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COMMUNICATION

Syntheses and properties of triborane(5)s possessing bulky diamino substituents on terminal boron atoms†

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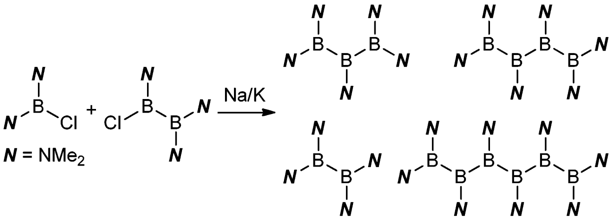
The present communication reports the chemistry of three linear triborane(5) compounds possessing bulky diamino substituents on the terminal boron atoms. Fluorotriborane 2 was synthesized by a reaction of boryllithium and $BF_3 \cdot OEt_2$. Halogen exchange reaction of 2 took place by a treatment with $ClSiMe_3$ to give the corresponding chlorotriborane(5) 3. Addition of silver tetraarylborate to 3 in ether afforded a hydroxylated triborane(5) compound 5 probably *via* an unstable cationic boron intermediate 4.

"Catenation" is a word describing the ability of an element to construct a long chain structure involving covalent bonds.[1] Many examples of catenation can be found as consecutive C–C bonds in organic chemistry and Si–Si bonds in polysilane chemistry. In contrast, boron, one of the closest neighbors to carbon in the periodic table, does not show catenation due to the following reason. In general, compounds containing multiple boron atoms tend to form a multinuclear structure through sharing the electrons by three or more orbitals as found in the B_2H_6 molecule and the polyborane structure because of the electron deficiency of the boron atom.[2,3] In the literature, only three types of examples for catenated boranes have been reported as triborane(5), tetraborane(6), and hexaborane(8).[4–6] These catenated boranes were synthesized by a reductive coupling of dimethylamino-substituted chloroborane and a similar chlorodiborane(4) by using a sodium/potassium alloy (Scheme 1).[7] Dimethylamino groups on the terminal boron atom of boranes could be converted to halogeno substituents (Cl, Br and I). The obtained terminal-halogenated boranes could also accept nucleophiles such as alkoxy, amino, alkyl, alkynyl, phosphino, and alkylthio groups onto their terminal boron atom.

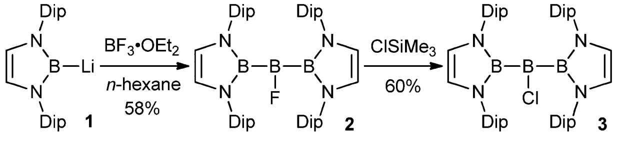
On the other hand, we recently reported a new boron-containing reagent, boryllithium **1**,[8–10] having an anionic charge and nucleophilicity on the boron center.[11] The anionic boron moiety in **1** could also be transferred to the other metals such as magnesium, copper, and zinc to form a series of boryl anion equivalents.[12–15] They could react with organic electrophiles to form a B–C bond in a nucleophilic manner. The high nucleophilicity of the boron center in boryl anion equivalents prompted us to explore new methods to synthesize catenated borane derivatives. Herein, we report syntheses and properties of triborane(5) derivatives using boryllithium **1**. In the reaction of chlorinated triborane(5) **3** with the silver tetraarylborate salt, the formation of the transient cationic boron compound **4** was suggested.



Scheme 1 Reported examples of linear borane.

Simple mixing of boryllithium **1**, generated in THF, with $BF_3 \cdot OEt_2$ in hexane gave fluorotriborane(5) **2** in 58% yield (Scheme 2). Resonances in the ^1H and ^{13}C NMR spectrum of **2** showed a highly symmetrical pattern with two distinct methyl, one methine, one backbone CH, and two aromatic signals. In the ^{11}B NMR spectrum of **2**, two signals at δ_B 83 and 25 were observed. The former signal could be assigned to the central boron atom from the integral ratio of two signals, although no ^{11}B–^{19}F coupling was observed probably due to significant broadening of the signal. It should be noted that the signal of the central boron atom appeared at a significantly lower-field compared to that (δ_B 60.2) observed in the reported pentakis(dimethylamino)triborane(5) compound.[5] This remarkable shift of ^{11}B resonance may be due to a less-effective overlap of p orbitals along the B–F bond in **2** compared to the B–N bond in the previously reported triborane(5) compounds.

The subsequent halogen exchange reaction of **2** could be achieved by a treatment of **2** with $ClSiMe_3$ to give the chlorinated triborane(5) **3** in 60% yield (Scheme 2). The features



Scheme 2 Syntheses of triborane(5)s **2** and **3** (Dip = 2,6-$^i Pr_2C_6H_3$).

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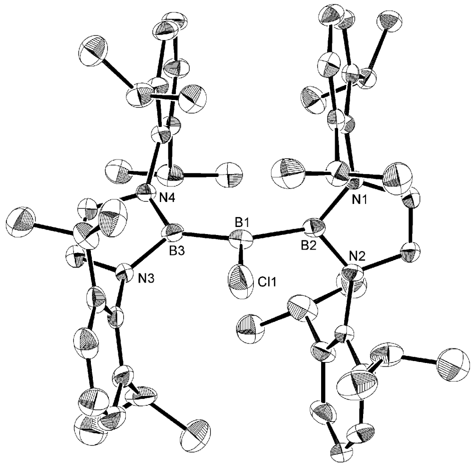


Fig. 1 ORTEP drawing of **3** (hydrogen atoms, minor parts of disordered isopropyl groups, and the co-crystallized THF molecule are omitted for clarity).

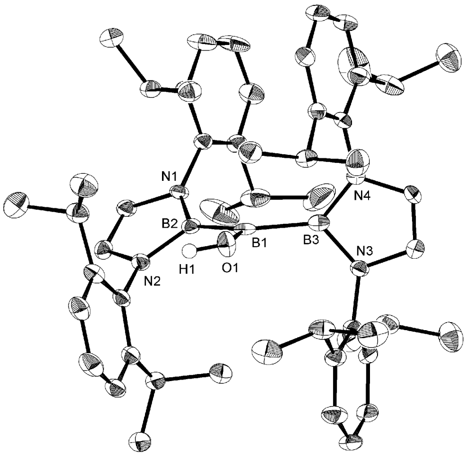


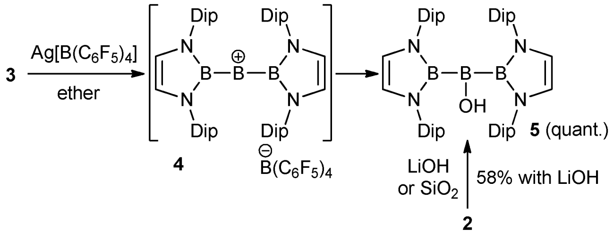
Fig. 2 ORTEP drawing of **5** (hydrogen atoms except for the hydroxy group, one of two independent molecules, and the co-crystallized *n*-hexane molecule are omitted for clarity).

of **3** in its ^{1}H and ^{13}C NMR spectra are similar to those of **2**. In the ^{11}B NMR spectrum of **3**, a lower-field shifted signal (δ_B 103) of the central boron atom compared to that in **2** was observed and it is probably due to less-overlapped p-orbitals on boron and chlorine atoms. Recrystallization of **3** from THF/*n*-hexane gave single crystals suitable for X-ray crystallographic analysis. The crystal structure of **3** is illustrated in Fig. 1. In the solid state, B–B lengths are 1.707(6) and 1.729(6) Å, which are in the range of B–B lengths in the reported triborane(5) and tetraborane(6) derivatives.[4–6] In contrast, the B–B–B angle of 141.5° in **3** is larger than those (120 ± 8°) in the reported linear boranes.[4–6] Despite the distortion around the central boron atom, the sum of the angles around each boron center is 360°, indicating their planarity. The B–Cl bond of 1.797(4) Å is similar to the typical values for B–Cl bonds.[1] Dihedral angles of Cl–B–B–N are 21.3° and 73.4°, showing that one boron-containing five-membered ring is close to being coplanar to the plane of the central boron atom and the other five-membered ring is almost perpendicular. This configuration may result from the steric repulsion between four bulky Dip groups.

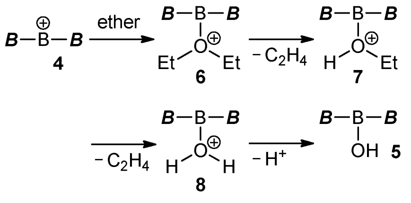
Treatment of chlorotriborane(5) **3** with silver tetrakis(pentafluorophenyl)borate in ether led to formation of a white precipitate and hydroxytriborane(5) **5** in quantitative yield as was observed in ^{1}H NMR (C_6D_6) of the crude product (Scheme 3).[16] Hydroxytriborane(5) **5** was independently synthesized and structurally characterized by X-ray crystallography (Fig. 2). Compared with **3**, the B–B lengths (av. 1.732 Å) in **5** are longer and the B–B–B angles (av. 135.5°) in **5** are smaller. The B–O bond distance was in the range of typical values for those in trialkoxyborane and tetraalkoxydiborane(4) derivatives as were observed in Cambridge crystallographic database. Existence of a hydroxy group in **5** was confirmed by the D_2O test in its ^{1}H NMR spectrum and ν_{OH} at 3524 cm^{-1} in its IR spectrum. It may be assumed that a cationic intermediate **4** was generated by an absorption of chloride on the silver cation to precipitate as AgCl. The diborylboryl cation **4** may be distinguished from the previously reported example of isolated boryl cations,[17,18] where the cationic boron center has one or two heteroatom(s) to gain a stabilization by pπ–pπ interaction between the boron and heteroatom(s). The lack of pπ–pπ stabilization may give anomalous instability to **4** to induce the further reaction of **4** with ether.

The possible reaction mechanism regarding the previously reported gas-phase reaction of the dimethylboryl cation with ether[19] is illustrated in Scheme 4. After the formation of **4**, the solvent ether immediately attacks the cationic boron center to form the diethylboryloxonium cation **6**.[20] Elimination of two ethylene molecules (detected by GC) from **6**, *via* two subsequent reactions including the formation of an ethyl cation and transfer of a proton,[21] induces the formation of dihydroboryloxonium **8**. Loss of a proton from **8** gives the hydroxylated product **5**.

In conclusion, boryllithium **1** reacted with $BF_3 \cdot OEt_2$ to give the corresponding fluorotriborane(5) **2** *via* double nucleophilic substitution by the boryl anion at the boron center of BF_3. The fluorine atom in **2** could be replaced with a chlorine atom by



Scheme 3 Reaction of **3** with $Ag[B(C_6F_5)_4]$.



Scheme 4 Plausible mechanism for the formation of **5** [***B*** = $B(NDipCH)_2$].

the reaction with $ClSiMe_3$ to afford the corresponding chlorotriborane(5) **3**. Treatment of **3** with the silver salt in ether gave the hydroxytriborane(5) **5**. Formation of **5** was explained by assuming an unstable cationic intermediate **4** and subsequent decomposition of the ether molecule.

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