Available online at www.sciencedirect.com

Journal of Organometallic Chemistry 672 (2003) 66–71

Journal of Organo metallic Chemistry

www.elsevier.com/locate/jorganchem

Reaction of a stable germabenzene with chalcogens: synthesis and structure of a novel germanium analog of pentathiepane, 1,2,3,4,5,6-pentathiagermepane

Norio Nakata, Nobuhiro Takeda, Norihiro Tokitoh *

Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan

Received in revised form 13 February 2003; accepted 13 February 2003

Abstract

Treatment of a germabenzene (**4**) bearing a Tbt group (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl) with elemental sulfur gave a 1,2,3,4-trithiagermolane (**5**) together with a novel 1,2,3,4,5,6-pentathiagermepane (**6**), which is the germanium analog of pentathiepane. On the other hand, the reaction of **4** with elemental selenium gave only 1,2,3,4-triselenagermolane (**7**). All the newly obtained polychalcogenides containing a germanium atom were characterized by NMR spectroscopy and elemental analysis. The molecular structures of **5** and **6** were determined by X-ray crystallographic analysis. In addition, the thermolyses of **5** and **6** were examined.

Keywords: Germabenzene; Pentathiagermepane; Trithiagermolane; Triselenagermolane; X-ray crystallographic analysis

---

1. Introduction

Much attention has been paid to the chemistry of cyclic polychalcogenides from the standpoints of chemical and physical properties as well as from that of biological activities [1]. In contrast to the widely explored chemistry of transition metal polychalcogenido complexes [2], very little has been known for cyclic polychalcogenides containing a heavier Group 14 element. We have already succeeded in the synthesis of 1,2,3,4,5-tetrachalcogenametallolanes, Tbt(R)ME_4 (M = Si, Ge, Sn, and Pb, E = S, Se), by taking advantage of an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt) [3], and revealed that their dechalcogenation reactions lead to the formation of the corresponding stable group 14–16 double-bond compounds, i.e., heavier congeners of ketones (heavy ketones) [4]. In addition, Tatsumi and co-workers recently reported the synthesis and structure of 1,2,3,4,5,6,7-hexathiagermepane, Dmp(R)GeS_6 (Dmp = 2,6-dimesitylphenyl) [5]. On the other hand, we have recently reported that the reactions of 2-sila- and 2-germanaphthalenes bearing a Tbt group with elemental sulfur and selenium afforded the novel five-membered trisulfides **1**, **2** and triselenide **3**, as shown in Scheme 1 [6,7].

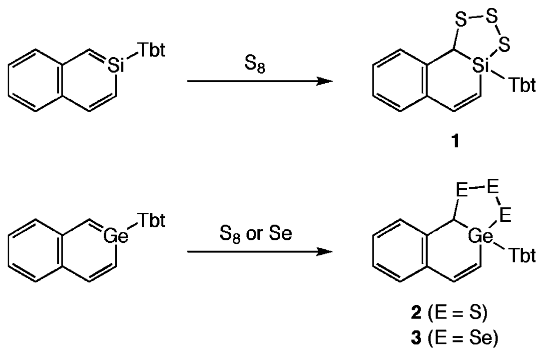
Although the chemistry of 1,2,3,4,5-pentathiepanes, which consist of five sulfur atoms and two vicinal sp^3 carbons, has been actively studied from interest in their synthesis, unique structures, and reactivities [8], there have been no reports on a heavier Group 14 element analog of 1,2,3,4,5-pentathiepane due to the limitation of synthetic methods. Here, we present the reaction of germabenzene **4** [9] bearing a Tbt group with elemental sulfur leading to the formation of 1,2,3,4-trithiagermolane **5** and a novel germanium analog of 1,2,3,4,5-pentathiepane, 1,2,3,4,5,6-pentathiagermepane **6**. Also,

---

* Corresponding author. Tel.: +81-774-38-3200; fax: +81-774-38-3209.

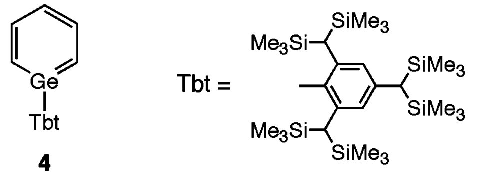
E-mail address: tokitoh@boc.kuicr.kyoto-uac.jp (N. Tokitoh).

0022-328X/03/$ - see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S0022-328X(03)00141-4



Scheme 1.

we describe the reaction of **4** with elemental selenium and the thermolyses of **5** and **6**.



2. Results and discussion

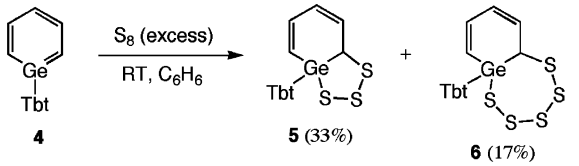
2.1. Reaction of germabenzene with elemental sulfur and selenium

Treatment of **4** with elemental sulfur (excess amount) in benzene at room temperature gave a Ge-containing cyclic trisulfide, 1,2,3,4-trithiagermolane **5** (33%), together with a novel Ge-containing cyclic pentasulfide, 1,2,3,4,5,6-pentathiagermepane **6** (17%), as colorless crystals (Scheme 2).

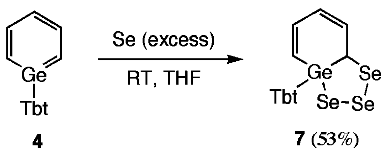
On the other hand, the reaction of **4** with elemental selenium in THF at room temperature afforded only a cyclic triselenide, 1,2,3,4-triselenagermolane **7**, as orange crystals in 53% yield (Scheme 3).

In the ^{77}Se-NMR spectrum of **7** (in C_6D_6), three signals were observed at 353, 554, and 784 ppm, which were assigned to the selenium atoms of the α-, γ-, and β-positions to the germanium atom, respectively, on the basis of the chemical shifts of the triselenide obtained by the selenation of the stable 2-germanaphthalene [6].

Since the polysulfides **5** and **6** and the triselenide **7** are relatively stable toward air and moisture, separation and purification of **5**, **6**, and **7** were performed by gel permeation liquid chromatography (eluent: $CHCl_3$) and subsequent preparative thin-layer chromatography (eluent: hexane). However, on standing in solution (benzene or $CHCl_3$) for a few hours, **5**, **6**, and **7** gradually decomposed with liberation of sulfur or red selenium to give complicated mixtures.



Scheme 2.



Scheme 3.

2.2. X-ray crystallographic analysis

The structures of polychalcogenides **5**, **6**, and **7** were satisfactorily confirmed by NMR spectroscopy and elemental analysis, and the molecular structures of **5** and **6** were finally determined by X-ray crystallographic analysis. The ORTEP drawings of **5** and **6** are given in Figs. 1 and 2 and the selected bond lengths and angles are listed in Tables 1 and 2, respectively.

The structure of **5** was successfully refined when the two overlapped disordered C_5GeS_3 rings of **5** (1:1 ratio) were assumed. The $GeCS_3$ ring of **5** adopts envelope-like conformation where the S(2) atom lies at about 1.04 Å out of the mean plane that consists of C(1), Ge(1), S(1), and S(3) atoms, while the previously reported five-membered triselenide **3** has a distorted half-chair conformation [7]. The seven-membered ring of pentasulfide

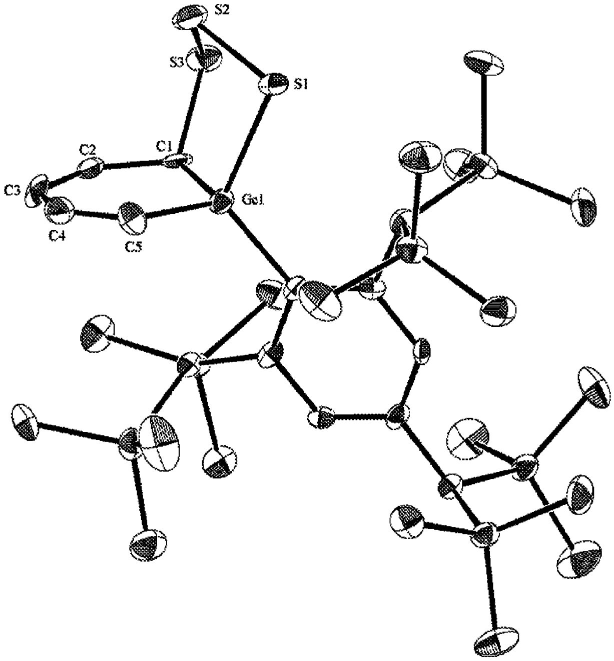


Fig. 1. ORPET drawing of trisulfide **5** (50% thermal ellipsoids).

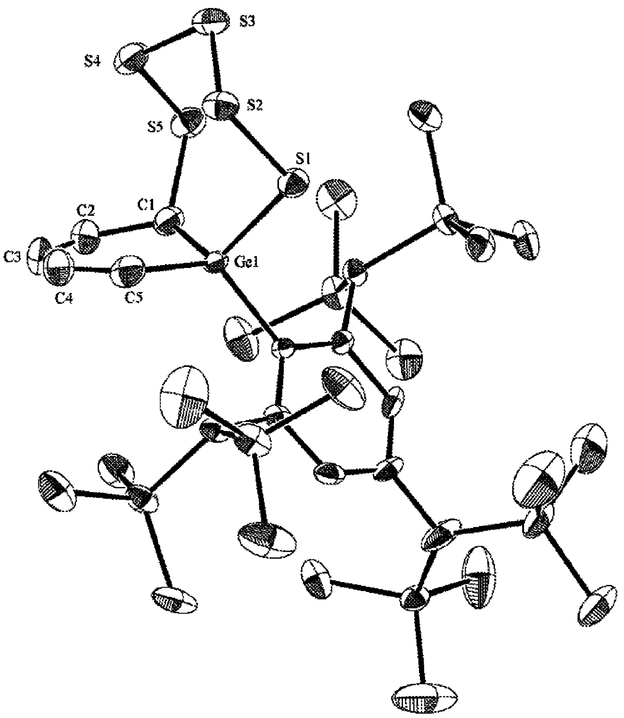


Fig. 2. ORPET drawing of pentasulfide **6** (50% thermal ellipsoids).

Table 1
Selected bond lengths (Å) and angles (°) for **5**

Bond lengths			
Ge(1)–S(1)	2.311(4)	S(1)–S(2)	2.046(6)
S(2)–S(3)	2.033(5)	S(3)–C(1)	1.843(14)
Ge(1)–C(1)	2.00(2)	Ge(1)–C(5)	1.857(15)
C(1)–C(2)	1.49(2)	C(2)–C(3)	1.37(2)
C(3)–C(4)	1.48(3)	C(4)–C(5)	1.340(19)
Bond angles			
Ge(1)–S(1)–S(2)	94.1(2)	S(1)–S(2)–S(3)	98.4(2)
S(2)–S(3)–C(1)	96.6(6)		

Table 2
Selected bond lengths (Å) and angles (°) for **6**

Bond lengths			
Ge(1)––S(1)	2.2603(16)	S(1)–S(2)	2.0540(19)
S(2)–S(3)	2.040(2)	S(3)–S(4)	2.062(2)
S(4)–S(5)	2.038(2)	S(5)–C(1)	1.831(5)
Ge(1)–C(1)	1.980(5)	Ge(1)–C(5)	1.941(5)
C(1)–C(2)	1.508(7)	C(2)–C(3)	1.342(8)
C(3)–C(4)	1.453(9)	C(4)–C(5)	1.331(8)
Bond angles			
Ge(1)–S(1)–S(2)	103.59(7)	S(1)–S(2)–S(3)	105.02(8)
S(2)–S(3)–S(4)	106.46(8)	S(3)–S(4)–S(5)	106.26(9)
S(4)–S(5)–C(1)	104.92(18)		

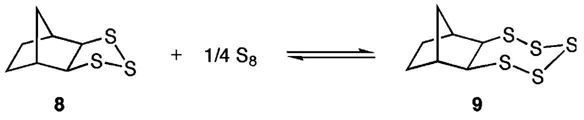
6 has a chair-like conformation, which is similar to the geometry of reported 1,2,3,4,5-pentathiepanes [8c,8e,8f]. The S–S bond lengths [2.033(5) and 2.046(6) Å for **5**; 2.038(2)–2.062(2) Å for **6**] in the $GeCS_3$ ring of **5** and in the $GeCS_5$ ring of **6** are almost equal to those for the corresponding carbon analogues, 1,2,3-trithiolanes [2.035(2)–2.056(2) Å] [10] and 1,2,3,4,5-pentathiepanes [2.025(2)–2.066(2) Å], respectively [8c,8e,8f]. Although the S–S–S bond angles [105.02(8)–106.46(8)°] in the $GeCS_5$ ring of **6** are roughly the same as those for 1,2,3,4,5-pentathiepanes [103.1(1)–106.2(1)°] [8c,8e,8f], the S–S–S bond angle [98.4(2)°] of **5** is slightly larger than those of 1,2,3-trithiolanes [92.5(1)–93.7(1)°] [10]. Furthermore, the Ge–S bond lengths of polysulfides **5** and **6** [2.311(4) Å for **5** and 2.2603(16) Å for **6**] are close to those for 1,2,3,4,5-tetrathiagermolane, Tbt(Mes)GeS_4 [2.320(2) and 2.257(2) Å] 3e and 1,2,3,4,5,6,7-hexathiagermepane, Dmp(R)GeS_6 [2.3004(9) and 2.2459(9) Å] [5].

2.3. Thermolyses of trisulfide 5 and pentasulfide 6

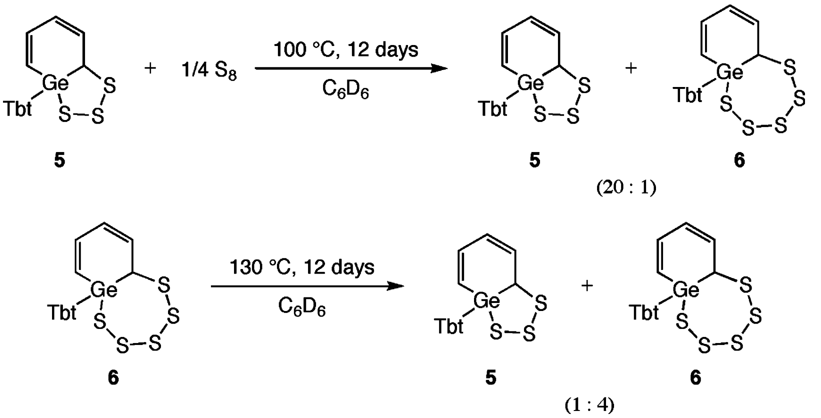
The thermal equilibrium between 1,2,3-trithioles and 1,2,3,4,5-pentathiepanes, which are unsaturated five-membered trisulfides and seven-membered pentasulfides, has already been known [11]. In addition, an equilibrium between 1,2,3-trithiolane **8** and 1,2,3,4,5-pentathiepane **9** in the presence of elemental sulfur has been reported (Scheme 4) [8a]. This equilibrium was rapidly attained in polar solvents, whilst the reverse process was slow. In these cases, the equilibrium lies to the trithiolane side.

The thermolyses of **5** and **6** were also investigated in a sealed NMR tube. The thermolysis of **6** in C_6D_6 at 100 °C for 12 days resulted in the formation of a mixture of **5** and **6** (the ratio of **5**–**6** was 1:4 as judged by ^{1}H-NMR signals), accompanied with the precipitation of S_8. In addition, the conversion of **5**–**6** was also observed in the thermal reaction of **5** with S_8 (two equivalents as S atom) in C_6D_6 at 130 °C for 12 days (the ratio of **5**–**6** was 20:1 as judged by ^{1}H-NMR signals) (Scheme 5).

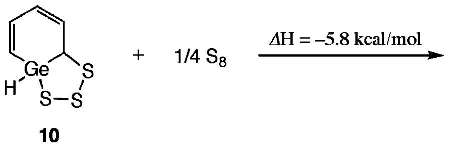
These observations indicate the interconversion reaction is possible between pentasulfide **6** and trisulfide **5** plus 1/4 S_8. However, it is considered that the equilibrium between **5** and **6** is not attained in these experiments, because the ratios of **5**–**6** are very different between the reaction started from **5** plus S_8 and that from **6**. Since the information for the thermodynamic stability of **5** and **6** could not be obtained experimentally, we carried out the theoretical calculation of the homodesmotic reaction between trisulfide **10** and pentasulfide **11** as model compounds (Scheme 6).



Scheme 4.



Scheme 5.



Scheme 6.

This homodesmotic reaction showed an exothermic reaction ($\Delta H = -5.8$ kcal mol^{-1}), and therefore pentasulfide **11** is more thermodynamically stable than trisulfide **10**.

3. Summary

We have succeeded in the formation of the 1,2,3,4-trithiagermolane **5** together with the novel 1,2,3,4,5,6-pentathiagermepane **6** by the sulfuration of germabenzene **4**, and their molecular structures were fully determined by the spectroscopic data and the X-ray structural analysis. On the other hand, the selenation of **4** gave only 1,2,3,4-triselenagermolane **7**. Further studies on the reactivities of **4** are currently in progress.

4. Experimental

4.1. General procedure

All experiments were performed in a glovebox filled with argon unless otherwise noted. ^{1}H-NMR (400 or 300 MHz), ^{13}C-NMR (100 or 75 MHz) and ^{77}Se-NMR (57 MHz) spectra were measured in $CDCl_3$ and C_6D_6 with a JEOL JNM AL-300 spectrometer at room temperature. Preparative gel permeation liquid chromatography (GPLC) was performed on an LC-908 (Japan Analytical Industry Co., Ltd) equipped with JAIGEL 1H and 2H columns (eluent: $CHCl_3$ and toluene). Electronic spectra were recorded on a JASCO Ubest-50 UV–vis spectrometer. 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. 1-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-1-germabenzene (**4**) was prepared according to the reported procedures [9]. THF, benzene and d_6-benzene were all dried over K mirror and distilled by trap-to-trap method before use.

4.2. Reaction of germabenzene 4 with elemental sulfur

To a solution of **4** (41.8 mg, 0.061 mmol) in benzene (1.0 ml) was added elemental sulfur (39.3 mg, 1.226 mmol) at room temperature, and the solution was stirred for 48 h. After the solvent was removed in vacuo, purification of the residue by GPLC (toluene) and PTLC (hexane) afforded 3a-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-3a,7a-dihydro-1,2,3-trithia-3a-germaindene (**5**) (15.1 mg, 31%) and 5a-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-5a,9a-dihydro-1,2,3,4,5,5a-benzopentathiagermepane (**6**) (8.9 mg, 17%) as pale yellow powder. **5**: m.p. 177–179 °C (dec.). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 0.04 (s, 36H), 0.05 (s, 18H), 1.34 (s, 1H), 2.04 (br s, 1H), 2.06 (br s, 1H), 3.95 (dd, $J = 1.2$, 5.4 Hz, 1H), 6.01 (ddd, $J = 0.9$, 5.4, 11.1 Hz, 1H), 6.27–6.31 (m, 1H), 6.30 (dd, $J = 0.9$, 13.5 Hz, 1H), 6.35 (br s, 1H), 6.46 (br s, 1H), 6.62 (ddd, $J = 0.9$, 6.6, 13.5 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 0.68 (q), 0.72 (q), 1.08 (q), 30.32 (d), 30.50 (d), 30.61 (d), 43.17 (d), 122.42 (d), 126.53 (s), 126.67 (d), 127.43 (d), 130.33 (d), 131.80 (d), 136.70 (d), 146.13 (s), 150.90 (s), 151.21 (s). *Anal.* Calc. for $C_{32}H_{64}GeS_3Si_6$: C, 48.89; H, 8.21%. Found: C, 48.78; H, 8.28%. **6**: m.p. 186–188 °C (dec.). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 0.02 (s, 9H), 0.02 (s, 9H), 0.03 (s, 9H), 0.05 (s, 9H), 0.07 (s, 9H), 0.09 (s, 9H), 1.31 (s, 1H), 2.11 (br s, 1H), 2.14 (br s, 1H), 4.00 (ddd, $J = 1.5$, 1.8, 4.8 Hz, 1H), 5.92 (dddd, $J = 0.9$, 1.5, 4.8, 10.5 Hz, 1H), 6.27–6.40 (m, 4H), 6.86 (ddd, 0.9, 6.9, 12.6 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 0.65 (q), 0.76 (q), 0.95 (q), 1.07 (q), 1.22 (q), 1.38 (q), 29.83 (d), 30.13 (d), 30.61 (d), 50.78 (d), 122.37 (d), 127.38 (d), 129.10 (d), 129.12 (d), 129.69 (s), 130.49 (d), 138.28 (d), 146.08 (s), 150.30 (s), 150.55 (s). *Anal.* Calc. for $C_{32}H_{64}GeS_5Si_6$: C, 45.20; H, 7.59%. Found: C, 45.21; H, 7.51%.

4.3. *Reaction of germabenzene **4** with elemental selenium*

To a solution of **4** (36.7 mg, 0.053 mmol) in THF (1.0 ml) was added elemental selenium (28.4 mg, 0.360 mmol) at room temperature, and the solution was stirred for 48 h. After the solvent was removed in vacuo, purification of the residue by GPLC (toluene) and PTLC (hexane) afforded 3a-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-3a,7a-dihydro-1,2,3-triselena-3a-germaindene (**7**) (26.1 mg, 53%) as orange crystals. **7**: m.p. 165–167 °C (dec.). ^{1}H-NMR (C_6D_6, 300 MHz) δ 0.13 (s, 27H), 0.19 (s, 18H), 0.22 (s, 9H), 1.45 (s, 1H), 2.48 (br s, 2H), 4.79 (d, $J = 6.0$ Hz, 1H), 5.63 (ddd, $J = 1.2$, 5.7, 10.5 Hz, 1H), 6.38–6.23 (m, 3H), 6.55 (br s, 1H), 6.65 (br s, 1H); ^{13}C-NMR (C_6D_6, 75 MHz) δ 0.85 (q), 0.90 (q), 1.09 (q), 1.43 (q), 1.46 (q), 1.48 (q), 29.93 (d), 30.05 (d), 30.94 (d), 40.97 (d), 123.07 (d), 125.56 (d), 128.12 (d), 129.10 (s), 132.73 (d), 133.73 (d), 135.58 (d), 146.16 (s), 151,69 (s), 152.01 (s); ^{77}Se-NMR (C_6D_6, 57 MHz) δ 353.1, 554.3, 784.2. *Anal.* Calc. for $C_{32}H_{64}GeSe_3Si_6$: C, 41.47; H, 6.96%. Found: C, 41.43; H, 7.14%.

4.4. *X-Ray crystallographic analysis of **5***

Crystal data: Formula $C_{32}H_{64}GeS_3Si_6$, MW = 786.14, triclinic, space group $P\bar{1}$, $a = 10.804(2)$, $b = 11.284(3)$, $c = 19.205(3)$ Å, $\alpha = 95.475(6)$, $\beta = 98.736(6)$, $\gamma = 106.634(10)$ °, $V = 2193.3(8)$ Å^3, $Z = 2$, $D_{calc} = 1.190$ g cm^{-3}, $\mu = 1.025$ mm^{-1}; R_1 $(I > 2\sigma(I)) = 0.086$, wR_2 (all data) = 0.213, GOF = 1.23 for 7584 reflections, 470 parameters, and 13 restraints. Colorless and prismatic single crystals of **5** were grown by the slow evaporation of its hexane solution at room temperature in a glovebox filled with argon. The intensity data were collected on a Rigaku/MSC Mercury CCD diffractometer with graphite monochromator Mo–K$_\alpha$ radiation ($\lambda = 0.71071$ Å) to $2\theta_{max} = 50°$ at 93 K. The structure was solved by direct methods (SIR97) [12] and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELX-97) [13]. All hydrogen atoms were placed using AFIX instructions, while all the other atoms were refined anisotropically. The structures of the overlapped and disordered C_5GeS_3 rings for **5** were restrained to be identical to each other using the DELU instruction. The occupancy of each fragment for **5** was refined with constraints that their sum is 1 (0.583(5): 0.417(5) for **5**).

4.5. *X-ray crystallographic analysis of **6***

Crystal data: Formula $C_{32}H_{64}GeS_5Si_6$, MW = 850.26, triclinic, space group $P\bar{1}$, $a = 9.030(4)$, $b = 13.192(6)$, $c = 19.627(9)$ Å, $\alpha = 89.858(11)$, $\beta = 89.397(10)$, $\gamma = 77.742(10)°$, $V = 2284.5(18)$ Å^3, $Z = 2$, $D_{calc} = 1.236$ g cm^{-3}, $\mu = 1.078$ mm^{-1}; R_1 $(I > 2\sigma(I)) = 0.066$, wR_2 (all data) = 0.156, GOF = 1.09 for 7855 reflections, 482 parameters, and 36 restraints. Colorless and prismatic single crystals of **6** were grown by the slow evaporation of its hexane solution at room temperature. The intensity data were collected on a Rigaku/MSC Mercury CCD diffractometer with graphite monochromator Mo–K$_\alpha$ radiation ($\lambda = 0.71071$ Å) to $2\theta_{max} = 50°$ at 93 K. The structure was solved by direct methods (SIR97) [12] and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELX-97) [13]. All hydrogen atoms were placed using AFIX instructions, while all the other atoms were refined anisotropically. The structures of the overlapped and disordered trimethylsilyl groups of *p*-position of the Tbt group for **6** were restrained to be identical to each other using the SIMU and DFIX instructions. The occupancy of each fragment for **6** was refined with constraints that their sum is 1 (0.828(8): 0.172(8) for **6**).

4.6. *Thermolysis of pentasulfide **6***

Pentathiagermepane **6** (12.4 mg, 0.015 mmol) was dissolved in C_6D_6 (0.5 ml) and the solution was put into a 5ϕ-NMR tube. After the NMR tube was evacuated and sealed, the mixture was heated at 100 °C for 12 days. The signals assignable to those of **5** and **6** were observed with a ratio of 1:4 in the ^{1}H-NMR spectrum.

4.7. *Thermal reaction of trisulfide **5** with elemental sulfur*

Trithiagermolane **5** (26.6 mg, 0.033 mmol) and elemental sulfur (1.4 mg, 0.043 mmol) were dissolved in C_6D_6 (0.5 ml) and the solution was put into a 5ϕ-NMR tube. After the NMR tube was evacuated and sealed, the mixture was heated at 130 °C for 12 days. The signals assignable to those of **5** and **6** were observed with a ratio of 20:1 in the ^{1}H-NMR spectrum.

4.8. *Homodesmotic reaction between **10** and **11***

The optimization of geometries and vibrational analysis for trisulfide **10**, pentasulfide **11**, and S_8 were calculated by using the Gaussian 98 program at B3LYP/6-31G(d) levels of density functional theory [14].

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-198915 (**5**) and -198916 (**6**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

This work was partially supported by a Grant-in-Aid for COE Research on Elements Science (No. 12CE2005) and Grants-in-Aid for Scientific Research (Nos. 14 204 064, 11 304 045, and 11 166 250) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References

[1] (a) R. Sato, T. Goto, M. Saito, J. Synth, Org. Chem. Jpn. 48 (1990) 797;
(b) B.S. Davidson, T.F. Molinski, L.R. Barrows, C.M. Ireland, J. Am. Chem. Soc. 113 (1991) 4709;
(c) M. Litaudon, M. Guyot, Tetrahedron Lett. 32 (1991) 911;
(d) A. Ishii, J. Nakayama, Rev. Heteroatom Chem. 19 (1998) 1;
(e) R. Okazaki, Phosphorus Sulfur Silicon 168-169 (2001) 41.

[2] Reviews on polychalcogenido complexes see: (a) M. Draganjac, T.B. Rauchfuss, Angew. Chem. Int. Ed. Engl. 24 (1985) 742;
(b) A. Müller, E. Diemann, Adv. Inorg. Chem. 31 (1987) 89;
(c) M.A. Ansari, J.A. Ibers, Coord. Chem. Rev. 100 (1990) 223;
(d) J.W. Kolis, Coord. Chem. Rev. 105 (1990) 195.

[3] (a) H. Suzuki, N. Tokitoh, S. Nagase, R. Okazaki, J. Am. Chem. Soc. 116 (1994) 11578;
(b) N. Tokitoh, T. Matsumoto, R. Okazaki, Tetrahedron Lett. 33 (1992) 2531;
(c) N. Tokitoh, H. Suzuki, T. Matsumoto, Y. Matsuhashi, R. Okazaki, M. Goto, J. Am. Chem. Soc. 113 (1991) 7074;
(d) N. Tokitoh, Y. Matsuhashi, R. Okazaki, Tetrahedron Lett. 32 (1991) 6151;
(e) Y. Matsuhashi, N. Tokitoh, R. Okazaki, Organometallics 12 (1993) 1351;
(f) T. Matsumoto, N. Tokitoh, R. Okazaki, M. Goto, Organometallics 14 (1995) 1008;
(g) M. Saito, N. Tokitoh, R. Okazaki, J. Organomet. Chem. 499 (1995) 43;
(h) M. Saito, N. Tokitoh, R. Okazaki, J. Am. Chem. Soc. 117 (1997) 11124;
(i) N. Tokitoh, N. Kano, K. Shibata, R. Okazaki, Organometallics 14 (1995) 3121.

[4] For reviews on the reactivity of heavy ketones see: (a) N. Tokitoh, Y. Matsuhashi, K. Shibata, T. Matsumoto, H. Suzuki, M. Saito, K. Manmaru, R. Okazaki, Main Group Met. Chem. 17 (1994) 55;
(b) N. Tokitoh, T. Matsumoto, R. Okazaki, Bull. Chem. Soc. Jpn. 71 (1999) 1665;
(c) R. Okazaki, N. Tokitoh, Acc. Chem. Res. 33 (2000) 625.

[5] T. Matsumoto, Y. Matsui, Y. Nakaya, K. Tatsumi, Chem. Lett. (2001) 60.

[6] K. Wakita, N. Tokitoh, R. Okazaki, S. Nagase, P.V.R. Schleyer, H. Jiao, J. Am. Chem. Soc. 121 (1999) 11336.

[7] N. Nakata, N. Takeda, N. Tokitoh, Chem. Lett. (2002) 818.

[8] (a) P.D. Bartlett, T. Ghosh, J. Org. Chem. 52 (1987) 4937;
(b) J. Nakayama, Y. Ito, A. Mizumura, Sulfur Lett. 14 (1992) 247;
(c) E.A. Chernyshev, O.V. Kuz'min, A.V. Lebedev, A.I. Gusev, N.I. Kirillova, N.S. Nametkin, V.D. Tyurin, A.M. Krapivin, N.A. Kubasova, J. Organomet. Chem. 252 (1983) 133;
(d) M. Kustos, R. Steudel, J. Org. Chem. 60 (1995) 8056;
(e) Y. Sugihara, H. Takeda, J. Nakayama, Tetrahedron Lett. 39 (1998) 2605;
(f) Y. Sugihara, H. Takeda, J. Nakayama, Eur. J. Org. Chem. (1999) 597.

[9] N. Nakata, N. Takeda, N. Tokitoh, J. Am. Chem. Soc. 124 (2002) 6914.

[10] (a) J. Emsley, D.W. Griffiths, R. Osborn, Acta Crystallogr. B35 (1979) 2119;
(b) W.H. Watson, P.C. Jain, P.D. Bartlett, T. Ghosh, Acta Crystallogr. C42 (1986) 332;
(c) Y. Sugihara, K. Abe, J Nakayama, Heteroatom Chem. 10 (1999) 638.

[11] (a) B.L. Chenard, R.L. Harlow, A.L. Johnson, S.A. Vladuchick, J. Am. Chem. Soc. 107 (1985) 3871;
(b) N. Tokitoh, H. Ishizuka, W. Ando, Chem. Lett. 2 (1988) 657.

[12] A. Altomare, M.C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna, J. Appl. Crystallogr. 32 (1999) 115.

[13] G.M. Sheldrick, SHELX-97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.

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