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 triethylaminborane complex $BH_3{\cdot}(C_2H_5)_3N$. 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 triethylamin borane complex the molar ratio of products is 1:1. When equimolar amount of triethyamminborane complex used, the selectivity of process shifted to formation of $[B_{10}H_{10}]^{2-}$ anion. However the formation of $[B12H12]^{2-}$ 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 $BH_3{\cdot}(C_2H_5)_3N$.

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Experimental

Starting reagents and solvents. All the starting substances including tetraphenylphosphonium chloride were produced by Aldrich. $NaBH_4$ 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]. $LiBH_4$ (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 $BH_3{\cdot}(C_2H_5)_3N$ was 95 ml (106 g, 85% calculated for $LiBH_4$). $n_D^{20} = 1.4425$.

Salts of $B_3H_8^-$ 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. ^{11}B and $^{11}B\{^1H\}$ 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 $(Ph_4P)_2[B_9H_9]$. Compound $Cs_2[B_9H_9]$ was preliminarily synthesized by "dry" pyrolysis of caesium octahydrotriborate [1]. Caesium octahydrotriborate (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 $Cs_2[B_9H_9]$ was dissolved in a minimal quantity of water alkalized with CsOH to pH 11, and $(C_6H_5)_4PCl$ (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, tetraphenylphosphonium nonahydro-*closo*-nonaborate (2.16 g, 2.76 mmol) was obtained. $^{11}B\{^1H\}$ NMR spectrum (CH_2Cl_2, δ, ppm): –2.38, –20.13; IR spectrum (suspension in vaseline oil), KBr, cm^{-1}: 2445w, 2416w, 2397w (ν_{BH}), 997m (δ_{BBH}), 724w (δ_{BBB}), yield 63%.

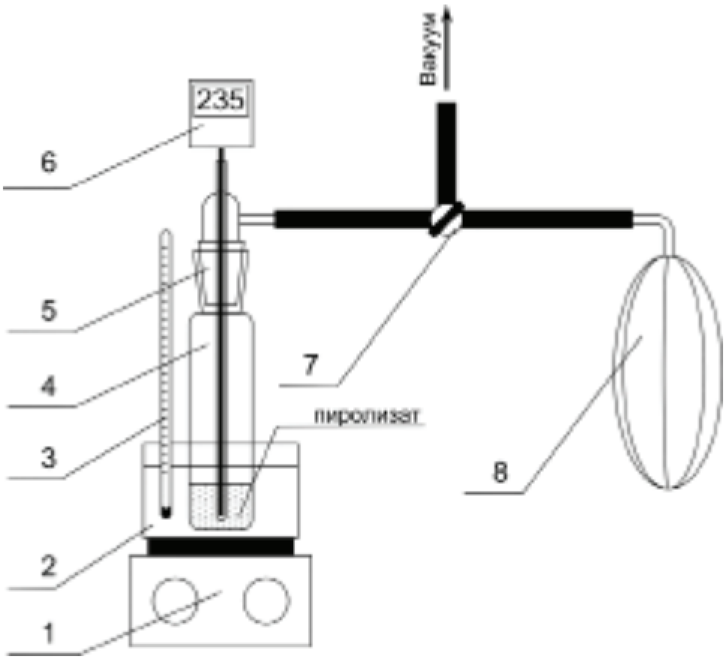


Figure 1. Installation for pyrolysis: 1 – electric heater; 2 – bath with Wood's alloy; 3 –mercury thermometer; 4 – test tube with ground glass joint; 5 – adapter with soldered tube for thermometer and with branch; 6 − digital thermometer; 7 − three-way cock; 8 − rubber squeeze bulb.

Interaction of $\{(C_6H_5)_4P\}_2[B_9H_9]$ *with* $BH_3\cdot(C_2H_5)_3N$

Method 1 (with an excess of $BH_3\cdot(C_2H_5)_3N$). $(Ph_4P)_2[B_9H_9]$ (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_2Cl_2 gave 0.21 g of $(Ph_4P)_2[B_{12}H_{12}]$: $^{11}B\{^1H\}$ NMR (CH_2Cl_2, δ, ppm): –14.98; IR spectrum (suspension in vaseline oil, KBr, cm^{-1}): 2474s, 2439s (ν_{BH}), 999m (δ_{BBH}), 723s (δ_{BBB}) and 0.19 g of $(Ph_4P)_2[B_{10}H_{10}]$: $^{11}B\{^1H\}$ NMR (CH_2Cl_2, δ, ppm): –0.52, –28.67; IR spectrum (suspension in vaseline oil, KBr, cm^{-1}): 2478s, 2435s (ν_{BH}), 995m (δ_{BBH}), 719s (δ_{BBB}).

Method 2 (with a deficit of $BH_3\cdot(C_2H_5)_3N$). $(Ph_4P)_2[B_9H_9]$ (0.5 g, 0.64 mmol) was added to 5 ml of toluene. Then borane triethylamine complex (0.095 ml, 0.64 mmol, ρ = 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}B NMR it consisted of $(Ph_4P)_2[B_9H_9]$: $^{11}B\{^1H\}$ NMR (CH_2Cl_2, δ, ppm): –2.38, –20.13; IR spectrum (suspension in vaseline oil, KBr, cm^{-1}): 2445s, 2416s, 2397s (ν_{BH}), 997m (δ_{BBH}), 724s (δ_{BBB}); $(Ph_4P)_2[B_{10}H_{10}]$: $^{11}B\{^1H\}$ NMR (CH_2Cl_2, δ, ppm): –0.50, –28.66; IR spectrum (suspension in vaseline oil, KBr, cm^{-1}): 2478s, 2435s (ν_{BH}), 995m (δ_{BBH}), 719s (δ_{BBB}) and $(Ph_4P)_2[B_{12}H_{12}]$: $^{11}B\{^1H\}$ NMR (CH_2Cl_2, δ, ppm): –14.99; IR spectrum (suspension in vaseline oil, KBr, cm^{-1}): 2474s, 2439s (ν_{BH}), 999m (δ_{BBH}), 723s (δ_{BBB}).

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 $[B_9H_9]^{2-}$ anion. The structure nonrigidity accounts for the lower stability of $[B_9H_9]^{2-}$ 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].

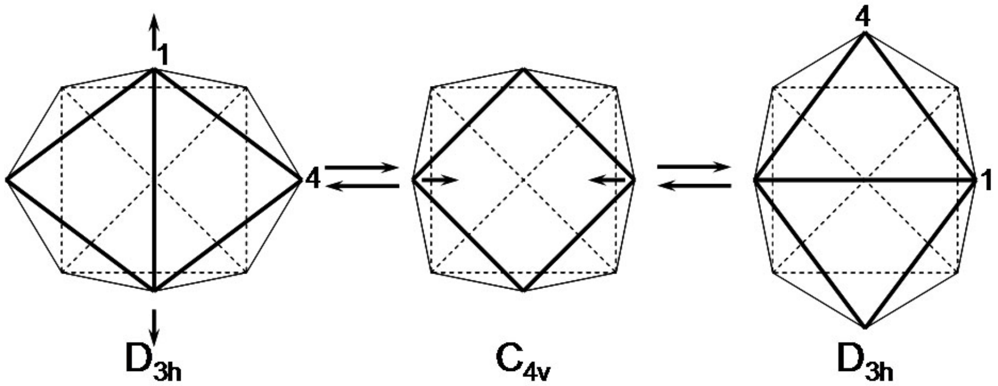
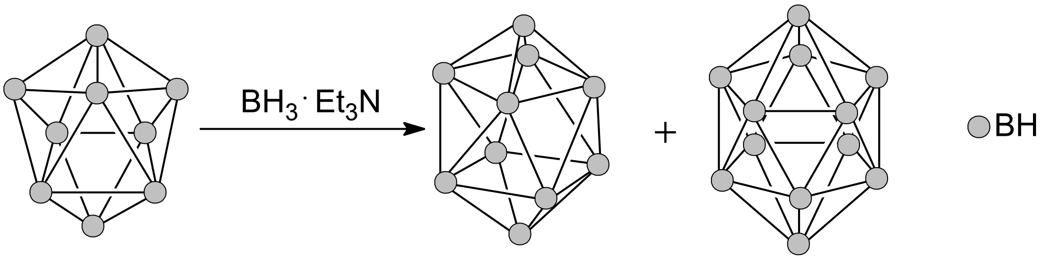


Figure 2. Scheme of a RSR (rhombus-square-rhombus) rearrangement in $[B_9H_9]^{2-}$ anion.

Practical confirmation of the capability of undergoing such rearrangements was obtained in works [13, 14]. The intermediate in them is the C_{4v} form of $[B_9H_9]^{2-}$ 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 $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$ 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 $^{11}B\{^1H\}$ 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.

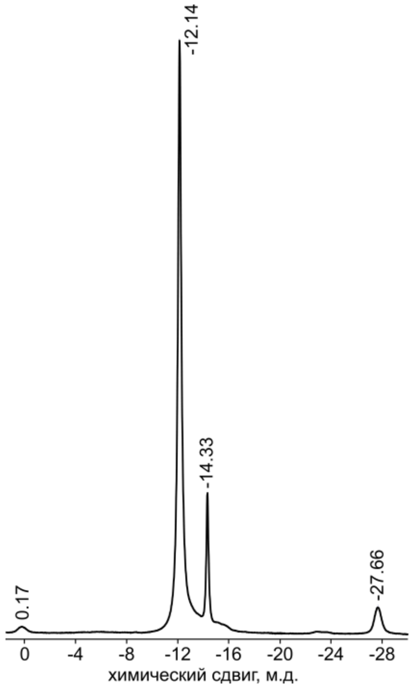


Figure 3. $^{11}B\{^1H\}$ NMR spectrum of the reaction mixture in dimethylformamide.
[химический сдвиг, м.д. means Chemical shift, ppm]

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 $^{11}B\{^1H\}$ 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 $[B_{12}H_{12}]^{2-}$ anion (–14.99 ppm) with the ratio of integral intensities 1:4:1.2. Thus, the molar ratio of *closo*-decaborate and *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 $[B_9H_9]^{2-}$ anion (–2.38 and –20.13 ppm).

Thus, the processes of homonuclear polyhedral extension studied by us are a basis for the development of methods for the preparation of *closo*-borates $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$, as well as their substituted derivatives. Note that at this stage of research we did not succeed in creating an approach enabling to prepare $[B_{10}H_{10}]^{2-}$ anion from $[B_9H_9]^{2-}$ anion in rather high selectivity because of the certain structural non-rigidity of $[B_{10}H_{10}]^{2-}$ anion and its tendency to processes of polyhedral extension.

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