

A typical reaction procedure follows. To a solution of LDA (10 mmol) in 30 mL of THF, maintained at  $-78^\circ\text{C}$  under an argon atmosphere, was added a solution of 0.46 g (2.5 mmol) of *N*-propionyl-*o*-chloroaniline (**1g**) in 20 mL of THF. After addition was complete, the solution of the dianion was allowed to come to  $25^\circ\text{C}$  and then irradiated for 3 h in a Rayonet Model RPR-240 photoreactor equipped with four 12.5-W lamps emitting at 350 nm. The reaction mixture was quenched with  $\text{H}_2\text{O}$ , acidified to pH 1 with 6 M HCl, and extracted with ether. The extracts were dried ( $\text{MgSO}_4$ ), filtered, and concentrated. Purification of the crude product by medium pressure chromatography (1:3 diisopropylamine-hexane) followed by recrystallization from ether-hexane afforded 0.27 g (73%) of **3g**, mp  $120\text{--}121^\circ\text{C}$  (lit.<sup>8</sup> mp  $124^\circ\text{C}$ ).

**Acknowledgment.** This work was supported by the National Science Foundation (CHE 77-13317) and the National Institutes of Health (NS 10197).

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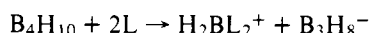
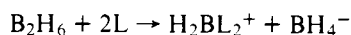
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### Unsymmetrical Cleavage of Boranes by Bis(trimethylphosphine)-Diborane(4). Formation of a Triboron Cation.

Sir:

Certain Lewis bases are known to react with diborane(6) and/or tetraborane(10) to give unsymmetrical cleavage<sup>1</sup> products of the boranes:



where L represents the Lewis base. Ammonia,<sup>2</sup> mono- and dimethylamine,<sup>3</sup> tetrahydrofuran,<sup>4</sup> and dimethyl sulfoxide<sup>5</sup> are typical of the bases that can effect the unsymmetrical cleavage of the boranes, and extensive work has been reported in the literatures<sup>6</sup> on the chemistry of the boronium cation  $\text{H}_2\text{BL}_2^+$ . Many other Lewis bases cleave the boranes "sym-

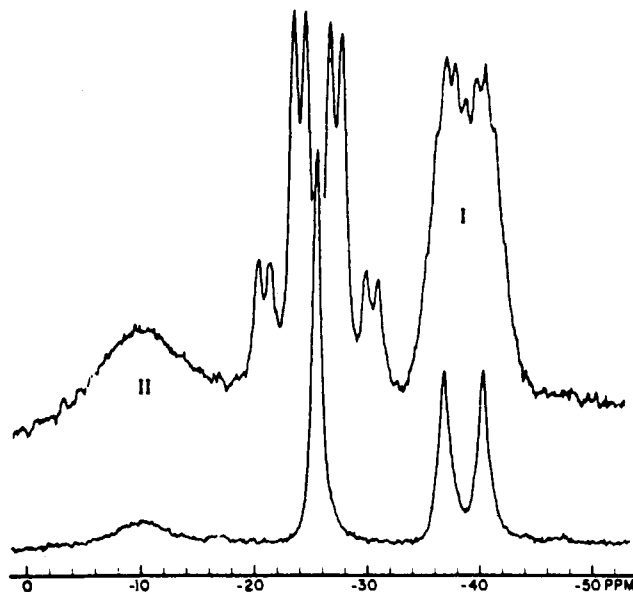
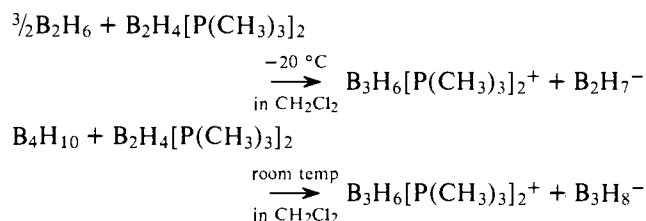


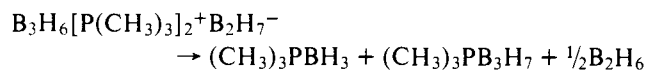
Figure 1.  $^{11}\text{B}$  NMR spectra of  $\text{B}_3\text{H}_6[\text{P}(\text{CH}_3)_3]_2^+ \text{B}_2\text{H}_7^- \cdot 1.5\text{B}_2\text{H}_6 + 1.0\text{B}_2\text{H}_4[\text{P}(\text{CH}_3)_3]_2$  in dichloromethane at  $-20^\circ\text{C}$ : upper, normal spectrum; lower, proton spin decoupled spectrum.

metrically"<sup>1</sup> to give the base adducts of borane(3) and triborane(7).

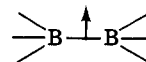
We now report that the reactions of an unconventional base bis(trimethylphosphine)-diborane(4) with  $\text{B}_2\text{H}_6$  and  $\text{B}_4\text{H}_{10}$  result in the unsymmetrical cleavage of the boranes, and that the cation produced by the reaction is a previously unreported triboron complex cation. The equations for the reactions are



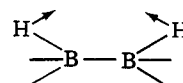
The  $^{11}\text{B}$  NMR spectra of the reaction products are shown in Figure 1 and 2. In addition to the signals of the  $\text{B}_2\text{H}_7^-$  ion at  $-25.8\text{ ppm}^7$  [ $\text{BF}_3\cdot\text{O}(\text{C}_2\text{H}_5)_2$  standard] and the  $\text{B}_3\text{H}_8^-$  ion at  $-30.5\text{ ppm}^8$ , a doublet signal (I,  $J_{\text{BP}} = 114\text{ Hz}$ ) and a broad singlet signal (II) are seen at  $-39.0$  and  $-10.5\text{ ppm}$ , respectively. The two signals are attributed to the new  $\text{B}_3\text{H}_6[\text{P}(\text{CH}_3)_3]_2^+$  cation. The  $\text{B}_3\text{H}_8^-$  salt can be isolated as a fairly stable solid at room temperature. The  $\text{B}_2\text{H}_7^-$  salt, however, is unstable at room temperature and decomposes according to the equation



On the basis of the established donor property of boron-boron single bonds<sup>9</sup>



and the known chelating property of two terminal hydrogen atoms attached to adjacent boron atoms<sup>10</sup>



the structure<sup>11</sup> shown in Figure 3 is proposed for the cation. Signals I and II are then assigned to the B(1,2) and B(3) atoms,

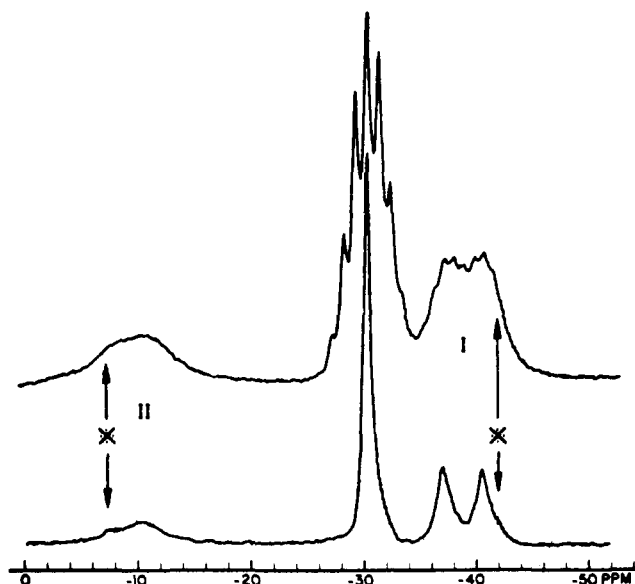


Figure 2.  $^{11}\text{B}$  NMR spectra of  $\text{B}_3\text{H}_6[\text{P}(\text{CH}_3)_3]_2 + \text{B}_3\text{H}_8^- \cdot 1.02\text{B}_4\text{H}_{10} + 1.00\text{B}_2\text{H}_4[\text{P}(\text{CH}_3)_3]_2$  in dichloromethane at  $+20^\circ\text{C}$ : upper, normal spectrum; lower, proton spin decoupled spectrum; \*, signals of the excess  $\text{B}_4\text{H}_{10}$  at  $-42.1$  and  $-7.2$  ppm.

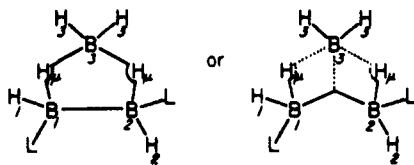
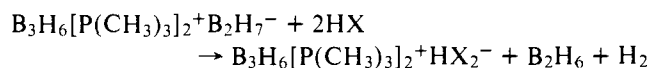


Figure 3. Structure proposed for the  $\text{B}_3\text{H}_6[\text{P}(\text{CH}_3)_3]_2^+$  ion [ $\text{L} = \text{P}(\text{CH}_3)_3$ ].

respectively. The cation as shown in the figure is isoelectronic with  $\text{L}'\text{B}_3\text{H}_7$  ( $\text{L}' = \text{Lewis base}$ ) and  $\text{B}_3\text{H}_8^-$  ion. Like its isoelectronic sister compounds, the cation appears to be fluxional with respect to a rapid tautomeric motion of hydrogen atoms around the  $\text{B}_3$  framework.<sup>12</sup> At  $-20^\circ\text{C}$  or above, the boron atoms see the six hydrogen atoms equally and therefore each member of the doublet signal I appears as a multiplet ( $J_{\text{BH}} = 28$  Hz, presumably a septet). The value of  $J_{\text{BH}}$  compares with the values, 35 and 33 Hz, which have been reported for  $(\text{CH}_3)_3\text{NB}_3\text{H}_7$  and  $\text{B}_3\text{H}_8^-$ ,<sup>8</sup> respectively. The  $^{11}\text{B}$  spin decoupled  $^1\text{H}$  NMR spectrum of the  $\text{B}_3\text{H}_8^-$  salt is also consistent with the model presented above. At  $+20^\circ\text{C}$ , in addition to the singlet signal of the  $\text{B}_3\text{H}_8^-$  ion at  $\delta$  0.21, two signals appear at  $\delta$  1.53 (doublet,  $\text{H}_{\text{CH}_3}$ ,  $J_{\text{HCP}} = 11.8$  Hz) and 0.93 (triplet,  $\text{H}_{\text{B}}$ ,  $J_{\text{HBP}} = 6.7$  Hz). The triplet signal is due to the coupling of the six hydrogen atoms to the two phosphorus atoms. The value of the coupling constant ( $J_{\text{HBP}}$ ) compares with that of 6.5 Hz which was found for a fluxional sister compound  $(\text{CH}_3)_3\text{PB}_3\text{H}_7$ .<sup>13</sup>

The newly discovered triboron cation is resistant to acids, but is sensitive to strong bases. Thus, when the  $\text{B}_2\text{H}_7^-$  salt of the cation is treated in  $\text{CH}_2\text{Cl}_2$  at  $-80^\circ\text{C}$  with excess anhydrous hydrogen chloride or bromide, 2 mol of the hydrogen halide were consumed by 1 mol of the salt, and 1 mol of each of hydrogen gas and diborane(6) was given off. The cation, however, remained intact as evidenced by the  $^{11}\text{B}$  NMR spectrum of the solution. See Figure 4. The  $^1\text{H}$  NMR spectrum of the same solution ( $-80^\circ\text{C}$ ) showed the signal due to the hydrogen dihalide ion ( $\delta$  11.5 for  $\text{HCl}_2^-$  and 7.88 for  $\text{HBr}_2^-$ )<sup>14</sup>. The equation for the reaction is



where  $\text{X} = \text{Cl}$  or  $\text{Br}$ . The hydrogen dihalide salts are unstable

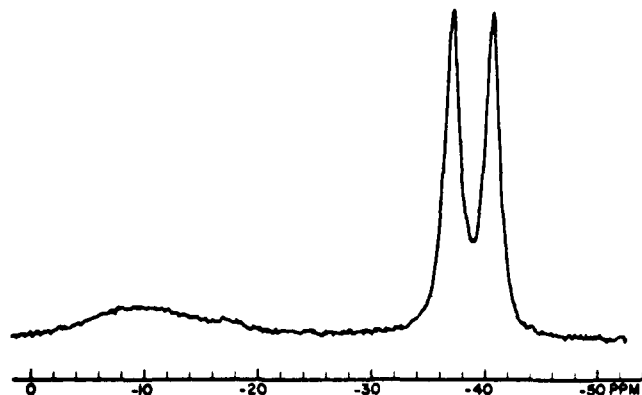
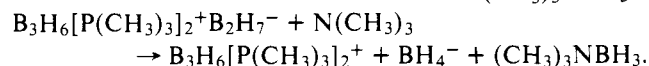
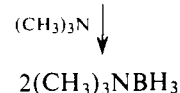
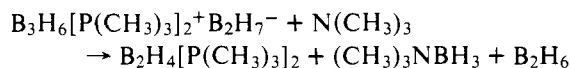


Figure 4. Proton spin decoupled  $^{11}\text{B}$  NMR spectrum of a solution obtained by the treatment of  $\text{B}_3\text{H}_6[\text{P}(\text{CH}_3)_3]_2 + \text{B}_2\text{H}_7^-$  with excess  $\text{HBr}$  at  $-80^\circ\text{C}$  in dichloromethane. Sample temperature was  $-60^\circ\text{C}$ .

at room temperature. When the  $\text{B}_2\text{H}_7^-$  salt is treated with an equimolar quantity of trimethylamine in  $\text{CH}_2\text{Cl}_2$  at  $-80^\circ\text{C}$ , however, the amine attacks both the cation and the anion. The two reactions that occur simultaneously are



The reaction products were identified by the  $^{11}\text{B}$  NMR spectrum of the reaction solution at  $-80^\circ\text{C}$ .

The low-temperature NMR spectra provided us additional information regarding the fluxional behavior of the cation. As the temperature is lowered, the doublet signal, I, in the normal  $^{11}\text{B}$  spectrum changes to a broad singlet, and then at about  $-70^\circ\text{C}$  it appears as a broad triplet (apparent  $J = 110$  Hz). In the proton spin decoupled  $^{11}\text{B}$  spectrum the signal I remains as a doublet. In the  $^{11}\text{B}$ -spin decoupled  $^1\text{H}$  spectrum of the  $\text{HCl}_2^-$  salt at  $-80^\circ\text{C}$ , the signals of the  $\text{H}_{\text{B}}$  atoms appear at three different shifts ( $\delta$  2.08, 0.63, and  $-0.62$ ) in an intensity ratio 1:1:1. The same feature is seen also in the proton spectra of the  $\text{HBr}_2^-$ ,  $\text{B}_2\text{H}_7^-$ , and  $\text{B}_3\text{H}_8^-$  salts. These changes observed in the low-temperature spectra are attributed to the slowing of the hydrogen atom motion to the point where the six  $\text{H}_{\text{B}}$  atoms become static, relative to the NMR time scale, as indicated in Figure 3. Thus, at the low temperatures the  $\text{B}(1,2)$  signal (1) appears as an apparent triplet in the normal spectrum ( $J_{\text{BP}} \approx J_{\text{BH}}$ ), and the signals of  $\text{H}(3)$ ,  $\text{H}(1,2)$ , and  $\text{H}(\mu)$  appear each separated at  $\delta$  2.08, 0.63, and  $-0.62$ , respectively. These assignments for the proton signals were confirmed by the single frequency  $^{11}\text{B}$  spin decoupling experiments.

The formation of triboron cations from diborane(4) adducts appears to be a general type of reaction. Thus, we have obtained, by the reactions similar to those described in this communication, several triboron cations which are identified as methyl and halogen derivatives of the parent  $\text{B}_3\text{H}_6[\text{P}(\text{CH}_3)_3]_2^+$  cation. Details of the syntheses and the characterization of these cations will be reported in due course.

**Acknowledgment.** The authors gratefully acknowledge support of this work by the U.S. Army Research Office through Grant DAAG29-79-C-0129.

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## Carbon-Carbon Bond Formation in the Reaction of Calcium Atoms with Ethers

Sir:

Although reactions of metal atoms with organic compounds have received considerable attention,<sup>1</sup> studies with the group 2 metals have been restricted largely to magnesium.<sup>2</sup> We report here some unusual reactions which occur when calcium atoms are codeposited with a large excess (~100:1) of an ether at -196 °C.

The codeposition of calcium atoms<sup>3</sup> with dimethyl ether at -196 °C resulted in the formation of a highly reactive orange-brown solid. Hydrolysis of this material leads primarily to a mixture of hydrocarbons, which were identified by GC-mass spectroscopy as methane, acetylene, ethylene, ethane, propyne, propene, propane, 1-butene, and 2-butene (cis and trans).<sup>4</sup> Some higher C<sub>6</sub> (C<sub>6</sub>H<sub>10</sub>, C<sub>6</sub>H<sub>12</sub>) and C<sub>8</sub> (C<sub>8</sub>H<sub>14</sub>) hydrocarbons and butanol were also detected.

When the organocalcium compound was hydrolyzed in D<sub>2</sub>O, the same mixture of products was produced, although in slightly different yields. The mass spectra of the products obtained from this reaction showed extensive incorporation of deuterium. These data are shown in Table I.

If one assumes that D<sub>2</sub>O labels each metal-carbon bond present in the organometallic, then it follows that extensive carbon-calcium bond formation has occurred during the codeposition process. The activation of inert bonds in hydrocarbons with metal atoms has also been observed very recently by others. Davis and Klabunde<sup>5</sup> observed the low temperature

**Table I.** Hydrolysis of the Codeposition Product of Calcium Atoms and Dimethyl Ether in D<sub>2</sub>O

product	composition, % <sup>a</sup>	yield, % <sup>b</sup>
CH <sub>3</sub> D, CH <sub>2</sub> D <sub>2</sub>	<1	trace
C <sub>2</sub> D <sub>2</sub> , C <sub>2</sub> HD	17	0.044
C <sub>2</sub> H <sub>3</sub> D	21	0.054
C <sub>2</sub> H <sub>5</sub> D, C <sub>2</sub> H <sub>4</sub> D <sub>2</sub>	2	0.012
C <sub>3</sub> H <sub>3</sub> D	<1	trace
C <sub>3</sub> H <sub>5</sub> D, C <sub>3</sub> H <sub>4</sub> D <sub>2</sub> , C <sub>3</sub> H <sub>3</sub> D <sub>3</sub>	1	0.001
C <sub>4</sub> H <sub>7</sub> D, C <sub>4</sub> H <sub>6</sub> D <sub>1</sub> (1-butene)	12	0.032
C <sub>4</sub> H <sub>7</sub> D, C <sub>4</sub> H <sub>6</sub> D <sub>2</sub> (2-butene)	21	0.054
C <sub>6</sub> H <sub>9</sub> D, C <sub>6</sub> H <sub>8</sub> D <sub>2</sub>	4	0.009
C <sub>6</sub> H <sub>11</sub> D, C <sub>6</sub> H <sub>10</sub> D <sub>2</sub>	15	0.042
C <sub>8</sub> H <sub>12</sub> D <sub>2</sub>	3	0.007

<sup>a</sup> Obtained from GC analyses. <sup>b</sup> Mole of product per mole of calcium vaporized.

cleavage of alkanes by small clusters of nickel atoms. Hydrolysis of the product yielded a mixture of alkanes, although no products with molecular weights higher than the starting alkanes were observed. Skell and his co-workers<sup>6</sup> have also observed the cleavage of carbon-hydrogen and carbon-carbon bonds in isoalkanes with zirconium and titanium atoms.

The codeposition of calcium atoms with several other ethers was also investigated. For example, hydrolysis of the product obtained from diethyl ether yielded the same mixture of alkanes, alkenes, and alkynes obtained from dimethyl ether; however, the mixture was much richer in acetylene and propyne.

Bromination of the organocalcium compound obtained from dimethyl ether leads to a complex mixture of bromides. Four of these were identified readily as methyl bromide, methylene bromide, bromoform, and tetrabromoethylene. Other products with empirical formulas C<sub>2</sub>H<sub>4</sub>Br<sub>2</sub>, C<sub>2</sub>H<sub>3</sub>Br<sub>3</sub>, C<sub>2</sub>H<sub>2</sub>Br<sub>4</sub>, C<sub>2</sub>HBr<sub>3</sub>, and C<sub>4</sub>H<sub>7</sub>Br<sub>3</sub> were detected by GC-mass spectroscopy. These compounds are thought to arise from bromolysis of carbon-calcium bonds as well as addition of bromine to the unsaturation present in the organometallic or the liberated alkene or alkyne.

An X-ray powder diffraction pattern of the cocondensation product of calcium and dimethyl ether showed the presence of Ca(OH)<sub>2</sub>, but neither CaO nor calcium carbide was detected. The use of X-ray powder patterns to detect products is not conclusive, however, since it is known that experiments of this type rarely give crystalline solids.

Since calcium atoms do not react with alkanes and perfluoroalkanes, it is likely that the oxygen group of the ether serves as an activating point. Oxidative insertion of calcium atoms into carbon-oxygen bonds yielding CH<sub>3</sub>OCaCH<sub>3</sub> or CH<sub>3</sub>CaOCaCH<sub>3</sub> probably follows. It is quite obvious, however, that extensive insertion of calcium atoms into either carbon-hydrogen or carbon-carbon bonds must also be invoked to account for the products obtained from the hydrolyses experiments. Matrix isolation experiments to delineate these steps are in progress.<sup>7</sup>

**Acknowledgment.** We gratefully acknowledge The Robert A. Welch Foundation (Grants C-490 and C-109) for support of this work.

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