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Facile and Mild Deboronation of *o*-Carboranes Using Cesium Fluoride

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Introduction

The nido monoanion $[7,8\text{-}C_2B_9H_{12}]^-$, which was first obtained by alcoholic base degradation of *o*-carborane[1] and substituted derivatives $[7,8\text{-}R'R''\text{-}7,8\text{-}C_2B_9H_{12}]^-$, are very important starting reagents for the syntheses of a wide range of metallacarborane compounds with potential applications as novel catalysts[2] and radiochemical drugs[3] as well as for the syntheses of several *nido*- and *closo*-carboranes and heteroboranes.[4] However, the deboronation using the potassium hydroxide/methanol or ethanol route is not suitable for carborane derivatives that contain functional groups susceptible to the attack of a strong base or nucleophile.[5] Although other deboronation reagents such as tertiary amines, hydrazine, ammonia, piperidine, and pyrrolidine are also available,[6] the recently found deboronation reagent, the fluoride ion,[5,7] is the most promising alternative because it is a very weak nucleophile but effective as well as easy to handle (no offensive odor).[8] Tetrabutylammonium fluoride (TBAF), the first reported fluoride ion source, readily degrades *o*- and *m*-carboranes under mild conditions to the corresponding nido monoanions $[Bu_4N][7,8\text{-}R'R''\text{-}7,8\text{-}C_2B_9H_{12}]$ and $[Bu_4N][7,9\text{-}R'R''7,9\text{-}C_2B_9H_{12}]$, respectively.[5,7,9] Nido structures have been used to synthesize more soluble analogues;[10] however, in tetrabutylammonium salt this deboronation method converts *o*-carborane to *nido*-carborane, which has extremely low hydrophilicity. The water solubility of the compounds containing carborane cages is one of the most important physical properties for potential BNCT (boron neutron capture therapy) reagents.[11] Furthermore, it is difficult to change the countercation to other salts. Getman has recently reported that potassium fluoride supported on alumina could deboronate *o*-carborane in acetonitrile and the countercation (K^+) in its nido anion $K[7,8\text{-}C_2B_9H_{12}]$ could be converted to $[P(C_6H_5)_3CH_3]^+$.[12] But the isolation of $K[7,8\text{-}C_2B_9H_{12}]$ itself was not achieved because of the concurrent presence of an unidentified hygroscopic solid that is formed from the reaction of the KF/alumina reagent with refluxing wet acetonitrile.[12] In seeking a mild and facile degradation route of *o*-carborane derivatives to produce water-soluble nido monoanions, we perceived that cesium fluoride is a good fluoride ion source that can be used as a base in various organic reactions and has higher solubility in methanol and ethanol than any other alkali metal fluoride.[13] Accordingly, we pursued the use of cesium fluoride as a deboronation base.

Herein we report that the CsF/ethanol pair is a very effective system for deboronating *o*-carborane derivatives to give the corresponding cesium salt of *nido*-carboranes in high yield, and it is mild enough to degrade *o*-carborane containing an ester bond without attacking the susceptible functional group.

Experimental Sections

^1H and ^{13}C NMR spectra were measured on a Bruker AVANCE 400 spectrometer operating at 400.13 and 100.61 MHz and were referenced to the internal solvent peaks. ^{11}B NMR spectra were obtained on a Bruker AM 300 spectrometer operating at 96.29 MHz using a coaxial tube containing MeCN-d_3 for the purpose of locking. External references for the chemical shifts are $BF_3\cdot Et_2O = 0.0$. IR spectra were recorded in KBr disks on a Bruker EQUINOX 55 FT-IR spectrometer.

Materials. *o*-Carborane, 1-methyl-*o*-carborane, and *m*-carborane, purchased from KATCHEM Ltd., were purified by sublimation under vacuum prior to use. Cesium fluoride, absolute ethanol, and other reagents were purchased from Aldrich and used as received. μ-1,2-Trimethylene-*o*-carborane (**1**) was synthesized by modifying the published method,[14] using 1-bromo-3-chloropropne instead of 1,3-dibromopropane. The synthesis of 3,3′-(3-(1,2-dicarba-*closo*-dodecaborane-1-yl)carbpropoxy)-2,2′-bipyridine (**2**) will be reported elsewhere.[15] Methanol, acetonitrile, and THF were dried according to the published procedures.[16] Other solvents were of reagent grade and used without further purification.

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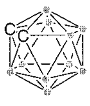
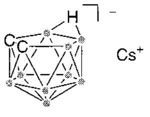
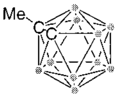
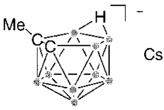
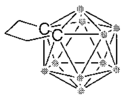
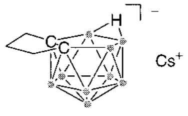
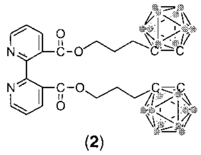
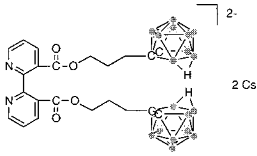
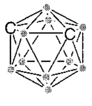
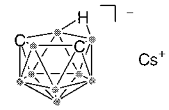
Table 1. Deboronation of *o*-Carborane Derivatives and *m*-Carborane

carboranes	solvent	equiv.[a]	time (h)	yield (%)	products
	ethanol	2	25	94	
	ethanol	3	25	92	
 (1)	ethanol	3	25	98	
 (2)	ethanol /THF (2:1 v/v)	3	27	87	
	ethanol	2	23	0[b]	

[a] Mole ratio of CsF/*o*-carborane cage. [b] No reaction.

General Deboronation Reactions. All the deboronations were carried out under an atmosphere of dinitrogen, but the workup was performed in the open air. In each experiment, 100 mg (0.69 mmol) of *o*-carborane and cesium fluoride of various molar ratios were dissolved in the indicated solvent of ca. 20 mL. The reaction mixtures were refluxed gently with stirring during the reaction and allowed to cool to room temperature. The percentage of deboronation in each reaction was calculated right after cooling by the integration sum of the in situ $^{11}B\{^1H\}$ NMR peaks originated from *o*-carborane and its nido monoanion. The wet condition of methanol was made by injecting a 10-fold amount of H_2O (125 μL) per *o*-carborane into the reaction mixture before refluxing.

Isolation of Cs[7,8-$C_2B_9H_{12}$]. A mixture of *o*-carborane (300 mg, 2.08 mmol) and cesium fluoride (632 mg, 4.16 mmol) in ethanol (20 mL) was stirred under reflux conditions for 25 h. The clear solution was dried by rotary evaporator to give a white solid that was dissolved in 40 mL of acetone. The solution was filtered off by glass frit to remove the white borate and washed several times with the same solvent. The white product obtained by the removal of the solvent of the filtrate in vacuo was recrystallized from H_2O to produce the white crystal (518 mg, 94% yield). The spectroscopic results and cell parameters of a single crystal for this compound are in agreement with the literature data.[4b,17] Anal. Calcd for $C_2H_{12}B_9Cs$: C, 9.02; H, 4.54. Found: C, 8.81; H, 4.81. ^1H NMR (400 MHz, MeOH-d_4): δ 1.72 (br, 2H), −3.01 (v br, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, MeOH-d_4): δ 43.4 (br, carborane C). $^{11}B\{^1H\}$ NMR (96.3 MHz, MeOH): δ −10.7(2B), −16.7 (3B), −23.1 (2B), −32.9 (1B), −37.6 (1B). IR (KBr, cm^{-1}): 2589 m, 2551 s, 2516vs, 2496 s, 2482 s, 1029 m, 988 w.

Deboronation of *o*-Carborane Derivatives (Table 1). A similar degradation procedure was employed to obtain cesium salts of nido monoanions of 1-methyl-*o*-carborane, μ-1,2-trimethylene-*o*-carborane (**1**), and 3,3′-(3-(1,2-dicarba-*closo*-dodecaborane-1-yl)carbpropoxy)-2,2′-bipyridine (**2**). The details of the reaction conditions are summarized in Table 1.

Preparation of Cs[7-methyl-7,8-$C_2B_9H_{11}$]. A mixture of 1-methyl-*o*-carborane (200 mg, 1.26 mmol) and cesium fluoride (572 mg, 3.77 mmol) in ethanol (30 mL) was stirred under reflux conditions for 25 h. The clear solution was dried in vacuo by rotary evaporator to give a white solid that was dissolved in 20 mL of acetone. The same workup and recrystallization procedures as above were employed to produce white crystals (324 mg, 92% yield). Anal. Calcd for $C_3H_{14}B_9Cs$: C, 12.85; H, 5.03. Found: C, 13.24; H, 5.01. ^1H NMR (400 MHz, MeOH-d_4): δ 1.62 (br, 1H), 1.33 (s, 3H), −2.65 (v br, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, MeOH-d_4): δ 55.5 (br, carborane C), 50.2 (br, carborane C), 25.4. $^{11}B\{^1H\}$ NMR (96.3 MHz, MeOH): δ −12.6(1B), −13.6 (1B), −15.4 (1B), −19.9 (2B), −21.3 (1B), −24.3 (1B), −35.9 (1B), −39.2 (1B). IR (KBr, cm^{-1}): 2927 w, 2859 w, 2518 vs, 1446 w, 1032 m, 991 w, 759 w.

Preparation of Cs[μ-7,8-trimethylene-7,8-$C_2B_9H_{10}$]. A solution of μ-1,2-trimethylene-*o*-carborane (**1**) (300 mg, 1.61 mmol) and cesium fluoride (741 mg, 4.88 mmol) in ethanol (30 mL) was stirred under reflux conditions for 25 h. The clear solution was dried under reduced pressure to give a white solid, which was dissolved in 20 mL of acetone again. The same workup and recrystallization procedures as described above were employed to produce white crystals (486 mg, 98% yield). Anal. Calcd for $C_5H_{17}B_9Cs$: C, 19.60; H, 5.26. Found: C, 20.45; H, 5.58. ^1H NMR (400 MHz, MeOH-d_4): δ 2.08 (m, 2H), 1.74 (m, 2H), 1.59 (m, 1H), 1.42 (m, 1H), −2.72 (v br, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, MeOH-d_4): δ 67.8 (br, carborane C), 35.4, 28.4. $^{11}B\{^1H\}$ NMR (96.3 MHz, MeOH): δ −13.8 (2B), −17.4 (1B), −21.5 (2B), −22.7 (2B), −34.8 (1B), −38.3 (1B). IR (KBr, cm^{-1}): 2950 w, 2861 w, 2496 s, 1444 w, 1065 m, 894 w, 742 s, 480 m.

Preparation of Dicesium 3,3′-(3-(Undecahydro-7,8-dicarba-*nido*-undecaborate-7-yl)carbpropoxy)-2,2′-bipyridine. A mixture of 3,3′-(3-(1,2-dicarba-*closo*-dodecaborane-1-yl)carbpropoxy)-2,2′-bipyridine (**2**) (400 mg, 0.62 mmol) and cesium fluoride (444 mg, 2.92 mmol) in 30 mL of ethanol/THF (2:1 v/v) mixed solvent was stirred under reflux conditions for 27 h. The precipitated cesium salt of the monoanion was collected as the first crop by filtration. The white solid taken by removing the solvent of the filtrate was dissolved in acetone, filtered, and washed several times with acetone. The second crop was obtained by drying the filtrate. The combined white solid was washed with small amounts of methylene chloride and recrystallized from acetone/Et_2O (486 mg, 87% yield). ^1H NMR (400 MHz, acetone-d_6): δ 8.70 (dd, J = 4.8, 1.7 Hz, 2H), 8.27 (dd, J = 7.9, 1.7 Hz, 2H), 7.54 (dd, J = 7.9, 4.8 Hz, 2H), 3.99 (m, 4H), 1.51 (m, 4H), 1.46 (m, 4H), 1.26 (m, 2H), −2.83 (v br, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, acetone-d_6): δ 167.2, 159.5, 151.5, 138.6, 128.0, 123.6, 66.1, 60.0 (br), 47.0

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(br), 36.3, 30.7. $^{11}B\{^1H\}$ NMR (96.3 MHz, acetone): δ −10.8 (2B), −13.8 (1B), −16.6 (1B), −18.2 (2B), −21.8 (1B), −33.0 (1B), −36.8 (1B). IR (KBr, cm^{-1}): 2955 w, 2850 w, 2510 vs, 1698 s, 1584 m, 1452 w, 1384 w, 1311 m, 1148 m, 1028 w, 778 m, 741 m.

Results and Discussion

Optimization of the Deboronation Conditions. To find the optimal reaction conditions, deboronation experiments were repeated with *o*-carborane by varying the temperature, the solvent, the molar ratio of CsF/*o*-carborane, and the reaction time. Under conditions of reflux for 20 h, 1 equiv of *o*-carborane (100 mg) is deboronated by 3 equiv of CsF in ethanol (100%), methanol (94%), methanol (wet) (95%), 2/1 ethanol/THF (98%), acetonitrile (35%), glyme (31%), and THF (3%). Alcohol was found to be the best solvent in deboronation using cesium fluoride under reflux conditions as expected from the high solubility of CsF in methanol and ethanol.[13c] Cesium fluoride is dissolved clearly in methanol and ethanol but has only marginal solubility in other solvents such as acetonitrile, THF, and glyme. The deboronation reaction proceeded much more slowly in acetonitrile and glyme than in ethanol, but only a minute quantity of *nido*-carborane was produced in THF. The mixed-solvent system of ethanol/THF (2:1 v/v) is also as effective as ethanol itself. Deboronation proceeded faster in ethanol than in methanol, which could be attributed to the higher boiling point of ethanol. At 60 °C, the reaction was retarded (3 equiv, 30 h, 79%), and at room temperature the reaction did not proceed at all even in ethanol.

The following ratios of *o*-carborane to CsF in refluxing ethanol to produce *nido*-carborane were studied: 1:1 (77%, 65 h), 1:1.5 (100%, 36 h), 1:2 (100% 20 h), 1:3 (100%, 15 h). Complete conversion of *o*-carborane to the nido anion was achieved with a CsF/*o*-carborane ratio of 1.5 or higher. As the molar ratio of cesium fluoride was increased, complete deboronation was achieved in a shorter time. However, the influence of increasing the amount of cesium fluoride from 2 to 3 times on the conversion percentage is rather insignificant compared to that from 1.5 to 2 times. Therefore, for the reaction conditions of ethanol as a solvent, CsF to *o*-carborane ratio of 2:1, 20 h of the reaction time and reflux temperature seem to be optimal for the complete conversion of *o*-carborane into its monoanion.

Deboronation Probed by ^{11}B NMR Spectroscopy. In the $^{11}B\{^1H\}$ NMR spectrum of an in situ reaction mixture obtained right after the complete deboronation of *o*-carborane (ethanol, 2 equiv, 20 h, reflux), three resonances, in addition to the nido-anion boron peaks, appear at 17.2 (br singlet), 1.8 (1:2:1 triplet, $J = 24$ Hz), and 0.6 ppm (1:3:3:1 quartet, $J = 13$ Hz). The relative intensity ratio of 9:1 of the sum of the integration for the *nido*-anion boron peaks to the three additional boron peaks indicates that a boron atom removed from an *o*-carborane cage by deboronation converts into three species. The multiplicity patterns of the three signals remain unchanged in the proton spin coupled ^{11}B NMR spectrum, implying that the coupling patterns of the three peaks are independent of the proton and likely to arise from fluorine atoms bonded to the boron atom. Therefore, the signals at 1.8 and 0.6 ppm originate from the species containing BF_2 and BF_3 units, respectively. It is worthwhile to note that $XYBF_2$ and XBF_3 fluoroborates, where X and Y could be solvent or OH group, have been reported as byproducts in the deboronation using $[Bu_4N]F$.[7a,b] The broad singlet at 17.2 ppm is presumably due to polyborate with no fluorine.[7c,18]

These three boron signals are also observed in deboronation processes of other *o*-carborane derivatives under various conditions. But the relative intensities of the three peaks vary with changing reaction time.[7b] The intensities of the fluoroborates' boron signals are larger than that of the polyborate at the earlier reaction period. As the reaction proceeds, the intensity of the polyborate signal increases at the expense of the intensities of the fluoroborates. In the case of the 2 mol ratio of CsF/*o*-carborane in ethanol, the three signals at 17.2, 1.8, and 0.6 ppm appear in ca. 1.1:1.5:1.0 ratio when the reaction time reaches 7 h and then in ca. 6.2:2.0:1.0 ratio when complete deboranation is reached at 20 h of the reaction time. The forgoing intensity variation indicates that the two fluoroborates are generated as initial byproducts and then transform into non-fluorine polyborate.[19]

Characterization and Physical Property. Table 1 shows that the degradation of several other *o*-carborane derivatives and thus the direct formation of their nido products as Cs salts in high yield can be also achieved by the CsF/ethanol route. Complete conversion of the parent carborane into its monoanion can be checked simply by the ^{11}B NMR spectrum measured in situ before workup. The nido monoanion derivatives could be easily identified by the characteristic NMR resonances: a broad peak of bridging or *endo*-H at −2 to −3 ppm in the ^{1}H NMR spectrum, weak and broad peak(s) of carborane carbons at 50−70 ppm in the ^{13}C NMR spectrum, and two peaks for B(1) and B(10) of *nido*-carborane at −30 to −40 ppm in the $^{11}B\{^1H\}$ NMR spectrum. The formation of fluorine-substituted nido monoanions, which was seen in other cases,[7c,20] was not observed in the deboronations reported in this paper. The byproducts and excess cesium fluoride have only marginal solubility in acetone, so the cesium salts of the *nido*-carboranes can be effectively isolated by extraction with acetone.

The direct and high-yield deboronation route to Cs salts of nido monoanions reported in this paper is very facile and effective. The cesium salts of nido monoanions have several experimental advantages over potassium or quaternary alkylammonium salts: they are a very useful synthon for metallacarbaboranes;[21] they are not as hydroscopic as potassium salt; they have moderate water solubility;[4b] and they give simpler ^{1}H and ^{13}C NMR spectra compared to quaternary alkylammonium salts. In addition, in the case of the deboronation of *o*-carborane ester-linked bipyridine (**2**), which requires mild deboronation conditions, the nido product was successfully obtained in high yield without breaking the ester bond, using CsF in a mixed solvent of ethanol/THF (2:1 v/v) where both cesium fluoride and **2** dissolve. The *m*-carborane, 1,7-$C_2B_{10}H_{12}$, was not degraded at all in ethanol under reflux conditions by cesium fluoride but was partially degraded by CsF under more intense conditions (di(ethylene glycol) methyl ether, 3 equiv, 100 °C, 25 h, 66% deboronation). The *m*-carborane is known to be more robust against deboronation and needs more vigorous reaction conditions.[7c]

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