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Studies on synthesis of boron and carborane cage derivatives

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ARTICLE INFO

Article history:
Received 01 November 2019
Received in revised form 02 January 2020
Accepted 11 February 2020
Available online 29 March 2020

Research Article

DOI: 10.30728/boron.641589

Keywords:
Borane,
Carborane,
Decaborane,
Dodecacarborane,
Undecaboran.

ABSTRACT

Weakly coordinating anions are extremely versatile species for capturing and characterizing cationic intermediates. Among these anions, carboranes and some boranes are known to be the most weakly coordinating anions. In this study, the carboranes and boranes were synthesized in order to use in different fields. $B_{11}H_{14}$- was synthesized from $NaBH_4$ and used to synthesize $CB_{11}H_{12}^-$. $CB_{11}H_{12}^-$ was synthesized by carbene addition to undecaborate. $B_{11}H_{14}^-$ was converted to $B_{10}H_{14}$ by oxidation and extrusion of one boron vertex. $CB_{11}H_{12}^-$ was methylated on boron vertex to get $HCB_{11}Me_{11}^-$. The methylated carborane cages are more hydrophobic and weakly coordinating anions.

1. Introduction

Boron and boron containing materials are already in use in various areas in today's modern life. One of the important boron containing chemicals is carborane. Although carboranes do not have immediate daily uses, they are constantly being researched to find use for them. In Turkey, recently such a quest has been embarked on. Nevertheless, until this study, carborane production has not been performed in Turkey to our best of knowledge. Sales of carboranes have many limitations because of their usage in defense industry as a military goods [1]. Besides many limitations, their high cost is an another factor that limiting studies about them. Despite all of these difficulties, carboranes and their derivatives have a very important role in the development of wide array of new materials.

Carborane clusters were produced in ZIP, HEF projects during World War II [2]. They are known as a high energy density materials and used as propellants for high burning composites [3,4]. Lithium rechargeable batteries are another field that dodecaborane derivatives can be used [5-7]. Lithium salts of dodecahydrododecaborane and dodecachlorododecaborane are examples of them. As mentioned before, boron clusters are thermally stable and polymers of dodecaborane and dodecacarbaborane clusters, too [8]. They can be also form non-linear optics materials [9] means liquid crystals at room temperature which can be used for electro-optics and ion selective electrode [10]. Dodecaborane was also studied for nuclear waste purification [11,12] because of its weak hydrogen bonds which can be formed between cluster and metal mono anion and dianion. Being used very much in organic chemistry, dodecaborane and dodecacarbaborane derivatives were also studied in medicinal chemistry. Boron Neutron Capture Therapy (BNCT) has led to this field [13,14]. Nuclear medicine [15], X-ray contrast agent [16-18] are other application areas that dodecaboranes have been used.

1.2. Carboranes

Boron can form many kinds of clusters which are polymeric or cage-like [19]. This study is focused on cage-like structures. High stability through covalent bonds of some boron molecular networks are comparable with carbon's covalent bond stabilities. Elemental boron and borax do not endanger human life but some boron hydrogen compounds have toxic properties hence, need caution during exposure [20].

Formally named as carbaboranes, carboranes are polyhedral molecular clusters of boron and carbon atoms. Despite the classical bonds of carbons in organaboranes, in carborane skeletons carbon atom neighbors 3 to 6 other atoms to stabilize the skeleton structure. Their stability comes from delocalization of electrons through nonclassical (*3c,2e* bonds) covalent bonds. Since mid-1950s, carboranes have been studied because of their bonding types and structures by theoreticians and boron chemists.

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Carborane structure was predicted before its synthesis and reported by William Lipscomb and Roald Hoffmann theoretically [21]. The structure of carboranes were predicted by pioneering of boron hydride chemist Alfred Stock [22]. The first carborane synthesis was performed in the post-World War II era through U.S. government program (i.e ZIP, HEF) to prepare high energy generating compounds of boron hydrides different from hydrocarbons for rocket and aircraft fuels. All of these syntheses were performed in secret in 1950s. Preparations, synthetic methods, and even their existence had not been known until late 1963 when they were reported in literatüre [23-33]. Idea of reality of carborane came after the discovery and isolation of the $B_{12}H_{12}^{2-}$ dianion by Pitochelli and Hawthorne as a $C_2B_{10}H_{12}$ cluster [34]. The number of carbons can vary in these structures. Widespread numbers are 1 or 2 for carbon atom but 3 and 4 even 5 and 6 carbon containing boron clusters have been observed (not isolated) [2].

1.2. $CB_{11}H_{12}^-$ anion

$CB_{11}H_{12}^-$ anion can be characterized by delocalized electron deficient bonding and skeletal bonds mostly known as low electron density bonds. $CB_{11}H_{12}^-$ has special stability; CH and BH^- units are isoelectronic of each other.

1.2.1. Synthesis of $CB_{11}H_{12}^-$ anion

$CB_{11}H_{12}^-$ can be synthesized with different methods and different smaller boron or carbon containing clusters such as from $B_{10}H_{14}$ which synthesis method and structure was proven [35,36]. These different methods are Boron insertion, carbon insertion, boron extrusion and carbon extrusion methods.

1.3. Boron insertion

Knoth was first scientist who has synthesized $CB_{11}H_{12}^-$ by boron insertion to $CB_{10}H_{13}^-$ and had a mixture of $CB_{11}H_{12}^-$ and CB_9H_{10} [37] (Scheme 1).

First development for Knoth's method was done by Heřmánek and his group [38]. $B_{10}H_{14}$, decaborane, was again used as a starting material at the last steps, instead of conversion of trimethylamine to hydrogen, like in Knoth's experiments, Heřmánek's group closed the cluster by addition of $(CH_3CH_2)_3NBH_3$ at 200 ºC. However, observations showed that one methyl group of amino was lost during this step, hence by the addition of dimethylsulfate, amino group trimethylated again and reduction was done in liquid ammonia by sodium to synthesize $CB_{11}H_{12}^-$. This method known as a basis method used by Katchem to produce $CB_{11}H_{12}^-$ for commercial porposes [39].

Other modifications came from groups of Fox and Hughes, to improve safer and efficient way [40]. Instead of using cyanide, isocyanides such as tert-butyl isocyanide and cyclohexylisocyanide were used.

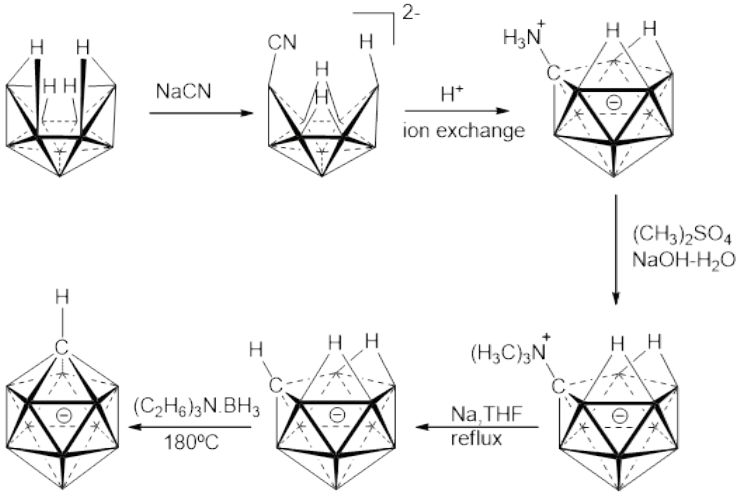
The most convenient method can be the group of Kennedy's method which basically has two steps and started from decaborane (Scheme 2). By taking advance of Brellochs reaction *nido*-decaborane turned to *arachno*-$CB_9H_{14}^-$. Then *closo*- cluster was synthesized by addition of $(CH_3)_2SBH_3$ [41] (Scheme 2).

1.4. Carbon insertion

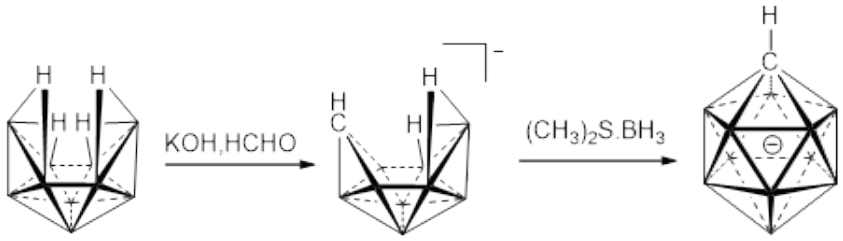
Boron insertion methods are multistep methods; hence carbon insertion can be seen as an easier method. Last added vertex to cluster is carbon in this insertions. Carborane can be synthesized from $B_{11}H_{14}^-$ by dichlorocarbene insertion [42]. Carbenoid formation mechanism in the process is not proven yet. However, DFT calculations on reaction pathway was done and accepted by scientists [43].

1.5. Carbon extrusion and boron extrusion

Carbon extrusion reactions are based on loss of carbon vertex from supercarboranes. Having more than twelve vertices on carboranes named them as super-

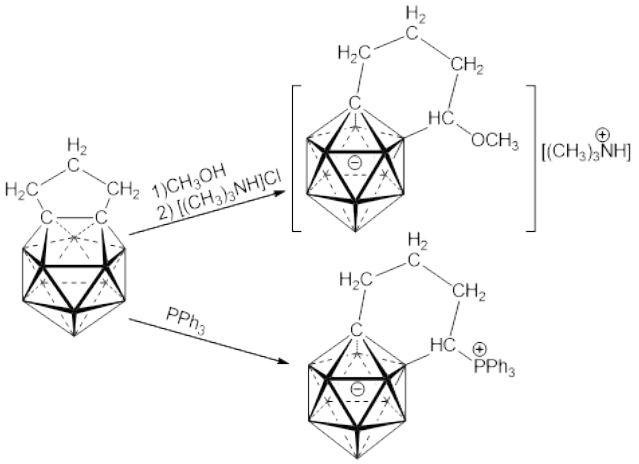


Scheme 1. Knoth's synthesis. Other vertices are B-H.



Scheme 2. Kennedy synthesis. Other vertices are B-H.

carboranes. 1,2-$(CH_2)_3$-1,2-$C_2B_{11}H_{11}$ is 13-vertex carborane which was transformed to a 12-vertex carborane also changed its position from *endo*- to *exo*- by treating with different kind of bases [44,45] (Scheme 3).



Scheme 3. Carbon extrusion reactions. Other vertices are B-H.

Even if carbon atom extrusions from carborane clusters seem rare reactions, they had been observed in different studies which were summarized by Maik Finze [46].

Boron extrusion reaction was observed with carbon atom extrusion while 2,3-$(CH_2)_3$-2,3-$C_2B_{12}H_{12}$ cluster converted from 14-vertex carborane to 12-vertex CB_{11} cluster [47].

2. Materials and methods

Caution ! During these reactions all required precautions should be taken! Gas mask, gloves, lab clothes and goggles should be used. All experiments should be done under good ventilated hood.

Structural determinations of compounds were done with the instruments as written below. ^{1}H and ^{13}C nuclear resonance spectra of compounds were recorded in $CDCl_3$, d_6-DMSO, d_6-Acetone and D_2O with Bruker Avance III Ultrashield 400 MHz NMR spectrometer. ^{11}B NMR spectra of compounds were recorded in 5 ml d_6-Acetone and D_2O with Magritek Spinsolve benchtop 60 MHz NMR spectrometer and also with Agilent Premium 600 MHz compact NMR Spectrometer. NMR spectra were processed with MestReNova processor. Infrared spectra were recorded with Thermo Scientific Nicolet iS10 ATR-IR spectrometer. Peak positions were reported in reciprocal centimeter (cm^{-1}). IR spectra were further processed with OriginPro 2016 program.

All starting materials and solvents were purchased from Sigma Aldrich/Merck and were used without further purifications.

2.1. Synthesis of [Na^+][nido-$B_{11}H_{14}^-$], (1) [48]

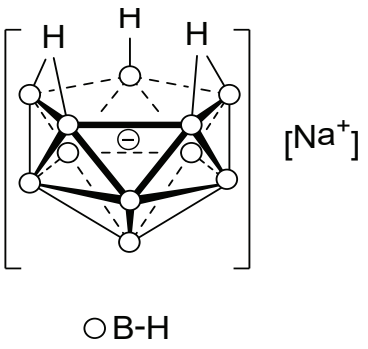


Figure 1. Molecular structure of [Na][$B_{11}H_{14}$].

$NaBH_4$ (60.00 g, 1.59 mol) was added into three necked round bottom flask and a big stirring bar was used to stir reaction. One neck of the round bottom flask was used for dropper, second one closed with septum and used for solvent addition. Argon gas was purged through all the setup and diglyme (450.00 ml) was taken with syringe from sealed diglyme glass bottle and was added to the round bottom flask. Reaction was stirred and heated until 105 ºC. Dropping funnel was filled with $BF_3.O(C_2H_5)_2$ (250.00 ml, 2.03 mol) and when reaction temperature rich to 105 ºC, $BF_3.O(C_2H_5)_2$ addition was started drop by drop from dropping funnel. Precipitates were formed during addition. After completion of addition reaction was stirred one more hour at 105 ºC, then cooled to room temperature. Reaction color was yellow. Reaction solution was filtered from medium frit with pump. Until all precipitates were formed to white color, they were washed with diglyme (approximately 100 ml of diglyme). Our product was in diglyme solution and without isolation it was used for further reaction. In Figure 1, molecular structure of the product was given.

Caution! During this reaction because of hydrogen

evolution and other small boron cages, acetone trap should be used and all required precautions should be taken before starting to this experiment.

2.1.1. Cation exchange of Compound 1 from Na^+ to $(CH_3)_3NH^+$

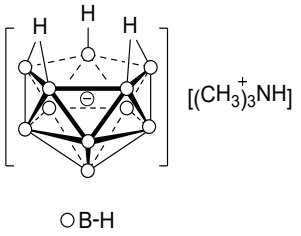


Figure 2. Molecular structure of $[(CH_3)_3NH][B_{11}H_{14}]$, (1).

Diglyme solution of sodium salt of compound **1** was evaporated until half of it evaporated with rotary vacuum evaporator and drop by drop deionized water (225 ml) was added and continued to evaporation of azeotrope solution (diglyme and water). This step was repeated six times until all diglyme was evaporated. $(CH_3)_3N.HCl$ (40.00 g, 0.40 mol) was added in to the homogeneous solution of compound **1** (sodium salt) and water. Immediately white crystals were formed and collected with filtration by using gapump filtration. For further purification acetone recrystallization or washing with diethyl ether to remove yellow impurities can be done. Crude product was 30.25 g. After purification yield was 28.65 g, 0.148 mol, 79 %. ^1H NMR in d6-acetone; 0.75-2.5 ppm (m). ^{11}B NMR in d_6-acetone; -14.11 (B-H), -15.99 (B-H) and -16.72 (B-H) ppm. In Figure 2, molecular structure of the product was given.

2.2. Synthesis of $[(CH_3)_3NH^+][closo\text{-}CB_{11}H_{12}^-]$, (2) [42]

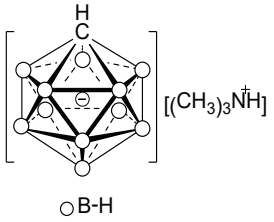


Figure 3. Molecular structure of $[(CH_3)_3NH][CB_{11}H_{12}]$, (2).

2.2.1. Method 1

Trimethylamine salt of compound **1** (6 g, 31.06 mmol) was dissolved in fresh distilled THF (120.00 ml) in the one necked round bottom flask. Argon gas was given to reaction and reaction medium was cooled to 0 ºC in an ice bath. NaH (60 w%, 20.00 g, 0.53 mol) was firstly washed with hexane (50 ml) to remove mineral oil and added to reaction slowly at 0 ºC. Remaining NaH solution was washed with ethanol. After 30 min stirring at room temperature. THF was evaporated to dryness under reduced pressure. After evaporation 100 ml THF and 5 ml $CHCl_3$ were added slowly and respectively to reaction. Reaction mixture was stirred for 2 hours at room temperature and ethanol (10 ml) was added drop by drop at 0 ºC in the ice bath and continued to stir reaction solution for 4 hours at ambient temperature. All reactions were performed under argon atmosphere. Deionized water (150 ml) was added drop by drop and THF was evaporated under reduced pressure. The reaction solution was acidified by addition of HCl (37 v%, 25.00 ml in 40.00 ml deionized water). Acidification was monitored with blue litmus paper. Residual THF and ethanol were also evaporated. $Me_3N.HCl$ (7.00 g, 73.24 mmol) was added to aqueous reaction mixture and white precipitates were formed. Solution was filtered and precipitates were collected. For further purification, methanol/hot water (1:9) recrystallization was done to yield 1.5 g of compound **2**. In Figure 3, molecular structure of the product was given.

2.2.2. Method 2

Diglyme solution of compound **1** (50 ml solution; asumed that solution has 2.00 g, 13.00 mmol $NaB_{11}H_{14}$) was taken with syringe and added into the 250 ml round bottom flask which is closed with septum and filled with argon gas. Reaction was stirred at 0 ºC in an ice-bath. NaH (4.40 g, 0.18 mol) was taken in a small beaker and washed with 20 ml distilled hexane. By decantation hexane and NaH was separated and nearly dry NaH was slowly added to the round bottom flask with spatula. After addition was completed, flask closed with septum and argon gas was given in a medium. Then, ethanol (10.00 ml) and $CHCl_3$ (5.00 ml) was taken in a same syringe and two reagents were mixed and added drop by drop to the round bottom flask at 0 ºC. Reaction was stirred at room temperature for overnight, then solvent was evaporated under reduced pressure. Water (40.00 ml) was added for solvent exchange and continued to evaporation to complete removal diglyme evaporation. After evaporation yellow precipitate was acidified with 37 v% 8.00 ml HCl in 60.00 ml water. Me_3NHCl (12.00 g, 0.13 mol) was added to water solution of the reaction and white precipitates were formed. Solution was filtered and precipitates were collected. For further purification, methanol/hot water (1:9) recrystallization was done to yield 1.02 g in overall reaction. ^1H NMR in d_6-acetone; 0.75-2.5 ppm (m), ^{13}C NMR in d_6-acetone; 47.5 ppm. ^{11}B NMR in d_6-acetone; -16.00 ppm (B-H),-14.00 ppm (B-H),-7.00 ppm (B-H). The IR spectrum consists of absorptions at 2500 cm^{-1}(vs) for B-H streching.

2.3. Synthesis of nido-$B_{10}H_{14}$, (3)

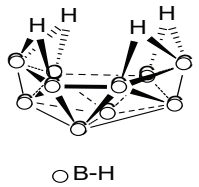


Figure 4. Molecular structure of $B_{10}H_{14}$, (3).

Caution! *Nido*-$B_{10}H_{14}$(decaborane) is neurotoxic matter. All lab safety equipments should be used. Most importantly proper gas mask has to be used.

2.3.1. Method 1

$NaBH_4$ (60.00 g, 1.59 mol) was introduced in 2000 ml 3 necked round bottom flask, then argon gas was given to the medium and diglyme (500.00 ml) was added by syringe. Pressure equilized dropper, condenser and gas inlet was used from necks. Reaction was heated to 105 ºC. Dropping funnel was filled with $BF_3.O(C_2H_5)_2$ (250 ml, 2.026 mol) and when reaction temperature reached to 105 ºC, $BF_3.O(C_2H_5)_2$ addition was started drop by drop from dropping funnel over 6 hours. Precipwww itates were formed during addition which were $NaBF_4$. When addition finished, reaction was stirred for 1 more hour at 105 ºC and then cooled to room temperature. Condenser was changed with simple distillation apparatus and deionized water (totally 1200 ml) was added drop by drop while the oil bath was heated until 130 ºC. After collecting 1200 ml diglyme-water azeotrope solvent, reaction was cooled down to room temperature and taken into the ice bath. $FeSO_4.7H_2O$ (4.80 g, 17.27 mmol) and 250 ml cyclohexane were added. 35 ml H_2SO_4 in 35 ml deionized water was cooled in fridge, then filled to the dropper and added drop by drop to the reaction medium in an ice bath. After finishing this addition, H_2O_2 (72.00 ml, 30 v%) was added to the dropper and added very slowly to the reaction medium in an ice bath. Reaction was stirred 1 more hour at room temperature and filtered using filter paper. Reaction flask was washed with 2*40 ml cyclohexane and poured over the filter cake. Then filter cake was washed with 100 ml more cyclohexane which is combined with filtrate. Then collected phases (cyclohexane and deionized water phases) were seperated. Cyclohexane phase was washed with 5*50 ml deionized water. At the next step, distillation was done from cyclohexane phase which was took 2 days. Distillation was done under argon gas and continued until approximately 50 ml solvent was stayed. Solution was kept at -18 ºC for over night. Formed crystals were filtered and dried in hood (2.5 g). ^{1}H NMR in d_6-acetone; 0-1.41 ppm (m), 2.42-4.41 ppm (m), ^{11}B NMR in d_6-acetone; -35.79 ppm (B-H),-0,59 ppm (B-H), 11.13ppm (B-H), 19.41 ppm (B-H). In Figure 4, molecular structure of the product was given.

2.3.2. Method 2

$NaBH_4$ (30.00 g, 0.79 mol) was introduced in 500 ml 2 necked round bottom flask, then argon gas was given to the reaction medium and diglyme (250.00 ml) was added by syringe. Reaction was heated to 105 ºC. Dropping funnel was filled with $BF_3.O(C_2H_5)_2$ (195.74 ml, 1.59 mol) and when reaction temperature reach to 105 ºC, $BF_3.O(C_2H_5)_2$ addition was started drop by drop from dropping funnel over 8 hours. Precipitates were formed during addition. Reaction was stirred for 1 more hour at 105 ºC and cooled to room temperature. Condenser was changed with simple distillation apparatus and deionized water (totally 785 ml) was added drop by drop while the oil bath was heated until 125 ºC. After collecting 1 L diglyme-water azeotrope solvent, reaction was cooled down to room temperature and taken into the ice bath. $FeSO_4.7H_2O$ (2.5 g, 8.99 mmol) and 125 ml cyclohexane were added. 18 ml H_2SO_4 in 18 ml deionized water was cooled in fridge, then filled to the dropper and added drop by drop in an ice bath. After finishing this addition, H_2O_2 (40.00 ml, 30 v %) was added to the dropper and added very slowly to the reaction in an ice bath. Reaction was stirred 20 more minutes in an ice bath and filtered using filter paper. Filter cake was washed with 100 ml cyclohexane and cyclohexane phase washed with water (4*40 ml), then evaporated at room temperature until crystal formation was observed and kept in fridge until crystallization was completed. Yield of this reaction was not determined because of neurotoxic property of decaborane. It is kept in cyclohexane and never dried or exposed to air. It was treated with acetonitrile for the next steps.

2.4. Synthesis of bis-(acetonitrile)-decaborane $(CH_3CN)_2B_{10}H_{12}$, (4)

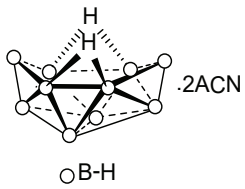


Figure 5. Molecular structure of $(CH_3CN)_2B_{10}H_{12}$, (4).

Compound **3** (from method 2) was kept in cyclohexane in closed round bottom flask. To remove cyclohexane from reaction medium syringe was used and stayed crystals were dissolved in acetonitrile (60.00 ml) and were taken into closed round bottom flask with syringe. Reaction was heated up until 82 ºC and refluxed for 2 hours and stirring was continued for one day at ambient temperature. By decantation solvent was removed from solids. Resultant product was 3.98 g. ^{11}B NMR in d_6-acetone; -40.00 ppm (B-H),-20.00 ppm (B-H), 0.00 ppm (B-H). The IR spectrum consists of absorptions at 2500 cm^{-1}(vs) for B-H streching. In Figure 5, molecular structure of the product was given.

2.5. Synthesis of undecamethyl-closo-dodecacarbaborate, $[(CH_3)_3NH^+][closo\text{-}HCB_{11}(CH_3)_{11}^-]$, (5)

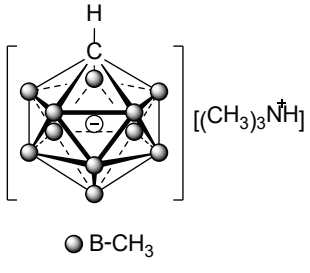


Figure 6. Molecular structure of $[(CH_3)_3NH][HCB_{11}(CH_3)_{11}]$, (5).

Suspension of $[(CH_3)_3NH^+][closo\text{-}HCB_{11}H_{11}^-]$ (0.09 g, 0.44 mmol) in $(CH_3)_3Al$ was prepared in the 50 ml round bottom flask which was flashed with argon and closed with septum. $(CH_3)_3Al$ (2 M in Heptane, 10.00 ml) was added with syringe. Gas outlet was also given to reaction to prevent overpressure medium. Then CH_3I (0.91 ml, 14.56 mmol) was added slowly and round bottom flask was taken into oil bath. Temperature was settled to 45 ºC and stirred for one week. After one week reaction was taken into sand-bath and settled with condenser. Reaction was stirred at 150 ºC for one more week. After this procedure reaction was cooled to room temperature and solvent was evaporated. Solid part was stirred in n-pentane (20.00 ml) for 20 minutes and decantation was done. Ethanol (20.00 ml) was added and stirred for 1 hour at room temperature. Filtration was done with sintered frit glass funnel by vacuum filtration. Solids on sintered frit glass funnel was dissolved with water and $(CH_3)_3N.HCl$ (0.10 g, 1.00 mmol) was added and the reaction solution was stirred. 1 ml CH_3OH was added and kept in hood for crystallization. Formed crystals were filtered and dried on filter paper then, dissolved with acetone (10.00 ml) and the solvent was evaporated. Product was 0.10 g. ^1H NMR Spectrum in d6-acetone; -1.00-0.00 ppm (m) (B-CH_3). In Figure 6, molecular structure of the product was given.

3. Results and Discussion

This study starts with converting $NaBH_4$ into *nido*-$B_{11}H_{14}^-$ anion, inturn, will be converted into decaborane (*nido*-$B_{10}H_{14}$) and *closo*-carboranes.

3.1. Conversion of $NaBH_4$ into nido-$B_{11}H_{14}^-$

This reaction involves $NaBH_4$ treated with $BF_3.O(CH_2CH_3)_2$. While reaction goes on, numerous volatile boron cages which are toxic (as literature indicates) were produced [49]. Therefore, a special reaction setup should be used (*vide infra*).

Na^+ salt of undecaborate (*nido*-$B_{11}H_{14}^-$) anion was synthesized according to Dunks' method [48]. Dunks and co-workers used mechanical stirrer, reservoir, pump, receiver and dry ice condenser which form very complicated setup for this synthesis. So, setup was simplified during previous works to reduce the expenses and to eliminate time-consuming steps within the safety rules. Our setup is formed from thermocouple magnetic stirrer, oil bath, two-necked round bottom flask, dropper with as equalizer, reflux condenser, trap, acetone trap. Lower boranes are volatile which can be pacified with acetone, so acetone trap has to be used to prevent breathe of unpredictable borane gases in case of their toxicity and presence in air. Stirring rate should be high enough during this reaction to prevent solidifying of precipitates. Using mechanical stirrer might work better. Addition of $BF_3.O(C_2H_5)_2$ should be done slowly to keep *ca.* 0.5 ml/min rate. During this reaction, it was shown in previous studies that there is also $B_3H_8^-$ anion formation [48].

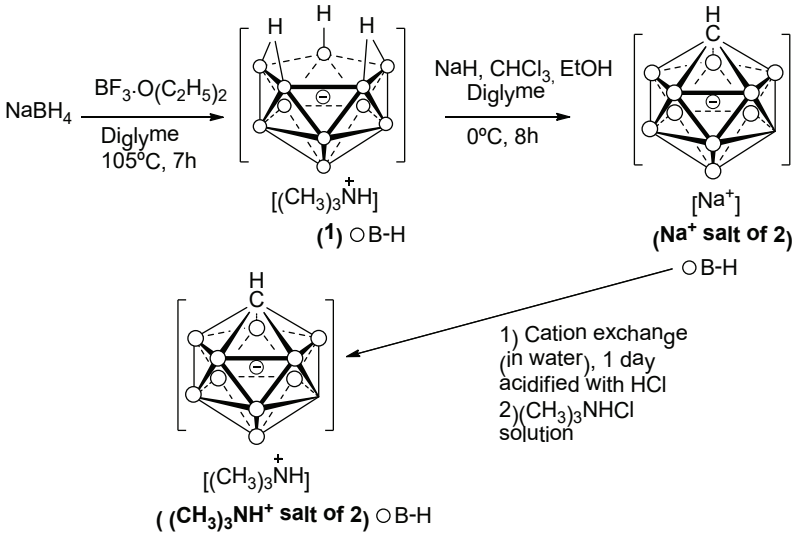
The yield of compound **1** was calculated according to this stoichiometry (Scheme 5). However, this stoichiometry is for $[Na^+][B_{11}H_{14}^-]$, yield (41%, assuming $NaBH_4$ is limiting reagent) was calculated for $[(CH_3)_3NH^+][B_{11}H_{14}^-]$ and assumed all synthesized sodium salts were converted to trimethylamine salt.

Cation exchange reaction was done for Na^+ salt of $B_{11}H_{14}^-$ to isolate this compound from water. Water was chosen as a solvent because $(CH_3)_3NH^+$ salt of *nido*-$B_{11}H_{14}^-$ has limited solubility in water. Na^+ salt of it can easily dissolve in water but trimethylammonium salt of it can be crystallized in water. With the help of water-diglyme azeotrope, diglyme was removed from reaction medium and solvent was exchanged to water. $NaB_{11}H_{14}$ is pyrohoric. Hence, cation exchange reaction was done from Na^+ to $(CH_3)_3NH^+$, not only for isolation of compound but also to make the salt stable. ^1H NMR of *nido*-$B_{11}H_{14}^-$ in d_6-acetone shows, B-H peaks ranging from 0.7-2.5 ppm due to boron coupling. This characteristic of *nido*-$B_{11}H_{14}^-$ ^1H NMR spectrum.

3.2. Synthesis of $[(CH_3)_3NH^+][closo\text{-}CB_{11}H_{12}^-]$, (3)

Before starting the synthesis of $[(CH_3)_3NH^+][closo\text{-}CB_{11}H_{12}^-]$ (**3**), all required precautions should be taken. Synthesis of compound **2** is not easy in terms of safety. That in our laboratory, several minor incidents occurred during this synthesis. The minor accidents could turn into extremely large accidents in the hands of unexperienced researchers. While synthesize compound **3** firstly Michl's method was tried [42]. By dichlorocarbene insertion to compound **1**, compound **2** can be synthesized. As a starting material $B_{11}H_{14}^-$ was preferred because as it was explained above, it can be synthesized in our laboratories. For this synthesis, after three unsuccessful attempt that resulted with explosions, synthesis was successfully achieved. If temperature is ambient temperature, the reaction is so fast that it is difficult to control that the reaction explodes.

The formation mechanism of $CB_{11}H_{12}^-$ was studied by Josef Michl's group using computational methods [43]. Hydride abstracts one proton of cage and borane cage will become dianion. At this step *in situ* formed dichlorocarbene can be attached on boron atom whose proton was taken. At this step there is two different ways that both all them were plausible mechanisms. At the first one, the removal of chloride ion was continued by carbon insertion into the cage which still has one chloride on it. Then, it was assumed that mechanism goes on because of insoluble NaH. NaH continues to abstract protons from cage and with the acidic work-up, cage was closed (Scheme 4). At the second way, which is also possible that has lower activation energy during the removal of chloride ion and also hydronium ion by NaH. But has one more step than first one that cage reconstructs itself.



Scheme 4. Reaction conditions for compound **2** according to Method 1.

Procedure for the sythesis of compound **3** was developed after explosions. Safety should be prior for scientists. *nido*-$B_{11}H_{14}^-$, (**1**), was not isolated in method 2 and reaction was continued in the same reaction flask to synthesis compound **2**.

Above mentioned reaction involves $B_{11}H_{14}^-$ as $(CH_3)_3NH^+$ salt. Then, to synthesize $CB_{11}H_{12}^-$ and separation, this compound was converted back Na^+ salt of it. This process was time consuming and involves risky steps in terms of safety. Therefore, we thought that after $[Na^+][B_{11}H_{14}^-]$ synthesis completed in diglyme and separation of $NaBF_4$ from the reaction mixture, we could treat $NaB_{11}H_{14}$ with NaH *in situ* then, treat them with EtOH and $CHCl_3$. This reaction also yields $[Na^+][CB_{11}H_{12}^-]$. However, the purification steps were lengthy and difficult. Synthesized $[Na^+][B_{11}H_{14}^-]$ was kept in diglyme which was reaction solvent at fridge until next step was achieved. It was assumed that formation yield of $[Na^+][B_{11}H_{14}^-]$ was 100%. Hence, for the next step equivalents were calculated according to this assumption. Reaction solvent was homogeneous and taken portions assumed that have same amounts.

For the synthesis $CB_{11}H_{12}^-$, steps were followed which were explained in experimental part. To avoid any explosion, excess EtOH can be added to the reaction after all additions were completed to inactivate excess NaH. Solution was acidified with HCl to be sure from protonation of carborane cage. After finishing reaction, yellow oily matter was observed which needs purification. Purification steps took many times until obtaining crystals from reaction by recrystallization. All purification steps were done by methanol and water by changing their ratios. Changing ratio did not work so, separation was also done during these crystallizations. Product was as a trimethylammonium salt which can precipitated in water and can be dissolved in MeOH. After many trials, all solvents were combined in order not to lose any product and then evaporated. After evaporation, 30 ml MeOH was added and oily matter was tried to be dissolved. Then filtration was done. 20 ml more MeOH was also added to wash undissolved oily substance. Dissolved part was yellow and residual matter was white. Collected MeOH phase was evaporated until approximately 5 ml solvent was left in the flask and 30 ml deionized water was added. Solution was kept at hood for two days to observe crystals. Formed crystals were filtered and same procedure was applied again. In that way, more purified products can be obtained.

3.3. Synthesis and Derivatization of nido-$B_{10}H_{14}$, (3)

For the synthesis of *nido*-$B_{10}H_{14}$, $NaB_{11}H_{14}$ is used as a starting material and was used as synthesized without any isolation and purification. For the next step, water-diglyme azeotrope was used to remove diglyme from reaction medium by solvent exchange reaction. Dunks and coworkers were also synthesized decaborane(14) and their reaction conditions and setup were modified to our laboratory [50]. Highly complicated and high price glass equipment did not want to use in our laboratory. Setup was designed in a simplest way to do this reaction easily and in a safe manner.

Thermocouple magnetic stirrer, oil bath, two-necked round bottom flask, $NaBH_4$ in diglyme, dropper with gas equalizer, $BF_3.O(CH_2CH_3)_2$, H_2SO_4 aqueous solution and H_2O_2, respectively, condenser, round bottom flask to collect water were used in this step.

While changing reaction setup from reflux to distillation setup, the reaction content was under argon gas. It is important to add water drop by drop in order to prevent bubbling and high pressure because of formation of H_2 and also to maintain same rate with the distillation. It is also necessary to give a vent to distillation apparatus in order not to pressurize the system. Solvent exchange step took three days until collecting

1 L of azeotrope solution. It might better use heating mantle in this step instead of oil bath to do faster distillation. As $B_{10}H_{14}$ is hydrophobic material as it is formed, it is transferred into cyclohexane phase during the reaction. Stirring should be always on and at high rate to maintain homogeneous solution. At this step, solution cannot be kept. It should be separated from water and precipitates. As mentioned before, decaborane is hydrophobic but when it stays in contact with water it starts to decompose to smaller borane cages. Hence, cyclohexane and water phases were separated immediately after filtration of reaction. During filtration more cyclohexane was used to wash precipitates and to collect all the product. Separation was done in extraction funnel and also cyclohexane phase was washed with water in order to remove other water soluble side products which were might still in the cyclohexane solution after filtration like $NaBF_4$, $B(OH)_3$ and Na_2SO_4. The presence of $B_{10}H_{14}$ was confirmed by addition of quinoline in a test tube in 1 ml cyclohexane decaborane solution. This red complex shows us the presence of $B_{10}H_{14}$ [51].

In method 1 for the synthesis of decaborane (compound **3**), after observing a red complex for cyclohexane phase and no red complex for water phase, we assumed that all produced decaborane was in cyclohexane. Because of the hydrophibic properties of the decaborane, cyclohexane phase should be distilled to remove water and excess cyclohexane from the reaction medium. Direct evaporation under reduced pressure of rotavap did not used because of the decaborane explosive properties and do not cause any sublimation of the product during evaporation. Crude decaborane might be explode around 100 ºC. So, distillation setup was used again. Distillation was done in oil bath and the temperature of the oil bath was not increased above 90 ºC and no vacuum was used for distillation. After compliting the distillation approximatly 50 ml cyclohexane phase was removed in reaction medium. Solution was taken from the oil bath and cooled to room temperature. Then kept at -18 ºC for overnight. Next morning formed crystals were filtered and dried in hood.

In method 2, after observing a red complex all decaborane product was converted to acetonitrile-decaborane complex to avoid from toxicity of decaborane and to easily undergo derivatization reaction. The decaborane acetonitrile complex was further characterized with IR spectroscopy. The peak at 2500 cm^{-1} shows the B-H stretching which is characteristic to borane cages. This is consistent with literature [52]. XRD, ^{1}H NMR and ^{11}B NMR results were also taken and given in the method parts. The results are consistent of previously published results. The reactions were summarized in Scheme 5 and Scheme 6.

Decaborane(14) was kept in cyclohexane in order to prevent its contact with air. Hence, cyclohexane was taken with syringe without taken formed crystals from a closed round bottom flask and acetonitrile was added. Crystals were used as they are in method 2, that is, some cyclohexane stayed in reaction the medium. Cyclohexane does not have any effect to next step so, dodecaborane(14) was used as it is. Solution was taken to other closed round bottom flask with syringe for starting to this reaction. 60 ml of acetonitrile was added and condenser was set up upper side of the round bottom flask. Reaction was heated up to 82 ºC with thermocouple and refluxed during 2 hours then stirred at ambient temperature for a day. By decantation all solvent was removed.

3.4. Derivatization of dodeca-closo-carbaborane, $CB_{11}H_{12}^-$

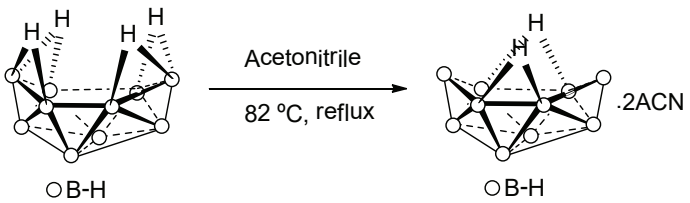
$[(CH_3)_3NH^+][CB_{11}H_{12}^{2-}]$, (**2**) crystals were methylated according to the mentioned procedure. Previously, such a reaction was accomplished with MeOTf [53]. MeOTf is extremely reactive and toxic. Therefore elimination of this chemical from a reaction is desired.

With the addition of $(CH_3)_3Al$ and CH_3I methylation reaction was performed. In this reaction, until addition of CH_3I, dissolvation of reactant could not be observed. The carborane was methylated on borons and observed with ^{1}H NMR spectrum, and this is consistent with published results. CH_3OH can dissolve product

$$17NaBH_4 + 20BF_3.O(C_2H_5)_2 \longrightarrow 2NaB_{11}H_{14} + 15NaBF_4 + 20\ O(C_2H_5)_2 + 20H_2$$

$$2NaB_{11}H_{14} + 20H_2O + 8H_2O_2 + H_2SO_4 \longrightarrow B_{10}H_{14} + 12B(OH)_3 + 18H_2 + Na_2SO_4$$

Scheme 5. Overall reaction for the synthesis of *nido*-$B_{10}H_{14}$.



Scheme 6. Formation of acetonitrile-decaborane complex.

completely and in water $(CH_3)_3NH^+$ salts can be precipitated so, they were chosen as a crystallization solvent with water. Formed crystals were filtered and dried on filter paper. Then, dissolved with acetone (10.00 ml) and solvent was evaporated. Acetone was used to purify product. While waiting for crystallization, little excess amount $(CH_3)_3N.HCl$ can also be precipitated. Hence, acetone was used that only dissolve product and do not dissolve $(CH_3)_3N.HCl$.

4. Conclusions

In this study, feasibility of synthesis of boron cages and carboranes were examined in our laboratories. The synthesis of such cages were successfully synthesized in our laboratories. Eleven vertex boron cages are relatively stable and were synthesized from $NaBH_4$. Synthesis of such compounds are relatively hard and long in terms of safety. This study proved that such synthesis could be done as experience gained with many failed experiments with minor accidents. Reactions were summarized in Scheme 7.

This study also proved that all of the carborane cages could be synthesized from $NaBH_4$, a relatively cheap and easy to handle compound. The hydride was converted to undecaborate cage with action of a Lewis acid, BF_3. Undecaborate was either converted to decaborane through an oxidation reaction or used as it is for the synthesis of $CB_{11}H_{12}^-$. Although these borate sodium salts are soluble in water, their $(CH_3)_3NH^+$ salts are insoluble. This makes isolation of these compounds affordable. The $(CH_3)_3NH^+$ salts are soluble in ethanol and methanol. With $CB_{11}H_{12}$ anion in hand, this compound could be converted to $HCB_{11}(CH_3)_{11}$ anion to increase the solubility of the salts in nonpolar solvents. Such a process previously done with MeOTf and CaH_2 in sulfolane. In this study, we discovered that CH_3I and $Al(CH_3)_3$ could do the methylation on $CB_{11}H_{12}$ anion where hydrides exchange with methyl group. It was also shown that the methylated carborane anion's cation could easily be exchanged with other cations (With this many nacked cations could be prepared in our laboratories.). Such compounds could be used to capture carbocations and characterize them. Decaborane(14) was also successfully synthesized from $B_{11}H_{14}^-$.

In short, this study proved that the strategically important boron and carborane cages could be synthesized in our laboratories. These compounds could also be further derivatized for many potential applications. Such synthesis need to be done by experienced persons. This experience was also gained through this study.

Acknowledgements

We would like to thank BOREN for funding (2018-30-06-30-004). We would also like to thank to METU BAP (YLT-103-2018-3662, BAP-07-02-2017-004-139). We would like to thank to Magritek for some ^{11}B NMR results.

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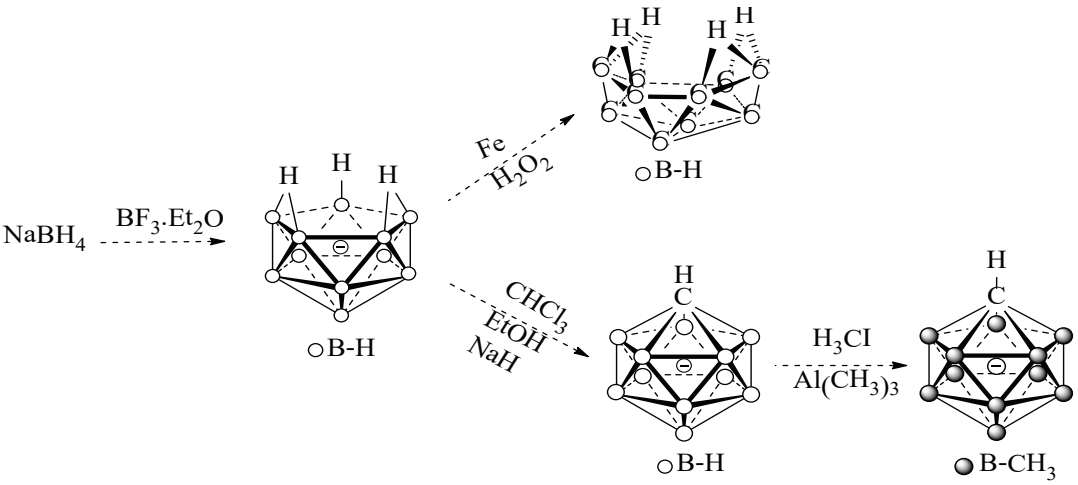

Scheme 7. General reaction scheme.

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