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The First *hypho*-Borane Dianion, Undecahydropentaborate(2−), $B_5H_{11}^{2-}$

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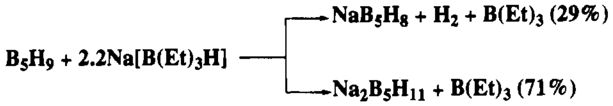
The field of pentaborane anion chemistry began with the synthesis of the *nido*-octahydropentaborate(1−), $[B_5H_8]^-$, in 1967 via deprotonation of *nido*-pentaborane(9), B_5H_9, using alkyllithiums[1] or metal hydrides.[2] Subsequently, the metastable *arachno*-decahydropentaborate(1−), $[B_5H_{10}]^-$, was reported in 1973 to be produced in the reaction of hexaborane(12), B_6H_{12}, with 2 equiv of ammonia.[3] The synthesis of *hypho*-dodecahydropentaborate(1−), $[B_5H_{12}]^-$, was reported in 1975 to be produced in the reaction of nonahydrotetraborate, $[B_4H_9]^-$, with $^1/_2$ equiv of diborane,[4] by a now classical cluster growth mechanism. The first dianion of a pentaborane was produced by reduction of pentaborane(9) with sodium naphthalide to form *arachno*-nonahydropentaborate(2−), $[B_5H_9]^{2-}$, reported in 1987.[5] We now report the reaction of pentaborane(9) with sodium triethylborohydride, $Na[B(Et)_3H]$, which produces the disodium salt of *hypho*-undecahydropentaborate(2−), $Na_2B_5H_{11}$ (**1**), by a novel hydride addition. This species appears to be the first *hypho* boron hydride dianion.

B_5H_9 reacts with sodium triethylborohydride in toluene solution at 0 °C to produce **1** in ca. 71% yield (based on starting B_5H_9), as shown in Scheme 1. The other major pentaborane product is NaB_5H_8, which is formed in a deprotonation side reaction and identified by its characteristic ^{11}B NMR spectrum. The concomitant production of H_2 in 29% yield (also based on starting B_5H_9) lends credence to the dual reaction pathway suggested in Scheme 1.

Isolation of **1** is accomplished by filtering the reaction mixture and washing the resulting white solid with diethyl ether. Since all species present in the reaction mixture other than **1** are very soluble in diethyl ether, **1** is isolated in a high degree of purity as an air-sensitive free-flowing white powder with very little loss by filtration of the diethyl ether slurry. Compound **1** appears to be quite stable *in vacuo* as a solid. In THF or DME solution, it decomposes slowly (over the course of several days) to $NaBH_4$ and NaB_3H_8, along with some other minor products.

Scheme 1. Product Distribution in the Reaction of B_5H_9 with $Na[B(Et)_3H]$ in Toluene[a]



[a] Yields are based on starting pentaborane(9).

The ^{11}B NMR spectrum of $Na_2B_5H_{11}$ consists of two resonances: a broad unresolved peak at −26.9 ppm (B(2−5)) and a doublet at −62.54 ppm (J = 83 Hz, B(1)). Such a spectrum is consistent with the previously proposed valence representation in Figure 1,[6] allowing for fluxionality of all hydrogens except the one on B(1). The high upfield chemical shift of the apical resonance in particular is often seen in *hypho*-pentaborane structures.[4,7−9] The structure of the dianion is probably similar to that of the isoelectronic diphosphine adduct of pentaborane(9), *hypho*-$B_5H_9[P(CH_3)_2]_2$, for which a single-crystal X-ray structure has been determined.[7] Figure 2 depicts a proposed structure for **1** based on substitution of hydrogens for the phosphine ligands in the determined structure. Such a structure is inferred from comparison of ^{11}B NMR spectra of these two species. The spectrum of the diphosphine adduct consists of four resonances; the basal resonances range from −19.6 to −31.8 ppm, in the same range as the basal resonance of **1**. The apical resonance of the diphosphine adduct is at −55.7 ppm. Considering the phosphine ligand coordinated at the apical position, this chemical shift is quite close to the apical resonance of **1**. Even closer agreement is seen between the ^{11}B NMR spectra of **1** and *hypho*-decahydro(trimethylphosphine)pentaborate(1−), $[B_5H_{10}{\cdot}P(Me)_3]^-$, which exhibits basal and apical resonances at −25.1 and −59.6 ppm, respectively.[9] The ^1H NMR spectrum of **1** consists of two resonances: a broad unresolved peak at −0.15 ppm corresponding to the fluxional basal

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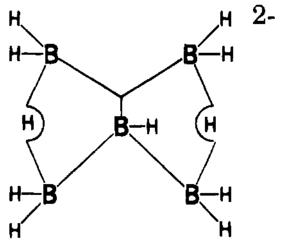

Figure 1. Possible valence representation for the undecahydropentaborate dianion. It should be noted that other representations are also allowed in accordance with the "STYX" rules.

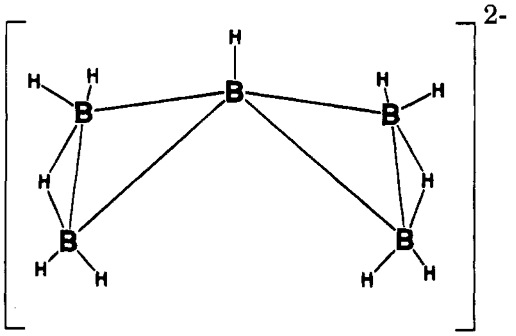

Figure 2. Proposed structure for the undecahydropentaborate dianion.

hydrogens and a quartet centered at −3.95 ppm corresponding to the lone static hydrogen on the apical boron.

Reactivity studies on **1** have been undertaken with the dual purpose of developing synthetic routes to new compounds and further characterizing the dianion. Several attempts were made to synthesize heteroboranes by reaction of **1** with species of the general formula X_2ER_n via metathesis mechanisms; however, in each case, B_5H_9 was produced as the only major boron-containing product. Reaction of **1** with Me_2SiCl_2 produced B_5H_9 nearly quantitatively,[10] identified on the basis of its ^{11}B NMR spectrum, and Me_2SiH_2, which was identified on the basis of its ^{1}H NMR and IR spectra. Reaction of **1** with $PhBCl_2$ and $MePCl_2$ also produced B_5H_9 cleanly; other products were not isolated.

Protonation of **1** by anhydrous HCl at −109 °C leads to the formation of B_5H_{11} and H_2 along with other boron hydrides, as identified by ^{11}B NMR.[11] Although the reaction is not clean, the only reasonable source for the B_5H_{11} is from bis-protonation of **1**, followed by loss of molecular hydrogen, similar to the formation of B_5H_{11} from protonation of $[B_5H_{12}]^-$.[4] Oxidation of **1** by $HgCl_2$ produces B_5H_{11} very cleanly; an ^{11}B NMR spectrum of the reaction mixture in dichloromethane shows only trace contamination by B_5H_9 and B_4H_{10}. Preliminary results involving reaction of 1-alkyl-*nido*-pentaboranes with Na[B(Et)$_3$H] indicate the production of alkylated derivatives of **1**; NMR evidence indicates retention of the alkyl group at the apical position on the pentaborane cage.

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Supplementary Material Available: ^{11}B and ^{1}H NMR spectra for compound **1** (2 pages). Ordering information is given on any current masthead page.

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[10] A ^{11}B NMR spectrum of the reaction product mixture showed B_5H_9 as the only major boron-containing product.

[11] A ^{11}B NMR spectrum of the reaction product mixture, in addition to B_5H_{11}, showed B_5H_9, B_4H_{10}, and a trace of B_2H_6.