



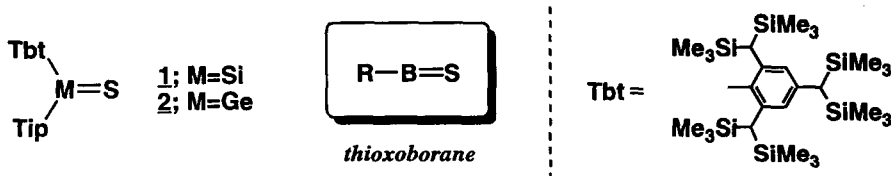
Formation and Reactions of a Thioxoborane, a Novel Boron-Sulfur Double-bond Compound

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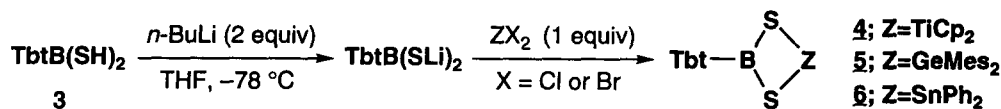
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Abstract: Thermolysis of an overcrowded tin-containing four-membered boracycle, 1,3,2-dithiastannaboretane derivative **6**, bearing an extremely bulky aryl group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt), on the boron atom in the presence of several 1,3-dienes in toluene at 120 °C gave the corresponding diene adducts of an initially formed thioxoborane (Tbt-B=S; **7**) together with a trimer of diphenylstannanethione **8**. Retro [4+2]cycloaddition of the diene adducts into the thioxoborane **7** is also described. Copyright © 1996 Elsevier Science Ltd

In recent years remarkable progress has been made in the chemistry of multiple-bond compounds containing heavier typical elements, especially in the field of thiocarbonyl compounds¹ and their heavy congeners.² In the course of our study on the kinetic stabilization of highly reactive organoheteroatom compounds, we have recently succeeded in the syntheses and isolations of the first stable silanethione [Tbt(Tip)Si=S (**1**); Tip = 2,4,6-triisopropylphenyl]³ and germanethione [Tbt(Tip)Ge=S (**2**)],⁴ *i. e.* heavier group 14 element analogues of thioketones, by taking advantage of a new and effective steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt hereafter), and revealed their unique structures and reactivities. On the other hand, very little is known for the chemistry of boron-sulfur double-bond compounds (thioxoboranes).⁵ The parent molecule, H-B=S, has been postulated as an intermediate in the reaction of hydrogen sulfide with elemental boron at 1000 °C,⁶ but no stable monomeric thioxoboranes have been known although some of them are isolated as oligomeric products such as dimer or trimer.⁷ In addition to the high reactivity and instability of thioxoboranes, the lack of a suitable synthetic route to the boron-sulfur double-bond species may hamper the progress of this field. Here, we wish to delineate the first example of the generation and trapping of a thioxoborane.

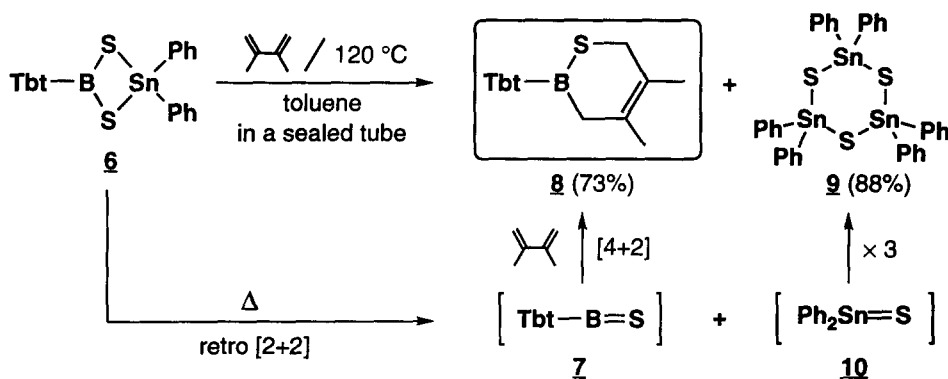


Recently, we have reported the synthesis and crystallographic structural analysis of the first stable dimercaptoborane bearing Tbt group, TbtB(SH)₂ **3**, and found that **3** can be utilized as a good precursor for the synthesis of a novel titanium-containing four-membered boracycle **4** (Z = TiCp₂; Cp = cyclopentadienyl) by way of its lithiation.⁸ Using this methodology we have succeeded in the synthesis of new types of dithiaborane derivatives containing heavier group 14 elements, a 1,3,2-dithiagermanoboretane derivative **5** (Z = GeMes₂; Mes = mesityl) and its tin-analogue **6** (Z = SnPh₂), as stable crystalline compounds (Scheme 1).^{9,10}



Scheme 1

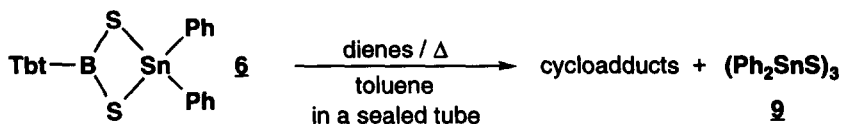
Since the structures of the four-membered rings of **5** and **6** are exactly those of [2+2]cycloaddition products of thioxoborane **7** (Tbt-B=S) with the corresponding germanethione (Mes₂Ge=S) and stannane-thione (Ph₂Sn=S), respectively, we examined the thermal retrocycloaddition of **5** and **6** in the presence of appropriate 1,3-dienes in the hope of trapping the regenerated thioxoborane **7**. On heating a toluene solution (20 ml) of the dithiastannaboretane **6** (53.1 mg, 0.059 mmol) at 120 °C for 5 days in a sealed tube in the presence of an excess amount of 2,3-dimethyl-1,3-butadiene (0.6 ml, 94 equiv.), 4,5-dimethyl-1,2-thiaboracyclohex-4-ene **8** (29.0 mg, 73%) was obtained together with the trimer of diphenylstannanethione **9** (15.9 mg, 88%) as shown in Scheme 2,¹⁰ while no change was observed for **5** even under severer reaction conditions (180 °C, 20 h).

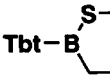
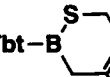
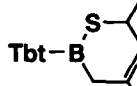
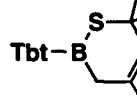


Scheme 2

The formation of **8** and **9** in the thermolysis of **6** can be reasonably interpreted in terms of the initial retro [2+2]cycloaddition of the dithiastannaboretane ring into the expected two 2π systems, *i. e.* thioxoborane **7** and diphenylstannanethione **10**, followed by [4+2]cycloaddition reaction of **7** with co-existing 2,3-dimethyl-1,3-butadiene and the self-trimerization of **10**, respectively. To the best of our knowledge, this is the first example of generation and trapping reactions of a thioxoborane.

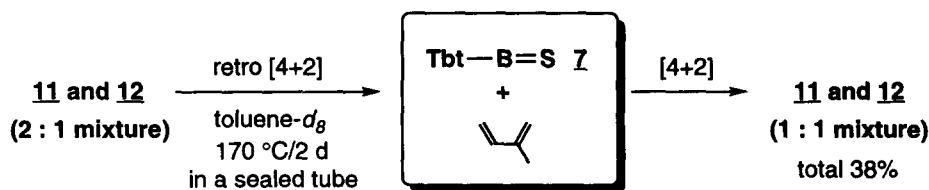
The effective generation of **7** from **6** and its high reactivity toward 2,3-dimethyl-1,3-butadiene prompted us to examine [4+2]cycloaddition reactions of **7** with other unsymmetric dienes, *i. e.* isoprene, 2-methyl-1,3-pentadiene, and 2,4-dimethyl-1,3-pentadiene. As shown in Table 1, all the three dienes afforded expected [4+2]cycloadducts with **7** in moderate to good yields. Although the cycloaddition reactions of **7** with dienes were found to proceed regioselectively in the cases of the latter two 1,3-pentadienes (entries 2 and 3) probably due to the considerable steric hindrance for the boron side of the thioxoborane unit in **7**, thermolysis of **6** at 120 °C in the presence of isoprene afforded both of the two possible regioisomers **11** and **12** in 62 and 31% yields, respectively (entry 1). The regioselectivity of cycloaddition of **7** with isoprene was almost lost at higher temperature (170 °C), suggesting an equilibrium between **11** and **12** via their retro [4+2]cycloaddition. Furthermore, we have found that the thermolysis of a 1:1 mixture of the isoprene adducts **11** and **12** at 170 °C in the presence of an excess amount of 2,3-dimethyl-1,3-butadiene resulted in exclusive formation of the diene-exchanged cycloadduct **8** in 70% yield.

Table 1. Thermolysis of Dithiastannaboretane **6 in the Presence of Unsymmetrical Dienes**

entry	diene	temp / °C	product (yield)
1			 + 
		120	11 (62%) 12 (31%)
		170	11 (33%) 12 (37%)
2		120	 13 (68%) — ^a
3		120	 14 (59%) — ^a

^a No the other regioisomer was obtained in these cases.

Cycloadduct **8** also underwent ready retro [4+2]-cycloaddition reaction at 170 °C in the presence of isoprene (excess) to give a 1:1 mixture of **11** and **12** (total 59%). These results showed that not only the dithiastannaboretane **6** but also the 1,2-thiaboracyclohex-4-enes here obtained can be used as good precursors for thioxoborane **7**.

**Scheme 3**

Finally, we have examined the retro [4+2]cycloaddition reaction of the diene adduct of thioxoborane **7** in the absence of an external trapping reagent. Monitoring by ¹H NMR spectroscopy of the thermolysis of the 2:1 mixture of **11** and **12** in toluene-*d*₈ at 170 °C for 2 days showed a gradual decrease of the molar ratio of **11** to **12** to 1:1, and a mixture of **11** and **12** (almost 1:1) was obtained in 38% yield after chromatographic separation (Scheme 3). These results suggest that thioxoborane **7** thus formed does not dimerize instantaneously but can survive as a monomeric species even in a hot solution at 170 °C and has a sufficient lifetime to un-

dergo [4+2]cycloaddition reaction with equimolar amount of the dissociated diene (isoprene) to regenerate an equilibrated mixture of the starting cycloadducts **11** and **12**.

In summary, we have succeeded in the generation of a kinetically stabilized thioxoborane Tbt-B=S (**7**), which is among a novel class of unsaturated organoboron compounds, and revealed its high dienophilic reactivity in the [4+2]cycloaddition reactions with 1,3-dienes. Further investigation on the structure and reactivity of **7** is currently in progress.

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REFERENCES AND NOTES

- Duss, F. In *Comprehensive Organic Chemistry*, Barton, D. H. R.; Ollis, W. D., Eds.; Pergamon Press:Oxford, U. K., 1979; Vol. 3, p 373-487.
- Tokitoh, N.; Okazaki, R. *Main Group Chemistry News* **1995**, 3, 4-11.
- Suzuki, H.; Tokitoh, N.; Nagase, S.; Okazaki, R. *J. Am. Chem. Soc.* **1994**, 116, 11578-11579.
- Tokitoh, N.; Matsumoto, T.; Manmaru, K.; Okazaki, R. *J. Am. Chem. Soc.* **1993**, 115, 8855-8856.
- Kroto, H. W. *Chem. Soc. Rev.* **1982**, 11, 435-491.
- a) Kirby, C.; Kroto, H. W.; Taylor, M. J. *J. Chem. Soc., Chem. Commun.* **1978**, 19-20. b) Kirby, C.; Kroto, H. W. *J. Mol. Spectrosc.* **1980**, 83, 1-14. c) Kirby, C.; Kroto, H. W. *J. Mol. Spectrosc.* **1980**, 83, 130-147. d) Kirk, R. W.; Timms, P. L. *J. Chem. Soc., Chem. Commun.* **1967**, 18-19.
- a) Becket, M. A.; Minton, P. R.; Werschkun, B. *J. Organomet. Chem.* **1994**, 468, 37-41. b) Männig, D.; Narula, C. K.; Nöth, H.; Wietelmann, U. *Chem. Ber.* **1985**, 118, 3748-3758. c) Hanecker, E.; Nöth, H.; Wietelmann, U. *Chem. Ber.* **1986**, 119, 1904-1910.
- Tokitoh, N.; Ito, M.; Okazaki, R. *Organometallics* **1995**, 14, 4460-4462.
- The molecular structures of newly obtained boron-containing metallacycles **5** and **6** have been determined definitively by X-ray crystallographic analysis, the details of which will be described elsewhere.
- All the new compounds described here gave satisfactory spectral and analytical data, among which those for compounds **6** and **8** are listed as representatives as follows.
6: colorless crystals, mp 175 °C (decomp); ¹H NMR(500 MHz, CDCl₃) δ 0.05 (s, 18H), 0.10 (s, 36H), 1.34 (s, 1H), 2.03 (br s, 2H), 6.24 (br s, 1H), 6.35 (br s, 1H), 7.55 (m, 6H), 7.90 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 0.64 (q), 0.85 (q), 29.70 (d), 30.18(d), 120.64 (d), 124.95 (d), 129.48 (d), 131.18 (d), 136.06 (d), 138.18 (s), 139.52 (s), 143.25 (s), 143.57 (s); ¹¹B NMR(86.4 MHz, CDCl₃) δ 74.5; ¹¹⁹Sn NMR(100 MHz, CDCl₃) δ -73.97. HRMS(FAB): m/z Calcd for C₃₉H₆₉Si₆S₂BSn: 900.2571. Found: 900.2475. Anal. Calcd for C₃₉H₆₉Si₆S₂BSn•0.5H₂O: C, 51.52; H, 7.76; S, 7.05. Found: C, 51.23; H, 7.77; S, 7.52.
8: colorless crystals, mp 176 °C (decomp); ¹H NMR(500 MHz, CDCl₃) δ -0.01 (s, 18H), 0.02 (s, 18H), 0.03 (s, 18H), 1.07 (br s, 2H), 1.29 (s, 1H), 1.82 (br s, 3H), 1.83 (br s, 3H), 2.14 (br s, 2H), 3.22 (br s, 2H), 6.19 (br s, 1H), 6.31 (br s, 1H); ¹³C NMR(125 MHz, CDCl₃) δ 0.65 (q), 0.94 (q), 19.75 (q), 21.51 (q), 29.51 (d), 29.97 (d), 33.37 (t), 35.77 (t), 120.87 (d), 124.87 (s), 125.31 (d), 127.91 (s), 128.18 (s), 142.51 (s), 143.69 (s). ¹¹B NMR(86.4 MHz, CDCl₃) δ 75.3. HRMS(FAB): m/z Calcd for C₃₃H₆₉Si₆SB: 676.3843. Found: 676.3829. Anal. Calcd for C₃₃H₆₉Si₆SB •0.5CH₂Cl₂: C, 55.90; H, 9.80; S, 4.45. Found C, 55.63; H, 9.71; S, 5.04.

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