HOMOATOMIC POLYHEDRAL EXTENSION

IN NONAHYDRO-closo-NONABORATE ANION \([B_9H_9]^{2-}\)

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Nonahydro-closo-nonaborate anion possess the property of structural nonrigidity because of
presence of three low-coordinated boron atoms. So it’s able to come into the reactions of
polyhedral extension. This paper is devoted to the reactions of homoatomic polyhedral
extension in nonahydrocloso-nonaborate anion \([B_9H_9]^{2-}\) in presence of triethylaminoborane
complex \(BH_3(C_2H_5)_3N\). It was shown that mixes of \([B_{10}H_{10}]^{2-}\) and \([B_{12}H_{12}]^{2-}\) salts in various
molar ratios had been formed as products. These ratios depend on proportion of reagents. In
presence of excess of triethylaminiborane complex the molar ratio of products is 1:1. When
equimolar amount of triethylaminoborane complex used, the selectivity of process shifted to
formation of \([B_{10}H_{10}]^{2-}\) anion. However the formation of \([B_{12}H_{12}]^{2-}\) still occurs in this conditions
but the molar ratio of \([B_{10}H_{10}]^{2-} : [B_{12}H_{12}]^{2-}\) is 5:1.

Keywords: boron hydrides, closo-borates, \(B_9H_9^{2-}\), \(B_{10}H_{10}^{2-}\), \(B_{12}H_{12}^{2-}\), polyhedral extension.

Introduction

\([B_9H_9]^{2-}\) anion belonging to the class of polyhedral compounds of boron was practically
out of the focus of attention of boron hydride chemistry experts, first of all, because of lack of well-
reproducible methods for its preparation \([1, 2]\). At the same time it holds a special position among
closo-borate anions. The presence of three low-coordinated boron atoms (apical vertices) in
\([B_9H_9]^{2-}\) anion determines its capability to undergo rearrangements and polyhedral extension \([3, 4]\)
and compression \([5]\) reactions, which was predicted by Lipscomb \([6]\) since before the actual
synthesis of \([B_9H_9]^{2-}\) anion. These features of nonahydro-closo-nonaborates are widely used for the
synthesis of hardly available polyhedral \([B_7H_7]^{2-}\) and \([B_8H_8]^{2-}\) anions, as well as for the synthesis of
ten-vertex heteronuclear clusters, metallaboranes.

However, the capability of \([B_9H_9]^{2-}\) anion to undergo homonuclear extension still remains
practically unstudied. This property of \([B_9H_9]^{2-}\) anion that causes the special timeliness of studying
its reactivity makes it possible not only using it (including low-molecular raw materials enriched
with \(^{10}\)B isotope) to obtain cluster boron compounds with a larger number of atoms, but also to
enrich the already well-studied chemistry of the highest polyhedral boranes.

The purpose of this work is to reveal specific features of \([B_9H_9]^{2-}\) anion polyhedral
homonuclear extension reactions in the presence of borane triethylamine complex \(BH_3(C_2H_5)_3N\).
Experimental

Starting reagents and solvents. All the starting substances including tetrphenylphosphonium chloride were produced by Aldrich. NaBH₄ with the content of the base material not less than 99% was used without additional purification. Triethylamine was shaken with solid potassium hydroxide within several days until potassium hydroxide darkening ceased, and then distilled under atmospheric pressure (bp = 89°C). High purity toluene and dimethylformamide were used without additional purification. Borane triethylamine complex was obtained according to the technique described in [7]. LiBH₄ (24 g, 1.08 mol) was placed into a 1-liter three-necked flask equipped with a magnetic stirrer and a drop funnel with a pressure compensator. Diethyl ether (400 ml) was added, and a flow of dry argon was passed for 15 min. Boron trifluoride etherate (55 ml, 63 g; 0.44 mol) was slowly added to the obtained suspension from the drop funnel. Resulting diborane was forced out of the flask by a continuous flow of dry argon and absorbed in another flask filled with 250 ml of triethylamine. When the gas evolution ceased, triethylamine was distilled off under atmospheric pressure. The residue was distilled in vacuum (bp = 101°C, p = 13 mm Hg). The yield of BH₃·(C₂H₅)₃N was 95 ml (106 g, 85% calculated for LiBH₄). nD = 1.4425.

Salts of B₃H₈⁻ anion were synthesized according to the technique developed by us before [8].

Methods of physico-chemical analysis. IR spectra of compounds suspensions in vaseline oil (Aldrich) were recorded within the range 4000–400 cm⁻¹ with the resolution 1 cm⁻¹ with the use of a hardware-software complex based on a VERTEX 70 IR Fourier spectrometer (BRUKER) with a combinational scattering module RAM II. ¹¹B and ¹¹B{¹H} NMR spectra of solutions of the studied compounds were recorded with the use of a Bruker AVANCE II-300 spectrometer at operating frequency 96.32 MHz with internal stabilization by deuterium. Boron trifluoride etherate was used as an external standard.

Synthesis of (Ph₄P)₂[B₉H₁₀]. Compound Cs₂[B₉H₁₀] was preliminarily synthesized by "dry" pyrolysis of caesium octahydrotriboride [1]. Caesium octahydrotriboride (7.6 g, 0.04 mol) was placed into an argon-filled installation, the scheme of which is presented in Figure 1. Then the installation was placed for 30 min into a bath with Wood’s alloy heated to 235°C. After cooling to room temperature the pyrolyzate was slowly added to 45 ml of water heated to 60–70°C, and the mixture was stirred for 15 min. An undissolved residue was filtered off, and 45 ml of water was added under stirring at 60–70°C for 15 min. An undissolved part was filtered off again and recrystallized from 150 ml of water. The obtained Cs₂[B₉H₁₀] was dissolved in a minimal quantity of water alkalized with CsOH to pH 11, and (C₆H₅)₄PĊl (2.24 g, 6 mmol) was added. The formed precipitate was filtered off, dried in the air and dissolved in a minimal quantity of dichloromethane.
An undissolved residue was separated by filtering, and the solvent was distilled off in a rotary evaporator. As a result, tetrphenylphosphonium nonahydro-cleso-nonaborate (2.16 g, 2.76 mmol) was obtained. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum (CH$_2$Cl$_2$, $\delta$, ppm): –2.38, –20.13; IR spectrum (suspension in vaseline oil), KBr, cm$^{-1}$: 2445w, 2416w, 2397w ($\nu_{\text{BH}}$), 997m ($\delta_{\text{BBH}}$), 724w ($\delta_{\text{BBB}}$), yield 63%.

Interaction of $[(\text{C}_6\text{H}_5)_{4}\text{P}]_2[\text{B}_9\text{H}_{10}]$ with BH$_3$·(C$_2$H$_5$)$_3$N

Method 1 (with an excess of BH$_3$·(C$_2$H$_5$)$_3$N). (Ph$_4$P)$_2$[B$_9$H$_9$] (0.5 g, 0.64 mmol) was added to 5 ml of borane triethylamine complex. The reaction mixture was stirred in the atmosphere of argon for 12 h at 130 °C. A precipitate (0.52 g) was filtered off. Fractional recrystallization from 10 ml of CH$_2$Cl$_2$ gave 0.21 g of (Ph$_4$P)$_2$[B$_{12}$H$_{12}$]: $^{11}\text{B}\{^1\text{H}\}$ NMR (CH$_2$Cl$_2$, $\delta$, ppm): –14.98; IR spectrum (suspension in vaseline oil, KBr, cm$^{-1}$): 2474s, 2439s ($\nu_{\text{BH}}$), 999m ($\delta_{\text{BBH}}$), 723s ($\delta_{\text{BBB}}$) and 0.19 g of (Ph$_4$P)$_2$[B$_{10}$H$_{10}$]: $^{11}\text{B}\{^1\text{H}\}$ NMR (CH$_2$Cl$_2$, $\delta$, ppm): –0.52, –28.67; IR spectrum (suspension in vaseline oil, KBr, cm$^{-1}$): 2478s, 2435s ($\nu_{\text{BH}}$), 995m ($\delta_{\text{BBH}}$), 719s ($\delta_{\text{BBB}}$).

Method 2 (with a deficit of BH$_3$·(C$_2$H$_5$)$_3$N). (Ph$_4$P)$_2$[B$_9$H$_9$] (0.5 g, 0.64 mmol) was added to 5 ml of toluene. Then borane triethylamine complex (0.095 ml, 0.64 mmol, $\rho$ = 0.777 g/ml) was added under stirring. The reaction mixture was refluxed (110 °C) under stirring for 12 h. A precipitate (0.52 g) was filtered off. According to $^{11}\text{B}$ NMR it consisted of (Ph$_4$P)$_2$[B$_9$H$_9$]: $^{11}\text{B}\{^1\text{H}\}$ NMR (CH$_2$Cl$_2$, $\delta$, ppm): –2.38, –20.13; IR spectrum (suspension in vaseline oil, KBr, cm$^{-1}$): 2445s,

![Figure 1](image_url)
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2416s, 2397s (νBH), 997m (δBBH), 724s (δBBB); (Ph4P)2[B10H10]: 11B{1H} NMR (CH2Cl2, δ, ppm): –0.50, –28.66; IR spectrum (suspension in vaseline oil, KBr, cm−1): 2478s, 2435s (νBH), 995m (δBBH), 719s (δBBB) and (Ph4P)2[B12H12]: 11B{1H} NMR (CH2Cl2, δ, ppm): –14.99; IR spectrum (suspension in vaseline oil, KBr, cm−1): 2474s, 2439s (νBH), 999m (δBBH), 723s (δBBB).

Results and Discussion

According to NMR data the nonahydro-closo-nonaborate anion exists in solutions mainly in the form of a tricapped triangular prism [1]. However, because of the existence of three low-coordinated boron atoms this form has structural nonrigidity, which, as stated above, was predicted since before the actual synthesis of [B9H9]2− anion. The structure nonrigidity accounts for the lower stability of [B9H9]2− anion as compared to other representatives of polyhedral boranes, as well as for the higher tendency to rearrangements. The mechanism of such rearrangements is described as a rupture of one of the edges of the triangular prism followed by the formation of a bond between two low-coordinated boron atoms (Figure 2) [9–12].

![Figure 2](image)

**Figure 2**. Scheme of a RSR (rhombus-square-rhombus) rearrangement in [B9H9]2− anion.

Practical confirmation of the capability of undergoing such rearrangements was obtained in works [13, 14]. The intermediate in them is the C4v form of [B9H9]2− anion, which has the shape of a one-capped square antiprism. Most likely, the existence of a square electron-excess face also determines the capability of the closo-nonaborate anion to undergo polyhedral extension reactions, including the addition of B–H fragments with the construction of ten- and twelve-vertex homonuclear polyhedra. Thus, the interaction of the closo-nonaborate anion both with an excess of borane triethylamine complex and with its deficit gives a mixture of [B10H10]2− and [B12H12]2− anions in various ratios:
Refluxing tetraphenylphosphonium nonahydro-closo-nonaborate in borane triethylamine complex results in the complete transformation of \([B_9H_9]^{2-}\) anion into \([B_{10}H_{10}]^{2-}\) and \([B_{12}H_{12}]^{2-}\) anions. The \(^{11}\text{B}\{^1\text{H}\}\) NMR spectrum of a solution of the reaction mixture in dimethylformamide, along with the main borane triethylamine signal at –12.14 ppm, shows three signals: at 0.17 and –27.66 ppm (\([B_{10}H_{10}]^{2-}\) anion) and –14.33 ppm (\([B_{12}H_{12}]^{2-}\) anion) with the ratio of integral intensities 1:4:5.9, respectively (Figure 3). Analysis of this ratio showed that closo-decaborate and closo-dodecaborate anions are formed in the molar ratio 1:1. The mixture is easily separated by fractional recrystallization from dichloromethane.

In order to increase the process selectivity towards the preparation of \([B_{10}H_{10}]^{2-}\) anion we used the equimolar quantities of borane triethylamine complex and a nonpolar solvent, toluene. The latter does not participate in the complex formation. However, the presence of \([B_{12}H_{12}]^{2-}\) anion in the reaction mixture was noted also in this case. The \(^{11}\text{B}\{^1\text{H}\}\) NMR spectrum of a solution of the reaction mixture in dichloromethane shows signals of \([B_{10}H_{10}]^{2-}\) anion (–0.50 and –28.66 ppm) and
of \([\text{B}_{12}\text{H}_{12}]^{2-}\) anion \((–14.99 \text{ ppm})\) with the ratio of integral intensities 1:4:1.2. Thus, the molar ratio of \textit{closo}-decaborate and \textit{closo}-dodecaborate anions in the mixture is 5:1.

In addition to the mentioned products, the spectrum of the solution also shows signals with a small relative integral intensity due to unreacted \([\text{B}_{9}\text{H}_{9}]^{2-}\) anion \((-2.38 \text{ and } –20.13 \text{ ppm})\).

Thus, the processes of homonuclear polyhedral extension studied by us are a basis for the development of methods for the preparation of \textit{closo}-borates \([\text{B}_{10}\text{H}_{10}]^{2-}\) and \([\text{B}_{12}\text{H}_{12}]^{2-}\), as well as their substituted derivatives. Note that at this stage of research we did not succeed in creating an approach enabling to prepare \([\text{B}_{10}\text{H}_{10}]^{2-}\) anion from \([\text{B}_{9}\text{H}_{9}]^{2-}\) anion in rather high selectivity because of the certain structural non-rigidity of \([\text{B}_{10}\text{H}_{10}]^{2-}\) anion and its tendency to processes of polyhedral extension.

The work was performed within the Program of basic research of the Presidium of the Russian Academy of Sciences No I.II32 and project No 14-13-01115 of the Russian Scientific Foundation. The IR spectra were recorded with the use of equipment of the Share Equipment Center “Research Scientific and Analytical Center of FSUE IREA”.

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