

Supporting Information

for

H^+ , CH_3^+ and R_3Si^+ Carborane Reagents: When Triflates Fail.

Christopher A. Reed

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General: Decaborane(14) was purchased from Katchem (www.katchem.cz). Purity was found to be important. Good quality decaborane is typically a free flowing white powder. If contaminated with pale yellow flakes or clumps, then step 2 in the synthesis of Cs(CHB₁₁H₁₁) typically fails. In that case, the decaborane must be purified by sublimation under vacuum. Small levels of impurities can be tolerated but a recrystallization of the Step 1 product is often necessary.

Air sensitive materials were handled in Vacuum Atmospheres gloveboxes (O₂, H₂O < 1 ppm), segregated according to solvent sensitivity. In particular, the syntheses and handling of silylium carboranes and carborane acids must be carried out in a drybox that is free of donor solvent vapors such as acetonitrile, ethers, alcohols etc.

Tetrahydrofuran was dried over blue Na/benzophenone for at least 2 days and freshly distilled under Ar immediately prior to use. Acetonitrile, benzene, hexane, ortho-dichlorobenzene (ODCB), triethylsilane, and toluene were dried following literature methods and stored in the glovebox over molecular sieves.¹ Bromotriphenylmethane was purchased from Acros Organics and used as received.

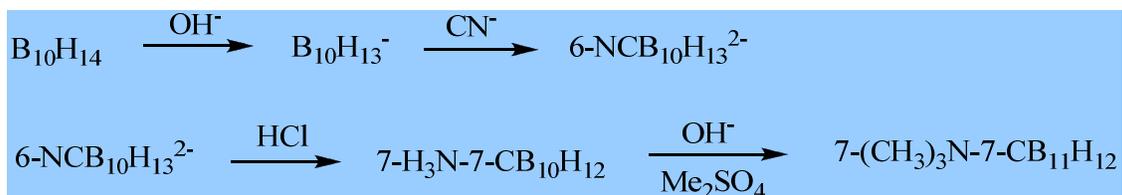
Syntheses are largely adapted from literature preps as indicated in the references below.

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Cs(CB₁₁H₁₂).²

Step One: Synthesis of 7-(CH₃)₃N-7-CB₁₁H₁₂ from B₁₀H₁₄.



- **Caution.** Care must be taken when working with decaborane(14) as it is extremely toxic. All actions performed with decaborane(14) should take place in a well ventilated fume hood and personal safety equipment should be utilized.

A one liter single-neck round bottom flask equipped with a magnetic stir bar was placed in an ice bath that rested on a stir plate and was secured in position. To this flask, 50 mL of pentane or hexanes was added and cooled for approximately 10 minutes. Colder temperatures are preferred because decaborane(14) decomposes slowly in water above 20 °C, but vigilant monitoring of the temperature is not required.

Decaborane(14) (12.2 g, 0.1 mol) was added and the stir bar was activated. A solution of NaOH (5.4 g, 0.11 mol) and NaCN (4.4 g, 0.11 mol) dissolved in 200 mL H₂O was separately chilled in an ice bath for approx. 15 minutes. This solution was then added dropwise to the decaborane(14) slurry via a separatory funnel. The round bottom flask was then packed with a large amount of ice and left to react overnight (12-16 hours). The decaborane(14) dissolves slowly as it reacts and the reaction is finished when no decaborane(14) solid remains. The two liquid phases should be clear and colorless, with an oily appearance at the interface.

The ice bath was refreshed by addition of new ice and salt was added to lower the temperature below 0 °C. The reaction mixture was allowed to cool below 0 °C. An addition funnel with the stopcock in the closed position was fitted via a ground glass joint to the reaction flask and charged with conc. HCl (50 mL). The top of the addition funnel was fitted with a ground glass hose connector which was attached via rubber hose to an inverted filter funnel in a beaker of NaOH (ca. 1M) to trap evolved HCN. The funnel must be clamped carefully just below the surface of the NaOH solution to prevent generation of a vacuum. The HCl solution was then added dropwise to the reaction mixture. Final acidity of the mixture was checked with litmus paper.

- **Caution.** During the addition of hydrochloric acid, effervescence of HCN occurs rapidly. HCN is toxic and caution must be taken to absorb the gas in the NaOH solution and work in a well ventilated fume hood. The NaCN solution should be disposed of in a safe manner.

Working in a fume hood, the pentane or hexanes, along with remnant HCN, was removed under reduced pressure. A single aqueous layer resulted. The round bottom flask was placed into a fresh ice bath and cooled again to 0 °C. An aqueous solution of NaOH (40g in 150mL) was prepared and cooled in a separate ice bath for

approximately 20 minutes. This was added gradually to the reaction mixture via a fresh addition funnel. While stirring vigorously, Me_2SO_4 (33 mL) was added dropwise by addition funnel. Typically, a white precipitate forms immediately, but in some cases there is a few minutes delay. The reaction mixture was stirred overnight.

- **Caution.** Care should be taken when handling the Me_2SO_4 (Carcinogen!). The addition funnel should be washed immediately with water to avoid an explosion hazard.

The precipitate was collected on a large, medium-porosity, glass fritted funnel and washed five times with 100 mL water aliquots and twice with 100 mL ethanol portions. The white solid, 7-(CH_3)₃N-7-CB₁₀H₁₂, was dried on the funnel via aspiration for approximately 2 hours and then recrystallized from acetonitrile (300 mL) (13.7 g, 72%).

The ^{11}B NMR spectrum of 7-(CH_3)₃N-7-CB₁₀H₁₂ in d_6 -acetone shows a pattern of 6 doublets as shown in Fig. 1.

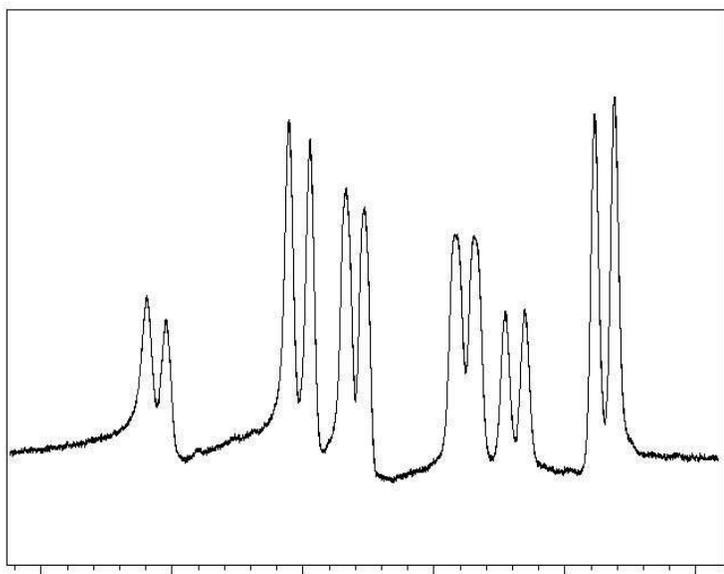


Figure 1. ^{11}B NMR of 7-(CH_3)₃N-7-CB₁₀H₁₂ in d_6 -acetone (unreferenced).

Step Two: Preparation of Cs(CB₁₀H₁₃) from 7-(CH₃)₃N-7-CB₁₀H₁₂.

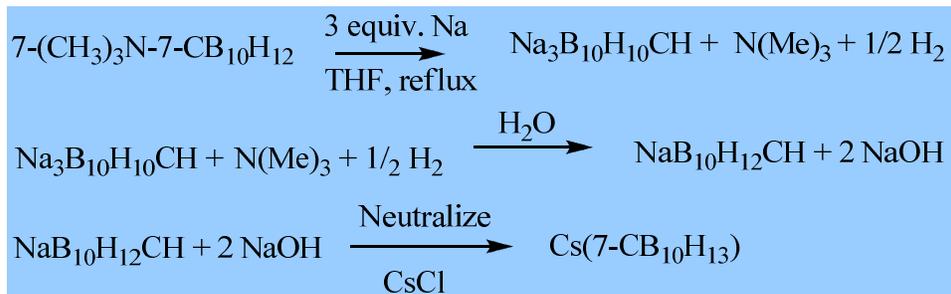
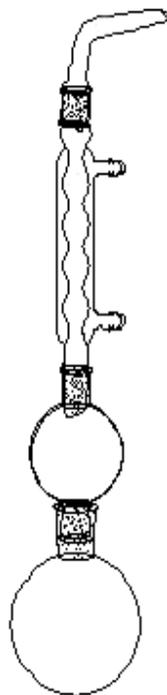


Figure 2. Step 2 apparatus.



Dry conditions are essential for the success of this step. A 2 L round-bottom flask was dried in an oven at 160 °C oven for approximately 3 hours then flame dried over a Bunsen burner. The flask was promptly placed under a dry argon atmosphere. With a magnetic stir bar inside, the flask was charged with 500 mL of dry, oxygen-free THF. The flask was clamped in place with a heating mantle on a magnetic stirrer. Approx. 10 g of sodium metal (cut into ca. 5x5x5 mm cubes) was placed in the round bottom flask, the magnetic stir bar was activated, and 7-(CH₃)₃N-7-CB₁₀H₁₂ (25 g from Step 1) was added with the aid of a wide-mouthed funnel. As shown in Fig. 2, an air condenser, pre-dried in an oven at 160 °C, was added followed by a water condenser. The system was kept under an Ar atmosphere with an oil bubbler vent. The solution was brought to strong reflux and progress was monitored by ¹¹B NMR beginning after 2 days of reaction time. Constant stirring is important and must be maintained to ensure reaction completion. Sometimes the reaction took up to 5 days to complete. A typical spectrum

of an incomplete reaction is shown in Fig. 3. Completion was determined by the presence of 5 rather than 6 doublets as seen in Fig. 4.

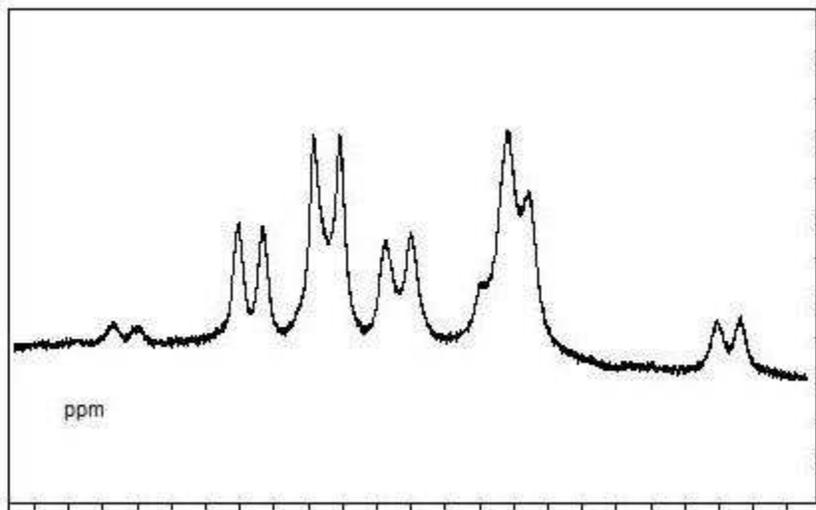


Figure 3. ^{11}B NMR spectrum of incomplete step 2 reaction (unreferenced).

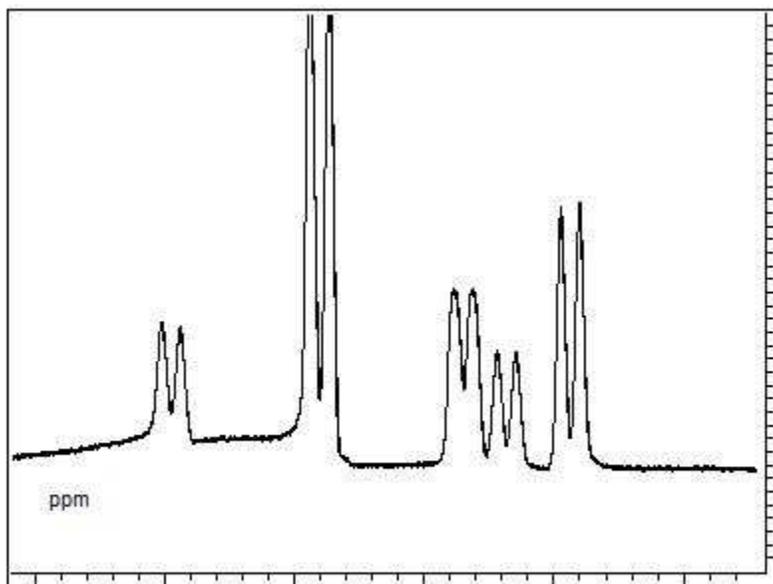


Figure 4. ^{11}B NMR of $\text{Na}(\text{CB}_{10}\text{H}_{13})$ in d_6 -acetone (unreferenced).

After completeness of the reaction had been determined, the milky white liquid containing considerable white precipitate was allowed to cool to room temperature and 95% ethanol was added slowly until the solution became clear (ca. 10 mL). The solution was decanted from any remaining sodium metal into another round-bottom flask and set aside. Occasionally, an ethanol-insoluble black precipitate persists in this reaction mixture. In this case, the solution was gravity filtered through paper.

- **Caution.** The excess sodium metal was destroyed by addition of isopropanol until gas evolution ceased, then 95% ethanol until no sodium metal is seen, and finally water.

To the decanted solution, water (100 mL) and ethanol (20 mL) were added. The solution was then placed on a rotary evaporator to remove the THF, triethylamine, and ethanol. A dry ice trap was used on the rotary evaporator to limit exposure to the evaporated chemicals. The rotary evaporation should be continued until a single layer of liquid is present in the solution. The round bottom flask was removed from the rotary evaporator and water (100 mL) and conc. HCl (50 mL) were added. The solution was verified to be acidic with litmus paper. If an oily black precipitate was present, it was removed by gravity filtration with filter paper. A solution of CsCl (20 g) in H₂O (50 mL) was added and a white precipitate formed immediately. This precipitate, Cs(CB₁₀H₁₃), was then collected on a large, medium-porosity, glass fritted funnel and dried in air.

Using an aspirator, the product was washed through the frit into a fresh 100 mL round-bottom flask by dissolution in acetone (ca. 20 mL). This solution was evaporated to dryness on a rotary evaporator and the product recrystallized from a minimum of boiling water (ca. 200 mL). Large colorless needles of Cs(CB₁₀H₁₃) were collected by filtration on a medium frit after allowing the solution to sit in a refrigerator overnight (23.9 g, 69%).

Step Three: Cs(CB₁₁H₁₂) from Cs(CB₁₀H₁₃).

To a 250 mL round bottom flask, Cs(CB₁₀H₁₃) (7.6 g) was added and placed under vacuum for approx. two hours to ensure dryness. Enough Et₃NBH₃ complex to just cover the solid was added (ca. 20 mL) along with a magnetic stir bar. The flask was then fitted with an air condenser, a Dean-Stark trap, a water condenser, and a ground glass adapter with hose connector, as shown in Fig. 5. The system was put under an Ar atmosphere with an oil bubbler vent.

The reaction mixture was heated in an oil bath whose temperature was thermostatically maintained at 190-200 °C for 48 hours. Excess Et₃NBH₃ was collected in the Dean-Stark trap.

The reaction mixture was allowed to cool and the volatile components were removed *in vacuo*. The resulting waxy solid was triturated with a mixture of toluene (75 mL) and methanol (1 mL). Pentane (100 mL) was added and the product was collected on a large, medium-porosity, glass fritted funnel and washed with pentane. The product was recrystallized from boiling water (ca. 300 mL) containing NaOH (0.5 g) and CsCl (3 g). The ¹¹B NMR spectrum showed 3 doublets as shown in Figure 6.

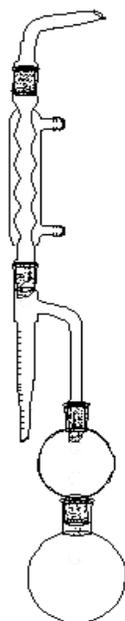


Figure 5. Step 3 apparatus.

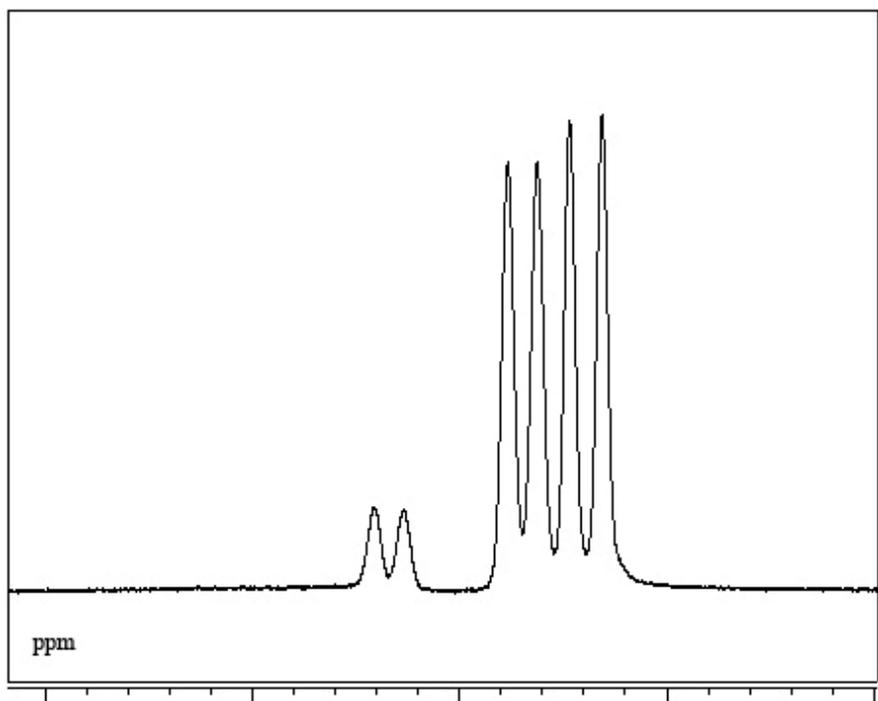
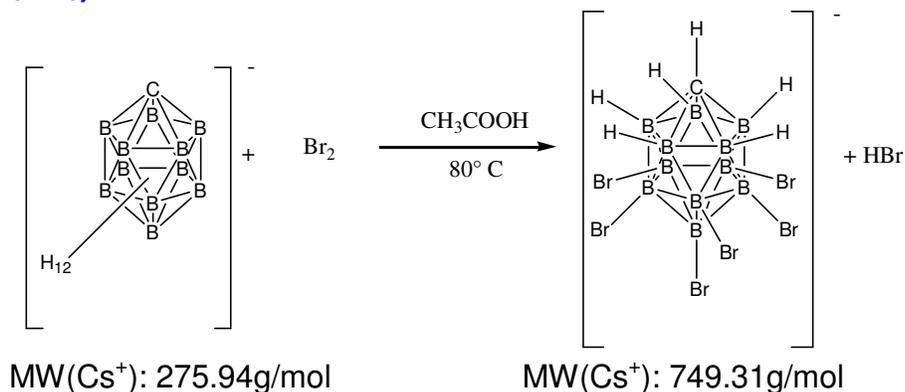


Figure 6. ^{11}B NMR of parent carborane anion $\text{CHB}_{11}\text{H}_{11}^-$.

$\text{Cs}(\text{CHB}_{11}\text{H}_5\text{Br}_6)^{\cdot 3}$



$\text{Cs}(\text{CHB}_{11}\text{H}_{11})$ (4 g) and glacial acetic acid (ca. 50 mL) were placed in a 500 mL three-neck round bottom flask containing a teflon stir bar. The round bottom flask was equipped with an efficient water-cooled condenser to prevent loss of bromine and fitted with a hose adapter above the condenser. Teflon rings were placed on all ground glass fittings to prevent leakage of bromine gas. Teflon tape was also used to seal the outside joints of the glassware. As shown in Fig. 7, a hose fitted with a funnel was attached to this adapter and minimally submerged (to prevent vacuum generation) into an aqueous solution of sodium hydroxide (to neutralize acetic acid vapors) and sodium sulfite (to reduce bromine). A pressure-equalizing addition funnel was then added to another neck and charged with bromine (ca. 15 mL). The third neck was closed to the atmosphere with a rubber septum. Bromine was added gradually over the course of 10 to 15 minutes. Caution must be exercised during this step, since accelerated addition leads to bromine evaporation. Glacial acetic acid (ca. 5 ml) was used to wash residual bromine from the funnel into the reaction mixture. The addition funnel was removed and the neck closed with a rubber septum or glass stopper. The round bottom flask was placed on a magnetic stirrer in a temperature-regulated oil bath in a fume hood and the temperature raised to 80° C.

After 12 hours, the progress of the reaction was monitored every 2 hours by withdrawing aliquots via syringe and determining the ^{11}B NMR spectrum (see Figs. 8 and 9). The reaction typically required a minimum of 24 hours to complete.

The product was isolated by removing the bromine and most of the acetic acid by evaporation to ca. 10 mL under vacuum. Care should be taken to prevent bromine from entering the vacuum pump oil and corroding the pump. Once visible signs of bromine were absent, water (ca. 200 mL) was added and the solution was heated to boiling. Na_2SO_3 (2 g) and NaOH (0.5 g) were added to raise the pH to attain a final pH of 6-7 (using indicator paper). A slightly brown solution was obtained. If this solution contained any insoluble material after 5 minutes of boiling, it was filtered hot through a medium frit. The resulting clear solution was brought to a boil again and CsCl (2 g) was added. The solution was allowed to cool slowly to room temperature and then transferred to a

refrigerator or ice bath. Small colorless crystals were formed, gathered via filtration onto a medium porosity glass frit funnel, and washed with cold water (ca. 50 mL). A second batch of product was obtained from the filtrate by evaporating the solvents and recrystallizing from boiling water (85% total yield).

The product was often deemed pure as judged by ^{11}B NMR (Fig. 9), but mass spectroscopy (Fig. 10) typically revealed the presence of some heptabrominated product arising from slight over-bromination. Successive recrystallizations from hot water may be used to improve the purity of the desired hexabrominated salt.

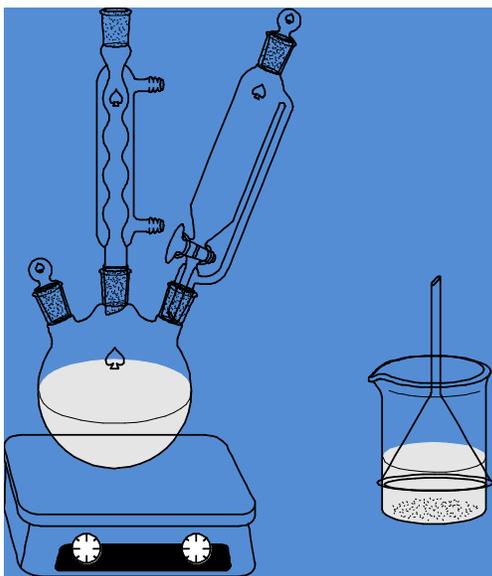


Figure 7.

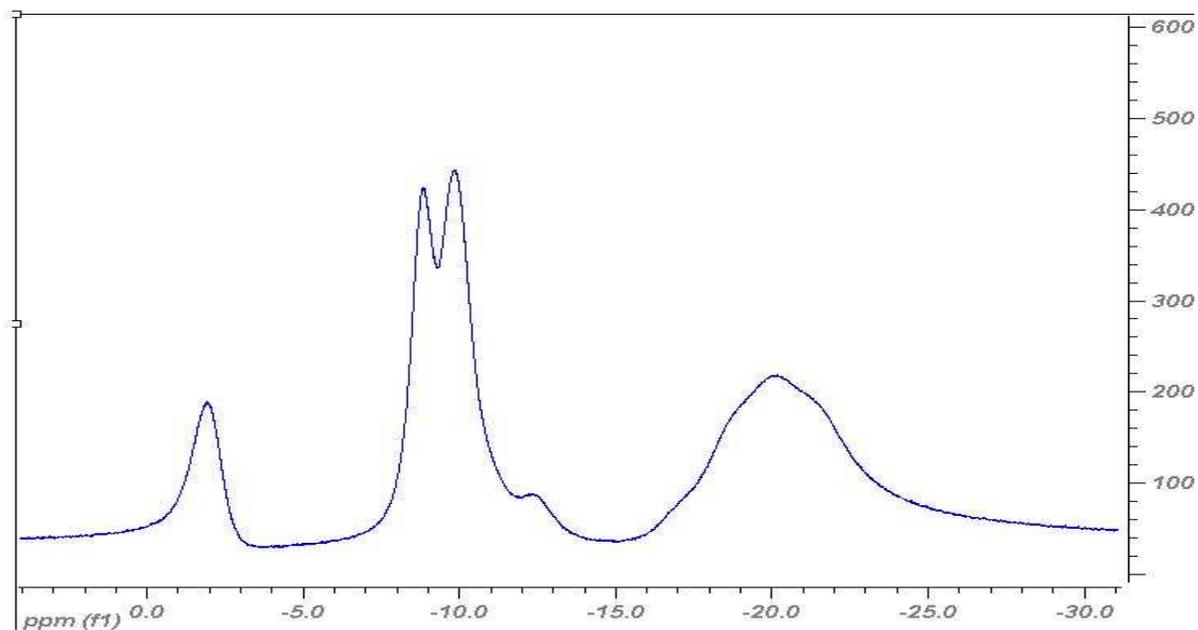
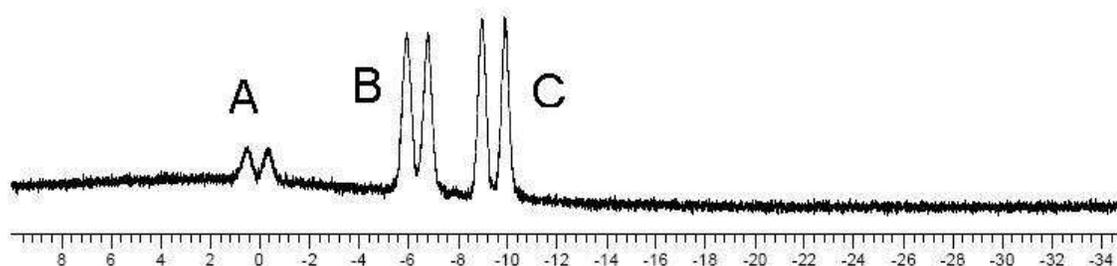
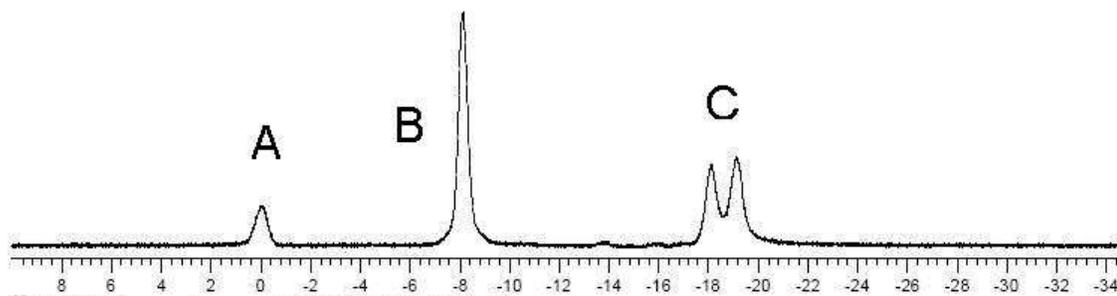


Figure 8. ^{11}B NMR (unreferenced) of reaction mixture (in mother liquor) showing incomplete hexabromination. This spectrum can be compared to those of the starting material and the fully hexabrominated material shown in Fig. 9.



^{11}B NMR spectrum of $[\text{Cs}^+][\text{CB}_{11}\text{H}_{12}^-]$



^{11}B NMR spectrum of $[\text{Cs}^+][\text{CB}_{11}\text{H}_6\text{Br}_6^-]$

Figure 9. ^{11}B NMR spectra (d_6 -acetone) of starting material and product (referenced to BF_3OEt capillary). A = 12, B = 7-11 and C = 2-5 positions.

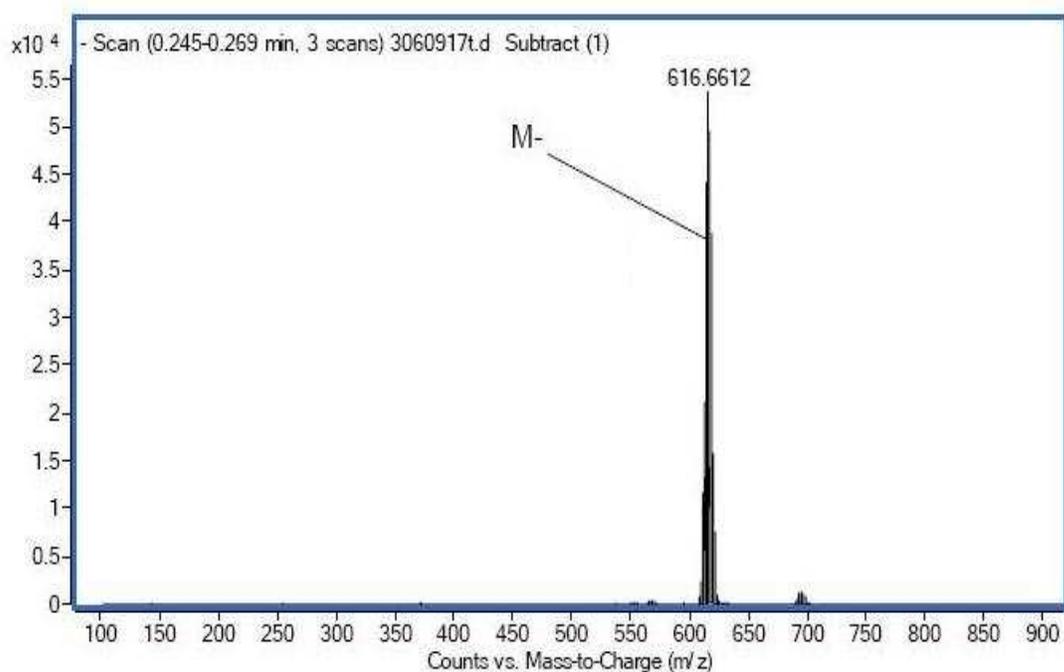


Figure 10. Anion electrospray ionization mass spectrum (from acetone solution) of a typical sample of NMR-pure $\text{Cs}(\text{CHB}_{11}\text{H}_5\text{Br}_6)$ (m/z 616.6) showing a small amount of $\text{Cs}(\text{CHB}_{11}\text{H}_4\text{Br}_7)$ (m/z 694).

$\text{Cs}(\text{CHB}_{11}\text{H}_5\text{Cl}_6)_3$

A 500 mL three-neck round bottom flask was placed into a temperature controlled oil bath inside a fume hood. To this flask, $\text{Cs}(\text{CHB}_{11}\text{H}_{11})$ (7 g, 0.025 mol), glacial acetic acid (220 mL), and a teflon magnetic stir bar were added. The flask was fitted with a water-cooled condenser and hose adapter connected via tygon tubing to an inverted filter funnel minimally submerged (to prevent vacuum generation) in a solution of NaOH (10 g/500 ml) and sodium sulfite (10 g) to scavenge liberated acid and excess chlorine. The pH of the scrubbing solution was checked periodically and more NaOH pellets were added if the solution started to become acidic. A lecture bottle of chlorine gas with a Monel valve was attached via tygon tubing to a fritted bubbler adapter submerged into the reaction mixture to deliver chlorine gas. The third neck was fitted with a rubber septum for reaction progress determination.

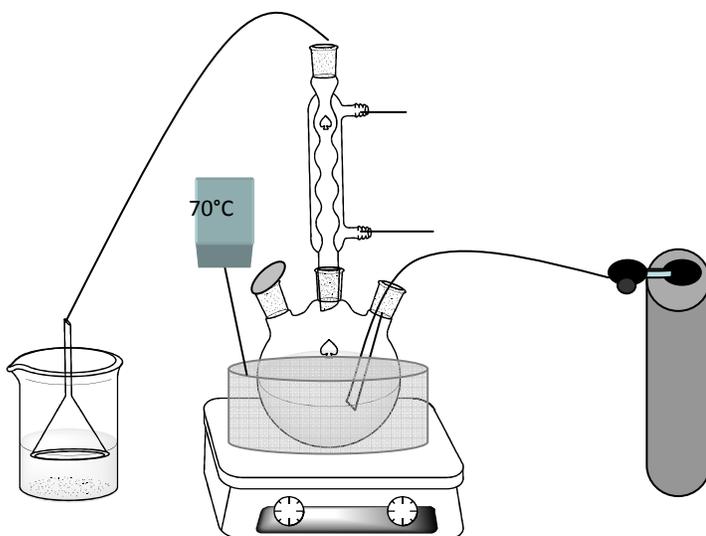


Figure11.

Chlorine was very slowly bubbled through the solution and the temperature of the bath was slowly raised to 70-75°C. While higher temperatures make the reaction proceed faster, they are not advised because over-chlorination can result. The reaction was monitored by ^{11}B NMR every hour for the first three hours and every 20-30 minutes thereafter.

When the reaction was complete, the flow of chlorine was ceased. Excess chlorine in the solution was removed either by bubbling with N_2 or by vacuum (using two liquid N_2 cold traps to prevent contamination of the pump). The solution was transferred to a single neck flask, and the three neck flask was rinsed into the single neck flask with small portions of water. The acetic acid was removed by rotary evaporation using a vacuum pump. Water (~200 mL) was added to the oily product and the mixture was transferred to a 600-mL beaker equipped with a teflon stir bar. If a precipitate formed, up to 200 mL of water was added to attain complete dissolution. The solution was

carefully neutralized by gradually adding sodium hydroxide pellets, checking for dissolution of the NaOH, and attaining a pH of 6-7 using indicator paper. Cesium chloride (~4 g) was added to the solution with stirring and the solution chilled in an ice bath for at least one hour. The precipitate was collected on a medium-porosity frit, washed with cold water, and air dried. The crude product was purified by recrystallization from a minimum of boiling water (10.5 g, 85%). Purity was checked by ^{11}B and ^1H NMR.

Cs(CHB₁₁Cl₁₁).⁴

- **Caution.** This reaction is carried out in a stainless steel pressure reactor. Appropriate cautions should be taken to prevent the explosive release of halogen gas.

Cs(CHB₁₁H₁₁) (2.0 g) was placed in a Teflon lined reactor (Berghof DAB-3) and dried by heating the apparatus in an oven at ca. 100°C for one hour. After cooling, iodine monochloride (68 g, 21 mL) and triflic acid (50 mL) were slowly added under a blanket of dry argon. The reactor was sealed (use torque specs from the instruction manual, ca. 30NM), placed behind blast shield protection, and heated to 200° C for 5 days. The reactor was cooled to room temperature and opened under a stream of argon. The contents were transferred to a round bottom flask and a trap-to-trap distillation, first at room temperature then at 160°C, was used to remove all of the liquid. Care was taken to minimize air exposure of the reaction mixture during these operations because the formation of H(H₂O)_n⁺ hydronium triflate salts makes the workup difficult. Water (450 mL) was added, the solid residue was stirred for an hour and filtered through a fine frit so that no cloudiness remained. The filtrate was evaporated to dryness under vacuum. Since traces of water greatly reduce the solubility of the product in acetonitrile, care was taken to minimize exposure of the reaction mixture to air during these operations. The solid was dissolved in acetonitrile (20 mL) and filtered through a fine frit. The filtrate was evaporated to dryness and the resulting solid heated to 160° C for a several hours under vacuum to remove volatiles. The solid was recrystallized by dissolution in hot water (60 mL) followed by addition of a few mL of acetonitrile and cooling (3.1 g, 65%). A second crop was obtained by concentrating the solution to 20 mL (1.0 g, 21%). ^1H NMR (300 MHz, CD₃CN): δ = 4.07 (s, 1H, C-H); ^{11}B NMR: see Figure 12.

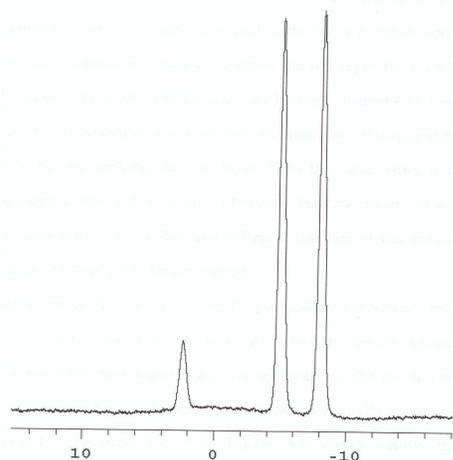


Figure 12. ^{11}B NMR spectrum of $\text{Cs}(\text{CHB}_{11}\text{Cl}_{11})$ in CD_3CN (unreferenced).

$\text{Ag}(\text{CHB}_{11}\text{H}_5\text{Br}_6)$.⁵

The purity of $\text{Cs}(\text{CHB}_{11}\text{H}_5\text{Br}_6)$ is absolutely essential to the success of the silver salt metathesis. It must be colorless, free of extraneous ^1H NMR signals, and neutral to pH indicator paper. This can be achieved by successive recrystallization from hot water.

$\text{Cs}(\text{CHB}_{11}\text{H}_5\text{Br}_6)$ (4.0 g, 5.3 mmol) was dissolved by simmering in a minimum quantity (ca. 100 mL) of high purity de-ionized water. When completely dissolved, one drop of conc. nitric acid was added to ensure a slightly acidic solution using indicator paper. Silver nitrate (1.0 g, 5.9 mmol) was dissolved in a minimum of high purity de-ionized water and added to the $\text{Cs}(\text{CHB}_{11}\text{H}_5\text{Br}_6)$ solution under low ambient light conditions. A white precipitate formed immediately. A colored precipitate is indicative of impurities or a basic solution. The mixture was simmered with stirring for **15 minutes** and allowed to cool to room temperature before filtering onto a medium (or fine) porosity glass frit. The white powder was allowed to air dry. The fine powder (3 g, 85%) was dried by transferring to a Schlenk tube wrapped in foil (to exclude light) and heated under vacuum at 90°C using a temperature controlled bath. The purity of this product was judged by the success of its use in the trityl salt preparation.

$\text{Ag}(\text{CHB}_{11}\text{H}_5\text{Cl}_6)$.⁵

This was prepared from $\text{Cs}(\text{CHB}_{11}\text{H}_5\text{Cl}_6)$ in a similar manner to $\text{Ag}(\text{CHB}_{11}\text{H}_5\text{Br}_6)$ using the same molar ratios of reagents except that no precipitate formed when the silver nitrate solution was added to a boiling solution of $\text{Cs}(\text{CHB}_{11}\text{H}_5\text{Cl}_6)$. Instead, the solution was removed from the heat and covered with Al foil to exclude light and allowed to cool to room temperature. The solution was placed in a refrigerator and allowed to crystallize overnight. After 24 hours, large colorless needles were observed. These were collected by filtration and washed with a small portion of ice-cold deionized water. The frit containing the crystals was covered with foil and air dried on the filter for one hour. The product was weighed to register the undried yield (ca. 85%), transferred to a

Schlenk tube, wrapped in foil, and placed under high vacuum. The Schlenk tube was heated under vacuum in a temperature-regulated oil bath at 90°C for 3 hours. Once dried, the colorless $\text{Ag}(\text{CHB}_{11}\text{H}_5\text{Cl}_6)$ was moved to the drybox and stored away from light. Since the solid slowly darkens with age and absorbs solvents and water from the atmosphere of the drybox, it is recommended that the material be used within a few weeks of preparation.

If colorless needles were obtained in the initial crystallization, the product generally proved to be pure. Otherwise, recrystallization from hot water is recommended.

$\text{Ag}(\text{CHB}_{11}\text{Cl}_{11})$.

$\text{Cs}(\text{CHB}_{11}\text{Cl}_{11})$ (3.75 g) and AgNO_3 (1.94 g) were dissolved in 500 mL of water. Acetonitrile (5 mL) was added, forming white precipitate. The suspension was extracted into toluene until no precipitate remained (3 x 500 mL). The toluene fractions were combined, filtered, and evaporated to dryness. The white solid was dissolved in CH_3CN (10 mL), filtered and evaporated to dryness. The resulting white product was dried at 100°C under vacuum for 1 hour (3.22 g, 89.4 %). ^1H NMR (300 MHz, CD_3CN): $\delta = 4.07$ (s, 1 H, C-H); see Figure 13. The small peak at $\delta = 2.1$ is an acceptable level of H_2O .

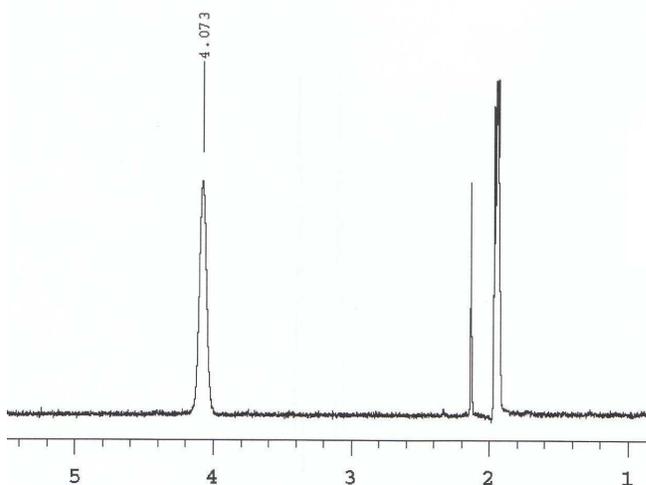


Figure 13. ^1H NMR spectrum of $\text{Ag}(\text{CHB}_{11}\text{Cl}_{11})$ in CD_3CN ($\delta = 1.9$).

$[(C_6H_5)_3C][CHB_{11}H_5X_6]$ for X = Cl or Br.⁵

In a high quality glovebox (O_2 , H_2O < 2 ppm), $Ag(CHB_{11}H_5X_6)$ (3 g, 4.1 mmol for X = Br, 6.6 mmol for X = Cl) was added to a 100 mL round bottom flask with a teflon stir bar. Dry toluene was added to just cover the solid. While stirring the slurry, dry acetonitrile was added dropwise until dissolution was achieved (ca. 3-5 mL). In a 5 mL glass vial, bromotriphenylmethane (trityl bromide) (1.3 g, 4.1 mmol for X = Br; 2.1 g, 6.6 mmol for X = Cl) was dissolved in toluene (2 mL) and added to the silver carborane solution yielding a red-orange (X= Br) or yellow-orange (X= Cl) solution and a precipitate (AgBr). The suspension was stirred for at least one hour and then filtered through a medium-porosity glass frit directly into a 100 ml round bottom flask. The AgX precipitate was washed with small aliquots of dry toluene:acetonitrile (4:1). The volume of the filtrate was carefully reduced to a few mLs under vacuum. The precipitate (red-orange for X= Br; yellow-orange for X=Cl) was collected and washed with small amounts of dry toluene followed by dry hexanes and dried under vacuum (70-80%).

$[(C_6H_5)_3C][CHB_{11}Cl_{11}]$.

In a glove box (O_2 , H_2O < 1 ppm), $Ag(CHB_{11}Cl_{11})$ (3.2 g) was dissolved in a mixture of dry toluene (50 mL) and dry acetonitrile (5 mL). A solution of triphenylmethyl bromide (2.05 g) in dry toluene (15 mL) was added and a yellow precipitate was formed. The suspension was stirred for 30 minutes then filtered onto a fine frit. The solid (AgBr) was washed with dry acetonitrile (5 mL) to dissolve any product. The filtrate was collected and partially evaporated to remove the acetonitrile. The product formed as an orange precipitate which was filtered off and washed with dry toluene followed by the dry hexane (3.69 g, 94%). 1H NMR (500 MHz, $CDCl_3$): δ = 2.06 (s, 3H, CH_3 toluene); δ = 3.08 (s, 1H; C-H); δ ~ 7.2 (m, 5 H ; C_6H_5 toluene), δ ~ 7.9 (br, 15 H; $(C_6H_5)_3C^+$ (see Fig. 14). The toluene solvate can be removed by heating the solid to 80°C under vacuum for several hours (see Fig. 15).

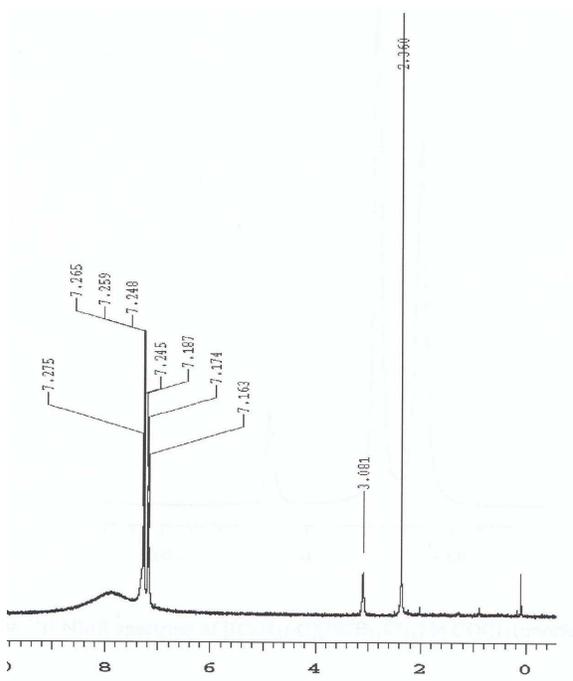


Figure 14. ^1H NMR spectrum of $[(\text{C}_6\text{H}_5)_3\text{C}][\text{CHB}_{11}\text{Cl}_{11}]$ in CDCl_3 .

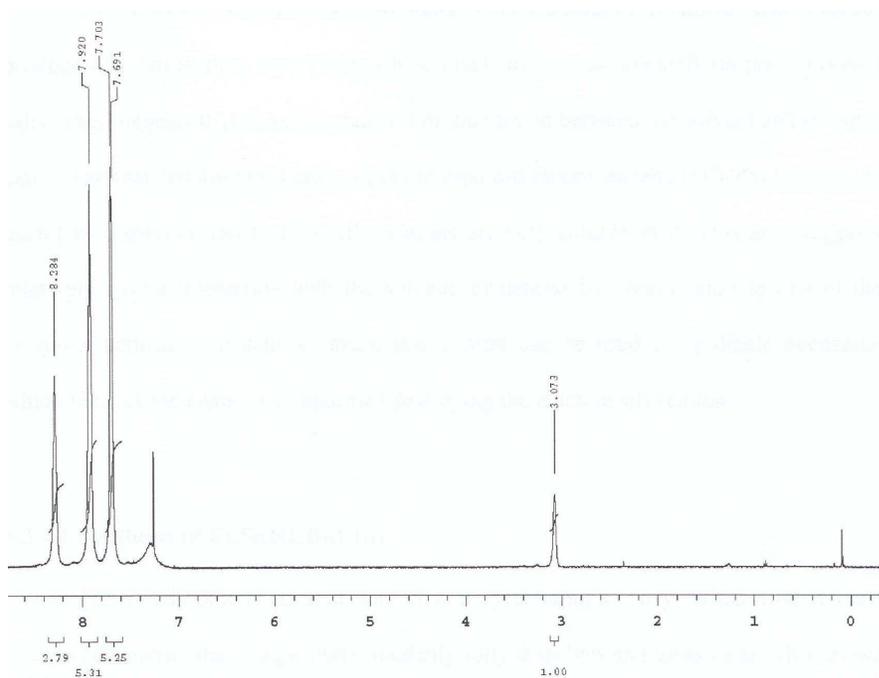


Figure 15. ^1H NMR (CDCl_3) spectrum of $[(\text{C}_6\text{H}_5)_3\text{C}][\text{CHB}_{11}\text{Cl}_{11}]$ after removal of the toluene solvate.

$(\text{Et}_3\text{Si})(\text{CHB}_{11}\text{H}_5\text{X}_6)$ for $\text{X} = \text{Cl}$ or Br ⁶

In a high quality glovebox (O_2 , $\text{H}_2\text{O} < 1$ ppm) free of donor solvent vapors, trityl salt $[(\text{C}_6\text{H}_5)_3\text{C}][\text{CHB}_{11}\text{H}_5\text{X}_6]$ (300 mg) was weighed into a small vial (ca. 5 mL) that contained a teflon micro stir bar. Enough toluene (~2 mL) was added to just cover the solid. The orange slurry was stirred and a few drops of triethylsilane were added. The vial was capped with a Teflon screw cap, sealed with Parafilm, and stirred until the solution became clear and colorless (20 mins to hours). Hexane (approx. 0.5 mL) was added and a white precipitate formed. This was quickly collected on a medium frit, washed twice with small aliquots of dry hexane (~ 1mL) and briefly air dried (90%). Because of its sensitivity to water and donor solvents, this material was typically used immediately rather than stored.

$[\text{Et}_3\text{Si}]_2\text{H}][\text{CHB}_{11}\text{Cl}_{11}]$.⁷

In a high quality glovebox (O_2 , $\text{H}_2\text{O} < 1$ ppm), free of donor solvent vapors, $[(\text{C}_6\text{H}_5)_3\text{C}][\text{CHB}_{11}\text{Cl}_{11}] \cdot \text{toluene}$ (605 mg) was covered with dry 1,2-dichlorobenzene (1.5 mL). To this suspension, Et_3SiH (0.5 mL) was added and stirred for 10 minutes. Dry hexanes (8 mL) were then added while stirring. The resulting precipitate was filtered off and washed with dry hexane (3 x 3 mL) (403 mg, 90%). ^1H NMR (500 MHz, SO_2) $\delta \sim 2.2$ - 2.4 (br, 15 H; $(\text{C}_2\text{H}_5)_3\text{Si}$, $\delta \sim 4.6$ (s, 1 H; C-H). The IR has a characteristic peak at 1875 cm^{-1} from $\nu\text{Si-H-Si}$ (see Fig. 16). The product may be recrystallized from ODCB by layering with hexane.

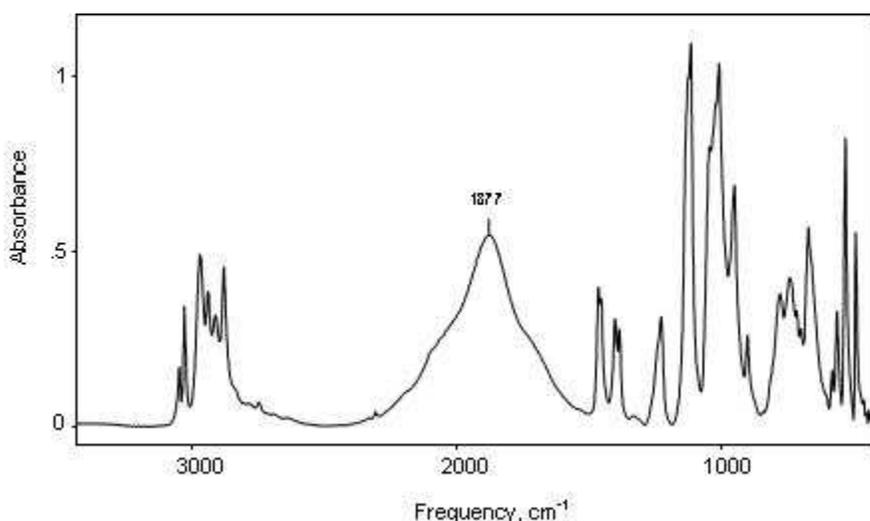


Figure 16. IR spectrum of $[(\text{Et}_3\text{Si})_2\text{H}][\text{CHB}_{11}\text{Cl}_{11}]$ in KBr with Si-H-Si stretch at 1875 cm^{-1} .

Et₃Si(CHB₁₁Cl₁₁).

In a high quality glovebox (O₂, H₂O < 1 ppm), free of donor solvent vapors, (C₆H₅)₃(CHB₁₁Cl₁₁)·toluene (275 mg) was covered with 1 mL of dry 1,2-dichlorobenzene. To this suspension Et₃SiH (51.9 mg, 0.72mL) was added and the mixture stirred about 1 hour until the suspension became white. Dry hexane (5 mL) was added while stirring. The resulting precipitate was filtered off and washed with dry hexane (3 x 2 mL) (148 mg, 62%). The IR spectrum is shown in Fig. 17. The ¹H and ¹¹B NMR are shown in Figs. 18 and 19 respectively.

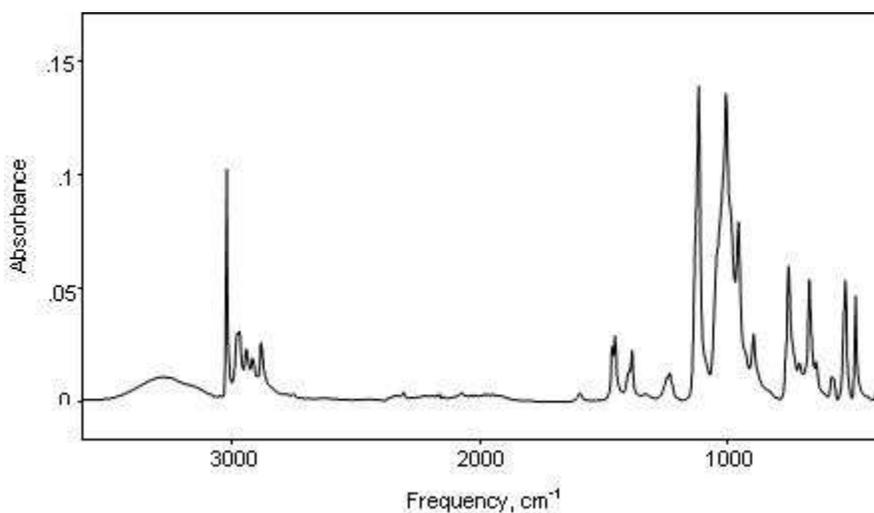


Figure 17. IR spectrum of Et₃Si(CHB₁₁Cl₁₁) in KBr.

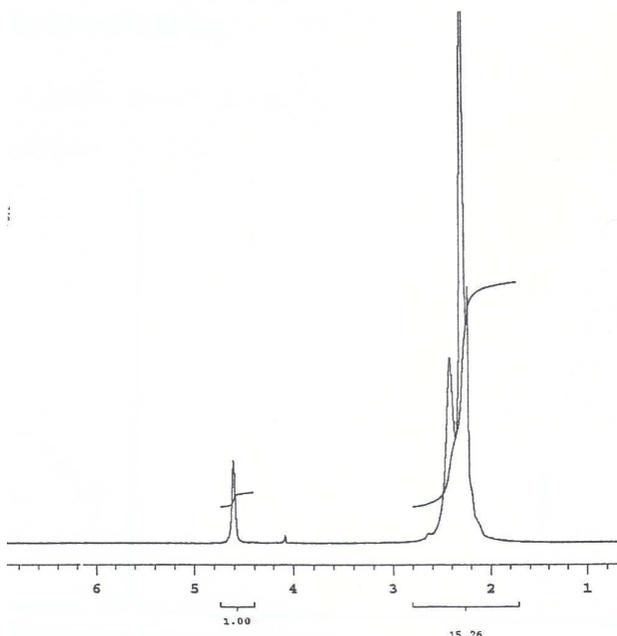


Figure 18. ^1H NMR spectrum of $\text{Et}_3\text{Si}(\text{CHB}_{11}\text{Cl}_{11})$ in SO_2

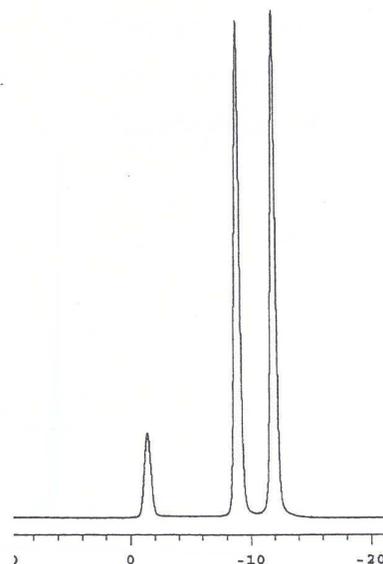


Figure 19. ^{11}B NMR spectrum of $\text{Et}_3\text{Si}(\text{CHB}_{11}\text{Cl}_{11})$ in SO_2

$\text{H}(\text{CHB}_{11}\text{Cl}_{11})$.⁸

In a heavy-walled Schlenk tube having a wide bore Teflon stopcock below the ground glass joint, enough dry HCl was condensed at liquid N_2 temperatures to just cover $[(\text{Et}_3\text{Si})_2\text{H}][\text{HB}_{11}\text{Cl}_{11}]$ (200 mg) and the mixture stirred at 0°C for 1 hour. The sample was re-cooled to -190°C and HCl was removed under vacuum (taking considerable care to protect the vacuum pump from HCl). The reaction vessel was allowed to warm to room temperature and pumped under vacuum for 1 hour (155 mg, 94%). The product was taken into the drybox and usually used immediately for reaction chemistry but greater purity can be obtained by sublimation at 150°C under high vacuum (diffusion pump). IR: see Fig. 20. ^1H NMR (500 MHz, SO_2 , -65°C): $\delta = 4.55$ (s, 1H; C-H_{carb}), 20.4 (s, 1H; H⁺), see Fig. 21. ^{13}C NMR (125MHz, SO_2 , -65°C): $\delta = 46.6$ (C-H).

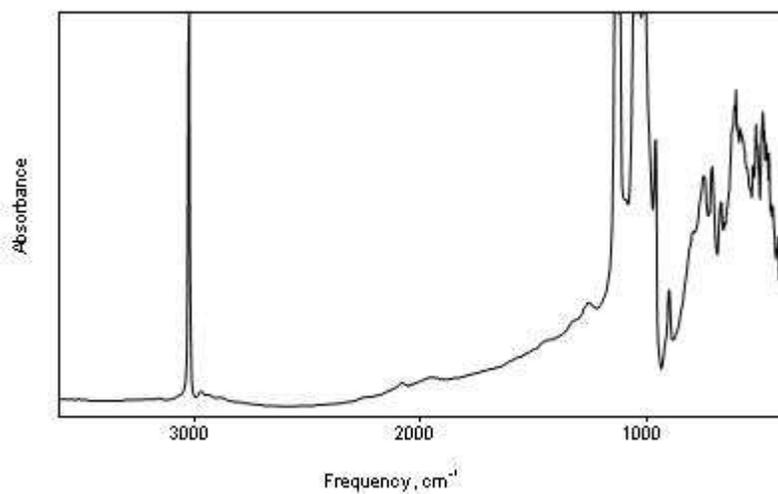


Figure 20. IR spectrum of solid $\text{H}(\text{CHB}_{11}\text{Cl}_{11})$ acid.

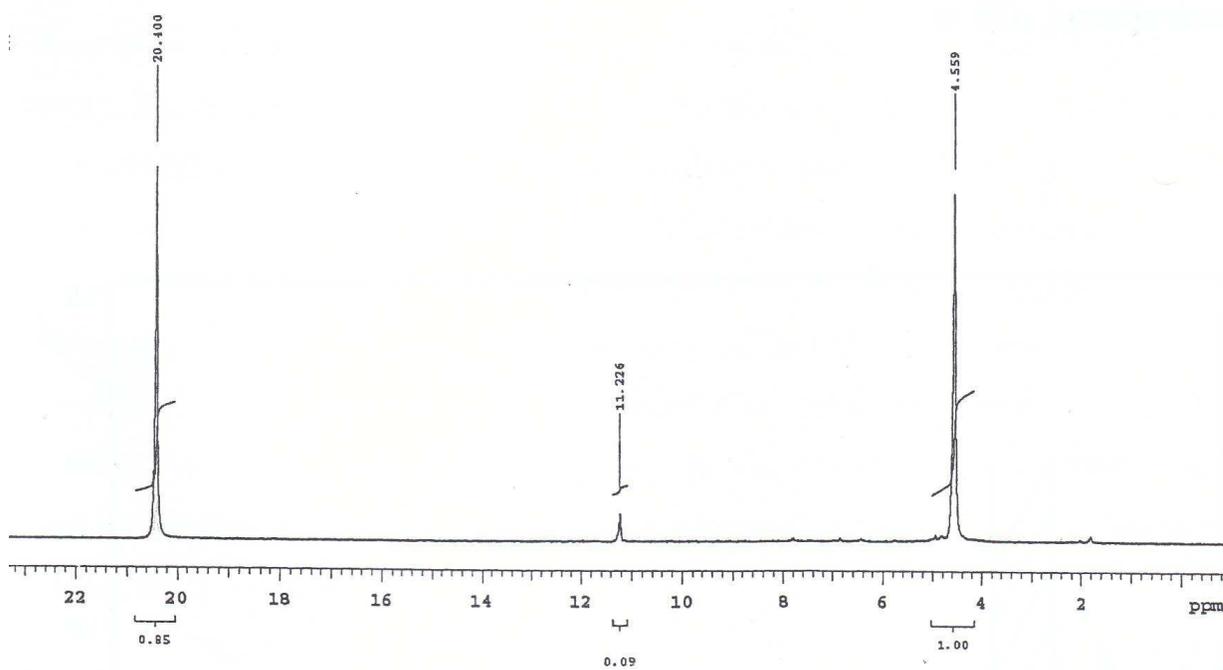


Figure 21. ^1H NMR spectrum of $\text{H}(\text{CHB}_{11}\text{Cl}_{11})$ in SO_2

[H(benzene)][CHB₁₁Cl₁₁].

In a high quality glovebox (O₂, H₂O < 1 ppm), Et₃Si(HB₁₁Cl₁₁) (372 mg) was covered with dry benzene (1.5 mL) and triflic acid (81.5 mg, 0.05 mL) was added while stirring. An off-white precipitate formed immediately which was filtered off and washed with dry benzene (2 mL) and hexane (2 mL) (237 mg, 79.8%). IR: See Fig 22.

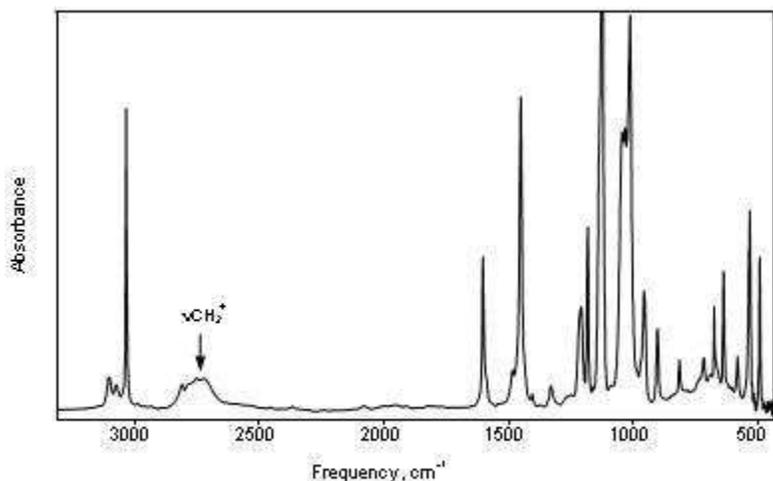


Figure 22. IR spectrum (KBr) of [C₆H₇][CHB₁₁Cl₁₁].

[H(toluene)][CHB₁₁Cl₁₁].

In a high quality glovebox (O₂, H₂O < 1 ppm), Et₃Si(HB₁₁Cl₁₁) (390 mg) was covered with dry toluene (1.5 mL) and triflic acid (85 mg, 0.06 mL) was added while stirring. An off-white precipitate formed immediately which was filtered off and washed with toluene (2 mL) and hexane (2 mL) (305 mg, 95.9%). IR: see Fig. 23.

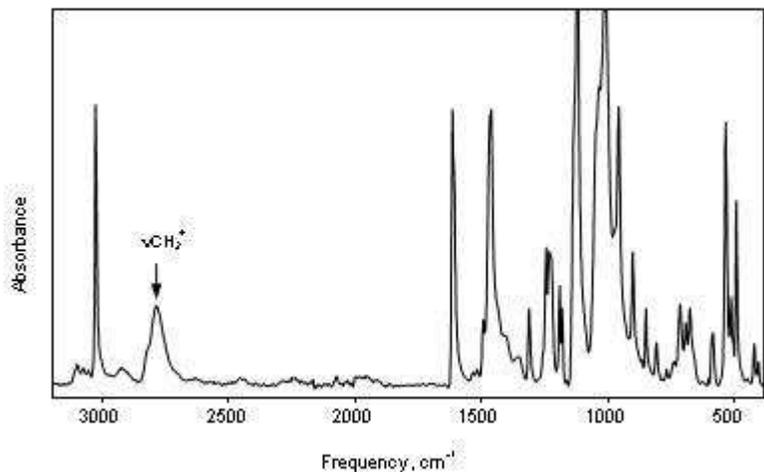


Figure 23. IR spectrum (KBr) of [(toluene)H][CHB₁₁Cl₁₁].

[H(pentamethylbenzene)][CHB₁₁Cl₁₁].

In a high quality glovebox (O_2 , $H_2O < 1$ ppm), $Et_3Si(HB_{11}Cl_{11})$ (562 mg) and $C_6H(CH_3)_5$ (122 mg) were covered with benzene (1.5 mL) and triflic acid (132 mg, 0.078 mL) was added while stirring. The precipitate was filtered off and washed with benzene (2 mL) and hexane (2 mL) (389 mg, 78%). IR: see Fig. 24.

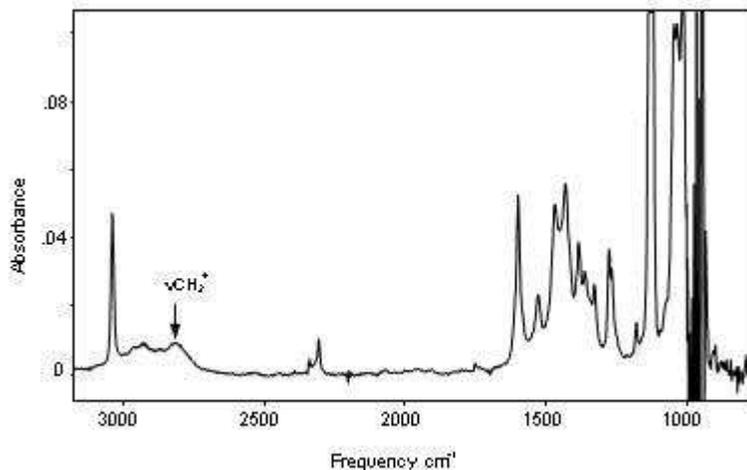


Figure 24. IR spectrum of [(pentamethylbenzene)H][CHB₁₁Cl₁₁] in CD₂Cl₂ (0.01 M).

CH₃(CHB₁₁Cl₁₁).

In a high quality glovebox (O_2 , $H_2O < 1$ ppm), dry hexane was added to $Et_3Si(CHB_{11}Cl_{11})$ (200 mg) to just cover the solid, followed by methyl triflate (0.031 ml, 1.1 equiv.) The suspension was immediately cooled to 0 °C and stirred 2 hours at 0 °C. The volatiles were then removed under vacuum to yield an off-white solid in quantitative yield.

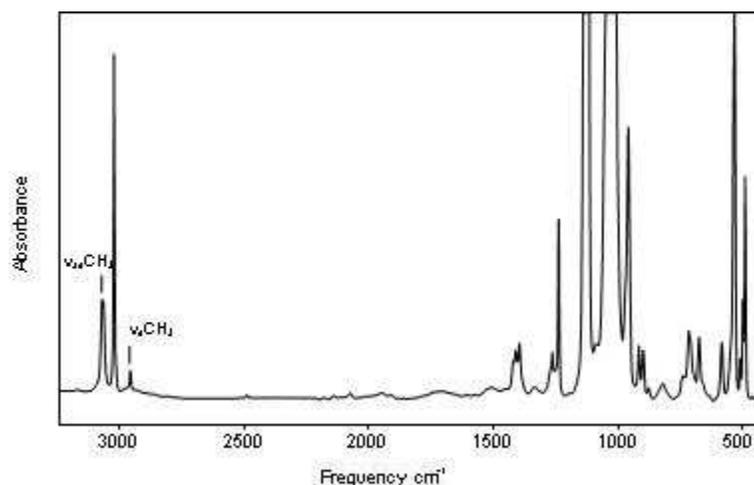


Figure 25. IR spectrum (KBr) of CH₃(CHB₁₁Cl₁₁).