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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.

<u>Keywords</u>: 1,3,2,4-dithiastannaboretane; thermolysis; boroncontaining 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 Cp₂TiCl₂, Mes₂GeBr₂, Ph₂SnCl₂, and TbtSbBr₂ resulted in the isolation of novel four-membered boracycles, 1,3,2,4dithiametallaboretanes 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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