Total Synthesis of $[Cs^+][CB_{11}H_{12}^-]$

Modified from Jeljnek et al. Coll. Czech. Chem. Comm. Vol 49 **1984** p1559

Work in a good fume hood and wear a labcoat, glasses and good gloves.

Step One: Synthesis of 7-trimethylamine-7-carba-*nido*-undecaborane

In a one liter round bottom flask was slurried:

50 mL of pentane or hexanes
12.2 g (0.1 mol) of decaborane
WARNING: Decaborane is extremely toxic and accumulates in the body fat!

The mixture was cooled with an ice bath. **See Note #1**
A solution of

5.4 g (0.11 mol) NaCN
4.4 g (0.11 mol) NaOH
200 mL H_2O

was cooled and slowly added to the slurry with an addition funnel. Care was taken to keep the temperature of the mixture below 20 °C. The decaborane dissolved slowly as it reacted. The solution stirred overnight at room temperature. **See Note #2.**

Note #1 Decaborane decomposes in water above 20 °C and is insoluble in 0 °C water. The temperature control is not absolutely critical, however a colder temperature is preferred.

Note #2 The reaction appears to be slow, probably due to the limited solubility of decaborane in water. Be patient as unreacted decaborane is difficult to separate from the reaction product and causes difficulties when present in the later steps of the synthesis. It is not advisable to increase the scale of this reaction, although
20 g and larger batch sizes are feasible.

After 16 hours, the solution was clear and colorless with an oily component (pentane or hexanes). The solution was cooled with an ice/salt bath to 0°C and

50 mL of conc. HCl

were added dropwise with an addition funnel. **This is VERY DANGEROUS due to the hydrogen cyanide gas generated!!!! See Note #3**

The acidification was verified by litmus paper, and a vacuum adapter was fitted to the flask. Vacuum from a water aspirator was used (IN THE FUMEHOOD) to remove the pentane (or hexanes) and any traces of HCN. The solution became clear and colorless, and the oily character was lost. The solution was cooled to 0 °C and a cold solution of

40 g NaOH
150 mL H_20

was added slowly to the mixture. The solution was stirred vigorously and

33 mL (0.35 mol) Me_2SO_4

with an addition were added slowly with an addition funnel. White precipitate formed immediately upon addition of Me_2SO_4. The reaction stirred overnight. The precipitate was collected on a large sintered glass frit funnel (or buchner). The solid was washed five times with 100 mL of DI water and then two times with 100 mL of ethanol. **See Note #4** The solid product was allowed to dry in the funnel before recrystallizing from ca. 300 mL acetonitrile. A total yield of 16.5 g (87%) of large white crystals was collected in two crops.

Note #3 This step must be performed in a fumehood because acidification liberates toxic hydrogen cyanide gas. As the HCl is added the solution will immediately effervesce. An addition funnel fitted with a hose adapter and hose which vents to a bubbler filled with NaOH solution (to neutralize the HCN) is best. Alternately, HCl can be added in 3mL aliquots by pipet. Close the fume hood for a few minutes after each aliquot is added before adding the next.

Note #4 Dimethylsulphate (Me_2SO_4) is also very toxic. It is extremely important to wash away the excess Me_2SO_4. This material will decompose rapidly if heated and poses an explosion hazard in addition to its toxicity.

Step Two: Preparation of $[Cs^+][CB_{10}H_{13}^-]$

In a 1000 mL 24/40 round bottom flask under argon atmosphere were added

13.7 g of 7-trimethylamine-7-carba-*nido*-undecaborane (FW = 191)
500 mL of THF *(dry and oxygen free)*

To this solution was added 5 g of sodium metal cut into small pieces. The solution was stirred and brought to strong reflux for at least 48 hours. **See Note #1.** A very gentle purge of inert gas helps vent the amine formed during the reaction.

After 48 hours the solution was white and milk-like in appearance with considerable precipitate. The mixture was cooled to room temperature and ethanol (95%, only a few mL are needed) was then added slowly until the solution became clear. The solution was decanted from the excess sodium and saved. Remaining sodium was destroyed with care. **See Note #2**.

To the decanted solution was added:

10 mL of ethanol
50 mL of water

The THF, trimethylamine and ethanol were then removed using a rotoevaporator (**Note #3**).

Another 50 mL of water was then added and the clear colorless solution was acidified with conc. HCl (approximately 25 mL) until blue litmus paper turned red

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Note #1 Reactions have been refluxed for 4-5 days with equally good if not better
results. The reaction length is variable and unpredictable, it is best to follow reaction by ^{11}B NMR.
Note #2 The sodium can be destroyed by carefully using isopropanol, then ethanol, and finally water once no traces of sodium metal are left.
Note #3 A dry-ice trap must be used on the rotoevaporator to capture the amine by-product that remains dissolved in the solution or else the entire laboratory will smell like bad fish.

The solution was then transferred to a 500 mL Erlenmeyer flask and cooled in

ice. (**Note #4**). A black oily precipitate may appear at this point and it can be removed by gravity filtration though a paper funnel. A solution of cesium chloride (10 g / 25mL) was then added to the solution ($NaCB_{10}H_{13}$) and a heavy white precipitate formed. The precipitate (product) was collected by filtration and dried in air. The solution can be reduced and material recrystallized from acetone/water mixtures. Check ^{11}B and ^{1}H NMR for purity (watch out for amine salt contamination). Insoluble material in the product such as cesium chloride and sodium chloride can be removed by dissolving the collected product in a minimum of acetone followed by gravity filtration, removal of the acetone by rotoevaporation, and if necessary recrystallization from hot water. Dry ***in vacuo*** before going on to part three.

Note #4 This solution should be clear and colorless (or almost colorless). Insufficient reaction time or heating will result in a yellow, *gooey* precipitate.

Step Three: Prep. of $CsCB_{11}H_{12}$

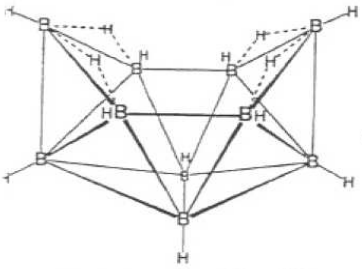
In a 250 mL 24/40 round bottom flask was placed:

7.6 g of Cs $CB_{10}H_{13}$

The flask was evacuated for approx. 30 min. to-ensure good dryness of the material. To the flask was added enough **Et_3NBH_3** to cover the solid. Stir. This mixture was then heated at 190-200°C for 24 hours (**Note #1**).
The progress of the reaction can be monitored by the amount of Et3N produced though 24-48 hours is sufficient for most runs. The volatiles were then removed *in vacuo* and the excess Et_3NBH_3 was recovered and recycled by a "trap-to-trap" distillation leaving a waxy solid. This waxy solid was then triturated with 75mL of toluene and 1 mL, of methanol. Cool to 0 °C, add 100 mL of pentane and filter to collect the product. Wash with more pentane (or hexane). Dry and check ^{11}B NMR. It is also a good idea to check the ^{1}H NMR for the presence of impurities, specifically Et_3NH^+. Recrystallize from water that has a few added pellets of NaOH and CsCl.

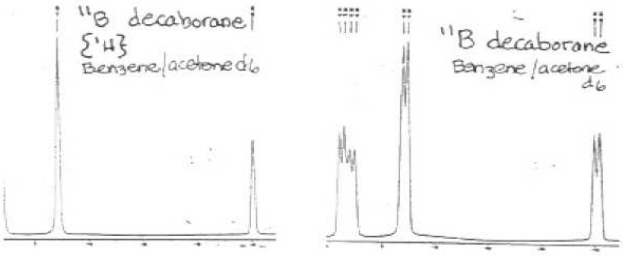
Note #1 Use an air-cooled condenser, then a Dean Stark trap (for the Et3N byproduct), and finally a water cooled condenser with an argon inlet on top. Heat with a reliable silicon oil bath, preferably with a thermostat setup in the fume hood. Do not heat beyond the flash point of the oil!

First Step in the Synthesis: Insertion of Carbon into $B_{10}H_{14}$.



$\xrightarrow{OH^-}$ $B_{10}H_{13}^-$ $\xrightarrow{CN^-}$ $6\text{-}NCB_{10}H_{13}^{2-}$

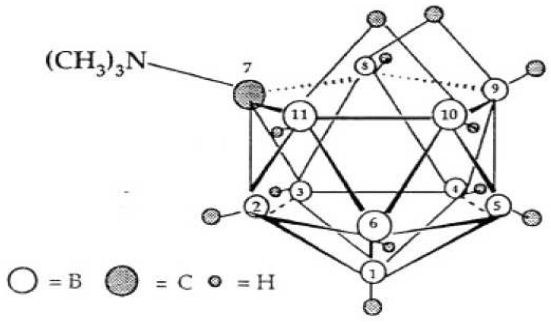
Decaborane, $B_{10}H_{14}$



conc. HCl, 0°C

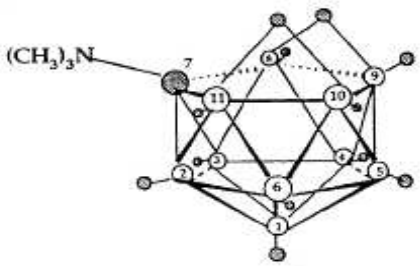
$7\text{-}H_3N\text{-}7\text{-}CB_{10}H_{12}$

OH^-, Me_2SO_4



7-Trimethylamine-7-carba-*nido*-undecaborane, I

Second Step in Synthesis: Reduction of the *nido* Carborane and Formation of it's Cesium Salt.



7-Trimethylamine-7-carba-*nido*-undecaborane, I

3 equiv. Na
THF, reflux

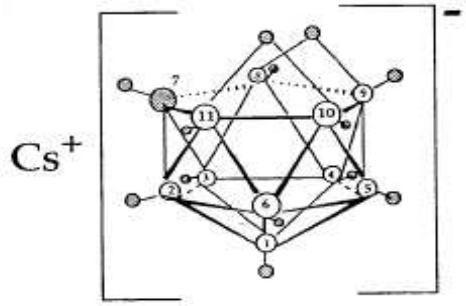
$Na_3B_{10}H_{10}CH$
$+ N(Me)_3 + 1/2\ H_2$

H_2O

$NaB_{10}H_{12}CH$
$+ 2\ NaOH$

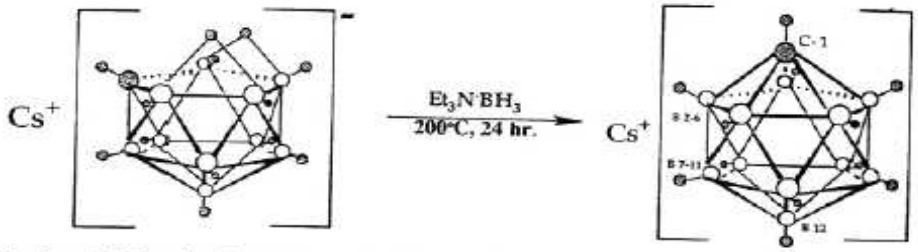
neutralize | CsCl

- NaCl



Cesium Tridecahydrocarbaundecaborate, II
$Cs[7\text{-}CB_{10}H_{13}]$

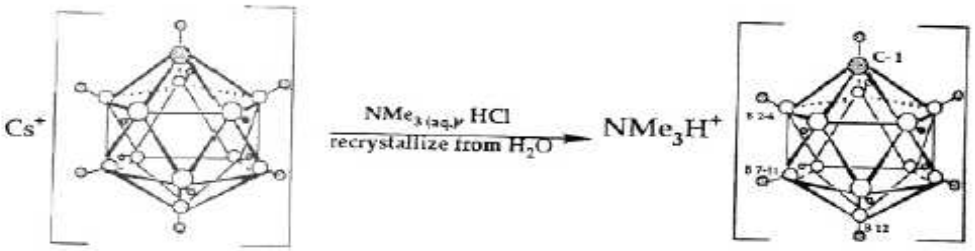
Third Step in the Synthesis- Closing the Cage:



Cesium Tridecahydrocarbaundecaborate, II
$Cs[7\text{-}CB_{10}H_{13}]$

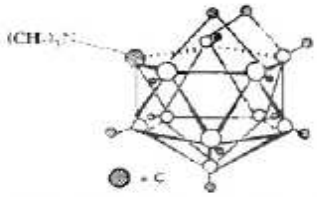
Cesium-1-carba-*closo*-dodecaborane

Making the trimethylammonium salt:

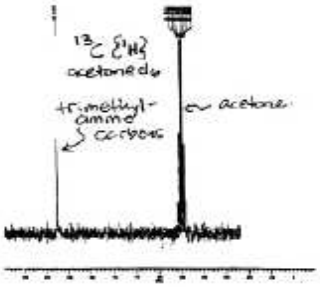


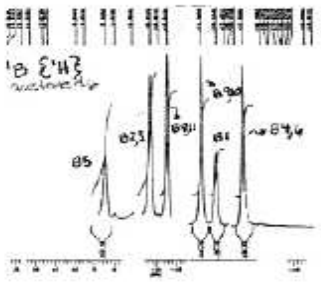
Trimethylammonium-1-carba-*closo*-dodecaborane

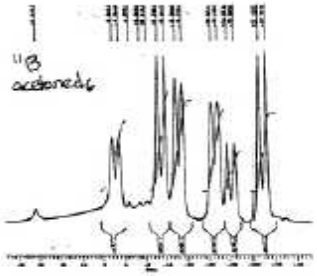
NMR Data for I and II:

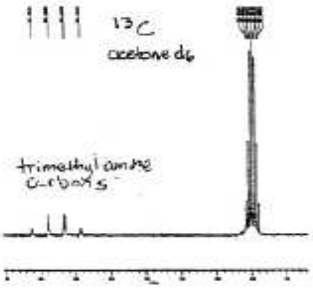


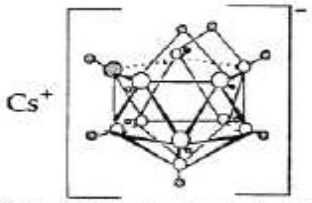
7-Trimethylamine-7-carba-*nido*-undecaborane, I



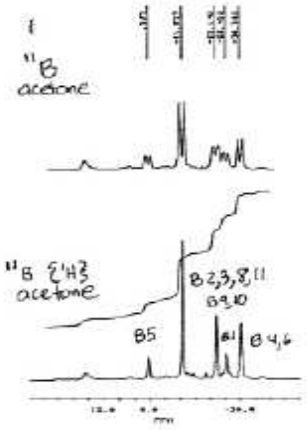




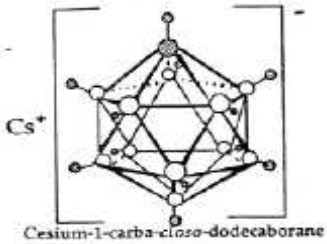




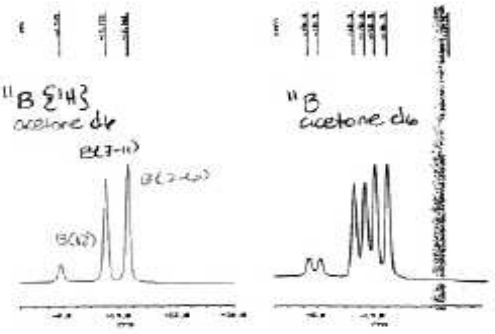
Cesium Tridecahydrocarbaundecaborate, II
$Cs[7\text{-}CB_{10}H_{13}]$

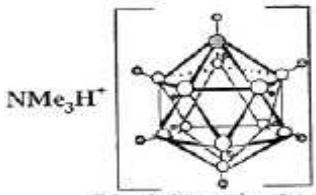


NMR Data for Cs-*closo*-1-[$CB_{11}H_{12}$]and NMe_3H^+-*closo*-1-[$CB_{11}H_{12}$]$^-$



Cesium-1-carba-*closo*-dodecaborane





Trimethylammonium-1-carba-*closo*-dodecaborane