

1,2,3,4,5,6,7-Hexathiagermepanes: Synthesis, Structures, and the Ring Contraction to 1,2,3,4,5-Tetrathiagermolanes

Tsuyoshi Matsumoto, Yosuke Matsui, Yukiko Nakaya, and Kazuyuki Tatsumi*†

Department of Chemistry, Graduate School of Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8602

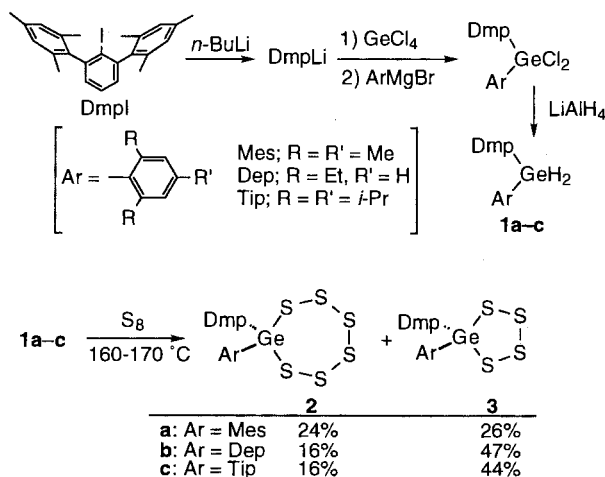
†Research Center for Materials Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8602

(Received October 18, 2000; CL-000948)

The first 1,2,3,4,5,6,7-hexathiagermepanes $\text{Dmp}(\text{Ar})\text{GeS}_6$ [Dmp =2,6-dimesitylphenyl, Ar = Mes, Dep (2,6-diethylphenyl), Tip (2,4,6-triisopropylphenyl)] were synthesized along with 1,2,3,4,5-tetrathiagermolanes by sulfurization of the corresponding dihydrogermanes. The hexathiagermepane $\text{Dmp}(\text{Tip})\text{GeS}_6$ slowly converted to the tetrathiagermolane with release of elemental sulfur owing to the steric hindrance.

Although transition metal polysulfides are ubiquitous,¹ chemistry of polysulfido compounds of group 14 elements is less developed.^{2,3} As an extension of our studies on transition metal chalcogenides, we have been interested in those having sterically protected germanium polysulfides. The structurally-characterized example of germanium polysulfides was limited to the 1,2,3,4,5-tetrathiagermolane.^{3a,b} Here we report the synthesis and structures of 1,2,3,4,5,6,7-hexathiagermepane, $\text{Dmp}(\text{Ar})\text{GeS}_6$, and experimentally made obvious that their ring size was controlled by steric effect.

Scheme 1.



The dihydrogermanes with bulky substituents **1a-c** were prepared as shown in Scheme 1. Recently Power et al. reported the high yield synthesis of Dmp_2Ge by the reaction of GeCl_2 (dioxane) with 2 equiv of DmpLi .⁴ When we reacted GeCl_4 with DmpLi , which was prepared in ether from DmpI and $n\text{-BuLi}$, DmpCl (51%) was formed. Addition of HMPA to the reaction system was found to suppress the formation of DmpCl , and we were able to synthesize $\text{Dmp}(\text{Ar})\text{GeH}_2$ in satisfactory yields by the subsequent treatment with ArMgBr and reduction by LiAlH_4 . The substitution by two or more Dmp groups was not observed even in the presence of excess DmpLi ,

presumably due to the steric congestion.

In a Schlenk tube were mixed the dihydrogermanes **1a-c** with elemental sulfur (30–40 equiv as S_8) and heated to 160–170 °C for 15–20 min. Most of excess sulfur was removed by recrystallization and the residue was chromatographed on silica gel to afford the new hexathiagermepanes **2a-c** along with the tetrathiagermolanes **3a-c**. The selectivity for **2** is higher for the reaction of dihydrogermane having a less bulky Ar group, i.e., Ar =Mes. On the other hand, the total yields of the germanium polysulfides **2** and **3** increase when a bulkier Ar group (Ar =Dep, Tip) is attached to germanium. In the case of sulfurization of Tip_2GeH_2 the yield of Tip_2GeS_4 was low (15%) and many uncharacterizable compounds were generated.⁵ Thus, it is important to choose a substituent of an appropriate size in order to isolate polysulfido compounds of germanium.

According to the ^1H NMR spectra, the hexathiagermepanes **2** are sterically tighter than the corresponding tetrathiagermolanes **3**. For instance, **2c** shows four doublets from 0.78 to 1.10 ppm attributed to four $i\text{Pr}$ groups of o -positions on Tip, while only one doublet at 0.83 ppm is observed in **3c**. Six methyl groups of Dmp are observed independently from 1.87 to 2.41 ppm in **2c**, despite two singlets at 1.87 and 2.29 ppm in **3c**.⁶

The structures of **2a,b** and **3a-c** were determined by X-ray analysis and those of **2b** and **3b** are shown in Figures 1 and 2, respectively.⁷

The 7-membered ring of **2b** assumes a chair conformation,

which is similar to the geometry of reported hexathiepanes, the carbon analogue.⁸ The S-Ge-S angle of **2b**, 104.68(4)°, is notably larger than that of **3b**, 99.31(3)°, which in turn forces the other bond angles around Ge to be smaller for **2b**.

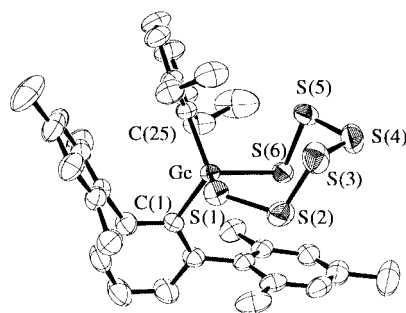


Figure 1. Structure of $\text{Dmp}(\text{Dep})\text{GeS}_6$ **2b**. Selected bond lengths (Å) and bond angles (Deg): Ge-S(1) 2.2459(9), S(1)-S(2) 2.063(2), S(2)-S(3) 2.053(2), S(3)-S(4) 2.050(2), S(4)-S(5) 2.036(2), S(5)-S(6) 2.022(2), S(6)-Ge 2.3004(9), S(1)-Ge-S(6) 104.68(4), Ge-S(1)-S(2) 99.40(5), S(1)-S(2)-S(3) 104.35(7), S(2)-S(3)-S(4) 107.51(7), S(3)-S(4)-S(5) 103.92(8), S(4)-S(5)-S(6) 106.52(7), S(5)-S(6)-Ge 110.32(6), S(1)-Ge-C(1) 111.38(9), S(1)-Ge-C(25) 105.83(9), S(6)-Ge-C(1) 105.04(9), S(6)-Ge-C(25) 113.93(9), C(1)-Ge-C(25) 115.6(1).

The Dep ring is situated nearly parallel to one Mes group of Dmp, and the two ethyl substituents of Dep point away from the Mes group, probably to avoid steric repulsion. Or, the parallelism may be caused by attractive π - π stacking interactions. The other Mes group of Dmp and the ethyl groups of Dep appear to protect sterically the 7-membered ring. This arrangement of substituents is also observed in **3b**.

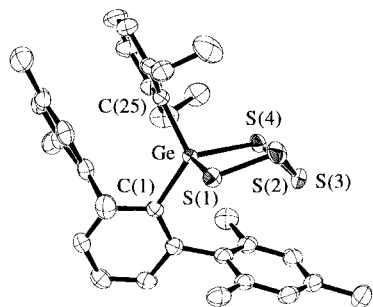
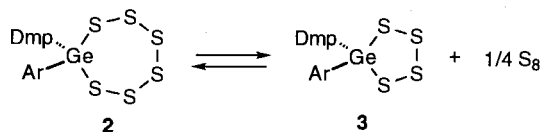


Figure 2. Structure of Dmp(Dep)GeS₄ **3b**. Selected bond lengths (Å) and bond angles (Deg): Ge-S(1) 2.2866(8), S(1)-S(2) 2.069(1), S(2)-S(3) 2.032(9), S(3)-S(4) 2.049(1), S(4)-Ge 2.2654(9), S(1)-Ge-S(4) 99.31(3), Ge-S(1)-S(2) 100.56(4), S(1)-S(2)-S(3) 99.26(5), S(2)-S(3)-S(4) 98.90(5), S(3)-S(4)-Ge 101.21(5), S(1)-Ge-C(1) 103.94(8), S(1)-Ge-C(25) 121.21(9), S(4)-Ge-C(1) 118.11(9), S(4)-Ge-C(25) 99.98(9), C(1)-Ge-C(25) 114.2(1).

Scheme 2.



The thermodynamic equilibrium between **2** and **3** deserves comments. The hexathiagermepane **2c** slowly converted to **3c** with release of elemental sulfur in hexane at room temperature while almost no change was discernible for **2a** in 2 days. The transformation was, however, accelerated by heating, and at 60 °C in hexane in 5 days, it reached to equilibrium in 1:1 (**2a** : **3a**) and 1:4 (**2c** : **3c**) ratio (Scheme 2). The conversion of **3c** to **2c** was also observed in the presence of 1 equiv of S₈ in hexane under reflux.⁹ The observation indicates that the ring size of the polysulfides is thermodynamically controlled by the size of the substituents on germanium.¹⁰

References and Notes

- Reviews on polychalcogenido complexes, see: a) A. Müller, E. Diemann, R. Jostes, and H. Bögge, *Angew. Chem., Int. Ed. Engl.*, **20**, 934 (1981). b) A. Müller, W. Jaegermann, and J. H. Enemark, *Coord. Chem. Rev.*, **46**, 245 (1982). c) M. Draganjac and T. B. Rauchfuss, *Angew. Chem., Int. Ed. Engl.*, **24**, 742 (1985). d) D. Coucouvanis, A. Hadjikyriacou, M. Draganjac, M. G. Kanatzidis, and O. Ilceperuma, *Polyhedron*, **5**, 349 (1986). e) A. Müller, *Polyhedron*, **5**, 323 (1986). f) A. Müller and E. Diemann, *Adv. Inorg. Chem.*, **89**, 31 (1987). g) M. R. DuBois, *Chem. Rev.*, **89**, 1 (1989). h) M. A. Ansari and J. A. Ibers, *Coord. Chem. Rev.*, **100**, 223 (1990). i) J. W. Kolis, *Coord. Chem. Rev.*, **105**, 195 (1990).
- "Comprehensive Organometallic Chemistry II," Pergamon Press, New York (1995), Vol. 2, pp.34–37, pp.166–174, and pp.293–296, and references cited therein.
- a) N. Tokitoh, H. Suzuki, T. Matsumoto, Y. Matsuhashi, R. Okazaki, and M. Goto, *J. Am. Chem. Soc.*, **113**, 7047 (1991). b) T. Matsumoto, N. Tokitoh, R. Okazaki, and M. Goto, *Organometallics*, **14**, 1008 (1995). c) H. Suzuki, N. Tokitoh, R. Okazaki, S. Nagase, and M. Goto, *J. Am. Chem. Soc.*, **120**, 11096 (1998). d) Y. Matsuhashi, N. Tokitoh, R. Okazaki, M. Goto, and S. Nagase, *Organometallics*, **12**, 1351 (1993). e) N. Tokitoh, N. Kano, K. Shibata, and R. Okazaki, *Organometallics*, **14**, 3121 (1995).
- R. S. Simons, L. Pu, M. M. Olmstead, and P. P. Power, *Organometallics*, **16**, 1920 (1997).
- T. Matsumoto, Y. Matsui, and K. Tatsumi, unpublished result.
- 2c**: colorless crystals; ¹H NMR(CDCl₃, 500 MHz) δ 0.78 (br d, *J* = 6.9 Hz, 3H), 0.80 (br d, *J* = 6.9 Hz, 3H), 1.00 (br d, *J* = 6.9 Hz, 3H), 1.10 (br d, *J* = 6.9 Hz, 3H), 1.23 (br d, *J* = 6.9 Hz, 6H), 1.87 (s, 3H), 2.02 (s, 3H), 2.23 (s, 3H), 2.30 (s, 3H), 2.33 (s, 3H), 2.41 (s, 3H), 2.82 (sept, *J* = 6.9 Hz, 1H), 3.09 (br sept, *J* = 6.9 Hz, 2H), 6.44 (br s, 1H), 6.84 (br s, 1H), 6.85 (br s, 2H), 6.86 (br s, 1H), 7.02 (br s, 1H), 7.02 (br d, *J* = 7.6 Hz, 1H), 7.12 (br d, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H). Anal. Found: C, 59.50; H, 5.72; S, 24.89%. Calcd for C₃₉H₄₈GeS₆: C, 59.91; H, 6.19; S, 24.61%. **3c**: light yellow crystals; ¹H NMR(CDCl₃, 500 MHz) δ 0.83 (d, *J* = 6.9 Hz, 12H), 1.20 (d, *J* = 6.9 Hz, 6H), 1.87 (br s, 12H), 2.29 (s, 6H), 2.79 (sept, *J* = 6.9 Hz, 1H), 2.98 (br sept, *J* = 6.9 Hz, 2H), 6.76 (br s, 4H), 6.84 (s, 2H), 7.00 (br d, *J* = 7.6 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 1H). Anal. Found: C, 65.59; H, 6.90; S, 17.51%. Calcd for C₃₉H₄₈GeS₄: C, 65.27; H, 6.74; S, 17.87%.
- The data collection was made with a Rigaku-AFC7R diffractometer for **2b** and a Rigaku-AFC diffractometer equipped with a MSC/ADSC Quantum 1 CCD detector for **3b**. The structures were solved by a Texsan package. Crystal data for **2b**: C₃₄H₃₈GeS₆, *M_r* = 711.62, monoclinic, space group *P*2₁/*n*, *a* = 11.346(5), *b* = 16.340(9), *c* = 18.989(7) Å, β = 100.82(3)°, *V* = 3458(2) Å³, *Z* = 4, *D_{calc}* = 1.367 g/cm³, *T* = 296 K, μ(Mo Kα) = 47.74 cm⁻¹, *R* = 0.046, *R_w* = 0.067, GOF = 2.63, 370 variables, 5518 unique reflections [*I* > 1σ(*I*)]. For **3b**: C₃₄H₃₈GeS₄, *M_r* = 647.50, monoclinic, space group *P*2₁/*c*, *a* = 10.9365(6), *b* = 10.4258(9), *c* = 27.5673(7) Å, β = 90.2677(5)°, *V* = 3143.2(3) Å³, *Z* = 4, *D_{calc}* = 1.368 g/cm³, *T* = 193 K, μ(Mo Kα) = 47.74 cm⁻¹, *R* = 0.067, *R_w* = 0.069, GOF = 0.90, 361 variables, 7199 unique reflections (all data). One methyl group on Dep is disordered.
- a) V. F. Fehér and J. Lex, *Z. Anorg. Allg. Chem.*, **423**, 103 (1976). b) Y.-N. Jin, A. Ishii, Y. Sugihara, and J. Nakayama, *Heterocycles*, **44**, 255 (1997).
- The equilibrium was reported between 1,2,3,4,5-benzopenathiepin and 1,2,3-benzotrithioles in the presence of amines. a) N. Tokitoh, H. Ishizuka, and W. Ando, *Chem. Lett.*, **1988**, 657. b) B. L. Chenard, R. L. Harlow, A. L. Johnson, and S. A. Vladuchick, *J. Am. Chem. Soc.*, **107**, 3871 (1985).
- The steric effect on the ring size was proposed previously. See ref 3.