A Novel Approach to an Oxoborane and Its Lewis Base Complex

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Abstract: Reaction of dimethyl sulfoxide (DMSO) with 1,3,2,4-dithiastannaboretane **3** bearing an extremely bulky aryl group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt), on the boron atom gave an oxoborane (Tbt–B=O; **4**), which formed a complex with DMSO stable in solution. The formation of the complex was confirmed by ^{11}B NMR and a [3+2] cycloaddition reaction with 2,4,6-tri-*t*-butylbenzonitrile oxide. © 1997 Elsevier Science Ltd.

In recent years much attention has been paid to the double-bond compounds of boron, among which stable methyleneboranes (RB=CR$_2$)[1] and iminoboranes (RB=NR)[2] have been isolated and extensively characterized. In contrast, very little is known for the chemistry of boron–group 16 element double-bond compounds. Our recent success[3] in the generation of a boron–sulfur double-bond compound (thioxoborane) bearing a new and effective steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt hereafter) promoted us to study a lighter congener, a boron–oxygen double-bond compound (oxoborane). We have already succeeded in the syntheses and isolation of the first stable silanethione [Tbt(Tip)Si=S; Tip = 2,4,6-triisopropylphenyl][4] and germanechalcogenones [Tbt(Tip)Ge=X; X=S, Se, Te],[5-7] *i. e.* heavier congeners of a ketone, by taking advantage of the Tbt group, and revealed their unique structures and reactivities.

Oxoboranes are considered to be an important intermediate in the combustion of boron compounds which are often utilized as rocket fuels.[8] However, no stable monomeric oxoborane has been known so far because of its high reactivity, although their cyclic trimers **1** are well-known and a dimer **2** bearing amino substituents has been isolated by Nöth et al.[9] Attempts to synthesize a kinetically stabilized oxoborane using a 2,4,6-tri-*t*-butylphenyl (Mes*) group, well known as an efficient steric protection group, have also been reported, but Mes*B=O is too unstable to be isolated and its intermediacy has been shown by trapping reactions[10] and intramolecular cyclization.[11]

oxoborane   **1**   **2**
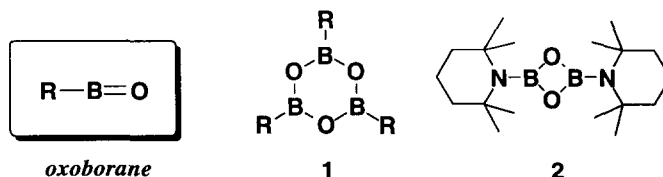
In addition to the high reactivity and instability, the lack of a suitable synthetic route to the boron–oxygen double-bond species obviously hampers the progress of chemistry in this field. Here, we wish to report a new and useful synthetic route to an oxoborane and the first oxoborane-Lewis base complex.

We previously reported the synthesis of a novel tin-containing four-membered boracycle **3** and the generation of a thioxoborane Tbt–B=S by its thermolysis.[3, 12] It occurred to us that oxidation of **3** could be a good synthetic approach to an oxoborane, Tbt–B=O **4**.

We first examined the oxidation of **3** with 2.5 equiv of dimethyl sulfoxide (DMSO) in the presence of a trapping reagent. Heating of a toluene solution of **3** and DMSO in the presence of Mes*CNO or methanol at 80 °C for 12 h in a sealed tube gave **5**[13] or **6** in high yields, respectively (Scheme 1).
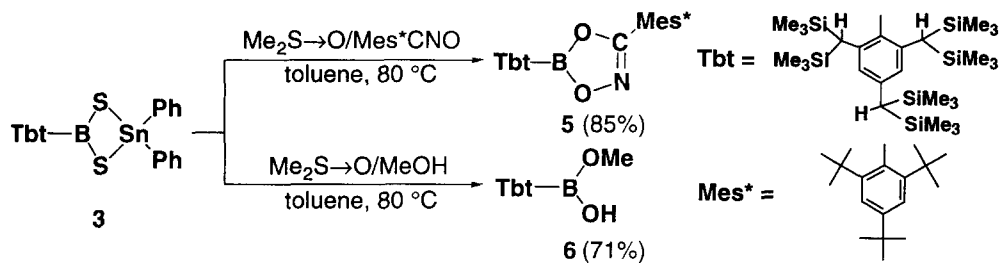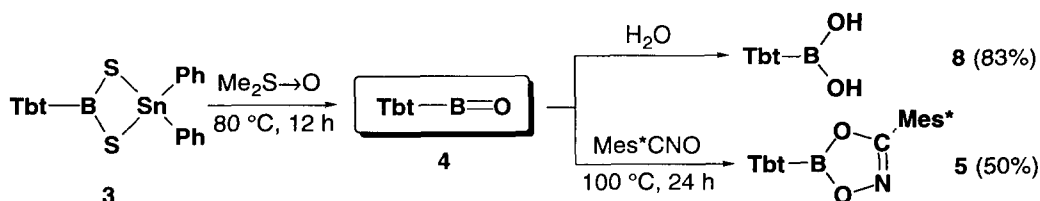

Scheme 1

The formation of **5** and **6** in these reactions can be reasonably interpreted in terms of the initial attack of the oxygen atom of DMSO to the boron center of **3** leading to oxathiaborirane **7** and diphenylstannanethione, followed by the elimination of a sulfur atom from **7** to form an oxoborane **4**, which would be trapped by Mes*CNO and methanol to give **5** and **6**, respectively.[14]
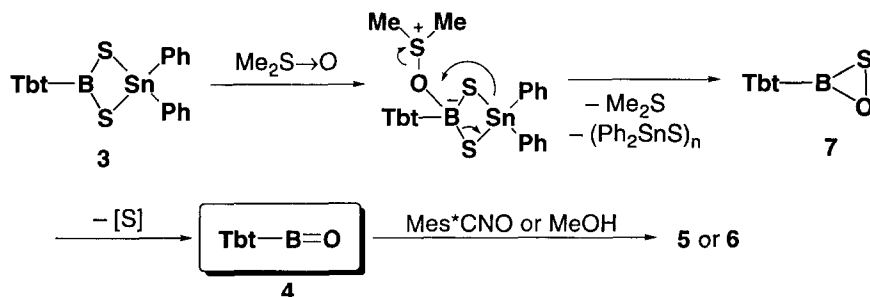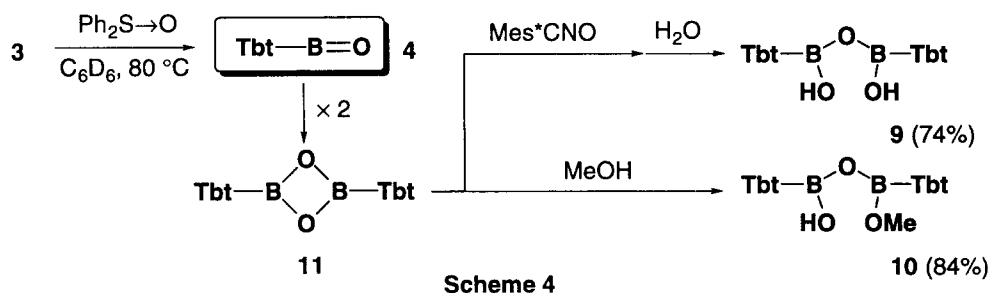

Scheme 2

The efficient generation of **4** from **3** prompted us to detect an intermediate of the reaction of **3** with DMSO by ^{11}B NMR. On heating a C_6D_6 solution of **3** and DMSO (2.5 equiv) at 80 °C for 12 h, a signal of ^{11}B NMR at 72.1 ppm due to **3** disappeared and a new signal was observed at 31.9 ppm. Usual workup of this solution resulted in the isolation of a dihydroxyborane **8**, a hydrolysis product of **4**, whereas heating of the solution in a glovebox for 24 h at 100 °C, after addition of Mes*CNO, afforded the [3+2]cycloadduct **5** in 50% yield. These results suggest the existence of a monomeric oxoborane **4** in solution (Scheme 3).


Scheme 3

However, oxidation of **3** with diphenyl sulfoxide (2.5 equiv) gave quite different results from those with DMSO. Although the reaction of **3** with diphenyl sulfoxide proceeded under the same conditions as that with DMSO, the ^{11}B NMR signal of the product was observed at 42.5 ppm, which was obviously different from that observed in the reaction with DMSO (δ 31.9). Addition of Mes*CNO to the reaction mixture under the same conditions as those with DMSO did not give the cycloadduct **5**, but a compound **9** was obtained along with diphenyl sulfide after usual workup. Furthermore, the addition of methanol to the reaction mixture gave a compound **10**. These results indicate that 1,3,2,4-dioxadiboretane **11**, a dimer of the oxoborane **4**, was formed in the reaction with diphenyl sulfoxide and it reacted with water or methanol to give **9** or **10**. The ^{11}B NMR signal observed at 42.5 ppm is most likely attributable to **11**.[15]

Scheme 4

The above-mentioned, seemingly strange discrepancy between the reactions of **3** with DMSO and diphenyl sulfide can be most reasonably explained as follows (Scheme 5). The oxoborane **4** is so reactive that it undergoes dimerization under the reaction conditions (80 °C) to give the dimer **11** in spite of being sterically protected by a Tbt group, as was observed in the reaction with diphenyl sulfoxide. On the other hand, in the reaction with DMSO, the oxoborane **4** is stabilized by coordination with DMSO as a Lewis base to form a complex **12**. The high electrophilicity of a doubly-bonded boron has been described.[1] The ^{11}B NMR (δ 31.9) is also consistent with the structure of **12** having two oxygen ligands. The trapping products **5** and **8** are most likely formed by the reaction with the oxoborane **4** which exists as a minor component in the equilibrium mixture with the complex **12**, although we cannot rigorously eliminate the possibility that **5** was formed directly from the complex **12**. The fact that diphenyl sulfoxide cannot make a complex with **4** can be interpreted in terms of steric repulsion upon coordination with the boron bearing an extremely bulky Tbt group as well as its weaker Lewis basicity than that of DMSO.

Scheme 5
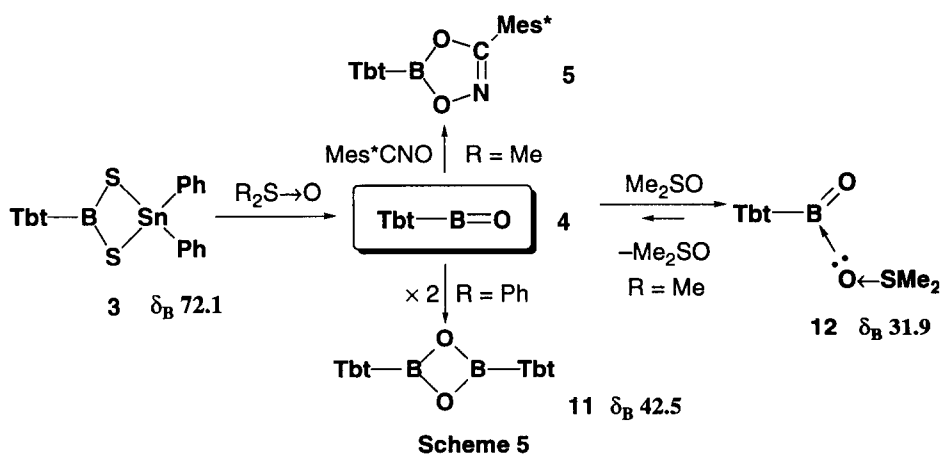
As far as we know, compound **12** is the first example of a Lewis-base complex of an oxoborane. Isolation, identification, and further reactions of this new organoboron compound are currently in progress.

REFERENCES AND NOTES

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13. All the new compounds described here gave satisfactory spectral and analytical data, among which those for compound **5** are listed as a representative as follows.
    5: colorless crystals, mp 197-199 °C; ^{1}H NMR(500 MHz, CDCl$_3$) δ 0.02 (s, 18H), 0.04 (s, 36H), 1.32 (s, 1H), 1.32 (s, 9H), 1.37 (s, 18H), 1.74 (br s, 1H), 1.81 (br s, 1H), 6.36 (br s, 1H), 6.48 (br s, 1H), 7.51 (s, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 0.44 (q), 0.72 (q), 29.40 (d), 29.79 (d), 30.80 (d), 31.23 (q), 33.11 (q), 37.46 (s), 118.34 (s), 119.65 (s), 121.43 (d), 122.39 (d), 126.26 (d), 145.73 (s), 149.80 (s), 150.28 (s), 151.23 (s), 152.29 (s), 165.06 (s); ^{11}B NMR(160 MHz, CDCl$_3$) δ 36.8. HRMS(FAB): *m/z* Calcd for C$_{46}$H$_{88}$BNO$_2$Si$_6$ 866.5602. Found: 866.5518. Anal. Calcd for C$_{46}$H$_{88}$BNO$_2$Si$_6$·1.5H$_2$O: C, 61.42; H, 9.86; N, 1.56. Found: C, 61.58; H, 9.78; N, 1.64.
14. The tin part of **3** was isolated as an unidentified insoluble white solid, probably polymers, along with a small amount of (Ph$_2$SnS)$_3$.
15. The [11]B chemical shift of 2,4-bis(2,4,6-tri-*t*-butylphenyl)-1,3,2,4-dioxadiboretane has been reported to be δ 33.5. See ref. 10.