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

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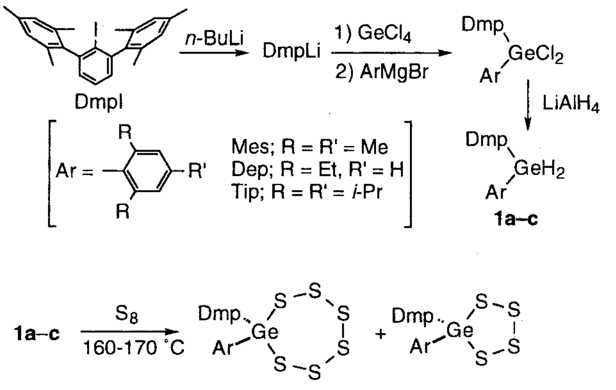
The first 1,2,3,4,5,6,7-hexathiagermepanes Dmp(Ar)GeS$_6$ [Dmp=2,6-dimesitylphenyl, Ar = Mes, Dep (2,6-diethylphenyl), Tip (2,4,6-triisopropylphenyl)] were synthesized along with 1,2,3,4,5-tetrathiagermolanes by sulfurization of the corresponding dihydrogermanes. The hexathiagermepane Dmp(Tip)GeS$_6$ 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, Dmp(Ar)GeS$_6$, and experimentally made obvious that their ring size was controlled by steric effect.

Scheme 1.



	2	3
a: Ar = Mes	24%	26%
b: Ar = Dep	16%	47%
c: Ar = Tip	16%	44%

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$_2$Ge 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*-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 Dmp(Ar)GeH$_2$ in satisfactory yields by the subsquent 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$_2$GeH$_2$ the yield of Tip$_2$GeS$_4$ 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 ^{1}H 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*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**.

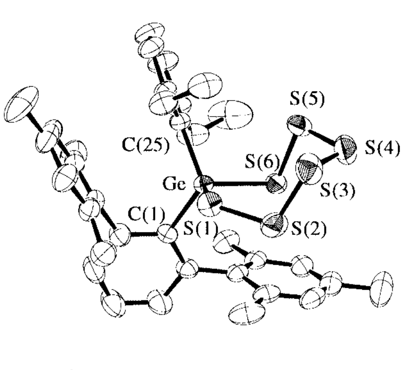


Figure 1. Structure of Dmp(Dep)GeS$_6$ **2b**. Selected bond lengths (Å) and bond angles (Deg): Ge-S(1) 2.2459(9), S(1)-S(2) 2.063(2), S(2)-S(3) 2.053(2), S(3)-S(4) 2.050(2), S(4)-S(5) 2.036(2), S(5)-S(6) 2.022(2), S(6)-Ge 2.3004(9), S(1)-Ge-S(6) 104.68(4), Ge-S(1)-S(2) 99.40(5), S(1)-S(2)-S(3) 104.35(7), 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**.

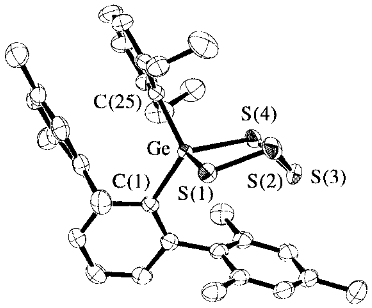
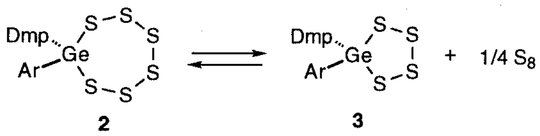


Figure 2. Structure of Dmp(Dep)GeS4 **3b**. Selected bond lengths (Å) and bond angles (Deg): Ge-S(1) 2.2866(8), S(1)-S(2) 2.069(1), S(2)-S(3) 2.032(9), S(3)-S(4) 2.049(1), S(4)-Ge 2.2654(9), S(1)-Ge-S(4) 99.31(3), Ge-S(1)-S(2) 100.56(4), S(1)-S(2)-S(3) 99.26(5), S(2)-S(3)-S(4) 98.90(5), S(3)-S(4)-Ge 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, accelarated 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 S_8 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

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5 T. Matsumoto, Y. Matsui, and K. Tatsumi, unpublished result.

6 **2c**: colorless crystals; ^{1}H NMR(CDCl$_3$, 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 $C_{39}H_{48}GeS_6$: C, 59.91; H, 6.19; S, 24.61%. **3c**: light yellow crystals; ^{1}H NMR(CDCl$_3$, 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 $C_{39}H_{48}GeS_4$: C, 65.27; H, 6.74; S, 17.87%.

7 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**: $C_{34}H_{38}GeS_6$, M_r = 711.62, monoclinic, space group $P2_1/n$, a = 11.346(5), b = 16.340(9), c = 18.989(7) Å, β = 100.82(3)°, V = 3458(2) Å^3, Z = 4, D_{calc} = 1.367 g/cm^3, 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 [$I > 1\sigma(I)$]. For **3b**: $C_{34}H_{38}GeS_4$, M_r = 647.50, monoclinic, space group $P2_1/c$, a = 10.9365(6), b = 10.4258(9), c = 27.5673(7) Å, β = 90.2677(5)°, V = 3143.2(3) Å^3, Z = 4, D_{calc} = 1.368 g/cm^3, 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.

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10 The steric effect on the ring size was proposed previously. See ref 3.