Anal. Calcd. for $B_{10}C_8H_{34}N_2$: B, 40.95; C, 36.34; H, 12.11; N, 10.60. Found: B, 40.96; C, 36.32; H, 13.91; N, 10.48.

Autoprotolysis of I in Acetonitrile.—A solution of 2.0 g. (7.5×10^{-3} mole) of I in 30 ml. of acetonitrile was heated to the reflux temperature and stirred under nitrogen for 4 hr. or until no more hydrogen was evolved. The solution was filtered and the filtrate was evaporated *in vacuo* to yield 1.5 g. (49% of theory) of solid. White crystals, m.p. 175°, were obtained from methylene chloride–pentane. The infrared spectrum contained NH bands at 2.9 μ and 3.1 μ and C=N absorption at 6.2 μ.

Anal. Calcd. for $B_{10}C_{10}H_{37}N_3$: B, 35.22; C, 39.06; H, 12.04; N, 13.67. Found: B, 36.20; C, 38.63; H, 11.90; N, 13.72.

Reaction of Amine Hydrochlorides and $\overset{+}{\mathrm{N}}\mathrm{a}B_{10}H_{13}X$.—The procedure was essentially the same for all compounds described in Table II.

In a 50-ml. round bottom flask were placed 5×10^{-3} mole of $\overset{+}{\mathrm{Na}}\overset{-}{\mathrm{B}}_{10}H_{13}X$, 20 ml. of tetrahydrofuran, and 7×10^{-3} mole of the desired amine hydrochloride. The solution was stirred and heated to the reflux temperature for 4 hr. while hydrogen was evolved. After filtering the solution, the filtrate was evaporated to dryness. The solid which was separated by filtration was washed well with water to remove starting material and then combined with the filtrate residue and recrystallized from methylene chloride–pentane. The yields of products are listed in Table II.

Protolysis of I in Acetonitrile Solution.—A 300-ml. round bottom flask containing 3.0 g. (1.1×10^{-2} mole) of I and 50 ml. of acetonitrile was evacuated on a vacuum line. Approximately one atmosphere of dry hydrogen chloride gas was introduced. Hydrogen was evolved as the reaction mixture was stirred. After 20 min., the contents of the flask was evaporated to dryness *in vacuo* and then extracted with methylene chloride. The methylene chloride-insoluble material, after being washed with water, yielded 2.0 g. (76% of theory) of white product, dec. pt. 171°. Recrystallization from acetonitrile gave light yellow crystals of $B_{10}H_{12}[(C_2H_5)_2NH](CH_3CN)$.

Anal. Calcd. for $B_{10}C_6H_{26}N_2$: B, 46.20; C, 30.74; H, 11.10; N, 11.96. Found: B, 45.66; C, 29.90; H, 11.46; N, 12.46.

Protolysis of I in the Presence of Diethyl Sulfide.—A suspension of 2.0 g. (7.5×10^{-3} mole) of I in 30 ml. of diethyl sulfide was placed in a 200-ml. round bottom flask and evacuated on a vacuum line. One atmosphere of hydrogen chloride was admitted and the reaction was allowed to proceed until 7.5×10^{-3} mole of hydrogen was evolved as measured in an attached Toepler system. The solution was evaporated *in vacuo* and the residue washed with water and dried. The yield of crude product was 1.6 g. (77% of theory). White crystals of $B_{10}H_{12}[(C_2H_5)_2NH][(C_2H_5)_2S]$ which melted at 124° were obtained from methylene chloride–pentane.

Anal. Calcd. for $B_{10}C_8H_{33}NS$: B, 38.21; C, 33.90; H, 11.65; N, 4.94. Found: B, 37.44; C, 33.92; H, 11.55; N, 4.88.

Acknowledgment.—This work was carried out under the sponsorship of the U. S. Army Ordnance Corps., Contract DA-01-021-ORD-11878.

Contribution from the Rohm and Haas Company, Redstone Arsenal
Research Division, Huntsville, Alabama

The Preparation and Reactions of B_9H_{13} (Ligand) Compounds[1a]

By Bruce M. Graybill, Anthony R. Pitochelli, and M. Frederick Hawthorne[1b]

Received February 6, 1962

Synthetic methods for the preparation of $B_9H_{13}X$ (X = ligand) species are described. Further reactions of $B_9H_{13}X$ compounds include (1) ligand displacement reactions, (2) proton abstraction to form $B_9H_{12}X$ anions, and (3) proton abstraction accompanied by ligand expulsion to produce the B_9H_{12} anion. Spectroscopic examination of a series of $B_9H_{13}(pyZ)$ (Z = substituent group on pyridine) revealed a correlation of excitation energy with the Hammett sigma constant of Z.

The synthesis[2] and structure[3] of an enneaborane-15 have been reported recently. The topological method of Dickerson and Lipscomb[4,5] allows the determined structure to be described as an icosahedral fragment of 5421 topology.

Previous workers[6,7] in the area of boron hydride

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(1) (a) Presented in part at the 138th National Meeting of the American Chemical Society, New York, N. Y., September, 1960, Abstracts, p. 45-N; (b) Department of Chemistry, The University of California, Riverside, California.

(2) W. V. Kotlensky and R. Schaeffer, *J. Am. Chem. Soc.*, **80**, 4517 (1958).

(3) R. E. Dickerson, P. J. Wheatley, P. A. Howell, and W. N. Lipscomb, *J. Chem. Phys.*, **27**, 200 (1957).

(4) R. E. Dickerson and W. N. Lipscomb, *ibid.*, **27**, 212 (1957).

(5) W. N. Lipscomb, *Advan. Inorg. Chem. Radiochem.*, **1**, 117 (1959).

(6) R. Schaeffer, private communication, 1956; methanolysis of 6,9-bis-(acetonitrile)-decaborane apparently produced a B_9 derivative.

(7) S. J. Fitch and A. W. Laubengayer, *J. Am. Chem. Soc.*, **80**, 5911 (1958).

chemistry have reported the preparation of products which appeared to be enneaborane derivatives. Recently, an entire series of enneaborane-15 derivatives ($B_9H_{13}X$ where X = ligand) were prepared and characterized.[1] Wang, Simpson, and Lipscomb[8] have reported the structure of a representative member[1] of this series, $B_9H_{13}(CH_3CN)$, as determined by single crystal X-ray diffraction studies. The boron atom arrangement in these compounds was found to be that of an icosahedral fragment differing from that which appears in the known B_9H_{15}.[2,3] The hypothetical parent hydride from which these derivatives may be formally derived[8] has the unfavorable topology 6330. The boron atom arrangement of $B_9H_{13}X$ compounds had been deduced previously from chemical[1] and B^{11} nuclear magnetic resonance spectra.[9] In this paper the preparation, chemical characterization, and further reactions of $B_9H_{13}X$ compounds are reported. Figure 1 presents the appoximate geometry of these materials.

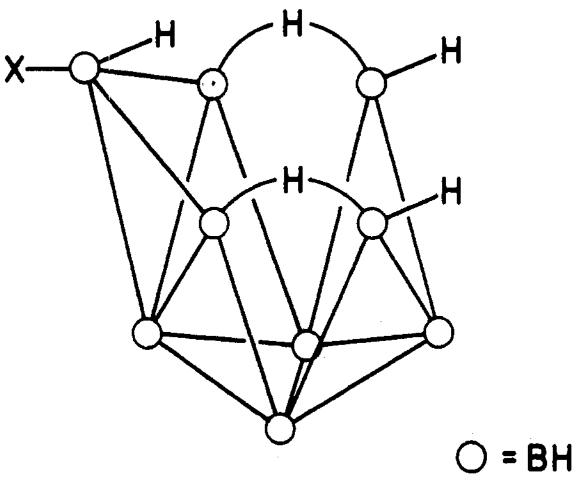

Fig. 1.—Approximate geometry of $B_9H_{13}X$.

Results and Discussion

Preparation of $B_9H_{13}X$ Compounds from $B_{10}H_{13}$-X Anions.—The reaction of two equivalents of diethylamine with one equivalent of decaborane produces the salt[1,10,11] $(C_2H_5)_2NH_2B_{10}H_{13}(C_2H_5)_2NH$, as shown in (1). The structure of the anion

$$B_{10}H_{14} + (C_2H_5)_2NH \overset{\text{fast}}{\rightleftarrows} (C_2H_5)_2\overset{+}{N}H_2B_{10}\overset{-}{H}_{13} \xrightarrow[\text{slow}]{(C_2H_5)_2NH} (C_2H_5)_2\overset{+}{N}HB_{10}\overset{-}{H}_{13}[(C_2H_5)_2NH] \quad (1)$$

of $(C_2H_5)_2\overset{+}{N}H_2B_{10}H_{13}(C_2H_5)_2\overset{-}{N}H$ has been deduced from chemical evidence[11] and is in accord with a $B_{10}H_{12}XX'$ configuration,[12] where X is diethylamine and X′ is a hydride ion.

Treatment of $(C_2H_5)_2\overset{+}{N}H_2B_{10}H_{13}(C_2H_5)_2\overset{-}{N}H$ with *aqueous* hydrogen chloride solutions was found to produce approximately 2.0 moles of hydrogen and 1.0 mole of boric acid per mole of salt. In this same reaction a new boron hydride derivative, formulated as $B_9H_{13}[(C_2H_5)_2NH]$, was produced in 95% yield. The composition of this new derivative was first deduced from (2) and

$$B_{10}H_{13}[(C_2H_5)_2NH]^- + H_3O^+ + 2H_2O \longrightarrow 2H_2 + B(OH)_3 + B_9H_{13}[(C_2H_5)_2NH] \quad (2)$$

its elemental analysis. Further chemical transformations followed by single crystal X-ray diffraction studies[8] of $B_9H_{13}(CH_3CN)$ confirmed this assignment (*vide ultra*). It is evident that the dimethylamine "aminate" of decaborane described by Fitch and Laubengayer[7] was the dimethylamine analog of $(C_2H_5)_2\overset{+}{N}H_2B_{10}H_{13}(C_2H_5)_2\overset{-}{N}H$ and that the acidolysis of this "aminate" produced $B_9H_{13}[(CH_3)_2NH]$.

The fact that $(C_2H_5)_2\overset{+}{N}H_2B_{10}H_{13}(C_2H_5)_2\overset{-}{N}H$ could be converted in high yield to an enneaborane-15 derivative suggested that other previously described[11] anions of the $B_{10}H_{13}X$ class also would undergo the acidolysis reaction. This was found to be the case. The $B_9H_{13}X$ compounds listed in Table I were prepared in high yields from the corresponding $B_{10}H_{13}X$ sodium salts (method A). Table I presents yields and characterization data for these materials. Figure 2 presents the B^{11} n.m.r. spectrum of $B_9H_{13}[(C_2H_5)_2NH]$.

Alcoholysis of $B_{10}H_{12}X_2$ Derivatives.—The original report[13] of the preparation of bis-(acetonitrile)-decaborane made reference to a methanolysis product which contained C=N absorption bands in the infrared. A similar compound (I) was prepared in 18% yield in this Laboratory by the treatment of bis-(acetonitrile)-decaborane with an excess of warm ethanol. Elemental analysis of pure crystalline I (m.p. 103° dec.)

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[8] F. E. Wang, P. G. Simpson, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **83**, 491 (1961).

[9] W. N. Lipscomb, private communication, correctly interpreted the B^{11} nuclear magnetic resonance spectra, February, 1960.

[10] M. F. Hawthorne, A. R. Pitochelli, R. D. Strahm, and J. J. Miller, *J. Am. Chem. Soc.*, **82**, 1825 (1960).

[11] B. M. Graybill, A. R. Pitochelli, and M. F. Hawthorne, Inorg. Chem., **1**, 622 (1962).

[12] J. Reddy and W. N. Lipscomb, *J. Chem. Phys.*, **31**, 610 (1959).

[13] R. Schaeffer, *J. Am. Chem. Soc.*, **79**, 1006 (1957).

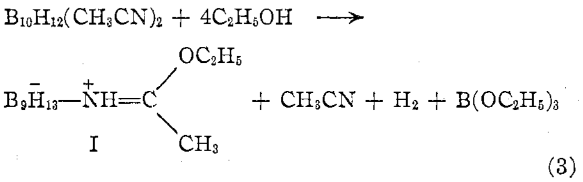
TABLE I

PREPARATION OF $B_9H_{13}X$ COMPOUNDS

X in $B_9H_{13}X$	Yield, % (method)	M.p., °C.	Analyses, % Calcd. B	C	H	N	Found B	C	H	N
Diethylamine	95(A), 75(B)	93–95	53.05	26.15	13.18	7.63	54.03	25.90	10.73	7.66
Ethylamine	65(A)	96–97	62.67	15.45	12.87	9.01	61.29	16.07	13.00	8.83
Triethylamine	88(A)	96–98	46.07	34.08	13.25	6.62	45.07	34.08	13.25	6.62
Triphenylphosphine	90(A), 85(B)	113	26.15	58.01	7.52	8.32[a]	25.28	57.20	7.32	8.16[a]
Acetonitrile	60(B)	>300	64.33	15.85	10.60	9.25	63.95	16.28	10.73	9.21
Pyridine	89(A), 62(B)	121	51.42	31.68	9.50	7.39	50.30	30.27	9.41	7.49
4-Methoxypyridine	65(B)	125	44.39	32.82	9.12	6.38	43.54	32.68	9.00	5.96
4-Methylpyridine	58(B)	125	47.88	35.40	9.83	6.88	47.32	36.32	10.15	6.65
4-Chloropyridine	72(B)	153	43.51	26.81	7.60	6.25	42.82	26.47	8.09	6.61
3-Chloropyridine	61(B)	106	43.51	26.81	7.60	6.25	42.67	26.70	7.87	6.37
4-Cyanopyridine	54(B)	167	45.42	33.59	7.93	13.06	44.10	33.84	8.04	12.87

[a] Analysis for phosphorus.

was in agreement with the empirical formulation $B_9H_{13}(CH_3CN)(C_2H_5OH)$. The infrared absorption spectrum of I contained bands at 3310 cm.$^{-1}$ (NH stretch); 2440, 2480, and 2525 cm.$^{-1}$ (BH stretch); and 1630 cm.$^{-1}$ (C=N stretch). The B^{11} n.m.r. spectrum of I was grossly identical to that of $B_9H_{13}[(C_2H_5)_2NH]$. The H^1 n.m.r. spectrum of I in the C–H region contained a strong singlet between the quartet and triplet characteristic of the ethyl group. The relative areas were approximately 2:3:3. The singlet thus is assigned as a methyl group which is attached to a carbon atom which bears no hydrogen. The structure of I thus may be represented as



$$B_{10}H_{12}(CH_3CN)_2 + 4C_2H_5OH \longrightarrow \underset{\text{I}}{\overset{-}{B_9H_{13}}\text{—}\overset{+}{N}H\text{=}C}\begin{matrix}\diagup OC_2H_5 \\ \diagdown CH_3\end{matrix} + CH_3CN + H_2 + B(OC_2H_5)_3 \qquad (3)$$

Bis-(diethyl sulfide)-decaborane[1,14] reacts rapidly with methanol at reflux temperature to produce copious amounts of hydrogen and a moderately stable derivative, which melts at 51°. The yields obtained in this reaction were of the order of 70%.[1] Characterization of the derivative as $B_9H_{13}[S(C_2H_5)_2]$ was accomplished by elemental analyses and a B^{11} n.m.r. spectrum which was characteristic of $B_9H_{13}X$ compounds (see Fig. 2).

In contrast to the alcoholysis reactions described above, bis-(triphenylphosphine)- and bis-(triethylamine)-decaborane did not react with ethanol at the reflux temperature. The relative ease with which the dialkyl sulfide and acetonitrile derivatives undergo this reaction may be attributed to facile displacement of these ligands by nucleophilic solvent followed by degradative reactions at the attached (6- or 9-) boron atom. The over-all reaction is expressed by (4).

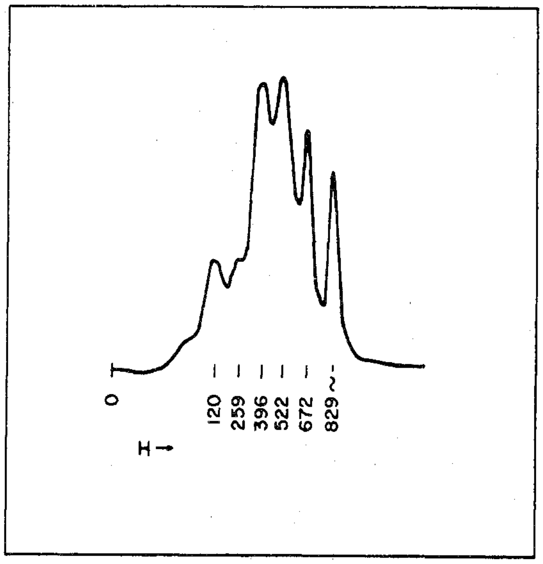


Fig. 2.—B^{11} n.m.r. spectrum of $B_9H_{13}[NH(C_2H_5)_2]$ in methylene chloride relative to methyl borate and at 12.8 Mc.

$$B_{10}H_{12}X_2 + ROH \longrightarrow B_{10}H_{12}X(ROH) + X$$
$$B_{10}H_{12}X(ROH) + 2ROH \longrightarrow B_9H_{13}X + B(OR)_3 + H_2 \qquad (4)$$

Although detailed mechanisms could be written for the transformations shown in (4), the presently available data do not warrant such a discussion.

Ligand Displacement Reactions with $B_9H_{13}SR_2$ Derivatives.—One of the characteristic reactions of $B_{10}H_{12}X_2$ molecules is their interconversion through ligand displacement reactions.[14, 15] These reactions are generalized in reaction 5, where

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(14) B. M. Graybill and M. F. Hawthorne, *J. Am. Chem. Soc.*, **83**, 2673 (1961).

(15) M. F. Hawthorne and A. R. Pitochelli, *ibid.*, **80**, 6685 (1958).

the ligand X′ is a more efficient ligand than X.

$$B_{10}H_{12}X_2 + 2X' \longrightarrow B_{10}H_{12}X'_2 + 2X \qquad (5)$$

Since $B_9H_{13}[S(C_2H_5)_2]$ resembled $B_{10}H_{12}[S(C_2H_5)_2]_2$[14] in a formal sense, ligand displacement reactions were attempted with the former material. The results obtained paralleled those obtained in the B_{10} series. The ligands chosen for study included acetonitrile, triethylamine, triphenylphosphine, diethylamine, and a series of substituted pyridines. The products derived from the substituted pyridines were employed in a spectroscopic study (*vide infra*). The triphenylphosphine, diethylamine, and substituted pyridine products were identical to those produced by reaction of the corresponding $B_{10}H_{13}X$ anions with aqueous acid and described in Table I (method A). Table I presents the yield and characterization data obtained (method B). The derivative $B_9H_{13}(CH_3CN)$ was employed for structure elucidation[8] and the derivatives reported in Table I exhibited B^{11} n.m.r. spectra characteristic of that compound.

$B_9H_{12}X$ Anions.—As seen in Table I, $B_9H_{13}(NH_2C_2H_5)$ was prepared by acidolysis of the $B_{10}H_{13}NH_2C_2H_5$ anion. Attempts to prepare this same derivative by the ligand displacement route were unsuccessful in that a compound of composition $B_9H_{13}(C_2H_5NH_2)_2$ was produced. This material exhibited an N–H stretching band at 2380 cm.$^{-1}$, which is characteristic of the $C_2H_5\overset{+}{NH_3}$ ion. In addition, acetonitrile solutions of $B_9H_{13}(C_2H_5NH_2)_2$ conducted electric current. Neutralization of $B_9H_{13}(NH_2C_2H_5)$ with one equivalent of ethylamine produced $B_9H_{13}(NH_2C_2H_5)_2$ in high yield. Other amines were strangely ineffective.

The pyridine derivative B_9H_{13}py is essentially colorless but absorbs strongly at 301 mμ (*vide infra*). Treatment of B_9H_{13}py with excess sodium hydride in tetrahydrofuran solution produced 90% of one mole of hydrogen and a blood-red solution. Exposure of this red solution to atmospheric oxygen resulted in rapid decolorization. Treatment of the red solution with anhydrous hydrogen chloride resulted in immediate decolorization. The starting material, B_9H_{13}py, was isolated in 75% yield from the neutralized solution. Thus, B_9H_{13}py may produce a highly colored anion which reacts rapidly with oxygen.

The results described above show that $B_9H_{13}X$ compounds may be converted to $B_9H_{12}X$ anions by abstraction of a proton. Wang, Simpson, and Lipscomb[8] propose a structure for these anions.

The B_9H_{12} Anion.—In contrast to the results reported above, treatment of $B_9H_{13}[S(C_2H_5)_2]$ with strong bases such as triphenylmethylene phosphorane or aqueous tetramethylammonium hydroxide resulted in the expulsion of the dialkyl sulfide ligand and a proton.[1] These reactions are illustrated in (6). The tetramethylammonium and the methyltriphenylphosphonium salts were water insoluble and gave the same B^{11} n.m.r. spectrum. The characterization of the tetramethylammonium salt has been reported recently.[16] The structure of the B_9H_{12} anion is ambiguous. Due to the relative instability of this new anion no molecular weight determinations were carried out. That the anion probably is similar in structure to the $B_9H_{13}X$ compounds is suggested by the formation of B_9H_{13}py in 55% yield from the tetramethylammonium salt and pyridinium chloride in tetrahydrofuran solution. In principle, at least, reactions of this type provide a third route to $B_9H_{13}X$ compounds.

$$B_9H_{13}[S(C_2H_5)_2] + (C_6H_5)_3PCH_2 \longrightarrow (C_6H_5)_3\overset{+}{P}CH_3 + B_9\overset{-}{H}_{12} + X$$
$$B_9H_{13}[S(C_2H_5)_2] + (CH_3)_4NOH \longrightarrow (CH_3)_4N^+ + B_9H_{12}^- + H_2O + X \quad (6)$$

$$B_9H_{12}^- + pyH^+ \rightarrow B_9H_{13}py$$

The methanolysis of the tetramethylammonium salt of the B_9H_{12} anion has been shown[16] to result in further degradation to the relatively stable triborohydride ion, $B_3H_8^-$. This degradation is of preparative importance.

Spectroscopic Evidence of Conjugation in B_9H_{13}py.—The topological method of Dickerson and Lipscomb[4,5] and the known structure of a representative $B_9H_{13}X$ compound[8] indicate that the boron atom bonding the ligand molecule (see Fig. 1) is hybridized sp^2. This same situation was postulated for the 6- and 9-boron atoms of $B_{10}H_{12}X_2$ compounds.[12] If pyridine or similar heterocyclic ligands are employed in the latter series, a remarkable absorption band appears in the visible region of the spectrum. This absorption has been interpreted[14] as a result of overlap between the π-electron cloud of the pyridine ring and a three-center, open B–B–B– orbital which has the symmetry properties of a p-orbital.

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

TABLE II

ULTRAVIOLET SPECTRA OF SUBSTITUTED PYRIDINE DERIVATIVES, $B_9H_{13}pyZ$

Substituent	*p*-CH_3O	*p*-CH_3	H	*p*-Cl	*m*-Cl	*p*-CN
Sigma constant for Z	−0.268	−0.170	0.0	0.226	0.373	1.000[a]
λ_{max}, mμ	284,236	276,222	301,269	315,269,230	318,278,240	358,282,246
Molar extinction coefficient × 10^{-3}	4.63, 6.38	6.75, 10.9	4.57, 5.51	4.87, 4.22, 12.0	4.41, 4.87, 4.84	5.46, Infl., 8.20

[a] σ of H. Jaffe, *Chem. Rev.*, **35**, 191 (1953).

Evidence for this interaction in the excited state was obtained from a satisfactory correlation of excitation energies and the Hammett sigma constant for substituents placed on the pyridine ligand.[14] It was not unexpected, therefore, to find a similar correlation of excitation energies of Hammett sigma constants for substituents, Z, placed on pyridine in the series $B_9H_{13}pyZ$. The required compounds are presented in Table I. Figure 3 presents a Hammett plot of $1/\lambda_{max}$ *vs.* the sigma constants for the substituents employed. Table II presents the spectroscopic data obtained in acetonitrile solution. Only the longest wave length band of each compound was employed in the correlation.

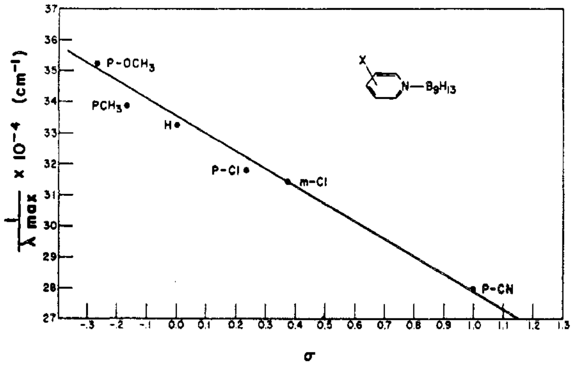

Fig. 3.—Correlation of excitation energies with σ-constants.

The correlation shown in Fig. 3 supports the previously stated arguments regarding the $B_{10}H_{12}(py)_2$ series[14] and at the same time provides additional evidence for the topological assignments of Wang, Simpson, and Lipscomb[8] in the $B_9H_{13}X$ series.

Experimental

Materials.—Decaborane was sublimed before use. All other reagents were commercially available materials of high purity. Bis-(diethyl sulfide)-decaborane, $B_{10}H_{12}[S(C_2H_5)_2]_2$, $B_9H_{13}[S(C_2H_5)_2]$, and the tetramethylammonium salt of the B_9H_{12} anion were prepared as previously described.[16] All $B_{10}H_{13}X$ anions employed in this study were prepared as previously described.[11] All solvents were dried by conventional methods.

Reaction of $(C_2H_5)_2NH_2{}^+B_{10}H_{12}NH(C_2H_5)^-$ with Aqueous Acid.—A 10.0-mmole sample of salt[11] was placed in a 200-ml. flask and dissolved in 70 ml. of distilled water. The flask was connected to a vacuum line carrying a Toepler pump and gasometer, frozen with liquid nitrogen, and evacuated. Through a side arm was added 5.0 ml. of concentrated hydrochloric acid in such a manner as to prevent the entrance of air. The reaction mixture was allowed to warm to room temperature and the evolved hydrogen (19.5 mmole corrected to STP) collected in the calibrated gasometer. The solid product (9.5 mmole, 95% yield) was separated by filtration, washed with a small quantity of water, and air-dried. Subsequent recrystallization from methylene chloride–pentane gave white crystals, m.p. 93–95°. The hydrogen analysis was low but this occasionally occurs with compounds of this type.

Anal. Calcd. for $C_4H_{24}B_9N$: B, 53.05; C, 26.15; H, 13.18; N, 7.63. Found: B, 54.03; C, 25.90; H, 10.73; N, 7.66.

The combined aqueous filtrate and washings were analyzed for boric acid by the conventional method; 10.1 mmoles of boric acid were found (theory 10.0).

General Procedure for the Acidolysis of $B_{10}H_{13}X$ Anions (Method A).—The sodium salts of $B_{10}H_{13}X$ anions[11] (where X is diethylamine, ethylamine, triphenylphosphine, or pyridine) were dissolved in a small quantity of water and treated with a slight excess of 6 *N* hydrochloric acid. Hydrogen was evolved and the $B_9H_{13}X$ products precipitated. The solid products were separated by filtration, air-dried, and recrystallized from methylene chloride–pentane. Yields were of the order of 65–95%. Analytical data and melting points appear in Table I.

Ethanolysis of Bis-(acetonitrile)-decaborane.—Bis-(acetonitrile)-decaborane[13] (40.0 g., 0.20 mole) was suspended in 300 ml. of ethanol and warmed gently under nitrogen in a flask equipped with a reflux condenser and mechanical stirrer. An exothermic reaction was initiated at about 60° and heating was discontinued. When the exothermic reaction had ceased the reaction mixture was cooled and flooded with water. The solid which separated was removed by filtration and washed thoroughly with cold water. The air-dried product was recrystallized from methylene chloride–pentane. The yield was 7.5 g. (19% theory), and the product (I) melted at 103° with decomposition.

Anal. Calcd. for $C_4H_{23}B_9NO$: B, 49.04; C, 24.17; H, 11.67; N, 7.05; Found: B, 48.28; C, 23.77; H, 11.28; N, 7.54.

Ligand Displacement Reactions with $B_9H_{13}[S(C_2H_5)_2]$ (Method B).—The general procedure employed in the preparation of $B_9H_{13}X$ derivatives (where X is triphenylphosphine, acetonitrile, triethylamine, diethylamine, and substituted pyridines) by ligand displacement is as follows: Two g. (1 × 10^{-2} mole) of pure $B_9H_{13}[S(C_2H_5)_2]$[16] was dissolved in 40 ml. of dry benzene and 1.1×10^{-2} mole of the desired ligand was added. The resulting solution was heated at the reflux temperature for 4 hr. in an inert atmosphere of dry nitrogen. The reaction mixture then was cooled and the solvent removed under reduced pressure at room temperature. The residual products were recrystallized from ethanol–water or methylene chloride–pentane. The reactions carried out with substituted pyridines were conducted at 25° for 4 hr. and the crude products were purified by chromatography on neutral alumina with methylene chloride solvent. Yields were of the order of 60–80%. Table II reports the analytical data and melting points obtained.

Preparation of $C_2H_5\overset{+}{N}H_3\overset{-}{B_9}H_{12}NH_2C_2H_5$.—A solution of 5.0 g. ($2.5 \times 10^{-2}$ mole) of $B_9H_{13}S(C_2H_5)_2$ in 40 ml. of dry benzene was heated with 4.5 g. (8.3×10^{-2} mole) of pure ethylamine at the reflux temperature. A dry nitrogen atmosphere was provided and a Dry Ice reflux condenser was employed. After 3 hr., the reaction mixture was cooled and the product separated. The crude product was recrystallized from ethanol–water to give 3.5 g. (70% theory) of pure $C_2H_5\overset{+}{N}H_3\overset{-}{B_9}H_{12}NH_2C_2H_5$, m.p. 180–181°.

Anal. Calcd. for $C_4H_{27}B_9N_2$: B, 48.55; C, 23.98; H, 13.49; N, 14.00. Found: B, 47.95; C, 22.99; H, 13.23; N, 14.41.

Preparation of the B_9H_{12}py Anion.—A 2.00-g. sample of B_9H_{13}py was dissolved in 15 ml. of pure tetrahydrofuran and treated with 1.0 g. of sodium hydride. The hydrogen evolved (9.40 mmoles; 10.6 mmoles theory) was collected with a Toepler pump and gasometer. As hydrogen evolution proceeded the solution turned blood-red. When hydrogen evolution had ceased the reaction mixture was filtered to remove excess sodium hydride. A vacuum line filtration apparatus was employed. A slight excess of dry hydrogen chloride was admitted to the red reaction mixture on the vacuum line and immediate decolorization resulted. In a separate experiment it was observed that air also caused rapid decolorization. The acidified reaction mixture was evaporated to dryness under vacuum and the residue chromatographed on neutral alumina with methylene chloride solvent. The purified material weighed 1.5 g. (75% recovery) and melted at 120–121°. The infrared spectrum of the product was identical to that of B_9H_{13}py.

Preparation of $(C_6H_5)_3\overset{+}{P}CH_3\overset{-}{B_9}H_{12}$.—An ethereal solution of triphenylmethylene phosphorane was prepared from 4.0 g. (1.1×10^{-2} mole) of triphenylmethyl phosphonium bromide and 13.2 ml. of 0.91 *M* butyllithium in 100 ml. of diethyl ether. The yellow phosphorane solution was added under nitrogen to a solution of 2.0 g. (1×10^{-2} mole) of $B_9H_{13}[S(C_2H_5)_2]$ dissolved in 15 ml. of diethyl ether. As the addition proceeded the yellow color disappeared and two phases separated. The lower phase crystallized and was removed by filtration. Purification was effected by recrystallization from methanol at low temperature. The purified material decomposed at 118–120°. The yield was 3.0 g. or 75% of theory.

Anal. Calcd. for $C_{19}H_{33}B_9P$: B, 26.00; C, 57.70; H, 8.02; P, 7.26. Found: B, 25.90; C, 56.91; H, 7.77; P, 7.00.

The Conversion of the B_9H_{12} Anion to B_9H_{13}py.—To 1.8 g. (1×10^{-2} mole) of the tetramethylammonium B_9H_{12} salt[16] suspended in 25 ml. of dry tetrahydrofuran was added 1.15 g. of pyridinium chloride. A nitrogen atmosphere was employed and the reaction mixture was stirred overnight, filtered, and the solvent removed *in vacuo*. The residue was chromatographed on alumina with methylene chloride solvent. Pure B_9H_{13}py, 1.0 g. (55% theory), m.p. 120–121°, was obtained.

Ultraviolet Absorption Spectra.—The spectra reported in Table II were obtained with a Beckman Model DK-1 spectrophotometer. Samples were accurately weighed and diluted with dry acetonitrile to produce approximately 10^{-4} *M* solutions.

Nuclear Magnetic Resonance Spectra.—The B^{11} n.m.r. spectra were obtained with a varian high resolution magnetic resonance spectrometer (10^4 gauss field) with a 12.8 Mc. B^{11} probe.