1,3,2,4-Diselenastannaboretane, a novel selenium-containing four-membered boracycle: synthesis, structure and thermal cycloreversion into a selenoxoborane

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Treatment of an overcrowded aryl trihydroborate bearing 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) group with Cp₂TiSe₅ followed by the addition of Ar₂SnCl₂ (Ar = Ph or Mes) and Ph₃P resulted in the isolation of novel selenium-containing four-membered boracycles, 1,3,2,4-diselenastan-naboretanes, the thermolysis of which in the presence of 2,3-dimethyl-1,3-butadiene or 2,4,6-tri-*tert*-butylbenzoni-trile oxide indicated the formation of a novel class of boron-containing doubly bonded compound, an arylselenoxoborane (Tbt)B=Se.

The chemistry of boracycles containing heavier group 16 elements has been much less investigated than that of the oxygen-containing counterpart such as boroxines [(RBO)₃] and other cyclic boronic esters owing to their high sensitivity toward air and moisture.1 Since a boron atom is known to prefer planartricoordinate geometry strongly, small ring compounds containing a boron atom generally have a large ring strain and are quite reactive. Recently, we have reported the synthesis and structures of several stable 1,3,2,4-dithiametallaboretanes, novel sulfur-containing four-membered boracycles, bearing a very bulky and effective steric protecting group, 2,4,6-tris[bis-(trimethylsilyl)methyl]phenyl (Tbt) group.² We have also described that one of those four-membered ring systems, i.e. a 1,3,2,4-dithiastannaboretane derivative, provides us with a new and facile route to the boron-oxygen and boron-sulfur doublebond compounds (oxoborane and thioxoborane, respectively), the synthetic methods to which have, so far, not been well established.^{3,4} By contrast, until now there have been very few reports on selenium-containing organoboranes.5

Here, we report the synthesis and crystal structure of a kinetically stabilized 1,3,2,4-diselenastannaboretane bearing the Tbt group, a novel selenium-containing four-membered boracycle, together with its thermolysis leading to the formation of an arylselenoxoborane (Tbt)B=Se. Oxoboranes and thioxoboranes are known to be important intermediates in the oxidation or sulfurization of elemental boron or other boron compounds and are widely studied from the viewpoints of theoretical and/or gas-phase chemistry.^{6,7} On the other hand, selenoxoboranes, selenium analogues of oxoboranes and thioxoboranes, are thought to be much less stable than oxoboranes and thioxoboranes, and there has been only one report on the gas-phase detection of a chloroselenoxoborane in the reaction of elemental boron with Se₂Cl₂ at 1000 °C.8 Although the synthesis and structure of 1,3,2,4-diselenadiboretane, a dimer of a selenoxoborane, has already been reported by Nöth and coworkers, no description was given for the intermediary selenoxoborane.9

The reaction of an overcrowded trihydroborate **2**, synthesized by the reaction of $(Tbt)B(OMe)_2$ **1** with LiAlH₄,² with titanocene pentaselenide followed by treatment with Ph₂SnCl₂

gave a novel five-membered boracycle, 1,2,4,3,5-triselenastannaborolane 3, as yellow crystals in 20% yield from 1 (Scheme 1). Although we have attempted the thermolysis of 3 in the hope of cycloreversion into the selenoxoborane (Tbt)B=Se, no change was observed even at 150 °C in the presence of 2,3-dimethylbuta-1,3-diene as a trapping reagent for a selenoxoborane. We next examined ring contraction of 3 to the 1,3,2,4-diselenastannaboretane by deselenation with Ph₃P. The reaction proceeded smoothly and quantitatively at ambient temperature to give the desired 1,3,2,4-diselenastannaboretane 4, a novel selenium-containing four-membered boracycle (Scheme 1). Compound 4 showed satisfactory spectral and analytical data, but single crystals suitable for X-ray crystallographic analysis were not obtained owing not only to the low crystallinity but also to its high instability in solution. On the other hand, 2,2-dimesityl-1,3,2,4-diselenastannaboretane 5, which was prepared from 1 and dichlorodimesitylstannane in 24% yield by a synthetic method similar to that of 4^{10} gave single crystals suitable for X-ray crystallographic analysis upon recrystallization from 1,2-dimethoxyethane. The crystal structure of 5 is shown in Fig. 1.[†]

The four-membered ring of **5** is not completely planar with the dihedral angle between planes B(1)–Se(1)–Se(2) and Sn(1)– Se(1)–Se(2) being 13.8° due to the steric repulsion between the Tbt group and one of the mesityl group on the tin atom. The geometry around the central boron atom is found to be perfectly trigonal planar ($\Sigma \angle B = 360^\circ$). The angle between the plane





Fig. 1 ORTEP drawing of 2,2-dimesityl-1,3,2,4-diselenastannaboretane 5 with thermal ellipsoid plots (40% probability). Selected bond lengths (Å) and angles (°). B(1)–C(1) 1.557(13), B(1)–Se(1) 1.962(11), B(1)–Se(2) 1.960(10), Se(1)–Sn(1) 2.557(1), Se(2)–Sn(1) 2.566(1), Sn(1)–C(2) 2.149(10), Sn(1)-C(37) 2.127(10), Se(1)–B(1)–Se(2) 114.1(5), Se(1)–B(1)–C(1) 123.2(7), Se(2)–B(1)–C(1) 122.7(8), B(1)–Se(1)–Sn(1) 82.4(3), B(1)–Se(2) -Sn(1) 82.2(4), Se(1)–Sn(1)–Se(2) 79.95(4), C(28)-Sn(1)–C(37) 117.3(3).

defined by B(1)–Se(1)–Se(2) and the aromatic ring plane of the Tbt group is 86.6°, suggesting no conjugative interaction of π -electrons on the Tbt group with the boron atom. These structural features of **5** are similar to those of the 2,2-dimesityl-1,3,2,4-dithiagermaboretane derivative reported by us.^{2b}

Since we have already shown that the 2,2-diphenyl-1,3,2,4-dithiastannaboretane derivative, a sulfur-analogue of 4, acts as a good precursor of a thioxoborane, (Tbt)B=S, on thermolysis,⁴ the thermolysis of 4 was also carried out in the expectation that it would dissociate into a boron–selenium double-bonded species (selenoxoborane) (Tbt)B=Se and diphenylstannaneselone.

When a toluene- d_8 solution of **4** and 2,3-dimethylbuta-1,3-diene in a sealed NMR tube was heated at 100 °C for 12 h, the starting material completely disappeared to afford 4,5-dimethyl-1,2-selenaboracyclohex-4-ene **6** (91%) along with the trimer **7** of diphenylstannaneselone **9** (75%) (Scheme 2). The formation of **6** and **7** clearly indicates the initial retro [2+2]cycloaddition of the diselenastannaboretane ring of **4** into the two units, *i.e.* selenoxoborane **8** and diphenylstannaneselone **9**, followed by the [4 + 2]cycloaddition reaction of **8** with coexisting 2,3-dimethylbuta-1,3-diene and the self-trimerization of **9**. To the best of our knowledge, this is the first example of the trapping reaction of a selenoxoborane. Similarly, thermolysis of **4** at 50 °C in the presence of 2,4,6-tri-*tert*-butylbenzonitrile oxide afforded the [3 + 2]cycloadduct of selenoxoborane **10** (59%)† together with **7** (45%). These results show that the



selenoxoborane has a double-bond character like oxoborane and thioxoborane previously reported.^{3,4}

In summary, we have succeeded in the isolation and crystallographic analysis of the first 1,3,2,4-diselenastannaboretane **4**. Compound **4** undergoes thermal cycloreversion into the overcrowded selenoxoborane (Tbt)B=Se, the formation of which was confirmed by the intermolecular [4+2]cycloaddition reaction with a diene.

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Notes and references

† Crystallographic data for 5: $C_{45}H_{81}BSe_2Si_6Sn$, M = 1087.07, monoclinic, space group $P2_1/n$, a = 21.053(5), b = 13.324(4), c = 21.341(5) Å, $\beta = 91.22(2)^{\circ}, V = 5634(2) \text{ Å}^3, Z = 4, D_c = 1.271 \text{ g cm}^{-3}, T = 173 \text{ K},$ F(000) = 2232.00, yellow prism with dimensions $0.65 \times 0.40 \times 0.10$ mm, μ (Mo-K α) = 19.00 cm⁻¹, $R(R_w)$ = 0.069(0.075). The intensity data (2 θ < 55°) for 1 were collected on a Rigaku AFC7R diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.71069$ Å), and 13870 reflections (13517 unique) were measured. The structure of 1 was solved by direct methods with SHELXS-86,11 expanded using Fourier techniques,12 and refined by the full-matrix least-squares methods using the TEXSAN crystallographic software package.¹³ All the non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were located in the calculated positions. The final cycles of the least square refinement were based on 6066 observed reflections $[I > 3\sigma |I|]$ and 497 variable parameters. The maximum and minimum peaks on the final difference Fourier map correspond to 3.48 and -1.04 e-/Å3, respectively. CCDC 182/1052.

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