

# The new approach to formation of exo boron–oxygen bonds from the decahydro-closo-decaborate(2-) anion



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## ABSTRACT

New methods of boron–oxygen bond formation in the decahydro-closo-decaborate(2-) anion have been worked out. The interaction between [closo-B<sub>10</sub>H<sub>10</sub>]<sup>2-</sup> and ethers in the presence of CF<sub>3</sub>SO<sub>3</sub>H has been considered. The degree of substitution in boron clusters depends on the amount of triflic acid and the synthetic conditions. The compounds obtained were characterized by IR and NMR (<sup>1</sup>H, <sup>11</sup>B and <sup>13</sup>C) spectroscopy. The crystal structures of some mono- and disubstituted derivatives of the closo-decaborate anion were determined by X-ray diffraction.

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## 1. Introduction

Investigation of the behavior of [closo-B<sub>10</sub>H<sub>10</sub>]<sup>2-</sup> in the presence of a Brønsted acid has been the subject of several publications. Depending on the type of acid, various processes have been performed. In the case of aliphatic carboxylic acids, this has entailed the substitution of hydrogen atoms and the formation of carboxonium derivatives of closo-decaborate anions [1–4]. In the case of strong inorganic acids, opening of the boron cluster cage takes place [5–7]. Hawthorne [5] and colleagues, in particular, investigated the interaction of closo-decaborate anions with triflic acid in the presence of benzene and cyclohexane. This process led to the formation of alkyl and aryl-*nido*-decaborane [6-(R)B<sub>10</sub>H<sub>13</sub>]. A hypothetical mechanism for the formation of such *nido*-decaboranes was described in Hawthorne's articles [5,6]. This mechanism comprised several successive stages of protonation of the closo-decaborate anions. In the first stage, the well-known anion [B<sub>10</sub>H<sub>11</sub>]<sup>-</sup> was observed, then this anion was protonated again and its closo-cage was initiated with the formation of the *nido*-borane.

Due to the low stability and high toxicity of *nido*-decaboranes, opening reactions of closo-decaborate clusters are not as common

as substitution processes of exo-polyhedral hydrogen atoms [8–12]. Therefore, most of the decahydro-closo-decaborate anion reactions have an EINS mechanism (electrophile-induced nucleophilic substitution) and lead to the formation of systems of the general formula [B<sub>10</sub>H<sub>10-n</sub>(Nu)<sub>n</sub>]<sup>(2-n)-</sup>, *n* = 1,2. In this case, Lewis acids (metal halides, organic and inorganic acids) act as electrophilic agents [13–15].

An alternative approach for hydrogen substitution in closo-decaborate anions is based on the use of the [B<sub>10</sub>H<sub>11</sub>]<sup>-</sup> anion as the starting cluster compound. Depending on the type of electrophilic agent and the synthetic conditions, derivatives of closo-decaborate with varying degrees of substitution and the position of the substituent can be prepared [16–20]. Use of [B<sub>10</sub>H<sub>12</sub>]<sup>-</sup> will provide an opportunity for the convenient preparation of disubstituted derivatives of closo-decaborate anions with the general formula [B<sub>10</sub>H<sub>8</sub>(Nu)<sub>2</sub>]<sup>0</sup>. The existence of this molecule has been assumed hypothetically in several articles, but no spectral evidence has been provided [16,21,22].

In the current research, we have paid the greatest attention to the synthesis of oxonium derivatives of closo-decaborate anions. Oxonium derivatives of closo-borates are suitable starting molecular platforms for further modifications for the creation of prospective compounds with various chemical and biochemical properties [23–26]. There are a few comprehensive reviews that describe the synthesis, chemical properties and some biological aspects of closo-borates with B–O bonds [27–29]. There are, at this time,

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many methods for the synthesis of oxonium derivatives of *closo*-decaborate anions [30–33]. These methods are also based on processes occurring by the EINS mechanism, but currently the regioselectivity of this process is not clearly understood. Furthermore, some of the methods used had some experimental difficulties; for example, in some work [32], anhydrous hydrogen chloride was used as an electrophilic agent. This method requires quite difficult apparatus for the synthesis of the oxonium derivatives of *closo*-decaborate anions.

The current research focuses on the development of new approaches for the synthesis of *closo*-decaborate anions with *exo*-polyhedral B–O bonds, based on the reaction of the  $[\text{B}_{10}\text{H}_{10}]^{2-}$  anion with ethers in the presence of  $\text{CF}_3\text{SO}_3\text{H}$ .

## 2. Experimental

**Materials.**  $(\text{Bu}_4\text{N})_2\text{B}_{10}\text{H}_{10}$  was prepared according to known procedures [34]. 2-Methyltetrahydrofuran (Aldrich, 99%) and  $\text{CF}_3\text{SO}_3\text{H}$  (Aldrich, 98%) were used without additional purification. Tetrahydropyran, 1,4-dioxane and dichloromethane were purified according to a known procedure [35].

Elemental analysis for carbon, nitrogen and hydrogen was carried out on a Carlo Erba CHNS3 FA 1108 Elemental Analyzer. Analysis of the boron content was conducted using an ICP MS on an iCAP 6300 Duo inductively coupled plasma-atomic emission spectrometer in the Shared Knowledge Center “Scientific Research Analytical Center FSUE IREA” with financial support from the GOVT (Ministry of Education and Science of the Russian Federation) in the framework of the Grant Agreement No.14.595.21.0001 dated 22 August 2014 (Unique Identifier for Applied Scientific Investigations (project) RFMEFI59514X0001).

IR spectra of the prepared compounds were recorded on an Infracum FT 02 Fourier transform spectrometer (Lumex Instruments Research and Production Company) in the region  $4000\text{--}300\text{ cm}^{-1}$ , with a resolution of  $1\text{ cm}^{-1}$ . Samples were prepared in Nujol (Aldrich).

NMR ( $^1\text{H}$ ,  $^{11}\text{B}$  and  $^{13}\text{C}$ ) spectra of solutions of the studied compounds in  $\text{CD}_3\text{CN}$  were recorded at the Shared Equipment Center of the Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, on a Bruker Avance II 300 spectrometer, operating at 300.3, 96.32 and 75.49 MHz, respectively, using an internal deuterium lock. Tetramethylsilane and boron trifluoride etherate were used as external references.

X-ray diffraction studies of 2–5 were performed at the Shared Equipment Center of the Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, on a Bruker APEX-II CCD diffractometer ( $\lambda\text{Mo} = 0.71073\text{ \AA}$ ,  $\varphi\text{--}\omega$  scan mode) [36]. The diffraction data were processed using the SAINT program [36] and an absorption correction based on equivalent reflections was applied with the SADABS program [36]. The structures were solved by the direct method and refined on  $F^2$  using the SHELXS-97 and SHELXL-2014/7 packages [37]. In **3**, the methyloxolane group is disordered over two positions with a common O(1) atom and a 0.864(3):0.136(3) ratio of site occupancies; in addition, one of the carbon atoms of the tetrabutylammonium cation is disordered over two equally occupied positions. In the structure of **4** there are three molecules per asymmetric unit. In molecule **4a**, the positions of the C(6) and C(8) atoms are split in the ratio 0.876(7):0.124(7); in the two variants of the chair conformation, the atoms C(6) and C(8) lie on opposite sides of the O(3)O(4)C(5)C(7) plane. Molecule **4b** is ordered. Molecule **4c** is disordered over two orientations in the ratio 0.685(4):0.315(4) (see Supplementary Data, Fig. 1s). The positions of the O(11) and O(11)A atoms coincide. The non-hydrogen atoms of the minor components in **3** and **4** were refined in an isotropic approximation using the SAME restraints. The thermal

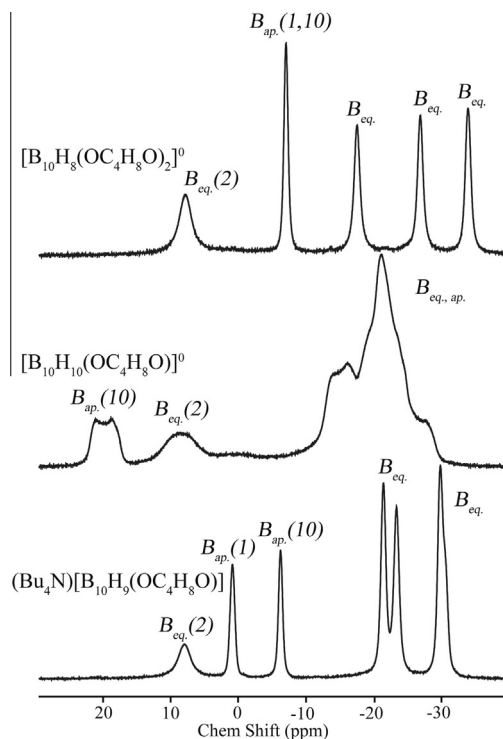


Fig. 1.  $^{11}\text{B}\text{--}\{^1\text{H}\}$  NMR spectra of  $(\text{Bu}_4\text{N})_2[\text{B}_{10}\text{H}_{10}]$ ,  $(\text{Bu}_4\text{N})[\text{B}_{10}\text{H}_{11}]$  and  $[\text{B}_{10}\text{H}_{12}]$ .

parameters of the atoms with low occupancies, the boron atoms in **4** and carbon atoms of the methyloxolane substituent in **3**, were taken to be equal and refined as free variables. All other non-hydrogen atoms in structures 2–5 were refined in the anisotropic approximation. The hydrogen atoms of the *closo*-borate polyhedra in **2** and **3**, as well as all H atoms in **5**, were localized on difference Fourier maps and refined in the isotropic approximation. The remaining H atoms in **2** and **3** and all H atoms in **4** were refined with the riding model in calculated positions with  $U_{\text{iso}} = 1.2U_{\text{eq}}$  of the parent atom. Crystal data, details of data collection and results of the structure refinements for 2–5 are summarized in Table 1.

### 2.1. Synthesis of monosubstituted oxonium derivatives of *closo*-decaborate

#### 2.1.1. Preparation of $(\text{Bu}_4\text{N})[2\text{-B}_{10}\text{H}_9\text{O}_2\text{C}_4\text{H}_8]$ (**1**)

A solution of 0.50 g (0.00082 mol) of  $(\text{Bu}_4\text{N})_2\text{B}_{10}\text{H}_{10}$  in a mixture of 10 ml of dichloromethane ( $\text{CH}_2\text{Cl}_2$ ), 20 ml of dioxane ( $\text{C}_4\text{H}_8\text{O}_2$ ) and 0.1 ml of  $\text{CF}_3\text{SO}_3\text{H}$  was heated for 4 h at  $50\text{ }^\circ\text{C}$  with stirring under an atmosphere of dry argon until gas ( $\text{H}_2$ ) ceased to be evolved. The solution was then concentrated on a rotary evaporator at  $35\text{ }^\circ\text{C}$ . The residue obtained was purified by column chromatography on silica gel eluting with a chloroform/acetonitrile mixture (2:1) to give 0.31 g (85%) of the title compound. IR (Nujol,  $\text{cm}^{-1}$ ):  $\nu(\text{BH})$  2452,  $\nu(\text{B--O})$  1370,  $\nu(\text{B--B--H})$  1104.  $^{11}\text{B}\text{--}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{CN}$ ,  $\delta$ , ppm): 6.2 (s, 1B),  $-0.9$  (d, 1B),  $-8.1$  (d, 1B),  $-23.4$  (d, 2B),  $-25.1$  (d, 2B),  $-31.9$  (d, 3B).  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ,  $\delta$ , ppm): 0.60–2.10 (m, 9H,  $\text{B}_{10}\text{H}_9$ ), 4.62 (t,  $J = 4.22\text{ Hz}$ , 4H,  $\text{CH}_2$  ( $\alpha$ )), 4.28 (t,  $J = 4.58\text{ Hz}$ , 4H,  $\text{CH}_2$  ( $\beta$ )), 3.19 (m, 8H,  $\text{Bu}_4\text{N}$ ), 1.65 (m, 8H,  $\text{Bu}_4\text{N}$ ), 1.42 (m, 8H,  $\text{Bu}_4\text{N}$ ), 1.00 (m, 12H,  $\text{Bu}_4\text{N}$ ).  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{CN}$ ,  $\delta$ , ppm): 82.9 ( $\text{CH}_2$  ( $\alpha$ )), 58.5 ( $\text{CH}_2$  ( $\beta$ )), 58.1 ( $\text{Bu}_4\text{N}$ ), 23.2 ( $\text{Bu}_4\text{N}$ ), 19.1 ( $\text{Bu}_4\text{N}$ ), 12.8 ( $\text{Bu}_4\text{N}$ ). Elemental Anal. Calc.: B, 24.14; C, 53.65; H, 11.93; N, 3.11. Found: B, 24.25; C, 53.8; H, 11.75; N, 3.07%.

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