl₃) δ 0.54 (q), 0.72 (q), 0.95 (q), 1.31 (q), 29.49 (d), 29.75 (d), 30.64 (d), 44.12 (d), 122.58 (d), 124.38 (s), 127.61 (d), 127.65 (d), 127.84 (d), 131.56 (d), 131.71 (d), 133.65 (s), 133.70 (d), 137.16 (s), 139.97 (d), 146.04 (s), 151.34 (s), 151.61 (s); ⁷⁷Se NMR (57 MHz, CDCl₃) δ 296.0, 531.4, 716.9; FABMS m/z 977 [M⁺], 819 [(M-Se₂)⁺], 740 [(M-Se₃)⁺]. Anal. Calcd for C₃₆H₆₆GeSe₃Si₆: C, 44.26; H, 6.81%. Found: C, 44.04; H, 6.82%.
- N. Nakata, N. Takeda, and N. Tokitoh, *Organometallics*, submitted.
- The intensity data for **6** were collected on a Rigaku/MSC Mercury CCD diffractometer. Crystal data of **6**: C₃₆H₆₆GeSe₃Si₆, fw = 976.90, T = 103 K, triclinic, space group $P\bar{1}$ (#2), a = 9.484(4) Å, b = 12.021(4) Å, c = 22.902(9) Å, α = 75.562(16)°, β = 81.901(18)°, γ = 68.746(13)°, V = 2352.8(15) Å³, Z = 2, D_{calcd} = 1.379 g/cm³, R_1 ($I > 2\sigma(I)$) = 0.045, wR_2 (all data) = 0.112 (CCDC 187028).
- S. Ogawa, T. Kikuchi, S. Niizuka, and R. Sato, *J. Chem. Soc., Chem. Commun.*, **1994**, 1593.
- 7**: mp 203–205 °C (decomp.); ¹H NMR (300 MHz, CDCl₃) δ 0.06 (s, SiMe₃, major), 0.13 (s, SiMe₃, major), 0.14 (s, SiMe₃, minor), 0.26 (s, SiMe₃, minor), 0.27 (s, SiMe₃, minor), 0.31 (s, SiMe₃, major), 0.34 (s, SiMe₃, minor), 1.42 (s, Tbt-*p*-methine, major), 1.44 (s, Tbt-*p*-methine, minor), 2.03 (br s, Tbt-*o*-methine, major), 2.28 (br s, Tbt-*o'*-methine, major), 2.43 (br s, Tbt-*o*-methine, minor), 2.69 (br s, Tbt-*o'*-methine, minor), 3.43 (s, GeCH, major), 3.93 (s, GeCH, minor), 6.12 (d, J = 7.2 Hz, Ar, major), 6.50–6.73 (m, Ar, major + minor), 6.90–7.06 (m, Ar, major + minor); ⁷⁷Se NMR (57 MHz, CDCl₃) δ -451.2 (major), -447.4 (minor). Anal. Calcd for C₇₂H₁₃₂Ge₂SeSi₁₂: C, 55.47; H, 8.53%. Found: C, 55.45; H, 8.50%. HRMS (FAB): found m/z 1561.5237 [(M + H)⁺], calcd for C₇₂H₁₃₃Ge₂SeSi₁₂ 1561.5167.