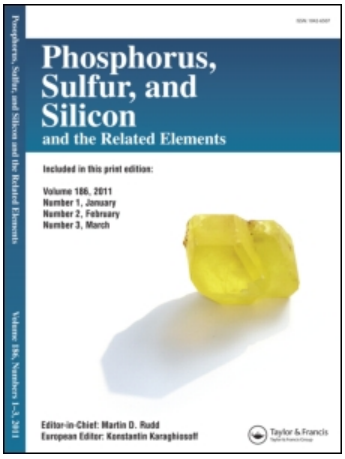

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Syntheses, Structures, and Properties of Novel Four-Membered Stannacycles, 1,3,2,4-Dichalcogenastannaboretanes

MITSUHIRO ITO, NORIHIRO TOKITOH* and RENJI OKAZAKI†

Department of Chemistry, Graduate School of Science, The University of Tokyo, 7–3–1 Hongo, Bunkyo-ku, Tokyo 113–0033, Japan

Syntheses of novel stannacycles, 1,3,2,4-dichalcogenastannaboretane derivatives bearing 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) group on the boron atom are presented. These newly obtained stannacycles were crystallographically analyzed. Thermolyses of these stannacycles are also described.

Keywords: 1,2,3,4-dichalcogenametallaboretane; germanium- or tin -containing cyclic compound; thermolysis; chalcogenoxoborane

INTRODUCTION

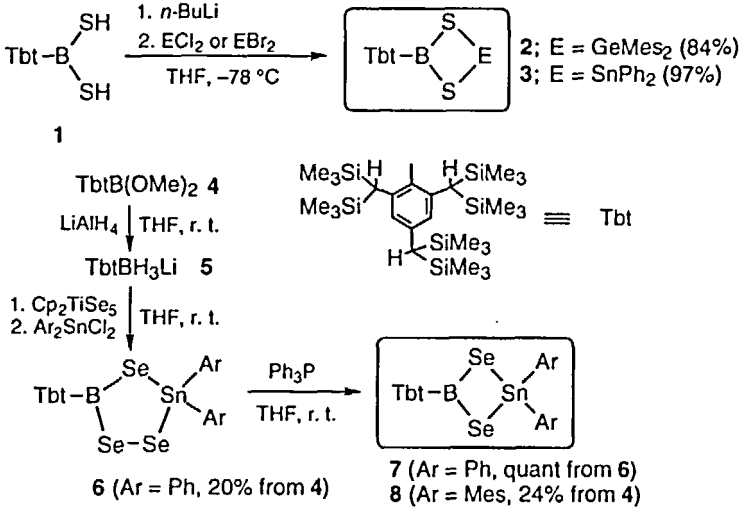
Although much attention has been paid to the chemistry of small-ring compounds containing heavier group 14 elements, very little is known for the properties of small-ring compounds containing boron and heavier group 14 elements.[1] Here, we present the syntheses of novel four-membered boracycles containing a germanium or tin atom in the ring system, *i. e.* 1,3,2,4-dithiametallaboretanes **2** and **3** and 1,3,2,4-diselenastannaboretanes **7** and **8**, kinetically stabilized by an effective steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt hereafter), together with their crystal structures and thermolysis.

* Institute for Fundamental Research of Organic Chemistry, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812–8581, Japan.
† Department of Chemical and Biological Sciences, Faculty of Science, Japan Women's University, Mejirodai, Bunkyo-ku, Tokyo 112–8681, Japan.

RESULTS AND DISCUSSION

Synthesis of 1,3,2,4-Dichalcogenametallaboretanes[2]

1,3,2,4-Dithiametallaboretanes **2** and **3** were synthesized by the reaction of dilithium thiolate of **1** with Mes_2GeBr_2 or Ph_2SnCl_2 in good yields, respectively, while 1,3,2,4-diselenastannaboretanes **7** and **8** were synthesized by the deselenation of the corresponding 1,2,4,3,5-triselenastannaborolane **6** prepared from the reaction of overcrowded trihydroborate **5** with Cp_2TiSe_5 and Ar_2SnCl_2 (Ar = Ph or Mes). The newly obtained cyclic compounds are stable toward air and moisture, indicating that the steric protection of the Tbt group is very effective.



Structural Properties of 1,3,2,4-Dichalcogenametallaboretanes

The structures of 1,3,2,4-dichalcogenastannaboretanes **2**, **3**, and **8** were crystallographically analyzed. ORTEP drawings of **3** and **8** are shown in Figures 1 and 2, respectively. In both cases the four-membered rings are nearly planar (fold angles of the four-membered ring; 10.9° for **2**, 3.9° for **3**, and 13.8° for **8**) and perpendicular to the

aromatic ring of Tbt group (dihedral angles between the four-membered ring and the aromatic ring plane of the Tbt group; 89.5° for **2**, 87.9° for **3**, and 86.6° for **8**). The geometries around the boron atom in their four-membered ring of **2**, **3**, and **8** were found to be perfectly trigonal planar ($\Sigma\angle B = 360°$), indicating that the core part of these small-rings around the boron atom is not so strained in spite of being embedded in the ring system. Thus, the strain of the four-membered rings is mainly imposed on the bonds bound to the germanium or tin atom.

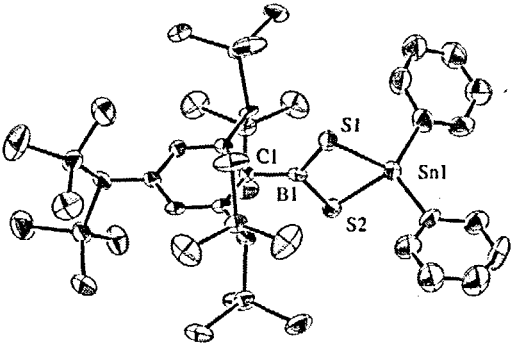


Figure 1. ORTEP drawing of **3**

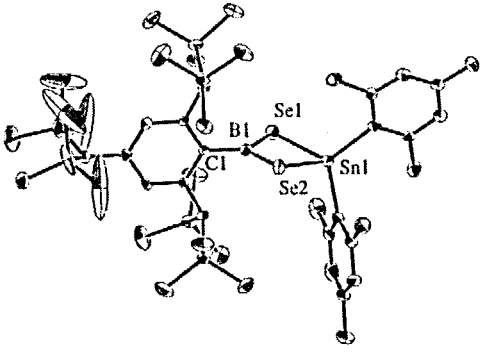
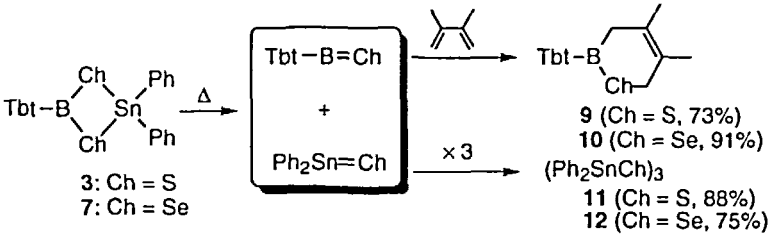


Figure 2. ORTEP drawing of **8**

Thermolysis of Dichalcogenastannaboretanes: Formation of

Thioxoborane (Tbt–B≡S) and Selenoxoborane (Tbt–B≡Se)[3]

The thermolysis of **3** and **7** in the presence of 2,3-dimethyl-1,3-butadiene afforded the [4+2]cycloadducts **9** and **10** of novel, chalcogenoxoboranes, *i. e.* boron–chalcogen double-bond species, together with a trimer of the corresponding diphenylstannanethione or -selone **11** and **12** in high yields, respectively.



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