at 44 °C and 11 Torr (87.7 g, 64.4% yield based on $SbCl_3$). (t-Bu)Me_2Sb was purified by fractional vacuum distillation two more times (55 °C at 20 Torr and 63 °C at 30 Torr): vapor pressure equation $\log P$ (mmHg) = 8.7082 − 2429/[T (K)]; mp 12–13 °C. ^1H NMR (C_6D_6): 1.07 ppm (s, 9 H, $(CH_3)_3C$), 0.55 ppm (S, 6 H, CH_3). ^{13}C NMR (C_6D_6): 29.8 ppm (q of septets, $(CH_3)_3C$, $^1J_{CH}$ = 125, $^3J_{CH}$ = 5.5 Hz), 20.9 ppm (s, $(CH_3)_3C$), 4.7 ppm (q, CH_3, $^1J_{CH}$ = 131 Hz). Anal. Calcd for $C_6H_{15}Sb$: C, 34.49; H, 7.24; Sb, 58.27. Found: C, 34.63; H, 7.20; Sb, 57.50.

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Registry No. (t-Bu)Me_2Sb, 138260-00-1; $SbCl_3$, 10025-91-9; (t-Bu)MgCl, 677-22-5; (t-Bu)$_2$MeSb, 138260-01-2.

Stabilization of Pentaborane(9) toward Air Oxidation and Facile Preparation of *nido*-$R_2C_2B_4H_6$ Clusters in Organic Solutions

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Summary: Solutions of pentaborane(9) in tetrahydrofuran (THF) were found to be indefinitely stable under inert conditions and relatively stable to dry air. Solutions exposed to the air were found to decompose slowly to boric acid. Similar stabilities were also found for other pentaborane(9) organic solvent systems including diglyme, diethyl ether, and hexane. No vigorous reactions with air or moisture, including pyrophoric or shock-sensitive behavior, were observed for any of the solutions investigated. The reaction of pentaborane(9) with triethylamine and either 3-hexyne or phenylacetylene in THF at room temperature was found to produce up to 80% of *nido*-2,3-$(CH_3CH_2)_2C_2B_4H_6$ and 20% of *nido*-2,3-(C_6H_5)-$HC_2B_4H_6$, respectively. In addition, the reaction of diphenylacetylene with the pentaborane(9)–THF solution and triethylamine was also explored to determine if the preparation of the synthetically very difficult *nido*-2,3-$(C_6H_5)_2C_2B_4H_6$ carborane could be achieved. The reaction was found to give a 21% yield of the *nido*-2,3-$(C_6H_5)_2C_2B_4H_6$ carborane after 1 day at room temperature. The nature of the interaction between pentaborane(9) and THF has been investigated by ambient- and low-temperature ^{11}B NMR studies.

The synthetic and organometallic chemistry of many small borane, heteroborane, and related systems has been made accessible through the use of *nido*-pentaborane(9), B_5H_9.[1] In fact, pentaborane(9) is an extremely versatile synthon in the preparation of a wide variety of boron clusters, including the larger boranes such as $[B_9H_{14}]^-$ anion, $B_{10}H_{14}$, and $B_{18}H_{22}$.[1d,2] Pentaborane(9), however, requires extreme caution in handling even under high-vacuum or inert-atmosphere conditions due to its explosive reactivity with air.[3,4] Thus, synthetic reactions requiring pentaborane(9) as a starting material are typically run on relatively small scales (typically less than 50 mmol per reaction vessel) and require laborious handling and safety precautions.[1,3,5] An alternative or modified method in which pentaborane(9) is stabilized but its reactivity not significantly altered is therefore of great practical interest.

Scheme I. Small Substituted Carborane Synthesis[5]

$$RC{\equiv}CR' + nido\text{-}B_5H_9 + N(CH_2CH_3)_3 \longrightarrow nido\text{-}RR'C_2B_4H_6 + H_3B{\cdot}N(CH_2CH_3)_3$$

$$\left\{\begin{array}{l}R = R' = \text{H, alkyl, phenyl, benzyl, indenyl, fluorenyl, adamantyl, naphthyl, etc...}\\ R = \text{H}, R' = \text{Phenyl, indenyl, fluorenyl, phenethyl, norbornadienyl, etc...}\end{array}\right\}$$

The small carboranes[6] and phosphinoboranes[7] derived from pentaborane(9) have been shown to exhibit a broad diversity in their structural and organometallic chemistry. The reactions of pentaborane(9) with unsaturated main-group compounds, such as alkynes[5] and phosphaalkenes,[7] produce a variety of both cage-inserted and cage-substituted cluster compounds. The neat reaction of alkynes with pentaborane(9) in the presence of amine bases such as triethylamine produces *nido*-2,3-$R_2C_2B_4H_6$ carborane clusters in up to 30% yield (Scheme I).[5,6] While this reaction has been shown to be a very general and useful

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method for the formation of these substituted carboranes, its relatively restricted yield and reaction scale has not provided the large amounts of carborane frequently required for multistep syntheses.

In this paper, we report the greatly increased stability of pentaborane(9) toward air oxidation in organic solutions. In order to probe the effect of the solvent on the reactivity of the pentaborane(9), we have used pentaborane(9)–THF solutions to prepare three carborane species *nido*-$RR'C_2B_4H_6$ ($R = R' = CH_3CH_2$, C_6H_5; $R = H$, $R' = C_6H_5$).

Results and Discussion

During our continuing synthetic studies of the reactions of pentaborane(9) and other borane clusters with unsaturated main-group species,[7] we have observed that pentaborane(9) in organic solutions is surprisingly air-stable at room temperature. We have, therefore, begun an investigation into the stability of pentaborane(9) in various organic solvents for possible application in overcoming some of the inherent difficulties typically encountered in the handling of pentaborane(9) in larger scale synthetic reactions. Many of the synthetic reactions which have been reported for pentaborane(9) involve reactions which occur without solvent.[5,6] In contrast, the use of ether solutions of the $B_5H_8^-$ anion have been frequently reported in the formation of pentaborane derivatives and metallaborane complexes.[1,8] The $B_5H_8^-$ anion is not, however, stable at room temperature and decomposes to form the $B_3H_8^-$ anion and the $B_9H_{14}^-$ anion.[1d,8j–l] Weak Lewis bases, such as THF, have been reported to facilitate the intramolecular hydrogen exchange between bridging and terminal hydrogens in the base of the pentaborane(9) cage.[8b,m,n] Complete hydrogen equilibration between all the basal and apical sites, however, was reported only when pentaborane(9) was placed in a stronger Lewis base such as 2,6-dimethylpyridine.[5d] In order to probe the potential synthetic utility of pentaborane(9)–THF solutions more fully, several stability and reactivity studies of pentaborane(9) in organic solvents have been completed and are described below.

THF solutions of pentaborane(9) in varying concentrations (0.03–0.2 M) were prepared and stored under inert-atmosphere conditions.[9] The potential decomposition of these solutions under inert conditions and upon exposure to air were monitored by ^{11}B NMR spectroscopy. In all solutions maintained under inert-atmosphere conditions, no decomposition of the pentaborane(9) was detected after standing at room temperature for over 1 month. When the solutions were exposed to a dynamic, dry-air atmosphere at room temperature, however, decomposition was found to occur more rapidly with complete decomposition occurring over several days. Upon exposure to a static air atmosphere, decomposition of the pentaborane(9) was observed to occur only very slowly. After 1 month, a 0.1 M solution still contained 59% of the original pentaborane(9). Similar reduced oxidation properties were also found for other organic solvents relative to neat pentaborane(9) including diglyme, diethyl ether, and hexane. No vigorous reactions with air or moisture, including pyrophoric or shock-sensitive behavior, were observed for any of the solutions investigated.

In order to probe the synthetic usefulness of the pentaborane(9)–THF solutions, we have investigated the solution-phase preparation of 2,3-diethyl-2,3-dicarba-*nido*-hexaborane(8), $(CH_3CH_2)_2C_2B_4H_6$, 2-phenyl-2,3-dicarba-*nido*-hexaborane(8), $(C_6H_5)HC_2B_4H_6$, and 2,3-diphenyl-2,3-dicarba-*nido*-hexaborane(8), $(C_6H_5)_2C_2B_4H_6$. The reaction of pentaborane(9) in THF and triethylamine with 3-hexyne at room temperature was found to cleanly produce the corresponding *nido*-2,3-$(CH_3CH_2)_2C_2B_4H_6$ cluster in up to 80% yield. The ^{11}B NMR spectra after 3 days clearly showed *only* the presence of the carborane product, $BH_3{\cdot}N(CH_2CH_3)_3$, and unreacted B_5H_9 with an approximate 1:1 ratio of carborane:pentaborane(9) observed. The carborane can be readily purified using trap-to-trap distillation according to literature procedures to provide the pure, solvent free-material in 74% yield.[5,9] As anticipated, reactions without triethylamine base did not produce the carborane. The analogous reaction between pentaborane(9)–THF, triethylamine, and phenylacetylene was found to produce the *nido*-2,3-$(C_6H_5)HC_2B_4H_6$ cluster in 20% yield.[5a,e] Finally, the reaction of diphenylacetylene, $C_6H_5C{\equiv}CC_6H_5$, with the pentaborane(9)–THF solution and triethylamine was also explored to determine if the preparation of the synthetically very difficult *nido*-2,3-$(C_6H_5)_2C_2B_4H_6$ carborane could be achieved.[10] The reaction was found to give a 21% yield of the *nido*-2,3-$(C_6H_5)_2C_2B_4H_6$ carborane after 1 day at room temperature. This behavior of pentaborane(9) solutions is consistent with the report that decaborane(14) forms both adducts and cleavage products with THF. These THF solutions were also found to catalyze the reaction of decaborane(14) with acetylenes to produce large cage carboranes.[11g] Thus, the use of pentaborane(9)–THF solutions provides a safe and convenient method for very cleanly preparing *nido*-2,3-$R_2C_2B_4H_6$ clusters in significantly higher yields and reaction purity than currently established procedures.[5]

The reaction of several borane clusters with Lewis bases, including ethers such as THF, has been investigated.[11–14] For borane clusters which contain BH_2 units, cleavage of the cluster occurred to produce a variety of predominantly smaller boranes and their derivatives. In particular, the reactions of the *arachno*-B_5H_{11} cluster with ethers and amines yield complex mixtures of boranes and their de-

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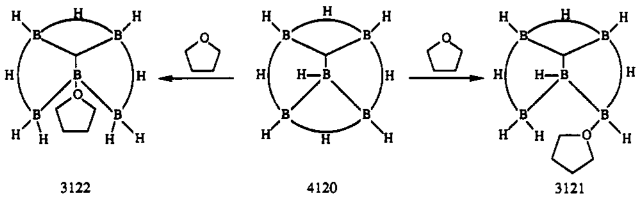

Figure 1. Topological representation of the possible coordination modes for THF on pentaborane(9).

rivatives including diborane(6), tetraborane(10), pentaborane(9), hexaborane(10), and nonaborane(15). Kodama[11a] has shown that, in the reaction of *arachno*-B_5H_{11} with THF at very low temperatures (<-33 °C), two products are formed in equilibrium. These compounds have been identified by reaction and spectroscopic techniques as $[B_4H_9^-][H_2B(THF)_2^+]$ and $B_5H_{11}\cdot THF$. Above -33 °C, however, an irreversible cleavage reaction occurs to produce $BH_3\cdot THF$, B_2H_6, $B_3H_7\cdot THF$, B_5H_9, and B_6H_{10}. As expected for a borane cluster without BH_2 units, we did not detect the formation of any cleavage products from the reaction of pentaborane(9) and any of the organic solvent systems, including THF.

^{11}B NMR studies at ambient and low temperatures provide some information on the nature of the interaction of the pentaborane(9) cage with the THF solvent. In one experiment, pure pentaborane(9) liquid was sealed in a glass capillary, inserted into a pentaborane(9)-THF solution, and held coaxially with the NMR tube. A single sharp resonance was observed in the ^{1}H-decoupled ^{11}B NMR spectrum for the apical boron atoms in the two environments. The chemical shifts for the basal boron resonances were, however, slightly different for the pure pentaborane(9) and the pentaborane(9) in the THF solution. The basal resonances were clearly resolved as two sets of overlapping ^{11}B-^{11}B-coupled quartets with the resonances from the pentaborane(9)-THF solution shifted ($\Delta\delta$ = 0.3 ppm) relative to the pure pentaborane(9). Low-temperature ^{11}B NMR studies of the pentaborane(9)-THF solution were unsuccessful in further resolving any more significant differences in the basal borons due to potential THF interactions.

Several possible structures and rationalizations exist for a proposed weak pentaborane(9)·THF adduct, leading to the increased facility of the carborane formation reaction in the THF solutions. In one possible structure, the THF is coordinated at the apical position of the cage. While this structural arrangement satisfies the observed equivalency of the basal boron atoms and is the observed structure for B_5H_9L species (where L = $P(CH_3)_3$),[13,14] it is thought to be an unlikely structure on the basis of Gaines' NMR studies of RB_5H_8 compounds.[8b,m,n] In addition, the charge distribution of B_5H_9 would suggest that the basal positions of the cage would be the more likely site of nucleophilic attack by THF.[15,16] The more likely structure thus involves coordination of the THF at the basal boron sites. These two possible single adduct structures based on the 3121 topology related to the *arachno*-B_5H_{11} parent structure are shown in Figure 1. These structures and rearrangements are similar to those proposed by Gaines, on the basis of elegant NMR B_5H_9-substitution investigations, for the facile intramolecular hydrogen exchange between bridging and terminal hydrogens in the base of the pentaborane(9) cage.[8b,m,n]

Detailed studies of the kinetics of oxidation of pentaborane(9) in organic solvents and their interactions with the pentaborane(9) cluster are now in progress in our laboratory. The potential safety and reactivity features of these pentaborane(9) solutions should provide greater facility in the exploration of pentaborane(9) and its derivative chemistry.

Experimental Section

Physical Measurements. Boron (^{11}B) NMR spectra were recorded on either a Cryomagnetics CM-250 or a General Electric QE-500 spectrometer operating at 80.26 or 160.45 MHz, respectively. Spectra were recorded in 5-mm (o.d.) tubes in both the coupled and decoupled modes and were externally referenced to BBr_3 (sealed in a glass capillary and held coaxially with the tube) at +40.0 ppm (positive chemical shifts indicate downfield resonances). Both proton broad-band decoupled and coupled spectra were routinely observed for each sample with a decoupling power of about 5 W. The variable-temperature studies were performed on the QE-500 spectrometer on a 0.1 M pentaborane(9)-THF solution from room temperature to -32 °C.

Materials. All solvents were ACS reagent grade. THF was distilled from sodium metal/benzophenone under a dry nitrogen atmosphere onto NaH. The solvent was then degassed by repeated freeze-thaw cycles and stored under vacuum prior to use.[9] Other solvents were dried with 4-Å molecular sieves and used without degassing. Pentaborane(9) was taken directly from our laboratory stock. 3-Hexyne, phenylacetylene, and diphenylacetylene were used as received (Aldrich). Triethylamine was dried over molecular sieves for several days prior to use. Pentaborane(9)-THF stock solutions for the synthetic studies of the carboranes were prepared by condensing the pentaborane(9) onto frozen THF (-196 °C). The solutions were then brought to room temperature slowly with constant stirring.

Stability Studies of *nido*-Pentaborane(9) in Organic Solvents. Several sets of experiments, including exposure of various pentaborane(9)-organic solvent solutions to both dynamic and static air atmospheres, were performed and are described below. No vigorous reactions with air or moisture, including pyrophoric or shock-sensitive behavior, were observed for any of the pentaborane(9) solutions investigated.

A. Stability in Dry Degassed Solutions. In a typical experiment, 0.1 M B_5H_9 solutions in THF were maintained under an inert atmosphere. The solution was monitored by ^{11}B NMR spectroscopy for potential decomposition. No changes were observed in the spectra after the solutions were allowed to stand for over 1 month at room temperature. Similar stabilities were also found for other organic solvents, including diglyme, diethyl ether, and hexane.

B. Stability to Air. In a typical experiment, 140 mL of a 0.03 M B_5H_9 solution in THF was placed in a 3-L flask. The flask was filled with a dry air atmosphere, and a flow of dry air was maintained through a "T" on the reaction flask [the dry air was obtained by passing a compressed air stream through a $CaSO_4$ drying system]. Aliquots of the solution were removed periodically and monitored by ^{11}B NMR spectroscopy for possible decomposition. The resonances for the B_5H_9 cage were found to decrease in intensity and new peaks at -6.5 and +19.0 ppm were observed to increase in intensity during the experiment. The B_5H_9 resonances and the resonance at -6.5 ppm were completely absent from the spectra after 2 days. Similar stabilities were also found for other organic solvent systems, including diglyme, diethyl ether, and hexane.

Numerous solutions (from 0.03-0.2 M) were placed in small vessels, opened to the atmosphere for at least 8 h and then closed. The solutions were found to slowly and partially decompose to boric acid over a period of several weeks.

Preparation of 2,3-Diethyl-2,3-dicarba-*nido*-hexaborane(8) and 2,3-Diphenyl-2,3-dicarba-*nido*-hexaborane(8) from Pentaborane(9) and Alkynes in THF. A. 2,3-Diethyl-2,3-dicarba-*nido*-hexaborane(8). (i) Without Triethylamine. In the reaction, 50 mL of a 0.1 M solution of B_5H_9 in THF was syringed onto 0.62 g (7.5 mmol) of 3-hexyne at -65 °C under an inert nitrogen atmosphere. The solution was allowed to warm slowly to room temperature and stirred for 3 days. No reaction

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was observed after this time, as monitored by ^{11}B NMR spectroscopy, and only resonances from the unreacted B_5H_9 were observed.

(ii) With Triethylamine. In a typical reaction, 50 mL of a 0.1 M solution of B_5H_9 in THF was syringed onto 0.62 g (7.5 mmol) of 3-hexyne at −65 °C under an inert nitrogen atmosphere, and the reaction was allowed to warm slowly to room temperature. The synthesis continued with the addition of 0.43 g (4.3 mmol) of dry triethylamine to this solution at room temperature. The reaction was allowed to stir for 3 days and was monitored during this time by using ^{11}B NMR spectroscopy. The ^{11}B NMR spectra showed gradual decrease in the B_5H_9 resonances [at (δ ppm) −12.7 (d, B(2–4), J_{BH} = 162 Hz), −52.6 (d, B(5), J_{BH} = 172 Hz)][16,17] and the formation and growth of peaks assigned to *nido*-2,3-$(CH_3CH_2)_2C_2B_4H_6$ [at (δ ppm) −0.8 (d, B(5), J_{BH} = 146 Hz), −3.9 (d, B(4,6), J_{BH} = 146 Hz), −47.0 (d, B(1), J_{BH} = 176 Hz)][5,17,18] and to $BH_3{\cdot}N(CH_2CH_3)_3$ [at (δ ppm) −11.9 (q, J_{BH} = 92 Hz].[16,17] After 3 days, only the product carborane (47%), $BH_3{\cdot}N(CH_2CH_3)_3$, and unreacted pentaborane(9) (53%) were observed. The carborane yields reported by ^{11}B NMR spectroscopy were determined by using a calibrated BCl_3 capillary standardized against known concentration of carborane solutions to generate a standard curve. Then, by comparison with this standard curve, the concentration of the carborane in the unknown sample was accurately determined.[19] Continued standing at room temperature for several days yielded 80% of the carborane. The pure carborane was isolated in 74% total yield by repeated trap-to-trap distillation operations with the pure carborane remaining in the 0 °C trap.[9,19] Refluxing the solution did not result in appreciably greater yields.

B. 2-Phenyl-2,3-dicarba-*nido*-hexaborane(8). In a 500-mL flask, 0.77 g (7.5 mmol) of $C_6H_5C{\equiv}CH$, 0.43 g (4.25 mmol) of $N(CH_2CH_3)_3$, and 50 mL of THF were mixed and degassed by repeated freeze–thaw cycles. The solution was cooled to −196 °C, and 0.32 g (5.0 mmol) of B_5H_9 was condensed into the flask using standard vacuum-line techniques.[9] The reaction was warmed with an ice bath to 0 °C and allowed to stir. After several hours, the reaction was allowed to warm slowly to room temperature with continued stirring. The ^{11}B NMR spectra showed a gradual decrease in the B_5H_9 resonances[16,17] and the formation and growth of peaks assigned to *nido*-2,3-$(C_6H_5)HC_2B_4H_6$.[5a–e] After 2 days at room temperature, a 20% yield of the product carborane was found by ^{11}B NMR spectroscopy.

C. 2,3-Diphenyl-2,3-dicarba-*nido*-hexaborane(8). A 500-mL flask was charged with 1.1 g (6.0 mmol) of $C_6H_5C{\equiv}CC_6H_5$, evacuated, and cooled to 0 °C. To this flask were added by syringe 0.35 g (3.5 mmol) of $N(CH_2CH_3)_3$ and 50 mL of dry 0.1 M pentaborane(9)–THF solution (5.0 mmol) under inert conditions. The resulting solution was then degassed by a freeze–thaw cycle and allowed to slowly warm to room temperature with continued stirring. The ^{11}B NMR spectra showed a gradual decrease in the B_5H_9 resonances and the formation and growth of peaks assigned to *nido*-2,3-$(C_6H_5)_2C_2B_4H_6$.[10] After 1 day at room temperature, 21% yield of the product carborane was found. Refluxing the solution did not result in a significantly improved yield of the carborane product.

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Registry No. THF, 109-99-9; B_5H_9, 19624-22-7; *nido*-$RR'C_2B_4H_6$ ($R = R' = CH_3CH_2$), 138062-03-0; *nido*-$RR'C_2B_4H_6$ ($R = H$, $R' = C_6H_5$), 138062-04-1; *nido*-$RR'C_2B_4H_6$ ($R = R' = C_6H_5$), 138062-05-2; $C_6H_5C{\equiv}CH$, 536-74-3; $C_6H_5C{\equiv}CC_6H_5$, 501-65-5; 3-hexyne, 928-49-4.

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[17] The ^{11}B data shown here are our data which are comparable with those reported earlier.[5,10]

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Attack of N-Nucleophile on a Coordinated Carbonyl Ligand: Structures of (7-Azabenzonorbornadiene)tetracarbonyliron Derivatives

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Summary: Three crystal structures of (N-substituted 7-azabenzonorbornadiene)$Fe(CO)_4$ derivatives have been studied for substituents 7-$MeSO_2$ (**1**), 7-*p*-ClC_6H_4 (**2**), and 7-*p*-MeC_6H_4 (**3**), respectively. In the solid state, an intramolecular interaction between the N-nucleophile and the nearby coordinated CO ligand is clearly seen. As the $N{\cdots}C{=}O$ contact distance becomes shorter, the O atom of Fe—C—O bends away from the N atom more, corresponding to a stronger interaction between the nucleophile and the coordinated CO.

The reactions of neutral iron carbonyls with nucleophiles have been extensively studied. The active site is generally the C atom of a coordinated CO. For a C-based nucleophile R^-, the immediate product is an anionic Fe–acyl species.[2] By analogy an O-based nucleophile RO^-, the first-stage product is an anionic iron carboxylate. Both are subsequently followed with various secondary reactions.[3]

When $Fe(CO)_5$ and R_2NH are mixed, a reaction ensures to yield initially the CO-inserted products.[4] A recent report on the nitrene-extrusion reactions mediated by $Fe_2(CO)_9$ indicates that an electron-withdrawing group or

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