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Simplified Synthesis of $B_{10}H_{14}$ from $NaBH_4$ via $B_{11}H_{14}^-$ Ion

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The synthesis of $B_{11}H_{14}^-$ ion from BH_4^- ion and acids, including $BF_3\cdot O(C_2H_5)_2$, BCl_3, $SiCl_4$, or alkyl halides, and the subsequent oxidation of the $B_{11}H_{14}^-$ ion to produce $B_{10}H_{14}$ using $Na_2Cr_2O_7$, $KMnO_4$, H_2O_2, or $H_2O_2/FeSO_4$ is described. An optimum procedure is suggested which can be scaled-up.

Introduction

A facile synthesis of tetradecahydroundecaborate(1−) ion, $B_{11}H_{14}^-$, from $BF_3\cdot O(C_2H_5)_2$ and $NaBH_4$ was previously described.[2] The major neutral product obtained from the sodium dichromate oxidation of an aqueous solution of $B_{11}H_{14}^-$ ion so prepared was decaborane(14), $B_{10}H_{14}$.[3] Thus $B_{10}H_{14}$ was made generally available for the first time by a relatively low-cost procedure which can be performed in standard laboratory apparatus.

A probable sequence of steps which results in the formation of $B_{11}H_{14}^-$ ion begins with the reaction of $BF_3\cdot O(C_2H_5)_2$ with excess BH_4^- ion in diglyme solvent to produce B_2H_6 (eq 1),

$$3BH_4^- + 4BF_3\cdot O(C_2H_5)_2 \rightarrow 2B_2H_6 + 3BF_4^- + 4O(C_2H_5)_2 \tag{1}$$

$${}^1/{}_2B_2H_6 + BH_4^- \rightarrow B_2H_7^- \tag{2}$$

$$2B_2H_7^- \rightarrow B_3H_8^- + BH_4^- + H_2 \tag{3}$$

$$5BH_4^- + 4BF_3\cdot O(C_2H_5)_2 \rightarrow 2B_3H_8^- + 3BF_4^- + 2H_2 + 4O(C_2H_5)_2 \tag{4}$$

$$17B_3H_8^- + 16BF_3\cdot O(C_2H_5)_2 \rightarrow 5B_{11}H_{14}^- + 12BF_4^- + 33H_2 + 16O(C_2H_5)_2 \tag{5}$$

$$17NaBH_4 + 20BF_3\cdot O(C_2H_5)_2 \rightarrow 2NaB_{11}H_{14} + 15NaBF_4 + 20H_2 + 20O(C_2H_5)_2 \tag{6}$$

which reacts further with BH_4^- ion to form $B_2H_7^-$ ion[4] (eq 2). The $B_2H_7^-$ ion thermally decomposes to $B_3H_8^-$ ion and BH_4^- ion[5] (eq 3), and thus the sequence continues until the BH_4^- ion is consumed. The overall process can be accomplished in one vessel,[6] producing $B_3H_8^-$ ion in approximately 65% yield on the basis of the stoichiometry of eq 4. If, however, $BF_3\cdot O(CH_2H_5)_2$ is added beyond the quantity represented by eq 4, the $B_3H_8^-$ ion reacts to form $B_{11}H_{14}^-$ ion[2] (eq 5). This sequence of reactions suggests that, under appropriate conditions, any reagent capable of producing B_2H_6 in the presence of BH_4^- ion may form $B_{11}H_{14}^-$ ion as in the case of $BF_3\cdot O(C_2H_5)_2$[2] (eq 6).

In addition to $BF_3\cdot O(C_2H_5)_2$, other Lewis acids and Bronsted acids have been shown to produce B_2H_6 when reacted with BH_4^- ion including BCl_3,[4] $AlCl_3$,[7] $ZnCl_2$,[8] $SnCl_2$,[9] H_2SO_4,[10] H_3PO_4,[11] and CH_3COOH,[12] and indeed B_2H_6 has been prepared from BH_4^- ion and alkyl halides.[4,13] With this background, a study directed toward the optimization of the synthesis of $B_{10}H_{14}$ via $B_{11}H_{14}^-$ ion was initiated.

Table I. Synthesis of $B_{11}H_{14}^-$ Ion from $NaBH_4$ and Acids

acid	$B_{11}H_{14}^-$ yield,[a] %	eq
$BF_3\cdot O(C_2H_5)_2$	63	6
BCl_3	46	8
$SiCl_4$	55	9
CH_3Cl	54	7
CH_2Cl_2	26	7
n-C_4H_9Cl	25	7
n-$C_5H_{11}Br$	67	7
n-$C_6H_{13}Br$	18	7

[a] Isolated as $(C_2H_5)_4N^+$, $(CH_3)_4N^+$, or $(CH_3)_3NH^+$ salts.

We report here the synthesis of $B_{11}H_{14}^-$ ion from BH_4^- ion and acids including $BF_3\cdot O(C_2H_5)_2$, BCl_3, $SiCl_4$, and alkyl halides and the subsequent oxidation of the $B_{11}H_{14}^-$ ion to produce $B_{10}H_{14}$ employing $Na_2Cr_2O_7$, $KMnO_4$, H_2O_2, and H_2O_2 in the presence of ferrous sulfate.

Results and Discussion

The procedure for the synthesis of $B_{10}H_{14}$ from BH_4^- ion involves three steps: (1) the synthesis of $B_{11}H_{14}^-$ ion from BH_4^- ion and an acid in a donor solvent, (2) exchange of the donor solvent for water, and (3) the oxidation of the aqueous solution of $B_{11}H_{14}^-$ ion to produce $B_{10}H_{14}$.

Step 1: Formation of $B_{11}H_{14}^-$ Ion. Sodium borohydride when treated with H_2SO_4, H_3PO_4, or CH_3COOH in diglyme solvent at 105 °C under conditions similar to those employed previously to synthesize $B_{11}H_{14}^-$ ion with $BF_3\cdot O(C_2H_5)_2$,[2] failed to produce detectable concentrations of BH-containing materials (by ^{11}B NMR). However BCl_3, $SiCl_4$, CH_3Cl, CH_2Cl_2, n-C_4H_9Cl, n-$C_5H_{11}Br$, and n-$C_6H_{13}Br$ did react with $NaBH_4$ under the conditions to produce $B_{11}H_{14}^-$ ion (Table I). The side products of the reaction of $NaBH_4$ with alkyl halides (eq 7) were hydrogen and the sodium halide and the alkane

$$11NaBH_4 + 10RX \rightarrow NaB_{11}H_{14} + 10RH + 10NaX + 10H_2 \tag{7}$$

corresponding to the alkyl halide starting material. While only hydrogen and sodium chloride were byproducts of the synthesis of $B_{11}H_{14}^-$ ion using BCl_3 (eq 8), $SiCl_4$ produced silane (42%) in addition to hydrogen and sodium chloride (eq 9).

$$17NaBH_4 + 5BCl_3 \rightarrow 2NaB_{11}H_{14} + 15NaCl + 20H_2 \tag{8}$$

$$22NaBH_4 + 5SiCl_4 \rightarrow 2NaB_{11}H_{14} + 5SiH_4 + 20NaCl + 20H_2 \tag{9}$$

The reaction of KBH_4 with $BF_3\cdot O(C_2H_5)_2$ in diglyme produced detectable concentrations of $B_3H_8^-$ ion and $B_{11}H_{14}^-$ ion. No BH_4^- ion was observed in the solution (by ^{11}B NMR) probably due to the low solubility of KBH_4 in diglyme. During

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the course of the experiment, the temperature of the off-gas scrubber (Experimental Section) increased markedly, indicating that a significant quantity of B_2H_6 was being evolved and destroyed in the scrubber with the evolution of heat. This suggests that, while B_2H_6 was readily formed, the concentration of BH_4^- ion in solution was too low to efficiently effect its complexation, and thus very little $B_{11}H_{14}^-$ ion was produced.

Treatment of $LiBH_4$ in diglyme (very soluble) with $BF_3 \cdot O(C_2H_5)_2$ produced $B_{11}H_{14}^-$ ion in 48% yield. Workup of the reaction mixture was complicated by the solvation of the Li^+ ions.

Even though a vigorous reaction occurred, no $B_{11}H_{14}^-$ ion was observed in a diglyme solution of $(C_2H_5)_4NBH_4$ which had been treated with $BF_3 \cdot O(C_2H_5)_2$. The solid filtered from the reaction mixture was largely $(C_2H_5)_4NBF_4$ with a detectable quantity of $(C_2H_5)_4NBH_4$ starting material.

Diglyme/bis(methoxyethyl) ether and diethylcarbitol/bis(ethoxyethyl) ether were found to be excellent solvents for the synthesis of $B_{11}H_{14}^-$ ion from $NaBH_4$ and $BF_3 \cdot O(C_2H_5)_2$. However, when 1,4-dioxane solvent was used (at 90 °C) no BH containing materials were observed in the reaction mixture.

Unless otherwise noted, all of the above reactions were conducted at 105 °C. A reaction of $NaBH_4$ and $BF_3 \cdot O(C_2H_5)_2$ in diglyme solvent conducted at 150 °C proceeded smoothly; however, no boron species other than BF_4^- ion was detected by ^{11}B NMR in the reaction mixture and no $B_{11}H_{14}^-$ ion salts could be isolated. The ^{11}B NMR spectrum of the reaction mixture from an experiment performed at 85 °C indicated the presence of BF_4^-, $B_3H_8^-$, $B_{11}H_{14}^-$, and $B_9H_{14}^-$ ions. Only traces of the latter ion had been observed in experiments performed at 105 °C. The presence of $B_9H_{14}^-$ ion supports the previous proposal that $B_9H_{14}^-$ ion is a probable intermediate in the buildup of polyhedral borane anions.[14]

Step 2: **Solvent Exchange.** The diglyme or diethylcarbitol solvent used in the synthesis of $B_{11}H_{14}^-$ ion was exchanged for water prior to the oxidation of the $B_{11}H_{14}^-$ ion. Even low concentrations of free ethereal solvent in the resulting aqueous solution were found to reduce the yield of $B_{10}H_{14}$ in the subsequent oxidation step. Control experiments showed that benzene/$B_{10}H_{14}$ solutions in contact with water (ambient temperature) were stable; however, the addition of diglyme (3:1 diglyme/$B_{10}H_{14}$) promoted hydrolysis of the $B_{10}H_{14}$ (half-life $\approx$ 60 h). Three methods of ethereal solvent removal were investigated.

(1) Vacuum distillation of the diglyme or diethylcarbitol solvent from the $B_{11}H_{14}^-$ ion reaction mixture removed approximately 85% of the solvent. The resulting semisolid in the reaction vessel complicated stirring and presented potential hazards associated with localized overheating.

(2) An interesting property of diethylcarbitol is that, while miscible with water at lower temperatures, it separates from water at temperatures >80 °C. Thus water could be added to reaction mixtures in which diethylcarbitol was employed and the solution heated. The diethylcarbitol layer could be decanted, leaving the $B_{11}H_{14}^-$ salts and other ionic reaction products in the aqueous layer. This method of solvent exchange proved difficult to operate in large-scale preparations and cannot be applied to reactions employing diglyme, which is miscible with water at all temperatures.

(3) Both diglyme and diethylcarbitol form constant-boiling mixtures with water (bp 99.6 and 98.4 °C at 1 atm, respectively). The distillate contains approximately 20 vol % ethereal solvent in each case.[15] Thus, addition of water to the cooled reaction mixture subsequent to the synthesis of $B_{11}H_{14}^-$ and the distillation (1 atm) of the ethereal solvent/water azeotrope proved to be the most facile solvent-exchange procedure attempted. Water was added to the reaction mixture at a rate equal to the rate that distillate was removed; thus the volume of the solution in the reaction vessel could be maintained constant to minimize stirring and over heating difficulties. Distillation was continued until the appropriate quantity of distillate had been collected. The cooled aqueous solution was suitable for use in the final oxidation step.

During the distillation of the diglyme/water azeotrope from the reaction mixture, which contained $B_{11}H_{14}^-$ ion and the other nonvolatile products, a small quantity of white solid was occasionally observed to collect in the condenser. A sample of the solid was characterized by spectral methods as n-$B_{18}H_{22}$.[16] It was reported previously that n-$B_{18}H_{22}$ was the major product of the protonation of $B_{11}H_{14}^-$ ion under anhydrous conditions.[17] The mechanism of the production of the n-$B_{18}H_{22}$ in the present system is unknown; however, its presence suggests that condensation of $B_{11}H_{14}^-$ ions may occur in the aqueous medium. The significance of such coupling reactions will be discussed below.

For economy, the ethereal solvents could be isolated from the aqueous solutions resulting from the above distillation and reused. The addition of toluene to the water/ether solutions followed by distillation of the toluene/water azeotrope (bp 85 °C, 1 atm, 18 vol % water[15]) using a distillation head capable of returning the toluene to the pot allowed complete removal of the water. Distillation of the toluene and a forerun of the ethereal solvent provided diglyme (bp 162 °C, 1 atm) or diethylcarbitol (bp 189 °C, 1 atm) sufficiently dry and pure for direct reuse in the synthesis of $B_{11}H_{14}^-$ ion.

Step 3: **Oxidation of $B_{11}H_{14}^-$ Ion to $B_{10}H_{14}$.** The aqueous solution of $B_{11}H_{14}^-$ ion from the solvent-exchange step above was acidified and treated with excess aqueous oxidizing agent. $B_{10}H_{14}$ produced was continuously extracted from the aqueous phase by a layer of immiscible organic solvent.

The conversion of $B_{11}H_{14}^-$ ion to $B_{10}H_{14}$ via the in situ oxidation of the $B_{11}H_{14}^-$ ion produced in step 1, in which diglyme solvent had been used, was as high as 53% (on the basis of a 70% yield of $B_{11}H_{14}^-$ ion in step 1 as indicated by ^{11}B NMR). A similar in situ oxidation of $B_{11}H_{14}^-$ ion synthesized in diethylcarbitol solvent produced $B_{10}H_{14}$ in only 26% conversion (again on the basis of the yield of $B_{11}H_{14}^-$ ion as indicated by ^{11}B NMR). Moreover, when isolated, pure $(CH_3)_3NHB_{11}H_{14}$ was converted to the potassium salt (to increase solubility) and subsequently oxidized under similar conditions, the conversion to $B_{10}H_{14}$ was only 15%. These results suggest that diglyme was instrumental in producing high yields of $B_{10}H_{14}$ in the oxidation step. For a test of this, the "diglymate", $NaB_{11}H_{14} \cdot 2C_6H_{14}O_3$ was prepared and crystallized from aqueous solution. Oxidation of the pure $NaB_{11}H_{14} \cdot 2C_6H_{14}O_3$ produced $B_{10}H_{14}$ in 48% conversion (comparable to the conversion obtained in the in situ oxidation of $B_{11}H_{14}^-$ ion above). A similar oxidation of the "dioxanate", $NaB_{11}H_{14} \cdot 2.5C_4H_8O_2$,[18] produced $B_{10}H_{14}$ in only 13% conversion. The diethylcarbitol/$B_{11}H_{14}^-$ ion complex was an oil and could not be compared. Thus, in the in situ oxidation of $B_{11}H_{14}^-$ ion to $B_{10}H_{14}$, the active species may be the $B_{11}H_{14}^-$ ion/diglyme complex.

Passage of air or oxygen through an aqueous $B_{11}H_{14}^-$ ion solution which contained $FeSO_4$ failed to produce $B_{10}H_{14}$ in detectable quantities. Hydrogen peroxide (30%) produced $B_{10}H_{14}$; however, the reaction was very slow, requiring 42 h to maximize the $B_{10}H_{14}$ yield. Potassium permanganate and

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Table II. Oxidation of $B_{11}H_{14}^-$ Ion[a] with Various Oxidizing Agents

oxidizing agent	mL of oxidant soln	equiv of oxidizing agent	time required, h	$B_{10}H_{14}$			
				g	mol	yield,[b] %	conversion,[c] %
H_2O_2/Fe(II)	72	1.34	2.7	8.55	0.070	74.9	44.0
$Na_2Cr_2O_7$	105	2.40	1.0	7.82	0.064	68.5	40.2
$KMnO_4$	1600	1.70	0.7	9.13	0.075	80.0	47.0
H_2O_2	130	7.72	42	7.99	0.065	70.0	41.1

[a] Prepared in situ from $NaBH_4$ (1.59 mol) and $BF_3 \cdot O(C_2H_5)_2$ in diglyme. [b] Based on eq 6 and 11. [c] Conversion of $NaBH_4$ to $B_{10}H_{14}$.

sodium dichromate both rapidly (<1 h) produced $B_{10}H_{14}$ in good yield. The low solubility of $KMnO_4$, however, required a reactor volume much larger than did sodium dichromate and also required careful control of pH to prevent precipitation of MnO_2. Hydrogen peroxide (30%) in the presence of $FeSO_4$ proved to be the optimum oxidizing agent in terms of yield and ease of operation (i.e., reactor size, disposal of reaction byproducts, and reaction time) (Table II).

The in situ oxidation (using $H_2O_2/FeSO_4$) of the $B_{11}H_{14}^-$ ion produced from alkyl bromides, alkyl chlorides, BCl_3, or $SiCl_4$ liberated bromine or chlorine, respectively, and those reactions were not studied further.

The stoichiometry of the oxidation of $B_{11}H_{14}^-$ ion to $B_{10}H_{14}$ was not unambiguously established. In the simplest process, 1 mol of $B_{10}H_{14}$ and 1 mol of $B(OH)_3$ would be produced for each mole of $B_{11}H_{14}^-$ ion employed (eq 10). No hydrogen

$$B_{11}H_{14}^- + 3H_2O \rightarrow B_{10}H_{14} + B(OH)_3 + 3H^+ + 4e^- \quad (10)$$

would be evolved, and 4 equiv of oxidizing agent would be consumed.

The experimental results were not consistent with the stoichiometry of eq 10, instead approximately 8 mol of hydrogen/mol of $B_{11}H_{14}^-$ ion was evolved, and 8 equiv of oxidizing agent were required to maximize the yield of $B_{10}H_{14}$. Furthermore, as discussed above, the conversion of $B_{11}H_{14}^-$ ion to $B_{10}H_{14}$ was very close to 50% for $NaB_{11}H_{14} \cdot 2C_6H_{14}O_3$ and for $B_{11}H_{14}^-$ ion formed in situ. These results suggest the possibility that two $B_{11}H_{14}^-$ ions were required to form one $B_{10}H_{14}$ in the oxidation step. Equation 11 best represents the experimental results. A possible first step in the oxidation

$$2B_{11}H_4^- + 36H_2O \rightarrow B_{10}H_{14} + 12B(OH)_3 + 18H_2 + 14H^+ + 16e^- \quad (11)$$

of $B_{11}H_{14}^-$ ion is the oxidative coupling of two $B_{11}H_{14}^-$ ions (with loss of two protons). For example, the oxidative coupling of $B_{10}H_{10}^{2-}$ ions by chemical[19] and electrochemical[20] procedures produced $B_{20}H_{18}^{2-}$ ion. Similarly, the chemical[21] and electrochemical[22] oxidative coupling of $B_{12}H_{12}^{2-}$ ion produced $B_{24}H_{23}^{3-}$ ion. Attempts in this study to isolate a coupled species from the reaction of $B_{11}H_{14}^-$ ion with ferric chloride using anhydrous conditions were unsuccessful. On one occasion, the addition of $(CH_3)_3NHCl$ to the aqueous mixture subsequent to the oxidation of $B_{11}H_{14}^-$ ion prepared in situ (with H_2O_2) produced a white precipitate. On the basis of the information presently available, the formulation favored for the precipitate is $[(CH_3)_3NH]_2B_{22}H_{24}$. The 80.5-MHz ^{11}B NMR spectrum (Figure 1) consisted of a high-field doublet of relative area 2, an overlapping set of resonances centered at approximately −16.9 ppm (upfield from $BF_3 \cdot O(C_2H_5)_2$[23] of relative area 19, and a low-field singlet of relative area 1. Anal. Calcd: B, 62.31; C, 18.85; H, 11.52; N, 7.33. Found: B, 62.15; C, 17.65; H, 12.00; N, 6.98. Equivalent weight: calcd, 191.02; found, 203.5. A structure consistent with the data is a B_{10} moiety singly bonded to a B_{12} moiety $[(B_{10}H_{13}-B_{12}H_{11})^{2-}$ ion]. Such a structure could arise from the oxidative coupling of two B_{11} fragments ($B_{11}H_{13}^{2-}$ ions) followed by the migration of one boron atom and loss of hydrogen. Further work is necessary to elucidate the composition and structure of this material.

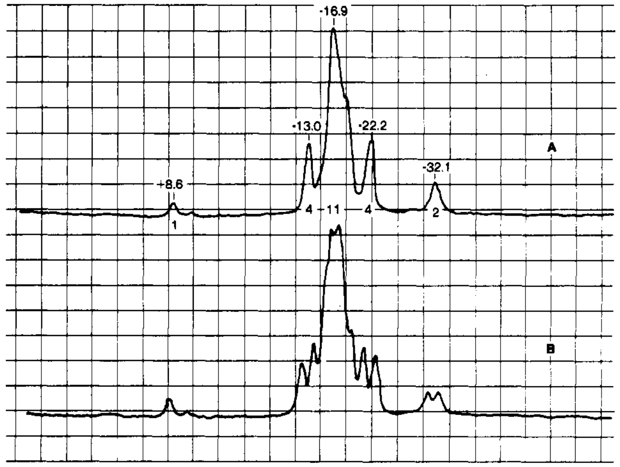

Figure 1. 80.5-MHz ^{11}B NMR spectrum of $[(CH_3)_3NH]_2B_{22}H_{24}$ measured in acetone: (A) proton decoupled, (B) undecoupled. Chemical shifts [ppm, relative to $BF_3 \cdot O(C_2H_5)_2$][23] are indicated. Relative areas appear beneath the peaks.

Clearly, the presence of $B_{22}H_{24}^{2-}$ (?) ion supports the proposal that the oxidation of $B_{11}H_{14}^-$ ion may involve two ions. In the subsequent hydrolysis of $B_{22}H_{24}^-$ ion, $B_{10}H_{14}$ was apparently the first intermediate capable of surviving the experimental conditions and, therefore, could be isolated. As noted by other authors, $B_{12}H_{12}^{2-}$ ion is relatively unstable under chemical oxidizing conditions[24] and is degraded to $B(OH)_3$.

Benzene, toluene, dichloromethane, hexane, cyclohexane, and 2,3-dimethylbutane were used as the organic phase to extract the product $B_{10}H_{14}$ from the aqueous phase during the oxidation. Benzene, toluene, and dichloromethane were found to extract colored impurities with $B_{10}H_{14}$ and each possessed undesirable physical or chemical properties (e.g., high freezing or boiling points, high density, etc.). Indeed dichloromethane may form shock-sensitive solutions of $B_{10}H_{14}$. Hexane and cyclohexane were found to be the optimum extractants of those investigated in terms of chemical and physical properties, availability, and economy.

Subsequent to the oxidation step, the organic phase which contained $B_{10}H_{14}$ was separated from the aqueous phase and dried, and $B_{10}H_{14}$ was isolated (such solutions of $B_{10}H_{14}$ were also used directly in the synthesis of carboranes).

The infrared, ^{11}B NMR, and mass spectra of the isolated $B_{10}H_{14}$ were identical with those of authentic samples.[25-28]

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GC–MS analysis of the concentrated liquor which remained after crystallization of the $B_{10}H_{14}$ contained peaks at *m/e* 138 ($CH_3B_{10}H_{13}^+$, two isomers), *m/e* 152 [$(CH_3)_2B_{10}H_{12}^+$, three isomers], and *m/e* 166 [$(CH_3)_3B_{10}H_{11}^+$, one isomer] and a minor peak at *m/e* 136 ($B_{11}H_{15}^+$) in addition to peaks which correspond to diglyme, organic extractant (i.e., hexane of cyclohexane), and $B_{10}H_{14}$.

Optimum Procedure. The optimum procedure for the synthesis of $B_{10}H_{14}$ in terms of yield and ease of operation based upon the results of this study is as follows. In step 1, $NaBH_4$ is treated with $BF_3{\cdot}O(C_2H_5)_2$ in diglyme solvent at 105 °C according to eq 6 to produce intermediate $B_{11}H_{14}^-$ ion. In step 2, water is added to the cooled reaction mixture, and the diglyme solvent is removed by distillation of the water/diglyme azeotrope. In step 3, the resulting aqueous solution of $B_{11}H_{14}^-$ ion is oxidized with hydrogen peroxide solution in the presence of $FeSO_4$, H_2SO_4, and hexane or cyclohexane. The organic phase (hexane or cyclohexane) is separated from the aqueous layer, dried, and concentrated in one step by distillation of the water/hexane (or water/cyclohexane) azeotrope followed by distillation of pure solvent. The concentrated $B_{10}H_{14}$ solution is cooled, and the crystalline $B_{10}H_{14}$ is isolated by filtration.

A linear scale-up of this procedure to 12-L vessels (19.0 mol of $NaBH_4$) in the laboratory and to 235-L vessels (370 mol of $NaBH_4$) in the pilot plant was achieved successfully. The average yield on the basis of eq 6 and 11 of $B_{10}H_{14}$ (10 runs) was 76% (44.7% conversion) in the laboratory, and reduced but satisfactory (>60%) yields were realized in the pilot plant.

Experimental Section

Sodium borohydride, potassium borohydride, lithium borohydride, and tetraethylammonium borohydride were obtained from Ventron Corp. and used as received. Diglyme (Ansul-141) was heated over sodium and benzophenone until a dark blue color was obtained and then was distilled at 60 °C (13 torr). Diethylcarbitol was obtained from Matheson, Coleman, and Bell (MCB) and treated with sodium and benzophenone prior to distillation at 74 °C (10 torr). Boron trifluoride–diethyl etherate (98%) was obtained from MCB and distilled from calcium hydride at 65 °C (41 torr). Hydrogen peroxide solution (31.2%, electronic grade) was obtained from PPG Industries and used as received. Silicon tetrachloride (technical grade) was obtained from Union Carbide and used as received. Boron trichloride and methyl chloride were obtained from Linde Specialty Gases and were used as received. All other materials were obtained from Fisher Scientific, were reagent grade, and were used as received. The temperatures were controlled with a Therm-O-Watch, I^{2}R Co., and liquid reagents were added with a Minipump, Milton Roy Co. The ^{11}B NMR spectra were measured with a Brucker Model HFX-90 spectrometer operating at 28.87 MHz with a Brucker Model B-SVZ proton decoupler operating at 90 MHz and with the 80.5-MHz research instrument at UCLA. Proton NMR spectra were measured with a Varian T-60 instrument. Infrared spectra were measured as Nujol mulls (solids) with a Beckman IR 5A spectrophotometer. Decaborane solutions were analyzed by the colorimetric method described by Hill and Johnston[29] using a Bausch and Lomb Spectronic 20. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

Preparation of the Aqueous $B_{11}H_{14}^-$ Ion (Optimum Procedure). The apparatus for step 1, the synthesis of intermediate $B_{11}H_{14}^-$ ion (Figure 2), consisted of a 2000-mL, three-neck flask equipped with a mechanical stirrer, a tube through which $BF_3{\cdot}O(C_2H_5)_2$ could be pumped from a reservoir (a pressure-equalized addition funnel could be used), and a side tube connected to a dry ice condenser and thence to an acetone-filled scrubber. The condensate was collected in a flask fitted to the side tube. A thermometer was passed through the side tube and into the reaction mixture and attached to the Therm-O-Watch. Under a slow stream of nitrogen, the flask was charged with 300 mL of diglyme and 60.0 g (1.59 mol) of $NaBH_4$. With stirring, the contents of the flask were heated to 105 °C, and 250 mL (2.04 mol) of $BF_3{\cdot}O(C_2H_5)_2$ was added at the rate of 40 mL/h. After the addition was complete (~6 h), the reaction mixture was maintained at 105 °C for 1 h and then allowed to cool to ambient temperature overnight under a nitrogen atmosphere.

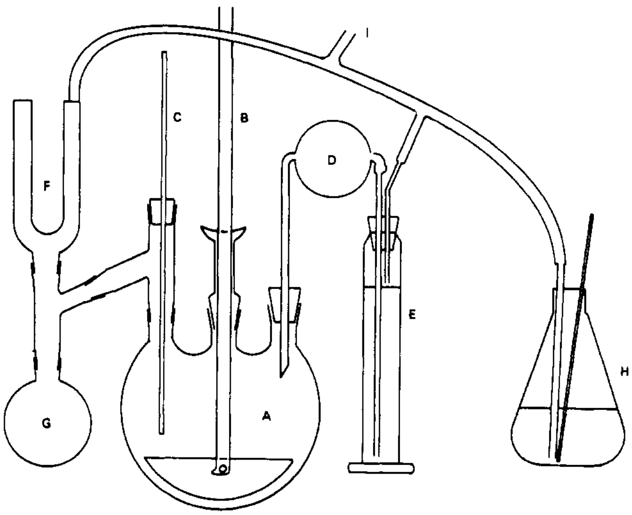

Figure 2. Apparatus used in the $B_{11}H_{14}^-$ ion forming step (step 1) consisted of a 2000-mL, three-neck flask (A) fitted with a mechanical stirrer (B), a thermometer (C), and a pump for the addition of $BF_3{\cdot}O(C_2H_5)$ (D) from the reservoir (E). The reaction off-gas passed through the dry-ice condenser (F) which condensed the ether into the receiver (G). The noncondensable gas passed through the condenser and into the acetone scrubber (H). Nitrogen was introduced at I.

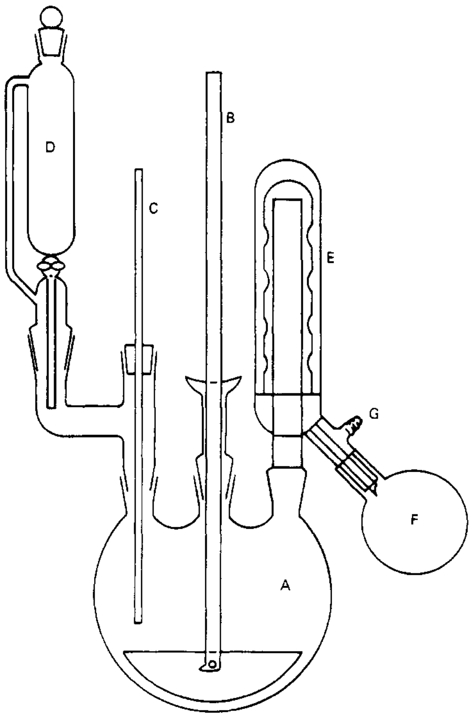

Figure 3. Apparatus used in the solvent exchange step (step 2) consisted of the same 2000-mL, three-neck flask used in the $B_{11}H_{14}^-$ ion forming step (A) fitted with a mechanical stirrer (B), a thermometer (C), a pressure-equalized addition funnel (D), a concentrator condenser (E), a receiver (F), and an opening (G) attached to a nitrogen bubbler which allowed gases produced to escape.

Solvent Exchange (Optimum Procedure). The apparatus for step 2, solvent exchange (Figure 3), was modified by replacing the ether trap with an addition funnel and the pump inlet with a water-cooled concentrator condenser and receiver. Water (800 mL) was added

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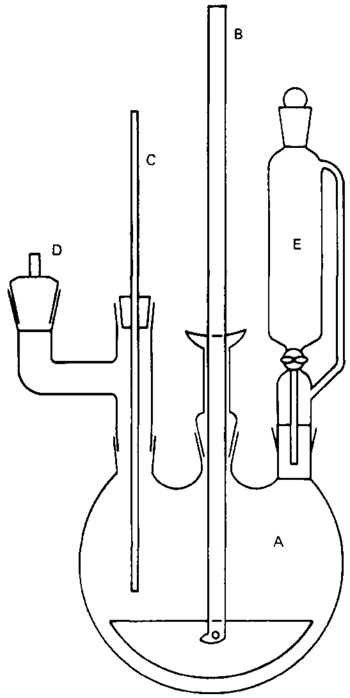

Figure 4. Apparatus used in the oxidation step (step 3) consisted of the 2000-mL, three-neck flask (A), equipped with a mechanical stirrer (B), a thermometer (C), an opening (D) attached to a nitrogen bubbler, and a pressure-equalized addition funnel (E).

slowly to the stirred mixture (gas evolution). The reaction mixture was heated (slowly to allow for gas evolution) to distill the water/diglyme azeotrope. An additional 400 mL of water was added during the distillation. The distillation was continued until 1243 mL of distillate had been collected (reaction-mixture temperature 112 °C). The reaction mixture was cooled to ambient temperature.

Oxidation of Aqueous $B_{11}H_{14}^-$ Ion with H_2O_2/$FeSO_4$ (Optimum Procedure). The apparatus for step 3, oxidation of $B_{11}H_{14}^-$ ion (Figure 4), was altered by replacing the condenser with an addition funnel and adding a gas outlet. Hexane (250 mL), sulfuric acid (62 mL, 50% v/v) and 4.4 g of $FeSO_4{\cdot}7H_2O$ were added. Over a period of 2.7 h, 72 mL (0.67 mol) of 31.2% H_2O_2 was added from the addition funnel to the stirred reaction mixture. The reaction temperature was allowed to increase to 35 °C and then maintained at 35 ± 5 °C throughout the addition (cooling was necessary). When the addition was complete, the mixture was filtered to remove yellow solids, and the filtrate was placed in a separatory funnel. The layers were separated, and the aqueous layer was washed with 2 × 100 mL portions of hexane. The combined hexane fractions were washed with 2 × 100 mL portions of water and dried over anhydrous $MgSO_4$. Analysis of the filtered hexane solution (1350 mL) indicated the presence of 8.55 g (0.070 mol) of $B_{10}H_{14}$.

Oxidation of Aqueous $B_{11}H_{14}^-$ Ion with $Na_2Cr_2O_7$. The aqueous $B_{11}H_{14}^-$ ion was prepared as above. To the solution were added H_2SO_4 (300 mL, 50% v/v) and benzene (500 mL). With stirring, a solution of 118.5 g (0.4 mol) of $Na_2Cr_2O_7{\cdot}2H_2O$ in 60 mL of water (105 mL total) was added over a period of 1 h. The temperature of the reaction mixture was allowed to increase to 30 °C. The mixture was transferred to a separatory funnel and the benzene layer separated. The aqueous layer was washed with 400 mL of benzene, and the combined benzene fractions were dried over anhydrous $MgSO_4$ and filtered. The benzene solution was analyzed and found to contain 7.82 g (0.064 mol) of $B_{10}H_{14}$.

Oxidation of Aqueous $B_{11}H_{14}^-$ Ion with $KMnO_4$. The aqueous $B_{11}H_{14}^-$ ion was prepared as above. The solution was transferred to a 5000-mL, three-neck flask which was fitted as in Figure 3 with a 2000-mL addition funnel. To the solution were added H_2SO_4 (150 mL, 50% v/v) and benzene (946 mL). A solution of 53.3 g (0.34 mol) of $KMnO_4$ and 160 mL of H_2SO_4 in 1600 mL of water was added with stirring over a period of ~40 min. The temperature of the reaction mixture was maintained at 10 °C with external cooling. The reaction mixture was transferred to a separatory funnel, and the benzene layer was separated and washed with 2 × 350 mL portions of water. The benzene fraction was dried over anhydrous $MgSO_4$ and condensed to an oil with use of a rotary evaporator and water aspirator. The oil was placed in a sublimer which was evacuated and then heated to 50 °C with the cold finger cooled with ice (0 °C). After the residual benzene had evaporated, $B_{10}H_{14}$ collected on the cold finger (9.13 g, 0.075 mol, mp 97.5–98.0 °C).

Oxidation of Aqueous $B_{11}H_{14}^-$ Ion with H_2O_2. The aqueous $B_{11}H_{14}^-$ ion was prepared as above. To the solution were added H_2SO_4 (130 mL, 65% v/v) and benzene (500 mL). A solution of H_2O_2 (130 g, 31.2%, 1.19 mol) was added over a period of 3 h with stirring. The reaction mixture was stirred at ambient temperature for 68 h, and aliquots of the benzene layer were periodically analyzed. The results showed that the concentration of $B_{10}H_{14}$ in the benzene layer maximized after approximately 42 h. The yield of $B_{10}H_{14}$ as indicated by analysis was 7.99 g (0.065 mol).

The aqueous layer was filtered, and 5.0 g of $(CH_3)_3NHCl$ in 20 mL of water was added. After 30 min, a fluffy, white precipitate formed and was isolated by filtration. The solid was recrystallized from acetone/water and dried under vacuum (0.73 g). A 0.1956-g sample was dissolved in 1 mL of acetonitrile and then diluted with 1 mL of water (no precipitate) and passed through an acidic Dowex 50W-8X column with ~40 mL of 1:1 acetonitrile/water solution. The resultant solution required 9.62 mL of 0.0999 N NaOH (0.9610 mequiv) to reach the equivalence point (pH meter). The equivalent weight thus determined was 203.5.

Oxidation of Isolated $B_{11}H_{14}^-$ Ion with H_2O_2/Fe(II). The $(CH_3)_3NH^+$ cation in sparingly water soluble $(CH_3)_3NHB_{11}H_{14}$ was exchanged for K^+ cation to facilitate the oxidation reaction. To a 500-mL Erlenmeyer flask fitted with a magnetic stirring bar were placed 10.6 g (0.19 mol) of KOH and 100 mL of water. The solution was cooled, and 15.3 g (0.08 mol) of purified, crystalline $(CH_3)_3NHB_{11}H_{14}$ was added. The reaction mixture was heated to boiling for 1 h to allow the liberated $(CH_3)_3N$ to evolve and then cooled to ambient. The solution was neutralized to pH 7 with 50% H_2SO_4 solution and then transferred to a 1000-mL, three-neck flask fitted as in Figure 3. To the flask were added H_2SO_4 (62 mL, 50% v/v), hexane (250 mL), and 4.4 g of $FeSO_4{\cdot}7H_2O$. A solution of H_2O_2 (72 mL, 31.2% g/g, 0.70 mol) was added over a period of 2.5 h with the temperature maintained at 30–35 °C. The layers were separated, and the hexane fraction was dried over anhydrous $MgSO_4$, filtered, and stripped to an oil with use of a rotary evaporator and a water aspirator. The product $B_{10}H_{14}$ (1.50 g, 0.012 mol) was sublimed from the oil in vacuo.

Preparation and Oxidation of $NaB_{11}H_{14}{\cdot}2C_6H_{14}O_3$. Aqueous $B_{11}H_{14}^-$ ion was prepared as above. The solution was allowed to stand at ambient temperature without stirring overnight. Crystals which formed were filtered from the solution and dissolved in 250 mL of ethyl ether. The ether solution was filtered and condensed to ~100 mL with use of a rotary evaporator and water aspirator. Water (300 mL) was added, and evaporation continued until all of the ether and about 50 mL of water had been removed. The crystals which had formed were filtered and air-dried (22.7 g). An additional 150 mL of water was stripped from the filtrate, and the crystals which formed were filtered and dried (13.6 g). After an additional 60 mL of water was stripped from the filtrate, 4.6 g of crystalline solid was isolated. The solids were combined and analyzed. Anal. Calcd: B, 29.75; C, 36.00; H, 10.50. Found: B, 30.01; C, 35.65; H, 10.71. A 0.2984-g sample was dissolved in 1 mL of acetonitrile and then diluted to 25 mL with water. The solution was passed through an acidic ion-exchange column (Dowex 50W-X8, 1 × 15 cm) with 50% (v/v) acetonitrile/water as eluant. A total of 50 mL of eluant was collected and titrated with 0.0999 N NaOH with use of a pH meter. The equivalence point was reached after 6.95 mL of NaOH had been added (0.694 mequiv). The equivalent weight of $NaB_{11}H_{14}{\cdot}2C_6H_{14}O_3$ was calculated as 424.26 and found to be 430. A 0.0211-g sample (0.0497 mol) of $NaB_{11}H_{14}{\cdot}2C_6H_{14}O_3$ was dissolved in $(CD_3)_2CO$ in an NMR tube, C_6H_5Cl (15μL, 0.1475 m mol) added as an internal standard, and the ^1H NMR spectrum measured. The theoretical ratios of the integrals of the C_6H_5Cl protons to the methyl and ethylene protons of the diglyme ligands in $NaB_{11}H_{14}{\cdot}2C_6H_{14}O_3$ are 1.235 and 0.927, respectively. The integral ratios found were 1.22 and 0.79, respectively. The ^{11}B NMR spectrum indicated the presence of about 12% BF_4^- ion in the sample as the only impurity. A 500-mL, four-neck flask fitted with a mechanical stirrer, thermometer, gas outlet, and an addition funnel was charged with 22.7 g (0.054 mol) of $NaB_{11}H_{14}{\cdot}2C_6H_{14}O_3$ and 50 mL of water. The mixture was stirred, and 150 mL of hexane, H_2SO_4 (32 mL, 50% v/v), and $FeSO_4{\cdot}7H_2O$ (2.0 g) were added. Over 3.4 h, H_2O_2 (25 mL, 31.2% v/v, 0.25 mol) was added. When the addition was complete, the mixture was transferred to a separatory funnel and the layers were separated. The hexane layer and the hexane wash of the aqueous layer were combined (390 mL), dried over anhydrous $MgSO_4$, and analyzed. The results indicated the presence of 3.2 g (0.026 mol) of $B_{10}H_{14}$ or 48% conversion from $NaB_{11}H_{14}{\cdot}2C_6H_{14}O_3$.

Preparation of $B_{11}H_{14}^-$ Ion in Diethylcarbitol and Its Subsequent Oxidation. The procedure and quantities of reagents used were identical with those used in the synthesis of $B_{11}H_{14}^-$ ion (in diglyme solution) described above. The resulting aqueous $B_{11}H_{14}^-$ ion was oxidized with use of $H_2O_2/FeSO_4$ exactly as described above. Analysis of the hexane layer indicated the presence of 4.2 g (0.034 mol) of $B_{10}H_{14}$.

Oxidation of $NaB_{11}H_{14}{\cdot}2.5C_4H_8O_2$. The synthesis of $NaB_{11}H_{14}{\cdot}2.5C_4H_8O_2$ has been described.[18] To a 500-mL, three-neck flask fitted as in Figure 3 were charged 20.0 g (0.053 mol) of $NaB_{11}H_{14}{\cdot}2.5C_4H_8O_2$, 50 mL of water, 150 mL of benzene, and 140 mL of 50% (v/v) H_2SO_4. Over 3 h a solution of 47.6 g of $Na_2Cr_2O_7{\cdot}2H_2O$ in 100 mL of water was added. When the addition was complete, the aqueous phase was separated and washed with 150 mL of benzene. The combined benzene fractions were dried over anhydrous $MgSO_4$ and analyzed. The analysis revealed the presence of 0.87 g (0.007 mol) of $B_{10}H_{14}$.

Preparation of $B_{11}H_{14}^-$ Ion with $NaBH_4$ and Amyl Bromide. The procedure to be described was used when liquid alkyl halides were employed. A 500-mL, four-neck flask fitted with a mechanical stirrer, thermometer, addition funnel, and gas-exit tube (which required gases produced to pass through a scrubber prior to venting) was charged with 6.0 g (0.159 mol) of $NaBH_4$ and 100 mL of diglyme. The stirred slurry was heated to 105 °C and 128 mL (0.693 mol) of neat *n*-amyl bromide was added over 5 h. When the addition was complete, the slurry was allowed to cool and then filtered with use of a medium-porosity glass frit. The solids were washed with 2 × 50 mL portions of ethyl ether and the washings combined with the diglyme fraction. The combined solutions were evaporated to an oil with use of a rotary evaporator first with a water aspirator and then with a mechanical vacuum pump. The oil was dissolved in 200 mL of water, and 12 g of $(CH_3)_4NCl$ was added. The precipitate was filtered and recrystallized from acetone/water to yield 2.0 g (0.010 mol, 67%) of $(CH_3)_4NB_{11}H_{14}$.

Preparation of $B_{11}H_{14}^-$ Ion from $NaBH_4$ and Methyl Chloride. The apparatus and procedure employed were identical with those described above with the exception that the addition funnel was replaced with a Pyrex sparge tube for the introduction of CH_3Cl. The rate of CH_3Cl addition was monitored with a rotameter; however, the total quantity added to the reaction was determined by the difference in the weight of the CH_3Cl tank before and after the addition. With use of 6.0 g (0.159 mol) of $NaBH_4$ and 29.7 g (0.58 mol) of CH_3Cl, 1.6 g (0.008 mol, 54% yield) of $(CH_3)_4NB_{11}H_{14}$ was isolated.

Preparation of $B_{11}H_{14}^-$ Ion from $NaBH_4$ and BCl_3. The procedure and apparatus employed were identical with those described above for the $B_{11}H_{14}^-$ ion synthesis using amyl bromide. With use of 33.1 g (0.875 mol) of $NaBH_4$ and 33.6 g (0.286 mol) of BCl_3 dissolved in 50 mL of diglyme, 9.07 g (0.047 mol, 46% yield) of $(CH_3)_3NHB_{11}H_{14}$ was isolated.

Preparation of $B_{11}H_{14}^-$ Ion from $NaBH_4$ and $SiCl_4$. A 500-mL, four-neck flask was attached to the manifold of a high-vacuum system through a 30-cm Vigreaux column and a stopcock. The remaining openings were fitted with a mechanical stirrer, a thermometer, and an addition funnel topped with a stopcock through which inert gas could be passed. The apparatus was evacuated and then swept with N_2. The flask was charged with 150 mL of diglyme and 3.8 g (0.10 mol) of $NaBH_4$ and then heated to 105 °C. A solution of 3.8 g (0.022 mol) of $SiCl_4$ in 30 mL of diglyme was added dropwise to the $NaBH_4$ solution. Volatile products were collected in three traps cooled to −196 °C. The reaction mixture changed gradually from tan to red. When the addition was complete, the flask and the attached apparatus were removed from the vacuum system and the contents filtered. The filtrate was stripped to an oil with use of a rotary evaporator and mechanical pump. The oil was dissolved in 200 mL of water, and excess $(CH_3)_4NCl$ was added. The precipitate was filtered and recrystallized from acetone/water to yield 1.0 g (0.005 mol, 55%) of $(CH_3)_4NB_{11}H_{14}$. The contents of the −196 °C (LN_2) trap (10.8 mol) were condensed into a 300-mL flask which contained 2.0 mL of $(C_2H_5)_3N$ and stirred at ambient temperature overnight. The flask was cooled to −78 °C (dry ice) and evacuated through a −196 °C trap. The residual oil (0.14 g) was $(C_2H_5)_3NBH_3$. The −196 °C traps contained 9.6 mmol (42.2% yield) of SiH_4 (identified by gas-phase IR).

Reaction of KBH_4 with $BF_3{\cdot}O(C_2H_5)_2$ in Diglyme. A 1000-mL, three-neck flask (Figure 1) was charged with 42.85 g (0.80 mol) of KBH_4 and 250 mL of diglyme and heated to 105 °C with stirring. Over 4 h, 125 mL (1.0 mol) of $BF_3{\cdot}O(C_2H_2)_2$ was added to the white slurry. During the addition of $BF_3{\cdot}O(C_2H_5)_2$, the temperature of the acetone scrubber increased to 50 °C and solids collected on the walls. When the addition was complete, the ^{11}B NMR spectrum of the acetone from the scrubber contained one broad peak at +16.8 ppm (downfield from $BF_3{\cdot}O(C_2H_5)_2$) which indicated the presence of $B(OH)_3$. ^{11}B NMR analysis of the diglyme solution indicated that both $B_3H_8^-$ and $B_{11}H_{14}^-$ ions were present in very low concentration; however, no BH_4^- ion was observed.

Reaction of $LiBH_4$ with $BF_3{\cdot}O(C_2H_5)_2$ in Diglyme. A 1000-mL, three-neck flask equipped as in Figure 1 was charged with 17.3 g (0.80 mol) of $LiBH_4$ and 150 mL of diglyme which dissolved the $LiBH_4$ with the evolution of heat. The flask was heated to 105 °C with stirring, and 125 mL (1.0 mol) of $BF_3{\cdot}O(C_2H_5)_2$ was added over 4 h. The stirring was stopped, and the flask was allowed to cool to ambient temperature. The slurry in the flask hardened as it cooled to a brittle mass. The mass was broken up and slurried in 250 mL of water, and 30 g (0.31 mol) of $(CH_3)NHCl$ in 150 mL of water was added. The precipitate which formed was filtered and then redissolved in 100 mL of acetone. Water (50 mL) was added and the solution boiled until solid just appeared. Crystals of $(CH_3)_3NHB_{11}H_{14}$ formed as the solution was allowed to cool. After the solution was dried under vacuum overnight, the yield of $(CH_3)_3NHB_{11}H_{14}$ was 8.7 g (0.045 mol, 48%).

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Registry No. $B_{10}H_{14}$, 17702-41-9; $B_{11}H_{14}^-$, 12448-05-4; $NaBH_4$, 16940-66-2; KBH_4, 13762-51-1; $LiBH_4$, 16949-15-8; $(CH_3)_3NHB_{11}H_{14}$, 12076-74-3; $(CH_3)_4NB_{11}H_{14}$, 52619-67-7; $(C_2H_5)_4NB_{11}H_{14}$, 12555-78-1; $NaB_{11}H_{14}{\cdot}2C_6H_{14}O_3$, 76862-07-2; $NaB_{11}H_{14}{\cdot}2.5C_4H_8O_2$, 12545-03-8; $BF_3{\cdot}O(C_2H_5)_2$, 109-63-7; BCl_3, 10294-34-5; $SiCl_4$, 10026-04-7; CH_3Cl, 74-87-3; CH_2Cl_2, 75-09-2; *n*-C_4H_9Cl, 109-69-3; *n*-$C_5H_{11}Br$, 110-53-2; *n*-$C_6H_{13}Br$, 111-25-1.