The reactivity of N,C,N-intramolecularly coordinated antimony(III) and bismuth(III) oxides with the sterically encumbered organoboronic acid 2,6-i-Pr$_2$C$_6$H$_3$B(OH)$_2$

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ABSTRACT

The reactivity of N,C,N-intramolecularly coordinated antimony(III) and bismuth(III) oxides (LMO)$_2$ [where M = Sb **1**, Bi **2** and L is an abbreviation for (2,6-Me$_2$NCH$_2$)$_2$C$_6$H$_3$] with sterically demanding organoboronic acid DipB(OH)$_2$ (where Dip = 2,6-i-Pr$_2$C$_6$H$_3$) was studied. Stoichiometric reactions of **1** and **2** with DipB(OH)$_2$ in 1:4 molar ratio gave compounds LM[OB(Dip) (OH)]$_2$ (where M = Sb **3**, Bi **4**). Compounds **3** and **4** are in solution liable to further dehydration leading to the formation of six-membered heteroboroxine rings LM[OB(Dip)]$_2$O (where M = Sb **5**, Bi **6**). Changing of the stoichiometry to 1(oxide):2(acid) led to the isolation of eight-membered heteroboroxine rings LM[OB(Dip)O]$_2$ML (where M = Sb **7**, Bi **8**), but both compounds are unstable in solution and slowly decomposed to **5** (or **6**) with concomitant elimination of oxides **1** (or **2**). Studied compounds were characterized by the help of multinuclear NMR spectroscopy, IR spectroscopy and in the case of **5** by single-crystal X-ray diffraction analysis.

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Introduction

The chemistry of organoboroxines as anhydrides of corresponding organoboronic acids, that contain central six-membered B$_3$O$_3$ ring, has recently attracted an increasing interest [1]. They are studied especially due to their potential applications as useful building-blocks in material science [2] and as reactants or catalysts in various organic transformation [3]. The chemistry of so-called heteroboroxines, i.e. compounds where one or two boron atoms within central six-membered rings are replaced by another element, is significantly less developed, but this field seems to become active again [4]. As a contribution to this area, we have recently (2013) reported on the synthesis and structure of stiba-, bisma- and stannaheteroboroxines containing central MB$_2$O$_3$ core (where M = Sb, Bi or Sn) [5]. These heteroboroxines are accessible via a facile one step procedure based on the reaction between either the oxides (LMO)$_2$ [where M = Sb **1**, Bi **2** and L is an abbreviation for (2,6-Me$_2$NCH$_2$)$_2$C$_6$H$_3$] or the organotin(IV) carbonate LSn(Ph) (CO$_3$) and an organoboronic acid [5]. Subsequent study on larger set of compounds showed that the successful formation of

desired heteroboroxines, especially in the case of stiba- and bisma-derivatives, strongly depends on the position of the substituent on the phenyl ring of used organoboronic acid [6]. It turned out that the utilization of ortho-substituted organoboronic acids did not lead to desired stiba- and bismaboroxines instead a mixture of products was observed [6]. This fact attracted our attention and closer inspection of the reactivity of **1** and **2** with sterically shielded organoboronic acids seems to be reasonable. Thus, we herein report on the reactivity of **1** and **2** with DipB(OH)$_2$ (where Dip = 2,6-i-Pr$_2$C$_6$H$_3$) as an example of sterically encumbered boronic acid.

Results and discussion

The reaction of **1** [7] and **2** [8] with 4 molar equivalents of DipB(OH)$_2$ gave within 5 min compounds LM[OB(Dip) (OH)]$_2$ (where M = Sb **3**, Bi **4**) as monitored by the help of ^{1}H and ^{13}C NMR spectroscopy (Scheme 1). Compound **3** was isolated as a white crystalline solid in nearly quantitative yield, which is well soluble in aromatic and chlorinated solvents, but only sparingly soluble in hexane. In contrast, compound **4** could not be isolated because during any attempt for its isolation it started to be contaminated by the bismaboroxine **6** (see further discussion). Nevertheless, the identity of **4** was tentatively suggested based on the NMR and IR data that are closely related to those found for **3** vide infra. The ^{1}H

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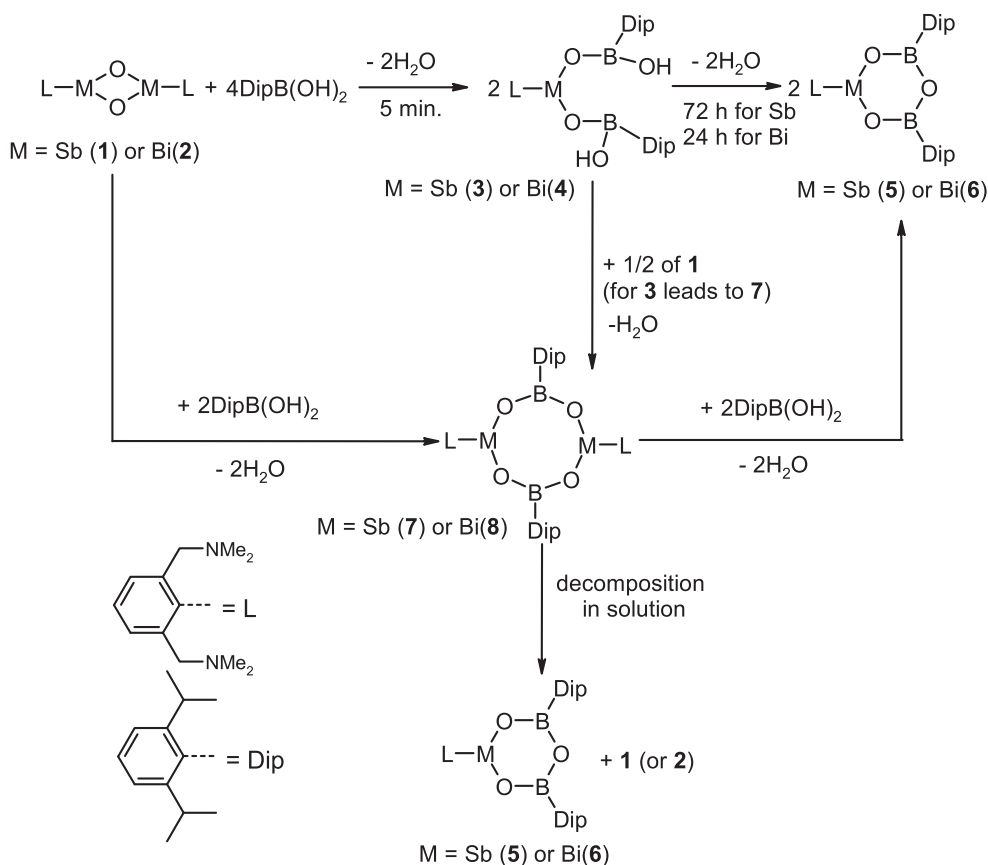
Scheme 1. Syntheses of **3**–**8**.

NMR spectra in both cases (**3** and **4**) established the presence of the ligand L and DipB groups in mutual 1:2 integral ratio. Thus, the ^{1}H NMR spectrum of **3** in C_6D_6 revealed an AX pattern at δ_A 2.84 and δ_x 4.51 ppm for CH_2N and two signals for magnetically non-equivalent $N(CH_3)_2$ groups, thereby proving *pseudo*-facial coordination of the ligand L. Next, the observation of two multiplets at δ 2.99 and 3.10 ppm and two overlapping doublets at δ 1.29 ppm together with their integral intensities established the presence of *i*-Pr units of two DipB groups. More importantly, a broad signal at δ 5.98 ppm was assigned to protons of two BO*H* groups. This signal is significantly down-field shifted in comparison with the chemical shifts (δ 4.18 ppm) found for B(O*H*)$_2$ protons in the parent acid DipB(OH)$_2$. The ^{13}C NMR spectrum of **3** was also consistent with the proposed structure (see the Experimental section). Although the bismuth congener **4** could not be isolated, the ^{1}H NMR spectrum (C_6D_6) observed after 5 min upon mixing of starting oxide **2** with 4 molar equivalents of DipB(OH)$_2$ closely resembled that obtained for **3**. Thus, this spectrum revealed an AX pattern at δ_A 3.25 and δ_x 4.54 ppm for CH_2N and two signals for magnetically non-equivalent $N(CH_3)_2$ groups and appropriate signals for *i*-Pr units of two DipB groups (broad signals at δ 1.34 and 3.08 ppm with expected integral intensity). The presence of two BO*H* groups in **4** was approved by the broad signal at δ 6.70 ppm with expected integration ratio in comparison with other signals in the spectrum. Furthermore, isolated samples of **3** and **4** (solvent was evaporated after 5 min from the post reaction mixture of starting **2** and DipB(OH)$_2$, thus analogous sample of **4** as was analyzed by ^{1}H and ^{13}C NMR spectroscopy *vide supra*) were also analysed by IR spectroscopy. In the IR spectrum of **3**, medium absorption of BOH groups at 3523 cm^{-1} accompanied with shoulder at 3536 cm^{-1} (3521 and 3540 cm^{-1} for

4) were found. The bands of ν_{OH} are not significantly broadened assuming the presence of isolated OH groups in the molecule, thereby proving the proposed structure of **3** and **4**.

Both compounds **3** and **4** are unstable in solution and after further dehydration gave heteroboroxines LM[OB(Dip)]$_2$O (where M = Sb **5**, Bi **6**). This reaction is smooth in the case of the bismuth compound (less than 24 h is usually necessary for a complete conversion of **4** to **6** as monitored by the help of ^{1}H NMR spectroscopy), while a complete dehydration from **3** to **5** took several weeks in a NMR tube in C_6D_6. Nevertheless, it may be accelerated by the addition of a drying agent on a preparative scale (see the Experimental section). Compounds **5** and **6** were isolated as white solids in good yields and are well soluble in chlorinated and aromatic solvents. The ^{1}H NMR spectra of **5** (and **6**) are analogous containing AX pattern at δ_A 2.60 and δ_x 4.49 ppm (δ_A 2.79 and δ_x 4.58 ppm for **6**) for CH_2N and two signals for magnetically non-equivalent $N(CH_3)_2$ groups and appropriate signals with expected integral intensity for *i*-Pr units of two DipB groups, i.e. one broad multiplet at δ 3.23 ppm (at δ 3.33 ppm for **6**) and a doublet at δ 1.37 ppm (at δ 1.39 ppm for **6**). The ^{13}C NMR spectra also revealed an expected set of signals consistent with proposed structures. Importantly, there was no signal of BO*H* protons in corresponding ^{1}H NMR spectra of **5** and **6** and similarly no BO*H* group was detected by IR spectroscopy. This finding proved the closure of the heteroboroxine rings in **5** and **6**. Molecular structure of **5** was unambiguously determined by the help of single-crystal X-ray diffraction analysis (Fig. 1). All attempts to obtain the molecular structure of **6** resulted only in seriously disordered structure (for details the Experimental section and Fig. S1) ruling out any detail description of this structure.