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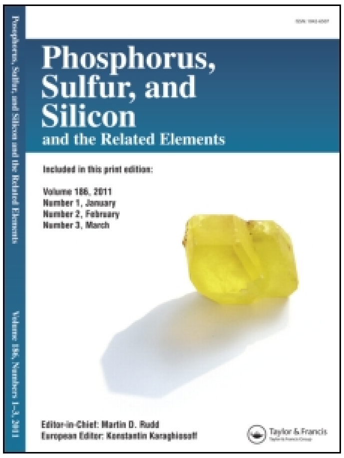

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Formation of Oxoborane and Thioxoborane from a Dithiastannaboretane Derivative

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FORMATION OF OXOBORANE AND THIOXOBORANE FROM A DITHIASTANNABORETANE DERIVATIVE

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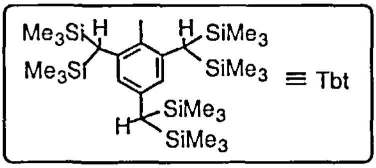
Reaction with an oxygen-donating reagent such as DMSO and thermolysis of a 1,3,2,4-dithiastannaboretane derivative bearing 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) group led to the formation of novel boron–group 16 element double bond compounds, oxoborane (Tbt–B=O) and thioxoborane (Tbt–B=S). The oxoborane and thioxoborane underwent cycloaddition reactions to give the corresponding adducts in good yields.

Keywords: 1,3,2,4-dithiastannaboretane; thermolysis; boron-containing doubly-bonded compounds; oxoborane; thioxoborane; cycloaddition

INTRODUCTION

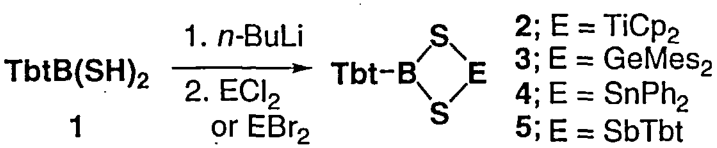
In contrast to the extensive studies on the stable methyleneboranes ($RB{=}CR_2$)[1] and iminoboranes (RB=NR),[2] very little is known for the chemistry of boron–group 16 element double-bond compounds.[3] We previously reported the synthesis of the first stable dimercaptoborane **1** bearing a 2,4,6-tris[bis(trimethylsilyl)methyl]-phenyl (Tbt) group and its facile transformation to the novel four-membered boracycles 2–5.[4, 5] Here, we present some reactions of the tin-containing four-membered boracycle **4** leading to the formation of a kinetically stabilized boron–oxygen double-bond compound (oxoborane) and its sulfur analogue (thioxoborane).

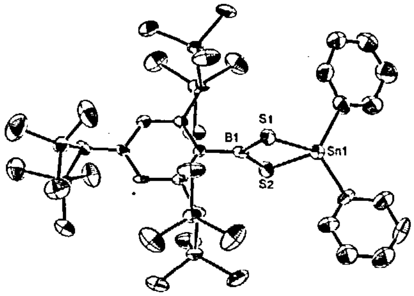


RESULTS AND DISCUSSION

Synthesis and Structure of 1,3,2,4-Dithiametallaboretanes

Dilithiation of the dimercaptoborane, $TbtB(SH)_2$ (**1**), which was synthesized by the sulfurization of the corresponding overcrowded lithium aryltrihydroborate bearing 2,4,6-tris[bis(trimethylsilyl)methyl]-phenyl (Tbt) group, followed by treatment with electrophiles such as Cp_2TiCl_2, Mes_2GeBr_2, Ph_2SnCl_2, and $TbtSbBr_2$ resulted in the isolation of novel four-membered boracycles, 1,3,2,4-dithiametallaboretanes **2-5** as stable crystals, respectively.

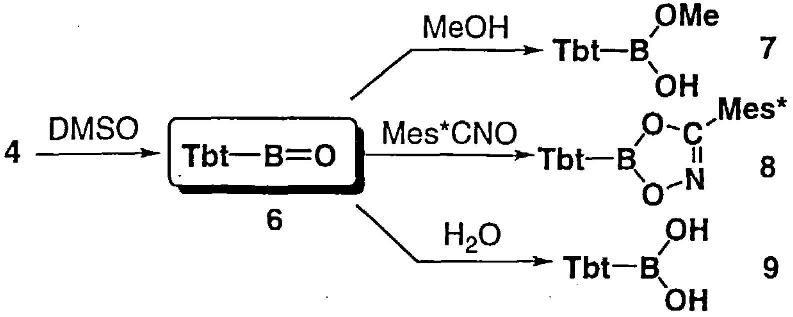




ORTEP drawing of **4**

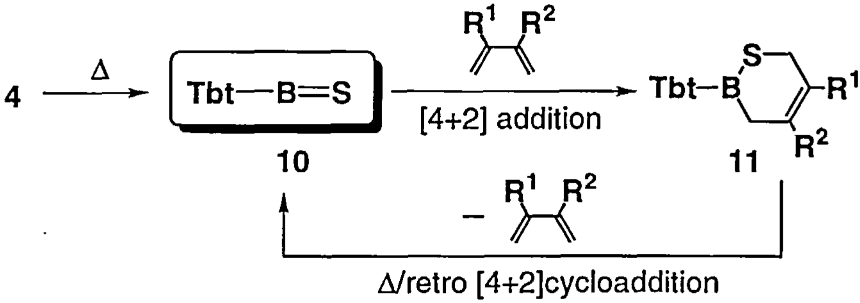
Formation and Reactions of Oxoborane (Tbt–B=O)[6]

The dithiastannaboretane **4** was found to be a good precursor for the oxoborane **6**. The reaction of **4** with dimethyl sulfoxide followed by the reaction with methanol and Mes*CNO (Mes* = 2,4,6-tri-*t*-butylphenyl) resulted in the formation of the expected methanol adduct **7** and [2+3]cycloadduct **8** of the oxoborane **6**. Exposure of **6** to moisture gave a hydrolysis product **9**.



Formation and Reactions of Thioxoborane (Tbt–B=S)[7]

The 1,3,2,4-dithiastannaboretane derivative **4** was found to undergo thermal retrocyclization to give a novel boron–sulfur double-bond compound (thioxoborane) **10**, the formation of which was confirmed by trapping reactions with 1,3-dienes giving **11**. Thioxoborane **10** was also generated by the thermal retro[4+2]cycloaddition reactions of the diene adduct **11**.



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