The boron-11 nmr spectrum of $H_2ClB_3N_3H_3$ was an unsymmetrical doublet. The higher field resonance was twice the size of the lower field resonance, but both resonances appeared symmetrical. This spectrum was the mirror image of the spectrum[7] of $H_2CH_3B_3N_3H_3$. The $^{11}$BH doublet ($\delta$ $-31.7$ ppm, $J$ = 133 Hz) is shifted downfield ($-2.5$ ppm) whereas the $^{11}$BCl resonance ($\delta$ $-27.4$ ppm) is shifted upfield ($+1.8$ ppm) relative to $H_3B_3N_3H_3$. The factors influencing these nmr shifts are not fully understood[7] and, therefore, no significance can be attached to their direction or magnitude.

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# The Formation of 2-Carba-*nido*-hexaborane(9) and Several of Its Alkyl Derivatives

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The reactions of 2,5-$C_2B_6H_8$ and its C-methyl or C,C′-dimethyl derivatives with tetramethylammonium borohydride have been investigated. The immediately formed ionic products, when treated with HCl gas, yield $CB_5H_9$ and several alkyl-substituted derivatives of $CB_5H_9$. This appears to be the first example of the removal of a carbon atom from a closed carborane polyhedron.

In the past few years carboranes have been reported which contain only one carbon atom in the polyhedral structure. They can all be considered members of the $CB_nH_{n+2}$ or the $CB_nH_{n+4}$ series. The former series includes $CB_5H_7$[1,2] and its ion $CB_5H_6^-$ [2] and the ions $CB_9H_{10}^-$, [3] $CB_{10}H_{11}^-$, [4] and $CB_{11}H_{12}^-$ [3] (which are formally derived from the hypothetical carboranes $CB_9H_{11}$, $CB_{10}H_{12}$, and $CB_{11}H_{13}$, respectively). The latter series includes $CB_5H_9$[5] and the ions $CB_{10}H_{13}^-$ [3] and $CB_{10}H_{11}^{3-}$ [6,7] (which are formally derived from the hypothetical carborane $CB_{10}H_{14}$).

We wish to report here the preparation of the parent member of the $CB_nH_{n+4}$ series where $n$ = 5, 2-carba-*nido*-hexaborane(9), $CB_5H_9$, and some of its methyl and ethyl derivatives in addition to those reported previously.[5,8–10]

## Experimental Section

**Apparatus and Procedures.**—All operations involving carboranes were carried out using standard high-vacuum techniques. An Aerograph Model A-350 gas chromatograph containing either a $^3/_8$ in. × 10 ft aluminum column packed with 30% Apiezon L on Chromosorb P or an 8 mm × 20 ft Pyrex column packed with 30% Apiezon L on Chromosorb P was employed. Helium was used as carrier gas at 60-cm$^3$/min flow rate for all separations. Injection was accomplished using an apparatus similar to that suggested by Jeffery and Kipping.[11] Samples were collected in traps cooled in Dry Ice–2-propanol. Infrared spectra of gases were obtained using a 10-cm Pyrex cell with sodium chloride windows with a Perkin-Elmer 137 sodium chloride spectrophotometer. Nuclear magnetic resonance measurements were obtained with a Varian Model A-60 for proton spectra and a Varian Model HA-100 operating at 32.1 Mc/sec for boron-11 spectra. Mass spectra were obtained using a Hitachi Perkin-Elmer RMU-6D mass spectrometer.

Diglyme (diethylene glycol dimethyl ether) was obtained from the Ansul Co. and distilled from sodium followed by distillation from $LiAlH_4$ at reduced pressure. It was stored and all transfers were made in a nitrogen-filled drybox. Tetramethylammonium borohydride was obtained from Ventron, Metal Hydrides Division, and recrystallized from acetonitrile before use. Hydrogen chloride was obtained from Matheson Co. and passed through a trap cooled in pentane slush ($-131°$) before use. Boron trichloride and methyl chloride were obtained from Matheson Co. and were passed through traps cooled in Dry Ice–2-propanol. 2,5-Dicarba-*closo*-octaborane(8), 2,5-$C_2B_6H_8$,[12] and its C-methyl and C,C′-dimethyl derivatives were prepared and purified according to literature methods.[13]

1. **Reaction of 2,5-$C_2B_6H_8$ and Tetramethylammonium Borohydride.**—To a 500-ml cylindrical flask containing a magnetic stirring bar to which a stopcock fitted with a water jacket about the joint was fixed was added 1.3664 g (15.4 mmol) of $(CH_3)_4NBH_4$.[14] The flask was evacuated, taken into the drybox, and

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filled with nitrogen followed by 8.0 ml of diglyme. The flask was cooled in liquid nitrogen and evacuated. The contents were allowed to warm to room temperature and stirred for 1 hr. The flask was again cooled in liquid $N_2$ and evacuated to remove any evolved gases; this was followed by the addition of 1.4985 g (15.5 mmol) of 2,5-$C_2B_6H_8$. The flask was closed and water was passed through the water jacket to cool the joint. The mixture was allowed to come to room temperature and then heated with stirring at 90° for 30 hr in an oil bath. The flask was cooled in liquid $N_2$ and approximately 8 mmol of noncondensable gases was removed. The flask was allowed to come to room temperature and the volatiles were condensed into a trap cooled in liquid $N_2$. This material consisted of diglyme and a trace of unreacted 2,5-$C_2B_6H_8$. The pale yellow residue in the flask was heated *in vacuo* at 90° for 15 hr to obtain a solvent-free solid. Four increments (13.0 mmol each) of HCl were added and allowed to remain for 20 hr each at room temperature followed, after each addition, by condensation of the volatiles in a trap cooled in liquid $N_2$. A white residue of $(CH_3)_4NCl$ remained. The combined fractions were then passed through traps cooled at 0° (ice), −98° (methanol slush), and −196° (liquid $N_2$). The 0° trap contained a small amount of a viscous material which was not characterized. The −196° trap contained 9.1 mmol of unreacted HCl which was identified by its infrared spectrum. The contents of the −98° trap (0.9248 g) were passed in approximately 0.25-ml increments through the 20-ft vpc column operating at 115°. Four major fractions were obtained (see Table I).

TABLE I

| Starting material | Products | m/e cutoff | $Rv^a$ | % yield$^b$ |
|---|---|---|---|---|
| 2,5-$C_2B_6H_8$ | $CB_5H_9$ | 76 | 1.00 | 18.5 |
| | 1-$CH_3CB_5H_8$ | 90 | 1.35 | 10.1 |
| | 3-$CH_3CB_5H_8$ | 90 | 1.69 | 12.1 |
| | 1,3-$(CH_3)_2CB_5H_7$ | 104 | 2.20 | 3.1 |
| 2-$CH_3$-2,5-$C_2B_6H_7$ | $CB_5H_9$ | 76 | 1.00 | 0.6 |
| | 2-$CH_3CB_5H_8$ | 90 | 1.31 | 25.1 |
| | 1,2-$(CH_3)_2CB_5H_7$ | 104 | 1.71 | 16.7 |
| | 2,3-$(CH_3)_2CB_5H_7$ | 104 | 2.08 | 6.5 |
| | 1,2,3-$(CH_3)_3CB_5H_6$ | 118 | 2.35 | 2.5 |
| 2,5-$(CH_3)_2$-2,5-$C_2B_6H_6$ | 2-$CH_3CB_5H_8$ | 90 | 1.31 | 10.0 |
| | 1-$C_2H_5$-2-$CH_3CB_5H_7$ | 118 | 2.86 | 26.8 |
| | 2-$CH_3$-3-$C_2H_5CB_5H_7$ | 118 | 3.27 | 14.5 |

$^a$ Average retention volume relative to 1.00 for $CB_5H_9$. $^b$ Based on starting carborane added.

2. **Reaction of 2-$CH_3$-2,5-$C_2B_6H_7$ and Tetramethylammonium Borohydride.**—The reaction was carried out exactly as above using 1.3560 g (15.2 mmol) of $(CH_3)_4NBH_4$, 8.0 ml of diglyme, and 1.7675 g (15.9 mmol) of 2-$CH_3$-2,5-$C_2B_6H_7$. The mixture was heated at 84° for 20 hr. The mixture was cooled to −196° and approximately 8.2 mmol of noncondensable gases was removed. The diglyme and a small amount of unreacted carborane were removed by distillation *in vacuo*. The yellow residue was heated *in vacuo* at 80° for 15 hr to remove residual solvent. Four increments (13 mmol each) of HCl were added and allowed to remain at room temperature for 20 hr each. The volatiles produced were condensed into a −196° trap after each addition, allowing the removal of noncondensable gases. A white residue of $(CH_3)_4NCl$ remained. The combined fractions were passed through 0°, −80° (Dry Ice–2-propanol), and −196° traps. The 0° trap contained a small amount of uncharacterized yellow oil. The −196° trap contained 5.5 mmol of HCl and traces of $B_2H_6$, $CH_3Cl$, and $BCl_3$, all identified by their infrared spectra. The contents of the −80° trap (0.8546 g) were passed through the 10-ft vpc column operating at 135° and five major fractions were collected (see Table I).

3. **Reaction of 2,5-$(CH_3)_2$-2,5-$C_2B_6H_6$ and Tetramethylammonium Borohydride.**—The reaction was carried out exactly as above using 2.0125 g (22.6 mmol) of $(CH_3)_4NBH_4$, 8.0 ml of diglyme, and 2.4403 g (19.5 mmol) of 2,5-$(CH_3)_2$-2,5-$C_2B_6H_6$. The mixture was heated at 122° for 35 hr. The mixture was cooled to −196° and approximately 12 mmol of noncondensable gases removed. The diglyme and a trace of unreacted carborane were removed by vacuum distillation. The yellow residue was heated *in vacuo* at 80° for 15 hr to remove residual solvent. Five increments (13 mmol each) of HCl were added and allowed to remain at room temperature for 20 hr each. The volatile products were condensed into a trap cooled to −196° after each addition, allowing the removal of noncondensable gases. A white residue of $(CH_3)_4NCl$ remained. The combined fractions were passed through 0, −80, and −196° traps. The 0° trap contained a small amount of uncharacterized viscous oil. The −196° trap contained 12.8 mmol of HCl identified by its infrared spectrum. The contents of the −80° trap (1.2496 g) were passed through the 10-ft vpc column operating at 150° and three major fractions were collected (see Table I).

**Reaction of 3-$CH_3CB_5H_8$ with HCl, $BCl_3$, and $CH_3Cl$.**—Into a 25-ml Pyrex bulb fitted with an nmr tube and a break-seal 1.0 mmol of HCl, 1.0 mmol of $BCl_3$, 1.0 mmol of $CH_3Cl$, and 1.0 mmol of 3-$CH_3CB_5H_8$ were condensed. The bulb was sealed. Boron-11 nmr spectra were taken beginning as soon as the bulb reached room temperature and each hour for 2 hr. The bulb was then heated for 3 hr at 100°. No significant change was observed in the spectra.

## Results and Discussion

The reaction between 2,5-$C_2B_6H_8$ or its C-methyl or C,C′-dimethyl derivatives with tetramethylammonium borohydride followed by treatment with HCl produces 2-carba-*nido*-hexaborane, $CB_5H_9$, and several of its alkyl derivatives.

Even though the removal of boron atoms from carborane polyhedra is known to occur pyrolytically,[15,16] chemically,[17–19] and photolytically,[20] this appears to be the first example of the removal of a cage *carbon* atom from such an environment.

In reaction 1 using 2,5-$C_2B_6H_8$ as the starting carborane, $CB_5H_9$, 1-$CH_3CB_5H_8$, 3-$CH_3CB_5H_8$, and 1,3-$(CH_3)_2CB_5H_7$ were obtained. These results indicate that one of the cage carbon atoms had been converted to a methyl group and a subsequent methyl cleavage and intermolecular migration yielded the products. Reaction 2 using 2-$CH_3$-2,5-$C_2B_6H_7$ as the starting carborane yielded $CB_5H_9$, 2-$CH_3CB_5H_8$, 1,2- and 2,3-$(CH_3)_2$-$CB_5H_7$, and 1,2,3-$(CH_3)_3CB_5H_6$. These results indicate that the methyl-substituted carbon atom remained in the polyhedron while the unsubstituted carbon atom was converted to a methyl substituent with subsequent cleavage and intermolecular migration to yield products. The alternative route in which the methyl-substituted carbon atom was converted to an ethyl group can be ruled out in view of the fact that no ethyl-substituted products were found. Reaction 3 using 2,5-$(CH_3)_2$-2,5-$C_2B_6H_6$ as the starting carborane yielded 2-$CH_3$-$CB_5H_8$, 1-$C_2H_5$-2-$CH_3CB_5H_7$, and 2-$CH_3$-3-$C_2H_5CB_5H_7$. These results indicate that one of the methyl-substituted polyhedral carbon atoms was converted to an

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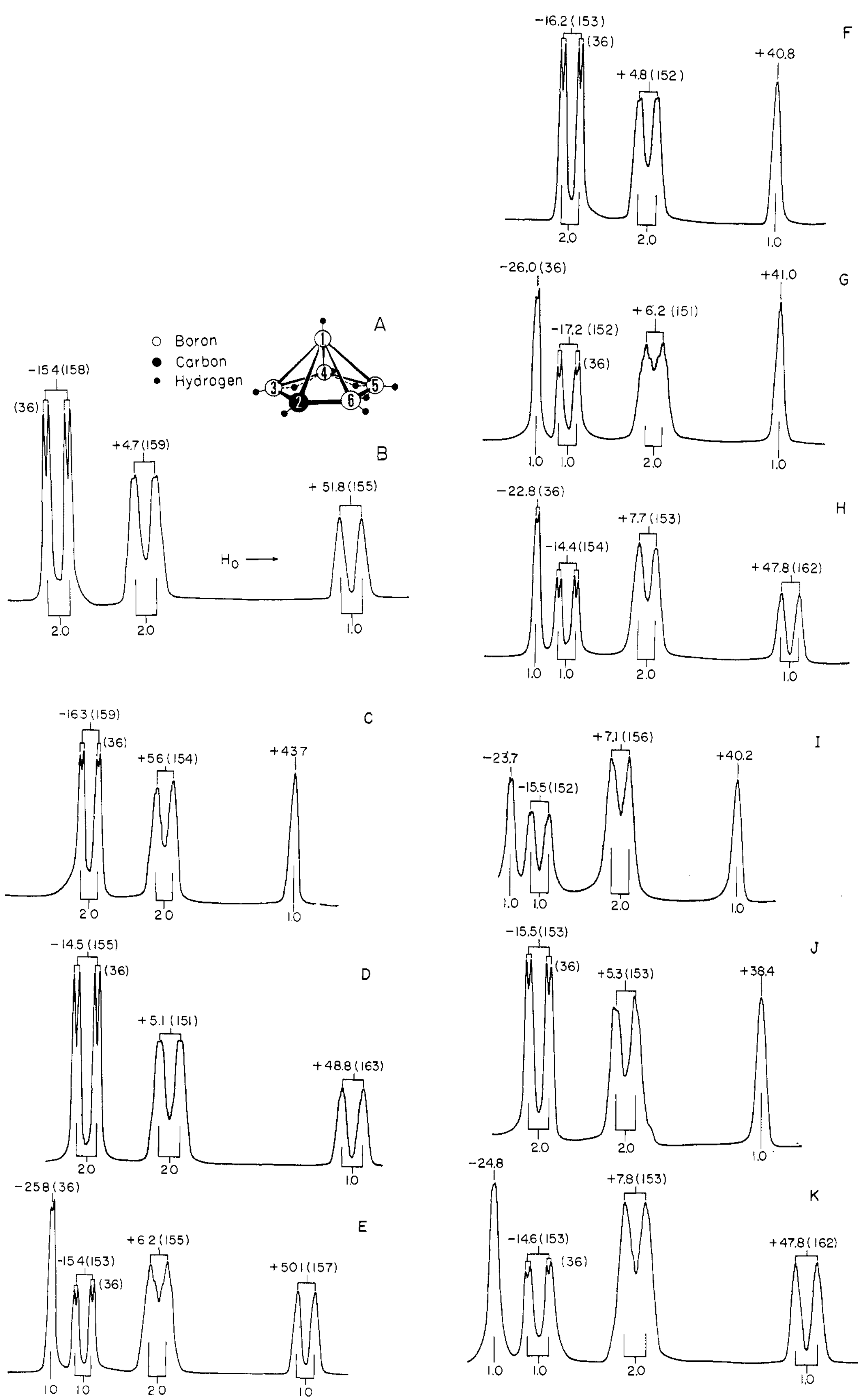

Figure 1.—(A) The molecular structure of 2-carba-*nido*-hexaborane(9), $CB_5H_9$. The 32.1-Mc/sec $^{11}B$ nmr spectra of $CB_5H_9$ (B), 1-$CH_3CB_5H_8$ (C), 2-$CH_3CB_5H_8$ (D), 3-$CH_3CB_5H_8$ (E), 1,2-$(CH_3)_2CB_5H_7$ (F), 1,3-$(CH_3)_2CB_5H_7$ (G), 2,3-$(CH_3)_2CB_5H_7$ (H), 1,2,3-$(CH_3)_3$-$CB_5H_6$ (I), 1-$C_2H_5$-2-$CH_3CB_5H_7$ (J), and 2-$CH_3$-3-$C_2H_5CB_5H_7$ (K). Chemical shifts (ppm, relative to $BF_3 \cdot O(C_2H_5)_2$) and coupling constants (cps) are indicated. Relative areas appear beneath the peaks.

ethyl substituent while the remaining polyhedral carbon atom, together with its attached methyl group, remained in the cage. A methyl diethyl derivative which would correspond to the dimethyl and trimethyl products obtained by an apparent methyl migration in reactions 1 and 2 and would require an intermolecular ethyl transfer was not observed possibly owing to low yield and/or its expected low volatility. In a separate experiment, 3-$CH_3CB_5H_8$ was treated with HCl, $BCl_3$, and $CH_3Cl$ to approximate reaction conditions in reaction 1 and none of the expected 1,3-$(CH_3)_2CB_5H_7$ was obtained. Thus, in these reactions we favor an intermolecular methyl transfer rather than an electrophilic methyl substitution, employing the by-products $BCl_3$ and $CH_3Cl$ observed in reaction 2.

**Nmr and Mass Spectra. $CB_5H_9$.**—The 32.1-Mc/sec $^{11}B$ nmr spectrum of $CB_5H_9$ (Figure 1B) consisted of three sets of doublets of relative areas 2:2:1 which are consistent with a five-boron-atom species in a pentagonal-pyramid structure containing one carbon atom in the base. We favor assignment of the doublet which occurs at −15.4 ppm to the 3,6 boron atoms rather than the 4,5 boron atoms because of the observed symmetrical and sharp bridge hydrogen coupling which indicates that these boron atoms are coupled strongly to only one type of bridge hydrogen atom. The doublet which occurs at +4.7 ppm was assigned to the 4,5 boron atoms. This doublet is apparently further split into triplets, though unresolved, due to coupling to two types of bridge hydrogen atoms. The 60-Mc/sec $^1H$ nmr spectrum consisted of a broad peak at $\tau$ 4.62 relative to internal tetramethylsilane (TMS), which was assigned to the single terminal CH resonance. The mass spectrum exhibited a sharp cutoff at $m/e$ 76 which corresponds to the $^{12}C^{11}B_5{}^1H_9{}^+$ ion.

**1-$CH_3CB_5H_8$.**—The 32.1-Mc/sec $^{11}B$ nmr spectrum of 1-$CH_3CB_5H_8$ (Figure 1C) consisted of two doublets and a singlet of relative areas 2:2:1, respectively. The singlet at highest field indicates apex substitution. The 60-Mc/sec $^1H$ nmr spectrum contained a broad peak of relative area 1 at $\tau$ 4.45 assigned to the single CH resonance and a broad peak of relative area 3 at $\tau$ 10.58 assigned to the apex methyl substituent relative to internal TMS. The mass spectrum exhibited a sharp cutoff at $m/e$ 90 which corresponds to the $^{12}C_2{}^{11}B_5{}^1H_{11}{}^+$ ion.

**2-$CH_3CB_5H_8$.**—The 32.1-Mc/sec $^{11}B$ nmr spectrum of 2-$CH_3CB_5H_8$ (Figure 1D) consisted of three doublets of relative areas 2:2:1, respectively. The 60-Mc/sec $^1H$ nmr spectrum consisted of a broad singlet at $\tau$ 7.92 relative to internal TMS which was assigned to the C–$CH_3$ resonance. The mass spectrum exhibited a sharp cutoff at $m/e$ 90 corresponding to the $^{12}C_2{}^{11}B_5{}^1H_{11}{}^+$ ion.

Table II

Infrared Spectra ($cm^{-1}$)[a]

$CB_5H_9$
3000 w, 2600 vs, 1900 s, 1850 m, 1500 vs, 1240 s, 1135 s, 990 m, 908 s, 722 m

1-$CH_3CB_5H_8$
3000 m, 2900 s, 2820 m, 2600 vs, 1930 s, 1870 s, 1460 vs, 1320 s, 1240 s, 1140 s, 1040 m, 970 m, 887 s, 758 s

2-$CH_3CB_5H_8$
2950 s, 2850 s, 2600 vs, 1900 s, 1480 vs, 1240 m, 988 vs, 910 s, 843 s, 836 s, 716 m, 710 m, 696 m, 683 m

3-$CH_3CB_5H_8$
3000 w, 2950 m, 2600 vs, 1920 s, 1470 vs, 1400 vs, 1330 vs, 1280 s, 1150 m, 1075 m, 1000 s, 888 s, 719 m

1,2-$(CH_3)_2CB_5H_7$
2920 s, 2850 m, 2600 vs, 1890 m, 1470 s, 1320 s, 1250 m, 1140 m, 1035 m, 990 s, 918 w, 896 m, 888 m, 852 w, 842 w, 735 m

1,3-$(CH_3)_2CB_5H_7$
3000 m, 2950 s, 2820 m, 2600 vs, 1950 m, 1900 m, 1470 s, 1380 vs, 1325 vs, 1270 s, 1140 s, 1070 m, 990 s, 898 m, 786 w, 743 m

2,3-$(CH_3)_2CB_5H_7$
2980 s, 2880 m, 2600 vs, 1900 m, 1480 s, 1430 s, 1320 s, 1270 m, 1060 m, 975 s, 885 m, 704 m

1,2,3-$(CH_3)_3CB_5H_6$
2950 s, 2600 vs, 1890 m, 1440 s, 1410 s, 1320 s, 1270 m, 1240 m, 1140 m, 1060 m, 1030 w, 1020 w, 975 m, 894 m, 810 w, 738 w

1-$C_2H_5$-2-$CH_3CB_5H_7$
2950 vs, 2600 vs, 1900 s, 1460 s, 1240 m, 1140 m, 1040 w, 986 s, 948 w, 918 w, 878 m, 852 w, 790 w, 728 w

2-$CH_3$-3-$C_2H_5CB_5H_7$
2950 vs, 2600 vs, 1900 m, 1460 s, 1430 s, 1310 w, 1240 w, 1070 w, 1060 w, 1025 w, 958 w, 932 w, 880 m, 807 w, 750 w, 712 w

[a] Abbreviations: vs, very strong; s, strong; m, medium; w, weak. Spectra taken in gas phase.

**3-$CH_3CB_5H_8$.**—The 32.1-Mc/sec $^{11}B$ nmr spectrum of 3-$CH_3CB_5H_8$ (Figure 1E) consisted of a singlet and three doublets of relative areas 1:1:2:1, respectively. The low-field singlet indicates substitution at the 3 position. The nonequivalence of the 4,5 positions is indicated by broadening of the doublet at +6.2 ppm. The 60-Mc/sec $^1H$ nmr spectrum exhibited a broad peak of relative area 1 at $\tau$ 5.10 assigned to the single CH resonance and a broad peak of relative area 3 at $\tau$ 9.20 relative to internal TMS which was assigned to the single B–$CH_3$ resonance. The mass spectrum exhibited a sharp cutoff at $m/e$ 90 which corresponds to the $^{12}C_2{}^{11}B_5{}^1H_{11}{}^+$ ion.

**1,2-$(CH_3)_2CB_5H_7$.**—The 32.1-Mc/sec $^{11}B$ nmr spectrum of 1,2-$(CH_3)_2CB_5H_7$ (Figure 1F) consisted of two doublets and a singlet of relative areas 2:2:1. The 60-Mc/sec $^1H$ nmr spectrum contained a broad peak of area 1 at $\tau$ 7.93 and a broad peak of area 1 at $\tau$ 10.62 relative to internal TMS which were assigned to the C–$CH_3$ and B–$CH_3$ resonances, respectively. The mass spectrum exhibited a sharp cutoff at $m/e$ 104 which corresponds to the $^{12}C_3{}^{11}B_5{}^1H_{13}{}^+$ ion.

**1,3-$(CH_3)_2CB_5H_7$.**—The 32.1-Mc/sec $^{11}B$ nmr spectrum of 1,3-$(CH_3)_2CB_5H_7$ (Figure 1G) consisted of a low-field singlet, two doublets, and a high-field singlet of areas 1:1:2:1, respectively. The 60-Mc/sec $^1H$ nmr spectrum consisted of three broad peaks of relative areas 1:3:3 at $\tau$ 5.08, 9.25, and 10.60 relative to internal TMS which were assigned to the resonances of the single C–H and methyl groups at the 3 and 1 positions, respectively. The mass spectrum exhibited a sharp cutoff at *m/e* 104 which corresponds to the $^{12}C_3{}^{11}B_5{}^1H_{13}{}^+$ ion.

**2,3-$(CH_3)_2CB_5H_7$.**—The 32.1-Mc/sec $^{11}B$ nmr spectrum of 2,3-$(CH_3)_2CB_5H_7$ (Figure 1H) consisted of a low-field singlet and three doublets of relative areas 1:1:2:1, respectively. The 60-Mc/sec $^1H$ nmr spectrum consisted of two broad peaks of equal area at $\tau$ 8.10 and 9.40 relative to internal TMS which were assigned to the resonances of the methyl groups at the 2 and 3 positions. The mass spectrum exhibited a sharp cutoff at *m/e* 104 which corresponds to the $^{12}C_3{}^{11}B_5{}^1H_{13}{}^+$ ion.

**1,2,3-$(CH_3)_3CB_5H_6$.**—The 32.1-Mc/sec $^{11}B$ nmr spectrum of 1,2,3-$(CH_3)_3CB_5H_6$ (Figure 1I) consisted of a low-field singlet, two doublets, and a high -field singlet of relative areas 1:1:2:1, respectively. The 60-Mc/sec $^1H$ nmr consisted of three peaks of equal areas at $\tau$ 8.05, 9.32, and 10.57 relative to internal TMS which were assigned to the resonances of the methyl groups at the 2, 3, and 1 positions, respectively. The mass spectrum exhibited a sharp cutoff at *m/e* 118 which corresponds to the $^{12}C_4{}^{11}B_5{}^1H_{15}{}^+$ ion.

**1-$C_2H_5$-2-$CH_3CB_5H_7$.**—The 32.1-Mc/sec $^{11}B$ nmr spectrum of 1-$C_2H_5$-2-$CH_3CB_5H_7$ (Figure 1J) consisted of two doublets and a singlet of relative areas 2:2:1, respectively. The 60-Mc/sec $^1H$ nmr spectrum consisted of a broad singlet of area 3 at $\tau$ 7.95 assigned to the C–$CH_3$ resonance and a partially resolved triplet of area 3.0 at $\tau$ 9.57 and a broad peak of area 2.1 at $\tau$ 10.23 relative to internal TMS, both assigned to the ethyl protons which are consistent with values previously observed.[10] The mass spectrum exhibited a sharp cutoff at *m/e* 118 which corresponds to the $^{12}C_4{}^{11}B_5{}^1H_{15}{}^+$ ion.

**2-$CH_3$-3-$C_2H_5CB_5H_7$.**—The 32.1-Mc/sec $^{11}B$ nmr spectrum of 2-$CH_3$-3-$C_2H_5CB_5H_7$ (Figure 1K) consisted of a low-field singlet and three doublets of relative areas 1:1:2:1, respectively. The 60-Mc/sec $^1H$ nmr spectrum consisted of a singlet of area 3 at $\tau$ 8.08 assigned to the C–$CH_3$ resonance and a singlet of area 4.6 at $\tau$ 8.89 assigned to the B–$C_2H_5$ resonance[10] relative to internal TMS. The mass spectrum exhibited a sharp cutoff at *m/e* 118 which corresponds to the $^{12}C_4{}^{11}B_5{}^1H_{15}{}^+$ ion.

The most significant feature of the infrared spectra of these compounds is the strong absorption between 1850 and 1950 cm$^{-1}$ due to bridge hydrogen vibrations.

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# A New Synthesis of Amine- and Phosphine-Boranes

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A new, rapid, and high-yield synthesis of borane adducts with amines and phosphines has been developed. It is based on the reaction of sodium borohydride and iodine in the presence of the donor. The procedure is applicable to adducts of ammonia, primary, secondary, and tertiary amines, di- and triamines, pyridines, triphenylphosphine, and diphosphines. The following new compounds have been prepared: 2-methoxypyridine–borane, 2,2′-dipyridyl–bis(borane), bis(diphenylphosphino)methane–bis(borane), and 1,2-bis(diphenylphosphino)ethane–bis(borane).

Amine–boranes constitute an important class of boron–nitrogen compounds since they or their derivatives provide a direct entry to the synthesis of aminoboranes or borazines[1,2] or to boron cations.[3–5] It is therefore of considerable importance to develop more simple and convenient methods of synthesis of amine–boranes from readily available starting materials. Present methods involve either direct combination of amine and diborane, reaction of ethereal lithium borohydride with ammonium salts,[6] transamination of an already formed amine–borane,[7,8] or less direct methods like reduction of an appropriate boron compound using hydrogen or borohydride.[9–11]

We wish to report here a convenient one-step synthesis of borane adducts using sodium borohydride, appropriate donors, and iodine. The method is simple and it gives boranes with good yield and high purity. The new method was successfully worked out for the synthesis of ammonia–borane, boranes of different aliphatic amines which include primary and secondary monoamines and tertiary di- and triamines, and boranes of substituted pyridines and for the synthesis of phenyl-substituted phosphine–boranes.

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