

**Table I.** Dark Reaction of Bromine with Trialkylboranes in Methylene Chloride Solvent<sup>a</sup>

| Organoborane from olefin  | Product                                  | Yield, % <sup>b</sup> |
|---------------------------|--|-----------------------|
| 1-Butene                  | 1-Bromobutane                            | 80                    |
|                           | 2-Bromobutane                            | 11                    |
| 2-Butene                  | 2-Bromobutane                            | 88                    |
| Isobutylene <sup>c</sup>  | Isobutyl bromide                         | 85                    |
| 2,4,4-Trimethyl-1-pentene | 1-Bromo-2,4,4-trimethylpentane           | 82                    |
| Cyclopentene              | Bromocyclopentane                        | 84                    |
| Cyclohexene               | Bromocyclohexane                         | 99                    |
| Norbornene                | <i>exo</i> -Bromonorbornane <sup>d</sup> | 88                    |

<sup>a</sup> Reactions were allowed to proceed for 24 hr at ~25° in a closed system using a 10% excess of bromine. <sup>b</sup> By glpc analysis. The yield is based on a maximum production of 1 mol of RBr from 1 mol of R<sub>3</sub>B (eq 1). <sup>c</sup> After 48 hr at ~25°. <sup>d</sup> The absence of the endo isomer was indicated by glpc analysis (<1%).

appearance at a much slower rate. Typical results for the reaction of bromine with tri-*sec*-butylborane in carbon tetrachloride are shown graphically in Figure 1.

These results are clearly incompatible with a mechanism involving the direct rupture of the carbon-boron bond by bromine. It requires that the bromine react with the organoborane in an initial fast reaction to produce an intermediate of relatively low volatility which is converted in a subsequent slow stage to the product.

Further support for this interpretation is provided by the observation that when the reaction is carried out under reduced pressure to facilitate escape of hydrogen bromide, the amount of alkyl bromide present in the reaction mixture decreases with a corresponding increase in the amount of hydrogen bromide present in the trap.

The following observations are significant in indicating that the first intermediate must be the  $\alpha$ -bromo-organoborane. The reaction of bromine with organoboranes containing one alkyl branch at the  $\alpha$  position, as in tri-*sec*-butylborane, proceeds more readily than corresponding organoboranes without this feature, such as tri-*n*-butyl- and triisobutylborane. Moreover, bromination of the xethyl di-*n*-octylborane yields only *n*-octyl bromide and no detectable amount of the xethyl bromide.  $\alpha$  bromination of the xethyl group is of course not possible. Finally, confirmation of the structure of the intermediate was achieved through study of the transfer reaction.<sup>6</sup>

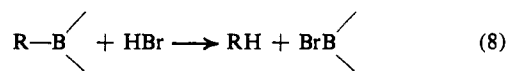
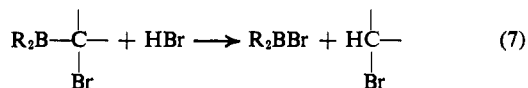
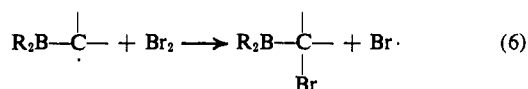
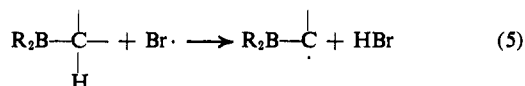
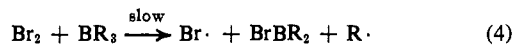
The mechanism we wish to propose involves free-radical chain bromination of the  $\alpha$  position of the organoborane, a free-radical bromination that proceeds rapidly even in the dark<sup>7</sup> (eq 5 and 6). The remarkably high reactivity of the organoborane toward attack by bromine atoms is indicated by the observation that even the use of cyclohexane as a solvent results in insignificant diversion of bromine atoms to this possible reactant. The precise nature of the initiation stage is uncertain, but may involve an attack of bromine on the organoborane<sup>8</sup> (eq 4). The hydrogen bromide

(6) Addition of water to the reaction mixture from tri-*sec*-butylborane at 0.5 hr (Figure 1), followed by oxidation with alkaline hydrogen peroxide, yields 32% 3,4-dimethyl-3-hexanol, the product anticipated for transfer of an alkyl group from boron to the  $\alpha$ -carbon position: D. J. Pasto and J. L. Meisel, *J. Amer. Chem. Soc.*, **85**, 2118 (1963).

(7) The reaction with bromine is greatly facilitated by light.

(8) For related reactions see A. G. Davies and B. P. Roberts, *Chem. Commun.*, 699 (1969).

produced in the substitution stage can then react preferentially to give the alkyl bromide<sup>9</sup> (eq 7) or competitively either with the intermediate or unreacted organoborane to give alkane (eq 8). This mechanism readily accounts for the available experimental observations.



Although the dark reaction of organoboranes in methylene chloride does provide a convenient route to certain organic bromides (Table I), the observation that it is possible to achieve a facile  $\alpha$  bromination of organoboranes in solution at room temperatures has enormous implication for the formation of carbon-carbon bonds and the synthesis of carbon structures.<sup>6</sup> We are exploring these implications.

(9) Methylene chloride evidently favors this step. The reaction course in this solvent is otherwise quite similar.

(10) Graduate research assistant on Grant No. GM 10937 from the National Institutes of Health.

\* Address correspondence to this author.

Clinton F. Lane,<sup>10</sup> Herbert C. Brown\*

Richard B. Wetherill Laboratory, Purdue University  
Lafayette, Indiana 47907

Received June 26, 1970

### Formation of a Novel Cobalt-Carborane Complex Involving the C<sub>2</sub>B<sub>6</sub>H<sub>8</sub><sup>4-</sup> Ligand Produced by Reduction of 1,7-C<sub>2</sub>B<sub>6</sub>H<sub>8</sub>

Sir:

The first bimetallic carborane complex formulated as [(B<sub>5</sub>C<sub>2</sub>H<sub>11</sub>)Co]<sub>2</sub>(B<sub>8</sub>C<sub>2</sub>H<sub>10</sub>)<sup>2-</sup> has been reported<sup>1</sup> in which two formal cobalt(III) atoms together with the apparent C<sub>2</sub>B<sub>8</sub>H<sub>10</sub><sup>4-</sup> ion complete a closed 12-atom polyhedron.

We wish to report the preparation of the first bimetallic 10-atom polyhedral carborane complex which we formulate as (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Co<sub>2</sub>C<sub>2</sub>B<sub>6</sub>H<sub>8</sub> (I). Treatment of 1,7-dicarba-*closo*-octaborane(8), 1,7-C<sub>2</sub>B<sub>6</sub>H<sub>8</sub>, with 2 equiv of sodium naphthalide in tetrahydrofuran followed by the addition of a fivefold excess of Na<sup>+</sup>-C<sub>5</sub>H<sub>5</sub><sup>-</sup> and excess CoCl<sub>2</sub> produced a mixture which included the complex C<sub>5</sub>H<sub>5</sub>CoC<sub>2</sub>B<sub>6</sub>H<sub>8</sub><sup>2-</sup> in addition to I. The green I was separated by column chromatography and recrystallized from hexane in 7.3% yield, mp 236–238°. *Anal.* Calcd for (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Co<sub>2</sub>C<sub>2</sub>B<sub>6</sub>H<sub>8</sub>: C, 41.76; B, 18.83; H, 5.22; Co, 34.17. Found: C,

(1) J. N. Francis and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **90**, 1663 (1968).

(2) G. B. Dunks, Ph.D. Dissertation, University of California, Riverside, Calif., 1970.

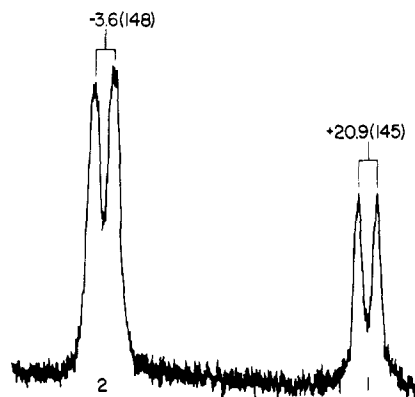


Figure 1. The 80.64-MHz  $^{11}\text{B}$  nmr spectrum of  $(\text{C}_5\text{H}_5)_2\text{Co}_2\text{C}_2\text{B}_6\text{H}_8$  taken in chloroform-*d*. Chemical shifts [ppm, relative to  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ ] and coupling constants (Hz) are indicated. Relative areas appear beneath the peaks.

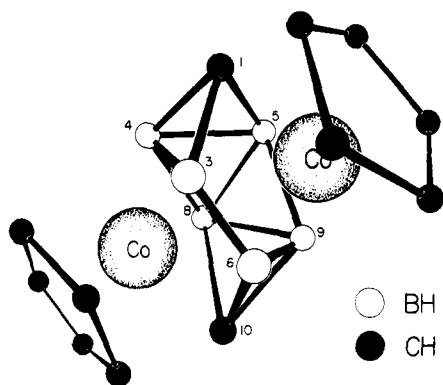


Figure 2. The proposed structure of  $(\text{C}_5\text{H}_5)_2\text{Co}_2\text{C}_2\text{B}_6\text{H}_8$ .

42.45; B, 18.02; H, 5.36; Co, 34.51. The mass spectrum exhibited a cutoff at  $m/e$  346 which corresponds to the  $^{59}\text{Co}_2^{12}\text{C}_{12}^{11}\text{B}_6^{1}\text{H}_{18}^+$  ion. The electronic spectrum determined in acetonitrile was as follows:  $[\lambda_{\text{max}}, m\mu (\epsilon): 233 (24,100), 324 (24,400), 548 (\text{sh}) (440), 652 (733)]$ . Figure 1 presents the 80.64-MHz  $^{11}\text{B}$  nmr spectrum of I in chloroform-*d* solution. The spectrum exhibits doublets of relative area 2 and 1. The 60-MHz  $^1\text{H}$  nmr spectrum consisted of a broad singlet of relative area 1 at  $\tau$  1.38 and a sharp singlet of area 5 at  $\tau$  4.92 which were assigned to polyhedral C-H and cyclopentadienyl protons, respectively. The proposed structure of I, presented in Figure 2, is consistent with the data if one assumes coincidental overlap of the resonances of the 4,9 and 5,8 boron atoms and resembles a bicapped Archimedean antiprism. Other possible structures cannot be excluded, however.

Finally, we wish to point out that the work reported herein represents the first example of the formation of a carborane ligand by direct electron addition to a closed polyhedral carborane. We are presently examining the scope of these reactions.

**Acknowledgment.** The authors wish to thank Drs. L. F. Warren for helpful discussion and R. J. Wiersema for measuring the 80-MHz  $^{11}\text{B}$  nmr spectra. We also thank Professor F. A. L. Anet and his coworkers for the use of the 80-MHz  $^{11}\text{B}$  nmr instrument. This

research was supported in part by the Office of Naval Research.

\* Address correspondence to this author.

Gary B. Dunks, M. Frederick Hawthorne\*

Contribution No. 2713  
Department of Chemistry, University of California  
Los Angeles, California 90024

Received September 4, 1970

## Evidence For A Small Ultraphosphate Molecule In Solution<sup>1</sup>

Sir:

During the last 20 years, a great deal has been learned<sup>2,3</sup> about the structure and properties of the condensed phosphates, which formerly made up one of the more confused and misunderstood areas of chemistry. There is, however, one region of composition—the ultraphosphates—about which there is still little known.

The ultraphosphates (which are defined as those compositions for which  $\text{M}_2\text{O}/\text{P}_2\text{O}_5 < 1.0$ , where M stands for 1 equiv of a cation or a single function of a covalently bonded moiety, such as an alkyl group) are found as infinite-network polymers of high viscosity exhibiting very broad  $^{31}\text{P}$  nuclear magnetic resonance (nmr) peaks, the broadness of which persists even when the viscosity is greatly diminished by addition of a nonreactive solvent. The branching  $\text{PO}_4$  groups, which are necessarily present in the ultraphosphate region of composition, almost always give rise to cross-linked network polymers. These are the sources of the physical properties observed for the ultraphosphate mixtures produced by the usual condensation or decondensation reactions.<sup>2,4,5</sup>

We have recently been putting considerable effort into the investigation of reactions of biochemical interest using  $^{31}\text{P}$  nmr, because recent advances<sup>6</sup> in the equipment are making  $^{31}\text{P}$  nmr considerably more useful in attacking biochemistry. As part of this general work, we have been looking into the nonaqueous phosphate chemistry of chemical dehydrating agents, such as trichloroacetonitrile<sup>7</sup> and dicyclohexylcarbodiimide,<sup>8</sup> and have found that, given sufficient time, these dehydrating agents will bring about condensation well into the ultraphosphate region of composition.<sup>9</sup> Further, although it is complicated and involves a number of concurrent and sequential reactions, condensation of inorganic phosphates with these dehydrating agents is

(1) This work was supported by the General Research Support Grant awarded to the University of Illinois, College of Medicine, a grant from the Research Board of the Graduate College, University of Illinois at the Medical Center, and Grants No. USPHS-11702, NSF-6403, and NSF-GP9525.

(2) J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. 1, Interscience, New York, N. Y., 1958, pp 706-716, 773-775.

(3) E. Thilo, *Advan. Inorg. Chem. Radiochem.*, **5**, 1 (1963).

(4) A. V. Kroll, *Z. Anorg. Allg. Chem.*, **76**, 387 (1912); **77**, 1 (1912); **78**, 95 (1912).

(5) E. J. Griffith and C. F. Callis, *J. Amer. Chem. Soc.*, **81**, 833 (1959).

(6) J. R. Van Wazer and T. Glonek in "Analytical Chemistry of Phosphorus Compounds," M. Halmann, Ed., Interscience, New York, N. Y., in press.

(7) F. Cramer and G. Weimann, *Chem. Ber.*, **94**, 966 (1961).

(8) G. Weimann and H. G. Khorana, *J. Amer. Chem. Soc.*, **84**, 4329 (1962).

(9) T. Glonek, T. C. Myers, and J. R. Van Wazer, *Bioinorg. Chem.*, in press.