CONTRIBUTION NO. 780 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION,
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Chemistry of Boranes. IV.[1] Phosphine Derivatives of $B_{10}H_{14}$ and B_9H_{15}

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Received April 9, 1962

The decaborane-14 derivative $B_{10}H_{13}P(C_6H_5)_2$ has been prepared from $B_{10}H_{13}MgI$ and $(C_6H_5)_2PCl$. The phosphino derivative was converted to a mixture of $B_9H_{14}P(C_6H_5)_2$ and $B_{10}H_{12}P(C_6H_5)_2^-$ by dissolution in protonic media. Formation of the anion derives simply from ionization of $B_{10}H_{13}P(C_6H_5)_2$ which behaves as a strong acid in aqueous media.

The Grignard derivative of decaborane-14 reacts smoothly with diphenylchlorophosphine to give a compound of the empirical formula $B_{10}H_{13}PR_2$. This compound may be considered structurally either as an R_2P substituted decaborane or an analog of the $B_{10}H_{12}$·base[2] structure, *i.e.*, $B_{10}H_{12}\cdot PHR_2$. The very high benzene solubility of the phosphorus derivative and an analogous arsenic compound is more typical of decaborane and substituted decaboranes than of the more polar and less tractable $B_{10}H_{12}$·base species. Further evidence, although negative in nature, against the $B_{10}H_{12}$·base formulation is the absence of M–H stretching absorption in the infrared spectra of the phosphorus and arsenic derivatives. Accordingly, we consider these compounds to be R_2M substituted decaboranes, and we are exploring the effect of the R_2M group on typical decaborane reactions.

The B^{11} n.m.r. spectra of the $B_{10}H_{13}MR_2$ compounds cannot be unambiguously interpreted. In the case of $B_{10}H_{13}P(C_6H_5)_2$, the B^{11} spectrum is similar to that of $B_{10}H_{14}$. Although the low field triplet of decaborane is replaced by a doublet (A_{BH} = 126 c.p.s.), the splitting in the high field doublet of $B_{10}H_{13}P(C_6H_5)_2$ is not significantly different from that in decaborane (A_{BH} = 167 and 159 c.p.s., respectively). Thus, it would appear safe to conclude that substitution has not occurred in the 2 or 4 positions. The studies of Dunstan, Blay, and Williams[3] suggest that reactions of $B_{10}H_{13}MgI$ usually yield decaboranes substituted at the 5 or 6 position.

Introduction of the phosphino group into decaborane significantly affects the reactivity of the B_{10} unit. In particular, $B_{10}H_{13}P(C_6H_5)_2$ shows little tendency to give $B_{10}H_{14}^{-2}$ derivatives[4] with neutral or anionic donors whereas decaborane readily forms such structures. The major reaction of $B_{10}H_{13}P(C_6H_5)_2$ with donor molecules or ions is proton loss with formation of the very stable $B_{10}H_{12}P(C_6H_5)_2^-$ ion.[5] Thus, this phosphinodecaborane functions like a strong monoprotic acid in aqueous media

$$H_2O + B_{10}H_{13}P(C_6H_5)_2 \longrightarrow H_3O^+ + B_{10}H_{12}P(C_6H_5)_2^-$$

This is analogous to decaborane's behavior in aqueous dioxane[6]

$$H_2O + B_{10}H_{14} \longrightarrow H_3O^+ + B_{10}H_{13}^-$$

However, $B_{10}H_{12}P(C_6H_5)_2^-$, unlike $B_{10}H_{13}^-$, is quite stable hydrolytically, and it does not accept donor ligands such as $(CH_3)_2S$ or CN^- to give $B_{10}H_{14}^{-2}$ structures. Cyanide ion addition to $B_{10}H_{13}^-$ to give $B_{10}H_{13}CN^{-2}$ is extremely fast in aqueous media[2] but under comparable conditions, $B_{10}H_{12}P(C_6H_5)_2^-$ shows no evidence of interaction with cyanide ion. Amines convert $B_{10}H_{13}P(C_6H_5)_2$ to amine salts of $B_{10}H_{12}P(C_6H_5)_2^-$ irrespective of the amine concentration. Decaborane, if in excess, also is converted by amines in non-aqueous media to amine salts of $B_{10}H_{13}^-$; however, excess amine yields compositions of the type $B_{10}H_{14}\cdot(\text{amine})_2$[7a] or amine-$H^+$ $B_{10}H_{13}\cdot\text{amine}^-$.[7b] Reduction of acceptor properties of the B_{10} unit by the phosphino group in $B_{10}H_{13}P(C_6H_5)_2$ and in

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[1] Paper III, E. L. Muetterties, R. E. Merrifield, H. C. Miller, W. H. Knoth, and J. H. Downing, *J. Am. Chem. Soc.*, **84**, 2506 (1962).

[2] W. H. Knoth and E. L. Muetterties, *J. Inorg. Nucl. Chem.*, **20**, 66 (1961), describe $B_{10}H_{12}\cdot S(CH_3)_2$.

[3] I. Dunstan, N. J. Blay, and R. L. Williams, *J. Chem. Soc.*, 5016 (1960).

[4] The $B_{10}H_{14}^{-2}$ structural class has been established by J. M. Reddy and W. N. Lipscomb, *J. Chem. Phys.*, **31**, 610 (1959). Examples of the various possible derivatives of $B_{10}H_{14}^{-2}$ are described by W. H. Knoth and E. L. Muetterties.[2]

[5] This is analogous to the $B_{10}H_{12}X^-$ ions reported by V. D. Aftandilian, H. C. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **83**, 2471 (1961).

[6] G. A. Guter and G. W. Schaeffer, *ibid.*, **78**, 3546 (1956).

[7] (a) M. F. Hawthorne, A. R. Pitochelli, R. D. Strahn, and J. J. Miller, *ibid.*, **82**, 1825 (1960); (b) M. F. Hawthorne, B. M. Graybill, and A. R. Pitochelli, Abstracts of Papers, 138th National Meeting, American Chemical Society, New York, N. Y., p. 45-N.

$B_{10}H_{12}P(C_6H_5)_2^-$ is expected if the filled nonbonding phosphorus orbital is involved to a significant degree in an overlap with a boron orbital. Further suggestion of involvement of the nonbonding orbital is the experimental finding that quaternization of the phosphorus atom in $B_{10}H_{13}P(C_6H_5)_2$ or in $B_{10}H_{12}P(C_6H_5)_2^-$ does not occur with methyl iodide or $(CH_3)_3S^+$.

In the characterization of this new anion, various salts and solvated acid forms were prepared. These gave no evidence of a PH stretching vibration in the infrared which is consistent with the $B_{10}H_{12}P(C_6H_5)_2^-$ formulation. Resistance to hydrolytic decomposition was strikingly high at least in comparison with $B_{10}H_{13}^-$. Neither hot strong aqueous alkali nor hot hydrochloric acid degraded the anion.

In the titration of $B_{10}H_{13}P(C_6H_5)_2$ with base in methanol or aqueous methanol, the neutral equivalent is significantly higher than theory, 340 *vs.* 306. This is due to a hydrolysis reaction that competes with the ionization process[8] in which the product is a neutral phosphine B_9 derivative

$$3H_2O + B_{10}H_{13}P(C_6H_5)_2 \longrightarrow B_9H_{14}P(C_6H_5)_2 + H_3BO_3 + H_2$$

The same mixture of products, *i.e.*, $B_{10}H_{12}P(C_6H_5)_2^-$ and the B_9 species, is obtained in the reaction of $B_{10}H_{13}P(C_6H_5)_2$ with alcohols and by work-up of the crude reaction product from $B_{10}H_{13}MgI$ and $(C_6H_5)_2PCl$ with aqueous ammonium chloride. It should be noted that since $B_{10}H_{12}P(C_6H_5)_2^-$ is very resistant to hydrolysis, this anion cannot be an intermediate in the formation of the B_9 species. Relative amounts of the B_9 species and the B_{10} anion formed appear independent of pH. In going from aqueous base to aqueous ether media to pure methanol, the yield of the anion drops from 60 to 41 to 24% and the yield of the B_9 compound rises sharply from ~0 to 24 to 58%.

The B_9 compound has the composition $B_9H_{14}P(C_6H_5)_2$. Since this derivative has weak but distinct infrared absorption in the PH stretching region (1330 cm.$^{-1}$), and since solubility characteristics are very similar to $B_9H_{13}S(CH_3)_2$, one may consider this as $B_9H_{13}PH(C_6H_5)_2$, analogous to $B_9H_{13}SR_2$[7b,9] and $B_9H_{13}NCCH_3$[7b,10] rather than $B_9H_{14}P(C_6H_5)_2$; however, a structural analysis is required before any decision can be made between the two possibilities. The B^{11} spectrum of this B^9 derivative is complex and not subject to unique interpretation although it bears a formal resemblance to the B^{11} spectrum of $B_9H_{13}S(CH_3)_2$.

General stability of the B_9 derivative is greater than the alkyl sulfide[9] analogs. Aqueous base, for example, does not rapidly extract a proton; and only a slow hydrolysis occurs at 25°. Bromination can be effected in methanol to give good yields of $B_9H_{13}BrP(C_6H_5)_2$ which still shows a weak, sharp infrared absorption in the PH stretching region.

Experimental

A. **$B_{10}H_{13}P(C_6H_5)_2$.**[11]—Twelve ml. of an approximately 2 *M* diethyl ether solution of methylmagnesium iodide was added to a solution of 0.029 mole of decaborane in 100 ml. of diethyl ether. Reaction was instantaneous as evidenced by methane evolution. To this clear yellow-to-green solution was added 0.0224 mole of diphenylchlorophosphine, and the resulting solution then was refluxed for about 3 hr. After this time the diethyl ether was removed by distillation, and about 100 ml. of petroleum ether was added to the solid reaction mixture which was heated to reflux and filtered while hot. The filtrate on cooling yielded 1.4 g. of white crystalline material, m.p. 136–137°. This material was recrystallized from hot cyclohexane. Yield of crude $B_{10}H_{13}P(C_6H_5)_2$ was 20%.

Anal. Calcd. for $B_{10}H_{13}P(C_6H_5)_2$: B, 35.3; P, 10.1; C, 47.0; H, 7.56; mol. wt., 306. Found: B, 35.8; P, 9.7; C, 47.3; H, 7.70; mol. wt., 341. By continuous extraction of the solid reaction mixture with petroleum ether, up to 75% yields of $B_{10}H_{13}P(C_6H_5)_2$ were obtained.

B. **$B_{10}H_{13}As(C_6H_5)_2$.**—About 9 ml. of a 2 *M* diethyl ether solution of methylmagnesium iodide was added to a solution of 0.024 mole of decaborane in about 100 ml. of diethyl ether. Then 5 ml. of a suspension of 0.016 mole of diphenylchloroarsine in diethyl ether was added to the reaction mixture, which was filtered and then refluxed for 18 hr. At the end of this period the diethyl ether was distilled from the reaction mixture, and 200 ml. of petroleum ether was added. The slurry was heated to reflux and filtered. The filtrate on cooling yielded a white crystalline solid that melted with decomposition at 180°.

Anal. Calcd. for $B_{10}H_{13}As(C_6H_5)_2$: As, 21.4; C, 41.1. Found: As, 21.6; C, 40.4.

This compound was readily crystallized from hot benzene or hot cyclohexane.

C. **$B_9H_{14}P(C_6H_5)_2$ and $B_{10}H_{12}P(C_6H_5)_2^-$.**—About 22 ml. of a 3 *M* solution of methylmagnesium bromide in diethyl ether was added to a solution of 0.059 mole of decaborane in about 150 ml. of ether. Then a suspension of 0.06 mole of diphenylchlorophosphine in about 25 ml. of ether was added to the reaction mixture which then was refluxed for 0.5 hour. On cooling, a solution of 125 g. of ammonium chloride in about 400 ml. of water was rapidly added to the reaction mixture. The ether layer was decanted, and to

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[8] Aqueous sodium hydroxide very slowly dissolves $B_{10}H_{13}P(C_6H_5)_2$ and the only product is $B_{10}H_{12}P(C_6H_5)_2^-$.

[9] B. M. Graybill, J. K. Ruff, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **83**, 2669 (1961).

[10] F. E. Wang, P. G. Simpson, and W. N. Lipscomb, *J. Chem. Phys.*, **33**, 1335 (1961).

[11] V. D. Aftandilian, U. S. Patent 3,013,041, Dec. 12, 1961.

this was added 50 ml. of toluene and about 400 ml. of *n*-heptane. Addition of the heptane precipitated a gummy solid. This was collected, dried, and then added to dichloromethane. The dichloromethane slurry was filtered, and the filtrate was evaporated to give a solid. The solid was recrystallized from a hot 50/50 mixture of ethanol and chloroform to give a colorless crystalline solid (average yield 0.014 mole or 24%), m.p. 170° with decomposition.

Anal. Calcd. for $B_9H_{14}P(C_6H_5)_2$: C, 48.6; H, 8.15; P, 10.5; B, 32.8. Found: C, 47.9; H, 8.14; P, 10.7; B, 31.7.

The dichloromethane-insoluble product was dissolved in water. Salts were precipitated by addition of concentrated aqueous solutions of CsF, $(CH_3)_3SI$, $(CH_3)_4NCl$, and ammoniacal $ZnCl_2$, and these were recrystallized from hot methanol–water mixtures. Average yield of the cesium salt per preparation was 0.024 mole or 41%.

Anal. Calcd. for $CsB_{10}H_{12}P(C_6H_5)_2$: Cs, 30.4; B, 24.6; P, 7.06; C, 32.8; H, 5.03. Found: Cs, 29.7; B, 24.6; P, 7.52; C, 32.8; H, 5.16.

Anal. Calcd. for $(CH_3)_3SB_{10}H_{12}P(C_6H_5)_2$: C, 46.8; H, 8.15; S, 8.37; B, 28.3. Found: C, 47.7; H, 8.33; S, 7.91; B, 28.0.

Anal. Calcd. for $(CH_3)_4NB_{10}H_{12}P(C_6H_5)_2$: C, 50 6; H, 9 04; B, 28.6; P, 8.44; N, 3.70. Found: C, 50.3; H, 9.07; B, 28.3; P, 7.71; N, 3.84.

Anal. Calcd. for $Zn(NH_3)_4[B_{10}H_{12}P(C_6H_5)_2]_2$: Zn, 8.78; N, 7.53; B, 29.1. Found: Zn, 9.17; N, 7.55; B, 28.5.

The hydrated form of $H^+B_{10}H_{12}P(C_6H_5)_2^-$ was prepared by passing an aqueous solution of the CH_2Cl_2-insoluble product through an ion exchange column packed with Amberlite IR-120 acid resin. The effluent was evaporated to give crystals.

Anal. Calcd. for $H_3O^+B_{10}H_{12}P(C_6H_5)_2^-\cdot H_2O$: B, 31.6; C, 42.1; H, 7.96; P, 9.05; neut. equiv., 342. Found: B, 32.2; C, 38.2; H, 8.69; P, 9.52; neut. equiv., 335.

Through a suspension of 0.01 mole of $CsB_{10}H_{12}P(C_6H_5)_2$ in 30 ml. of dimethylformamide was passed hydrogen chloride gas until the slurry was essentially saturated with HCl. The solid was recovered by filtration and was recrystallized from a hot toluene–chloroform–acetonitrile mixture to give colorless crystals of $H^+[HCON(CH_3)_2]_2$-$B_{10}H_{12}P(C_6H_5)_2^-$.

Anal. Calcd. for $H[HCON(CH_3)_2]_2B_{10}H_{12}P(C_6H_5)_2$: C, 47.8; H, 8.26; N, 6.20; B, 23.8; P, 6.86. Found: C, 46.4; H, 8.18; N, 6.17; B, 23.8; P, 6.74.

The characteristic Cs^+ and $(CH_3)_4N^+$ salts of $B_{10}H_{12}P$-$(C_6H_5)_2^-$ were obtained by neutralization of the above acid forms and addition of CsF or $(CH_3)_4NCl$.

The alternative preparation of $B_9H_{14}P(C_6H_5)_2$ and $CsB_{10}H_{12}P(C_6H_5)_2$ consisted of reaction of 0.016 mole of $B_{10}H_{13}P(C_6H_5)_2$ with 500 ml. of ethanol. This slurry was stirred for 3 min. during which time hydrogen was evolved. Filtration yielded 0.0037 mole of $B_9H_{14}P(C_6H_5)_2$, which was identified by analysis, melting point, and infrared spectrum. The filtrate was treated with 10 ml. of concentrated aqueous $(CH_3)_4NOH$ and diluted 1/2 with water to give 0.0069 mole of $(CH_3)_4NB_{10}H_{12}P(C_6H_5)_2$.

A slurry of 0.0033 mole of $B_{10}H_{13}P(C_6H_5)_2$ and 50 ml. of methanol was stirred for 25 min. A total of 0.065 l. of hydrogen was evolved (theory 0.073 l. for complete conversion to $B_9H_{14}P(C_6H_5)_2$). The slurry was evaporated to dryness, and the residue was extracted with a 90–10 CH_2Cl_2–C_2H_5OH mixture to give 0.0019 mole (58% yield) of $B_9H_{14}P(C_6H_5)_2$. The gummy residue was treated with water and filtered. Addition of $(CH_3)_4NCl$ to the filtrate gave 0.0008 mole (24% yield) of $(CH_3)_4NB_{10}H_{12}P(C_6H_5)_2$. Boric acid was identified as a product of the reaction by infrared analysis.

D. $B_9H_{13}BrP(C_6H_5)_2$.—To a solution of 0.02 mole of $B_9H_{14}P(C_6H_5)_2$ in 200 ml. of dichloromethane was added a solution of 0.02 mole of bromine in 50 ml. of dichloromethane. There was an immediate reaction as evidenced by the loss of bromine color. The reaction solution was evaporated to a solid which then was recrystallized twice from a hot 50/50 mixture of chloroform and ethanol to give colorless needles, m.p. 143°.

Anal. Calcd. for $B_9H_{13}BrP(C_6H_5)_2$: B, 25.9; Br, 21.4; P, 8.28; C, 38.5; H, 6.18. Found: B, 25.7; Br, 21.3; P, 8.38; C, 37.8; H, 6.59.

Stability of $B_{10}H_{12}P(C_6H_5)_2^-$.—A solution of 0.00683 mole of $CsB_{10}H_{12}P(C_6H_5)_2$ in 250 ml. of CH_3OH, 100 ml. of H_2O, and 45 ml. of concentrated hydrochloric acid evolved no hydrogen in 6 days at 25° and 3 hr. at 70°. Only $CsB_{10}H_{12}P(C_6H_5)_2$ was recovered from the solution on evaporation. Similarly, hydrogen chloride did not detectably react with a suspension of $CsB_{10}H_{12}P(C_6H_5)_2$ in benzene at 75°.

$CsB_{10}H_{12}P(C_6H_5)_2$ (0.00683 mole) was added to 100 ml. of 4 *N* NaOH and sufficient methanol was added to dissolve all the cesium salt. No hydrogen was evolved in a period of 4 hr. The solution was heated to 80° for 30 min. Then cesium fluoride was added; the solution was cooled and partially concentrated. Crystals of a hydrate of $CsB_{10}H_{12}P(C_6H_5)_2$ were obtained. These crystals on recrystallization from hot methanol–water, to which a few drops of concentrated hydrochloric acid were added, gave the nonhydrated form of $CsB_{10}H_{12}P(C_6H_5)_2$.

Neutralization of $B_{10}H_{13}P(C_6H_5)_2$.—A solution of 0.0045 mole of $B_{10}H_{13}P(C_6H_5)_2$ in 25 ml. of water and about 90 ml. of dioxane was titrated with 0.1 *N* NaOH. A typical strong acid titration curve was obtained. The neutral equivalent was, however, 340 *vs.* a theoretical value of 306. To the neutralized solution was added CsF, and concentration yielded crystals of a dioxanate of $CsB_{10}H_{12}P(C_6H_5)_2$ contaminated with $B_9H_{14}P(C_6H_5)_2$. This crude mixture was treated with hot 90–10 water–methanol and filtered. The insoluble material proved to be $B_9H_{14}P(C_6H_5)_2$, 0.0004 mole. The filtrate on cooling yielded pure $CsB_{10}H_{12}P(C_6H_5)_2$. In this titration, correction for the degradation of B_{10} to B_9 that occurred in the dioxane–water solution prior to titration gave a value of 312 for the neutral equivalent.

When a slurry of 0.0033 mole of $B_{10}H_{13}P(C_6H_5)_2$ in aqueous sodium hydroxide (*ca.* 0.3 *N*) was stirred for 2 hr., about half the phosphinodecaborane dissolved. On filtration, the insoluble, unreacted $B_{10}H_{13}P(C_6H_5)_2$ was recovered; the filtrate on addition of CsF gave $CsB_{10}H_{12}P$-$(C_6H_5)_2$. There was no evidence for the formation of the B_9 derivative.

A slurry of 0.00294 mole of $B_{10}H_{13}P(C_6H_5)_2$ with a solution of 0.09 mole of KCN in 80 ml. of H_2O was stirred for 3 days (no hydrogen evolved) and then filtered. The insoluble material, 0.2 g., was unreacted $B_{10}H_{13}P(C_6H_5)_2$. The filtrate on addition of CsF gave $CsB_{10}H_{12}P(C_6H_5)_2$.

The weight of the cesium salt was 0.6 g. (0.00136 mole). The conversion was 46% and the yield was 60%.

A solution of 0.0033 mole of $B_{10}H_{13}P(C_6H_5)_2$ in 25 ml. of water, 120 ml. of dioxane, and 5 ml. of concentrated hydrochloric acid was allowed to stand for 7 hr. The total hydrogen evolved was 0.041 l. Then 50 ml. of water was added and the solution was evaporated to 1/4 the original volume. The resulting slurry was filtered to give 0.0005 mole of the insoluble $B_9H_{14}P(C_6H_5)_2$. The filtrate on addition of $(CH_3)_4NCl$ yielded 0.0025 mole of $(CH_3)_4NB_{10}H_{12}P(C_6H_5)_2$.

Reaction of $B_{10}H_{13}P(C_6H_5)_2$ with Amines.—Addition of 10 ml. of triethylamine to a solution of 0.01 mole of $B_{10}H_{13}P(C_6H_5)_2$ in dichloromethane resulted in heat evolution and slow separation of a solid. No hydrogen evolved. The solid was repeatedly recrystallized from hot toluene–dichloromethane, m.p. 216–217°.

Anal. Calcd. for $(C_2H_5)_3NHB_{10}H_{12}P(C_6H_5)_2$: B, 26.6; P, 7.63. Found: B, 26.3; P, 7.89.

The infrared spectrum of this compound was essentially identical to that of crystalline solid obtained by adding $(C_2H_5)_3NHCl$ to a solution containing $B_{10}H_{12}P(C_6H_5)_2^-$.

CONTRIBUTION NO. 763 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION,
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Chemistry of Boranes. V.[1] First Example of a B_{11} Hydride, the $B_{11}H_{14}^-$ Anion

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Received June 9, 1962

Ethereal decaborane reacts with metal borohydrides at 90° to give $M^+B_{11}H_{14}^-$. Spectral data suggest that the anion $B_{11}H_{14}^-$ has high symmetry and appear consistent with the $B_{11}H_{14}^-$ structure hypothesized by Moore, Lohr, and Lipscomb. In strong base, $B_{11}H_{14}^-$ ionizes and salts of $B_{11}H_{13}^{-2}$ can be isolated from these solutions.

We wish to report the synthesis of a new boron hydride derivative, the first example of a B_{11} species, which has been isolated in the form of a salt $M^+B_{11}H_{14}^-$ from the essentially quantitative reaction of decaborane and sodium or lithium borohydride at elevated temperature

$$MBH_4 + B_{10}H_{14} \xrightarrow[R_2O]{90°} MB_{11}H_{14} + 2H_2 \qquad (1)$$

We have confirmed the findings of Hough and Edwards,[2] who reported that $NaB_{10}H_{13}$, diborane, and hydrogen are the sole products of reaction 1 when effected at 25°.

$$\begin{array}{l} MBH_4 + B_{10}H_{14} \xrightarrow[R_2O]{25°} \\ \qquad MB_{10}H_{13} + \begin{array}{c} H_3B{\cdot}OR_2 \\ \uparrow\downarrow \\ B_2H_6 + R_2O \end{array} + H_2 \qquad (2) \end{array}$$

The obvious implication to be drawn from these data is that reaction 1 involves a sequence of steps including reactions 2 and 3, and, in fact, we

$$R_2O{\cdot}BH_3 + MB_{10}H_{13} \xrightarrow{90°} MB_{11}H_{14} + H_2 + R_2O \qquad (3)$$

found that ethereal B_2H_6 and $NaB_{10}H_{13}$ do form $NaB_{11}H_{14}$ at 45°. The $B_{11}H_{14}^-$ salts were isolated from the reaction mixtures as etherates, $NaB_{11}H_{14}{\cdot}2.5$dioxane and $LiB_{11}H_{14}{\cdot}2$dioxane. These etherates dissolve readily in water and from metathesis reactions in such aqueous solutions, crystalline, non-solvated cesium, tetramethylammonium, trimethylsulfonium, and triethylammonium salts of $B_{11}H_{14}^-$ have been isolated.

The infrared spectrum of $B_{11}H_{14}^-$ is quite simple and suggests a high symmetry for this anion. The B–H stretch at 2530 cm.$^{-1}$ is structureless, and there is no bridge B–H absorption. No contemporary structure appears consistent with these data, but such a possibility cannot be excluded from consideration.

The proton magnetic resonance spectrum of aqueous solutions of $NaB_{11}H_{14}$ consists of a water resonance and a broad multiplet which has a high field shoulder. Effective spin decoupling of the boron and hydrogen nuclei by superposition of a saturating boron rf. field yields a proton spectrum consisting of the water resonance, two very closely spaced peaks of similar intensity (total relative

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[1] Paper IV, E. L. Muetterties and V. D. Aftandilian, *Inorg. Chem.*, **1**, 731 (1962).

[2] W. V. Hough and L. J. Edwards, 133rd National ACS Meeting, Division of Inorganic Chemistry, Paper No. 69, San Francisco, Calif., 1958.