given respectively in Figures 1C (high field) and 2B (low field) for the purpose of comparison. The striking similarities among the spectra are quite apparent, particularly in the upfield region where each displays a pair of methyl peaks, d and c near −3.5 ppm (Ileu FG5),[11] except for an obvious extra three methyl groups in the region of −12 ppm for the PMe_3 ligand. These similarities suggest that the PMe_3 complexes are low spin like the CN^- complexes. The low-field regions are also similar, except for a methyl group that is in the region of 35 ppm for metMbPMe$_3$ and in the region of 27 ppm for metMbCN.[12,13] In all cases, the protein methyl peaks all exhibit intensities of 1:3 vs the methyl ligand peak. Since the resolved heme methyl assignments have been previously obtained for metMbCN,[12,13] we propose the same assignment for metMbPMe$_3$. However, the detailed interpretation leading to a description of the metMbPMe$_3$ structure must await definitive assignment of the heme methyl peaks and protein peaks based on nuclear Overhauser effects and 2D NMR methods. Such studies are in progress.

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Contribution from the Department of Chemistry,
The Ohio State University, Columbus, Ohio 43210

High-Yield Preparation of the Tetradecahydroundecaborate(1−) Anion, $[B_{11}H_{14}]^-$, from Pentaborane(9)

Narayan S. Hosmane,[1] Joseph R. Wermer, Zhu Hong,[2]
Thomas D. Getman, and Sheldon G. Shore*

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An earlier report from this laboratory[3] described the use of pentaborane(9), B_5H_9, as a source for practical syntheses of several higher boron hydride species and the *nido*-carborane 5,6-R,R′-5,6-$C_2B_8H_{10}$ (R,R′ = CH_3,CH_3; H,H). In the course of this work it was observed that excess B_5H_9 employed in the preparation of $[B_9H_{14}]^-$ or reaction temperatures higher than room temperature led to the presence of significant amounts of a $[B_{11}H_{14}]^-$ impurity in the product. By exploitation of these observations, it was found that B_5H_9 and $[B_9H_{14}]^-$ react in a 0.4/1 molar ratio to form $[B_{11}H_{14}]^-$ essentially quantitatively. This result in turn led to a high-yield, "one-pot" preparation of $[B_{11}H_{14}]^-$ from the reaction of B_5H_9 with a metal hydride (NaH or KH) or a metal alkyl (*tert*-butyllithium, *t*-BuLi).

Experimental Section

B_5H_9 was obtained from Callery Chemical Co., Callery, PA. It was purified by passing it through a U-trap maintained at −78 °C and collected in a second U-trap cooled to −111 °C. NaH and KH were obtained from the Aldrich Chemical Co. as mineral oil dispersions. The oil was washed away with dry pentane,and the compounds were stored in a controlled-atmosphere glovebox until use. Hydride activity was determined by reaction with methanol and measurement of the H_2 gas formed by using a calibrated Toepler system. *tert*-Butyllithium was obtained from the Aldrich Chemical Co. as a 2.17 M solution in pentane and refrigerated until use. $[(CH_3)_4N]Cl$, CsCl, and bis(triphenylphosphine)nitrogen(1+) chloride, (PPN)Cl, were obtained from the Aldrich Chemical Co. These salts were dried at 120–140 °C under high vacuum prior to use. Glyme (1,2-dimethoxyethane) was distilled from sodium benzophenone ketyl before use. Materials were handled by using standard vacuum-line and inert-atmosphere techniques.[4] Boron-11 and 2D ^{11}B–^{11}B NMR spectra were obtained at 96.3 MHz on a Bruker MSL-300 NMR spectrometer. Boron-11 decoupled proton NMR spectra were obtained on a Bruker WM-300 spectrometer. Fourier transform infrared (FT-IR) spectra were obtained on a Mattson Cygnus 25 spectrometer using KBr windows.

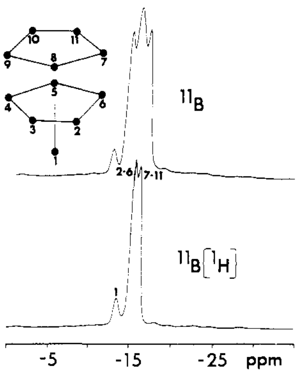

Figure 1. 96.3-MHz boron-11 NMR spectra of $K[B_{11}H_{14}]$ in glyme.

In a typical preparation, 373 mg of KH (97% active, 9.02 mmol) was reacted with 1.39 g of B_5H_9 (22.0 mmol) in 10 mL of dry glyme in a 500-mL reaction vessel. the KH was first loaded in the drybox, and the reaction vessel was then evacuated on the vacuum line. The volatile materials were condensed into the vessel at −196 °C. The vessel was allowed to warm to ambient temperature and heated to 85 °C for 20 h by using an oil-bath heater. During this time there was a gradual yellowing of the reaction solution. The reaction solution was then allowed to cool, and 32.3 mmol of H_2 gas was measured on a calibrated Toepler system and pumped away. Removal of the volatile materials under high vacuum ($<10^{-3}$ mmHg) left a yellow gum. Heating this yellow gum to 90 °C for 24 h, while the volatiles were being removed under dynamic vacuum, produced a yellow solid, $K[B_{11}H_{14}]$, in 85% yield. The IR spectrum in THF or glyme showed a single broad absorption in the B–H stretching region at 2527 cm^{-1}.

$Li[B_{11}H_{14}]$ was synthesized by syringing 1.00 mL (2.17M, 2.17 mmol) of *t*-BuLi in pentane into a nitrogen-filled flask through a septum. The flask was cooled to −196 °C, and the nitrogen was evacuated on the vacuum line. Glyme (5–6 mL) and B_5H_9 (5.91 mmol) were then condensed into the flask at −196 °C. The reaction was then completed by using the method given above. $[(CH_3)_4N]B_{11}H_{14}$ was obtained by the reaction of 359 mg of KH (99% active, 8.88 mmol), 1.00 g of $[(CH_3)_4N]Cl$ (9.17 mmol), and 1.31 g of B_5H_9 (20.9 mmol) in 15 mL of glyme by using a method similar to that given above. KCl produced in the metathesis reacton was separated by filtration of the glyme solution. Volatiles were pumped away, leaving behind 1.83 g (8.83 mmol, 99% based on B_5H_9) of yellow, free-flowing product. $CsB_{11}H_{14}$ was similarly prepared by the addition of CsCl to the B_5H_9, MH reaction mixture. Anal. Calcd for $CsB_{11}H_{14}$: Cs, 49.98; B, 44.71; H, 5.31. Found: Cs, 49.99; B, 45.16; H, 5.38. $PPN[B_{11}H_{14}]$ and $[(C_6H_5)_4P]B_{11}H_{14}$ were obtained by metathesis of $K[B_{11}H_{14}]$ or $Na[B_{11}H_{14}]$ with (PPN)Cl and $[(C_6H_5)_4P]Br$, respectively.

Discussion

The reaction of $K[B_9H_{14}]$ with 0.4 equiv of B_5H_9 in glyme at 85 °C for 20 h produced $[B_{11}H_{14}]^-$ in essentially quantitative yield, according to eq 1. Boron hydride was not present in the volatiles.

$$K[B_9H_{14}] + 0.4B_5H_9 \xrightarrow[20\ h]{glyme,\ 85\ °C} K[B_{11}H_{14}] + 1.8H_2 \quad (1)$$

The boron-11 NMR spectrum of the nonvolatile product (Figure 1) indicated the presence of $[B_{11}H_{14}]^-$ as the only boron-containing product. Since $[B_9H_{14}]^-$ is readily produced from the reaction of 1.8 equiv of B_5H_9 with KH or NaH in glyme at room temperature,[3,5,6] it was convenient to adapt this procedure to a

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(1) Department of Chemistry, Southern Methodist University, Dallas, TX.

(2) Department of Chemistry, Wuhan University, Wuhan, China.

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"one-pot" synthesis of $[B_{11}H_{14}]^-$ from B_5H_9 by altering the ratio of reactants and increasing the reaction temperature. When B_5H_9 and KH were reacted in a 2.4:1 molar ratio (B_5H_9:KH) in glyme at 85 °C, the only nonvolatile boron hydride product was K[$B_{11}H_{14}$], as indicated from its boron-11 NMR spectrum. A very small amount of B_2H_6 was recovered from the volatile reaction products. Approximately 3.5 equiv of H_2 gas was evolved in the reaction. The use of NaH instead of KH produced similar results. The formation of $[B_{11}H_{14}]^-$ from this reaction is illustrated in eq 2.

$$2.2B_5H_9 + MH \xrightarrow{\text{glyme, 85 °C}} M[B_{11}H_{14}] + 3.4H_2 \qquad (2)$$

In a similar reaction Li[$B_{11}H_{14}$] was prepared from *t*-BuLi and B_5H_9. When B_5H_9 and *t*-BuLi were reacted in a 2.4:1 molar ratio (B_5H_9:*t*-BuLi) in glyme at 85 °C, the major nonvolatile boron-containing product (>85%) was Li[$B_{11}H_{14}$], as indicated from its boron-11 NMR spectrum. A small amount of B_2H_6 was identified in the volatile reaction products by IR spectroscopy. Approximately 3.9 equiv of H_2 gas was evolved in the reaction. The formation of Li[$B_{11}H_{14}$] from this reaction is illustrated in eq 3.

$$2.2B_5H_9 + t\text{-BuLi} \xrightarrow[\text{20 h}]{\text{glyme, 85 °C}} Li[B_{11}H_{14}] + 2.4H_2 + t\text{-BuH} \qquad (3)$$

In addition to the preparative reactions cited above, it was found that 1 equiv of B_2H_6 also reacts with K[B_9H_{14}] under the same conditions to produce $[B_{11}H_{14}]^-$ in essentially quantitative yield based upon analysis of the volatiles and the boron-11 NMR spectrum of the nonvolatile product. Although the reaction of B_5H_9 with Na[BH_4] has been previously shown to produce $[B_{11}H_{14}]^-$, this preparation provides much lower yields of $[B_{11}H_{14}]^-$ along with other anionic species ($[B_3H_8]^-$ and $[B_{12}H_{12}]^{2-}$) and employs the use of high-pressure equipment.[7] The procedure reported here produces pure $[B_{11}H_{14}]^-$ in yields that are in excess of 90% based on B_5H_9 and is carried out in standard Pyrex laboratory apparatus. It is especially attractive in view of the large stockpile of B_5H_9 in government inventories. Other synthetic methods for the preparation of $[B_{11}H_{14}]^-$ not based upon B_5H_9 have also been reported previously.[8-11]

The boron-11 NMR spectrum of $[B_{11}H_{14}]^-$ reported earlier[8] was obtained at 19.1 MHz and does not show resolution of the signals. The boron-11 NMR spectrum shown here (Figure 1), obtained at 96.3 MHz consists of three doublets at −12.5 (J = 146 Hz), −14.1 (J = 156 Hz), and −14.9 ppm (J = 138 Hz), in a ratio of 1:5:5, corresponding to boron atoms 1, 2–6, and 7–11, respectively. The assignments were made by employing 2D ^{11}B–^{11}B NMR spectroscopy. The 2D ^{11}B–^{11}B NMR spectrum clearly shows that there is coupling between the two planes of atoms and that the capping atom is coupled to only one of the planes, allowing the assignment given above. The boron-11-decoupled proton NMR spectrum (300.3 MHz) is in good agreement with the boron-11 NMR spectrum, showing three signals for the terminal hydrogens and a single signal for the bridging hydrogens at 1.93 (1 H, terminal), 1.72 (5 H, terminal), 1.28 (5 H, terminal), −3.67 ppm (3 H, bridge).

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Contribution from the Department of Chemistry,
Brooklyn College of the City University of New York,
Brooklyn, New York 11210

Peroxoborates. Interaction of Boric Acid and Hydrogen Peroxide in Aqueous Solution

Richard Pizer* and Cherryl Tihal

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The interaction of hydrogen peroxide with boric acid has been studied by a wide variety of experimental techniques including conductivity measurements,[1] pH measurements,[2] Raman spectroscopy,[3] and, most recently, ^{11}B NMR spectroscopy.[4] While the crystal structure[5] of sodium peroxoborate shows a cyclic dimeric peroxoborate anion with bridging peroxo groups and two four-coordinate boron atoms ($B_2(O_2)_2(OH)_4{}^{2-}$), various solution studies have been interpreted in a number of ways ranging from a proposal[3] that one monomeric four-coordinate peroxoborate anion ($(HO)_3BOOH^-$) is the only significant species in solution to the assertion[2] that "...quantitative interpretation of the (pH titration) data requires the postulation of about six peroxyborate species". We have previously used[6] pH methods successfully to determine stability constants for complex formation of boron acids with bidentate chelating ligands. Application of those methods to the study of peroxoboron species permits quantitative evaluation of equilibrium constants for the formation of three peroxoboron species at pH ≤9. High-field ^{11}B NMR spectroscopy was used in conjunction with the pH methods in a qualitative sense in order to determine the minimum number of boron-containing species as a function of pH.

Experimental Section

Boric acid and hydrogen peroxide (Fisher) were used as received. All pH experiments were performed at μ = 0.1 M (KNO_3) and 25 °C. Hydrogen peroxide solutions were freshly prepared just prior to use and standardized[7] by titration with standard $KMnO_4$. Solutions were prepared with freshly boiled water, and titrations were carried out under a N_2 atmosphere. No attempt such as addition[3] of EDTA was made to inhibit the decomposition of H_2O_2. Instead, following each titration the reaction mixture was immediately titrated against standard $KMnO_4$. The peroxide, whether bound or free,[2] is oxidized by $KMnO_4$. In all cases, the decrease in concentration of peroxide during the experiment was less than 1%.

Phenylboronic acid and *tert*-butyl hydroperoxide (Aldrich) were used as received. pH titration experiments were carried out on the $C_6H_5B(OH)_2/H_2O_2$ and the $B(OH)_3/(CH_3)_3COOH$ systems to determine the effect of reactant acidity on the measured equilibrium constants. Standardization of $(CH_3)_3COOH$ solutions was accomplished by titration[8] with standard $S_2O_3{}^{2-}$ in the presence of excess I^-.

^{11}B NMR spectra were run at a frequency of 128 MHz on a JEOL GX 400-MHz NMR spectrometer. Quartz tubes (10 mm) were used since strong ^{11}B resonances occur in Pyrex.[9] All solutions were 0.1 M KNO_3 with ~25% D_2O used as a frequency lock. All solutions were freshly prepared, and the pH was checked just before running the ex-

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