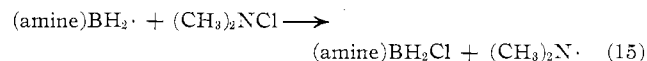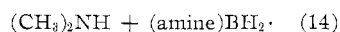approximately equal amount of other products shows that other reactions are occurring.

Since a possible side reaction could be attributed to the presence of "BH_3," the reaction between $(CH_3)_2$-NCl and B_2H_6 was investigated. The nmr spectra of the reaction mixtures showed that the reaction is complicated and that products similar to those in the borohydride reaction are produced. The fact that the order of addition of the reagents in the dimethylchloramine–borohydride reaction made little difference in the products produced shows that if "BH_3" is responsible for the side reactions, it is produced from eq 12 and not by the reduction of amine–chloroborane

$$(CH_3)_2HNBH_2Cl + BH_4^- \longrightarrow$$
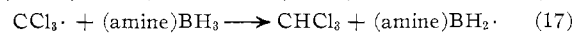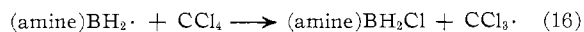$$(CH_3)_2HNBH_3 + Cl^- + \text{"}BH_3\text{"} \quad (13)$$
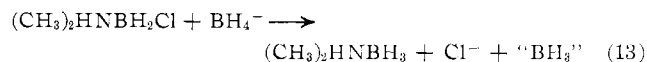
There is some evidence which supports a free-radical chain mechanism for the chlorination step of the amine–boranes, eq 14 and 15. The reaction with $(CH_3)_3$-

$$(CH_3)_2N\cdot + (amine)BH_3 \longrightarrow$$
$$(CH_3)_2NH + (amine)BH_2\cdot \quad (14)$$

$$(amine)BH_2\cdot + (CH_3)_2NCl \longrightarrow$$
$$(amine)BH_2Cl + (CH_3)_2N\cdot \quad (15)$$

NBH_3 is accelerated by a free-radical initiator, di-*t*-butyl peroxyoxalate, while the reaction with $(CH_3)_2$-$HNBH_3$ shows an induction period. Another obser-

vation which supports a free-radical chain mechanism is the production of $CHCl_3$. The production of chloroform can be explained by a branching in the free-radical chain, e.g.

$$(amine)BH_2\cdot + CCl_4 \longrightarrow (amine)BH_2Cl + CCl_3\cdot \quad (16)$$
$$CCl_3\cdot + (amine)BH_3 \longrightarrow CHCl_3 + (amine)BH_2\cdot \quad (17)$$

Based on bond-dissociation energies,[16] both reactions are energetically favorable. It is difficult to conceive of any other mechanism which accounts for the concurrent production of $CHCl_3$.

As yet an unresolved difficulty in this mechanism is the nature of the initiation process. There is no evidence for low-energy homolysis of a B–H bond and $(CH_3)_2NCl$ is usually assumed to proceed with heterolytic cleavage. The fact that the reaction with $(CH_3)_2NCl$ proceeds more slowly when both oxygen and moisture are excluded shows that the initiation step is rather complicated. A confirmation of the free-radical nature of these reactions and the initiation step must await further study.

(16) (a) T. L. Cottrell, "The Strength of Chemical Bonds," 2nd ed, Butterworth and Co. Ltd.. London, 1958, Table 11.5.1; (b) E. L. Muetterties, "The Chemistry of Boron and Its Compounds," John Wiley and Sons, Inc., New York, N. Y., 1967, p 13.

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Pentaborane(9) Derivatives. II.[1] Synthesis of Di- and Trisubstituted Methyl-, Methylchloro-, and Methylbromopentaboranes. Detailed Nuclear Magnetic Resonance Studies

By PHILIP M. TUCKER, THOMAS ONAK, and JOHN B. LEACH

Several new polysubstituted pentaborane derivatives are reported. These include 2-Br-3-$CH_3B_5H_7$, 1-Cl-2-$CH_3B_5H_7$, 2-Cl-1-$CH_3B_5H_7$, 2-Cl-3-$CH_3B_5H_7$, 2-Cl-4-$CH_3B_5H_7$, 1,2,3-$(CH_3)_3B_5H_6$, 2,3,4-$(CH_3)_3B_5H_6$, 2-Cl-1,3-$(CH_3)_2B_5H_6$, 2-Cl-1,4-$(CH_3)_2$-B_5H_6, 2-Cl-3,4-$(CH_3)_2B_5H_6$, 3-Cl-2,4-$(CH_3)_2B_5H_6$, and 1-Cl-2,3-$(CH_3)_2B_5H_6$. The ^1H and ^{11}B nmr spectra of these and of some previously reported pentaborane derivatives are totally assigned. Substituent effects on the chemical shifts of contiguous, neighboring, and *trans* borons have been determined and are found to be additive for polysubstituted pentaboranes. An additivity relationship has also been found for the chemical shifts of bridge hydrogens in differing environments. Long-range coupling (*ca.* 6–7 Hz) between the apex boron and the attached methyl hydrogen of 1-methyl derivatives appears to be a general occurrence. A Friedel–Crafts alkylation of 2-methylpentaborane produces chlorinated derivatives of pentaborane in addition to the expected 1,2-dimethylpentaborane. Base-catalyzed rearrangement studies on polysubstituted pentaboranes lend experimental support to a "minimum atomic motion" mechanism.

Introduction

In an earlier report[1] the preparation of some pentaborane(9) derivatives was described and ^1H and ^{11}B nmr spectra were recorded in as much detail as was possible at that time. More recently several new pentaborane derivatives have been described; among

these are μ-trimethylsilyl-pentaborane(9),[2] group IV derivatives of pentaborane(9),[3] chloro derivatives of pentaborane(9),[4] iodo- and fluoropentaboranes,[5] phosphinopentaboranes,[6] and metal carbonyl derivatives of

(1) Part I: T. Onak, G. B. Dunks, I. W. Searcy, and J. Spielman, *Inorg. Chem.*, **6**, 1465 (1967).

(2) D. F. Gaines and T. V. Iorns, *J. Am. Chem. Soc.*, **89**, 4249 (1967).

(3) D. F. Gaines and T. V. Iorns, *ibid.*, **90**, 6617 (1968).

(4) D. F. Gaines and J. A. Martens, *Inorg. Chem.*, **7**, 704 (1968).

(5) A. B. Burg, *J. Am. Chem. Soc.*, **90**, 1407 (1968).

(6) A. B. Burg and H. Heinen, *Inorg. Chem.*, **7**, 1021 (1968).

TABLE I

INFRARED SPECTRA OF POLYSUBSTITUTED DERIVATIVES OF PENTABORANE(9)

Compound	Main infrared bands, cm^{-1}
2-Cl-1-CH$_3$B$_5$H$_7$ (I)[a]	3400 vw, br, 3000 m, sh, 2950 s, sh, 2930 s, 2850 s, 2615 vs, 2090 vw, 1935 w, 1825 m, 1755 m, 1605 w, 1530 w, sh, 1480 m, sh, 1448 s, 1384 vs, 1350 vs, 1328 s, sh, 1270 s, br, 1225 s, br, 1136 w, br, 1093 m, 1065 s, sh, 1040 vs, br, 988 s, 936 ms, 885 vs, 836 m, 792 m, 664 s
1-Cl-2-CH$_3$B$_5$H$_7$ (II)[b]	2950 m, 2900 mw, 2820 w, 2600 vs, 2360 w, 2320 vw, sh, 1800 m, br, 1650 vw, 1620 vw, 1460 ms, sh, 1418 vs, 1380 vs, 1360 sh, br, 1316 ms, 1210 sh, br, 1180 vs, 1150 w, 1120 m, sh, 1104 s, 1068 s, 1000 m, 917 s, sh, 905 s, 985 vs, 840 m, 783 m, 736 m, 678 s, 650 ms
2-Cl-3-CH$_3$B$_5$H$_7$ (III)[a]	2970 m, 2920 w, 2830 vw, 2610 vs, 1900–1650 multiplet, w, br, 1580 w, br, 1550 w, 1500 w, sh, 1480 m, sh, 1460 ms, sh, 1440 s, sh, 1425 s, sh, 1400 vs, sh, 1380 vs, 1340 s, sh, 1260 w, br, 1155 s, 1100 mw, 1060 s, sh, 1045 s, br, 1000 m, br, 910 s, 864 m, 827 m, 714 w, 633 s
2-Cl-4-CH$_3$B$_5$H$_7$ (IV)[a]	2975 m, 2930 w, 2850 vw, 2610 vs, 1900–1650 multiplet, w, br, 1580 w, br, 1550 w, 1530 w, 1500 w, sh, 1480 m, 1460 ms, sh, 1440 s, sh, 1425 s, sh, 1405 vs, 1470 w, br, 1340 vs, sh, 1300 m, sh, 1200 w, 1150 w, 1105 ms, 1075 m, sh, 1049 vs, 989 ms, 875 s, 775 m, 675 w, vbr, 630 m, vbr
2-Br-3-CH$_3$B$_5$H$_7$ (V)[a]	2950 m, 2925 w, 2830 vw, 2600 vs, 1900–1700 w, br, 1580 m, br, 1420 sh, 1380 vs, br, 1330 m, sh, 1240 w, vbr, 1145 ms, 1095 w, 1025 s, 988 m, br, 903 s, 880 sh, br, 838 m, br, 770 w, br, 706 w, br, 633 s, br
2-Cl-1,3-(CH$_3$)$_2$B$_5$H$_6$ (VI)[a]	2960 s, 2925 s, 2830 m, 2600 vs, 1950–1550 mw, br, multiplet, 1460 m, sh, 1430 s, sh, 1380, 1355, 1333 vs, br overlapping, 1225 ms, br, 1120 ms, br, 1044 vs, 985 ms, br, 901 vs, 825 ms, br, 715 ms, br, 685 s, br, 655 s, br
2-Cl-1,4-(CH$_3$)$_2$B$_5$H$_6$ (VII)[a]	2960 s, 2925 s, 2840 m, 2600 vs, 1900–1600 multiplet, w, br, 1590 mw, br, 1460 w, sh, 1430 s, sh, 1370 vs, br, 1330 s, 1230 m, br, 1110 ms, br, 1030 s, br, 970 w, vbr, 858 s, br, 740 w, vbr, 670 mw, vbr
2-Cl-3,4-(CH$_3$)$_2$B$_5$H$_6$ (VIII)[a]	2980 m, 2930 mw, 2850 w, 1485 w, sh, 1460 m, sh, 1430 s, sh, 1370 vs, br, 1330 s, sh, 1260 m, br, 1165 w, vbr, 1105 ms, 1050 s, 1012 ms, 900 s, 860 m, br, 775 m, 680 w, br
3-Cl-2,4-(CH$_3$)$_2$B$_5$H$_6$ (IX)[a]	2980 m, 2930 mw, 2840 w, 1580 w, vbr, 1460 m, sh, 1430 s, sh, 1400 vs, br, 1348 vs, br, 1280 m, br, 1162 w, 1125 ms, br, 1053 s, 1016 ms, 972 w, 916 s, 857 m, br, 772 w, br, 746 m, br, 678 w, br
1-Br-2-CH$_3$B$_5$H$_7$[b]	2970 m, 2930 m, 2830 w, 2610 vs, 1820 ms, br, 1650 w, 1605 w, 1520 w, sh, 1480 m, sh, 1460 s, sh, 1425 vs, 1390 vs, 1350 s, sh,1320 s, 1185 s, 1168 vs, 1100 vs, 1061 s, 1032 w, 1003 ms, 919 s, 903 s, 885 vs, 845 m, br, 786 m, 740 m, sh, 730 ms, 683 s, br, 655 s, br, 628 s, br
2,3,4-(CH$_3$)$_3$B$_5$H$_6$ (XI)[a]	3460 vw, 3260 vw, br, 3030 w, 2975 s, 2940 ms, 2855 mw, 2595 vs, 2425 vw, 2075 vw, br, 1900 w, sh, 1850 w, br, 1815 w, sh, 1750 w, sh, 1725 w, br, 1680 w, sh, 1580 w, br, sh, 1540 w, sh, 1490 m, sh, 1412 vs, br, 1380 w, br, 1360 vs, sh, 1325 s, sh, 1275 w, br, 1177 w, 1111 s, 1028 w, 979 mw, 913 ms, sh, 896 s, 784 w, 737 w, 656 mw, sh

[a] Gas phase. [b] Thin film (see Experimental Section).

pentaborane(9).[7] Many of the resonances in ^{1}H nmr spectra reported in these papers have been only partially assigned due to overlapping peaks or because certain compounds have an equal number of chemically different bridge, terminal, or substituent protons. In an earlier communication[8] a procedure was outlined that would enable these spectra to be totally assigned. Here, we report details of the preparation of some new polysubstituted pentaborane derivatives and give total assignments for the ^{1}H and [11]B nmr spectra of these compounds using this technique. In the course of these studies, an attempt is made empirically to correlate substituent effects among these new pentaborane derivatives as well as some of those previously reported.

Experimental Section

Materials.—Methyl chloride, hydrogen chloride, boron trichloride, and chlorine were obtained from the Matheson Co., Inc., pentaborane was obtained from Olin Mathieson Chemical Co., Inc., aluminum chloride was from J. T. Baker Chemical Co., and hexamethylenetetramine was from Matheson Coleman and Bell. Boron trichloride was vacuum fractionated to remove traces of chlorine and hydrogen chloride; chlorine was vacuum fractionated to remove hydrogen chloride. Hexamethylenetetramine was sublimed prior to each experiment into an apparatus designed for the rearrangement reactions (*vide infra*). This apparatus was connected *via* a constricted tube (later sealed) to a reservoir from which the hexamethylenetetramine was sublimed.

1-Methyl-, 2-methyl-, 1,2-dimethyl-, 2,3-dimethyl-, 1-chloro-, 2-chloro-, 1-bromo-, 2-bromo-, and 1-bromo-2-methylpentaboranes were prepared as previously described (see footnotes in reference

1). All chemicals were handled in conventional high-vacuum equipment, and all samples were purified prior to spectral analysis on a high-vacuum, low-temperature fractionating column.

Infrared Spectra.—These were all recorded on a Beckman IR-5 instrument and, where possible, in the gas phase; some compounds were of too low volatility for this and were handled in a thin-film cell similar to that described by Burg and Kratzer[9] except that the cell employed a Teflon stopcock and the plates were mounted in Kel-F wax.[10] These procedures were necessitated by the air and moisture sensitivity of the compounds. Spectra are presented in Table I.

Nuclear Magnetic Resonance.—The proton spectra (Table II) were recorded using three spectrometers: Varian A-60, Varian HA-100,[11] and Varian HR-220.[12] Proton spectra are referenced to tetramethylsilane (τ 10.00) as internal standard.

The boron-11 spectra were recorded at 32.1 MHz using the HA-100 instrument. Decoupled proton spectra were run while irradiating at 32.1 MHz employing an NMR Specialties Model HD-60 spin decoupler modified for use with the HA-100 and Hewlett-Packard Model 200CD wide-range audio oscillators, in a manner previously described.[8] Conversely, decoupled [11]B spectra were recorded at 32.1 MHz with the heteronuclear decoupler operating at 100 MHz.

Boron-11 spectra were referenced to boron trichloride (δ −46.8)[13] as external secondary standard using the conventional side-band techniques. Chemical shift values thus determined were then converted to values relative to boron trifluoride di-

(7) D. F. Gaines and T. V. Iorns, *Inorg. Chem.*, **7**, 1041 (1968).
(8) P. M. Tucker and T. Onak, *J. Am. Chem. Soc.*, **91**, 6869 (1969).
(9) A. B. Burg and R. Kratzer, *Inorg. Chem.*, **1**, 728 (1962).
(10) Halocarbon Products Corp., Hackensack, N. J.
(11) The instrument at California State College at Los Angeles was obtained through Grant GP-8347 from the National Science Foundation.
(12) The HR-220 nmr spectrometer was available at California Institute of Technology through Grant GP-8540 from the National Science Foundation.
(13) Determined relative to BF$_3$·O(C$_2$H$_5$)$_2$ (δ 0.0) in separate experiments. This procedure was necessary due to the proximity of the compound [11]B resonances to δ 0.0.

Table II

Pentaborane Derivatives: NMR Chemical Shifts and Coupling Constants[a]

Compound	Proton environment	$\tau_{exptl}\ (\tau_{calcd}),$[b] ppm	J, cps	Boron environment	$\delta_{exptl}\ (\delta_{calcd}),$[c] ppm	J, cps
Pentaborane	H–B(1)	9.47	175	B(1)–H	53.1 (53.1)	178
	H–B(2, 3, 4, 5)	7.51	166	B(2, 3, 4, 5)–H	13.4 (13.4)	162
	H$_\mu$(2, 3, 4, 5)	12.28 (12.3)	33			
1-Methylpentaborane	H–B(2, 3, 4, 5)	7.58	165	B(1)–CH$_3$	45.3 (44.8)	
	H$_\mu$(2, 3, 4, 5)	12.06 (12.1)	36	B(2, 3, 4, 5)–H	13.3 (12.5)	167
	H–C	9.96				
2-Methylpentaborane	H–B(1)	9.54	170	B(1)–H	51.5 (51.6)	176
	H–B(3, 5)	7.73[d]	164	B(2)–CH$_3$	−1.6 (−1.0)	
	H–B(4)	7.73[d]	164	B(3, 5)–H	13.5 (13.6)	169
	H$_\mu$(2, 5)	11.66 (11.7)		B(4)–H	19.1 (18.6)	165
	H$_\mu$(3, 4)	12.43 (12.4)				
	H–C	9.66				
1,2-Dimethylpentaborane	H–B(3, 4, 5)	7.66[d]	136	B(1)–CH$_3$	43.6 (43.3)	
	H$_\mu$(2, 5)	11.45 (11.5)		B(2)–CH$_3$	−1.1 (−1.9)	
	H$_\mu$(3, 4)	12.05 (12.2)		B(3, 5)–H	13.2 (12.7)	158
	H–C(1)	9.95		B(4)–H	17.6 (17.7)	160
	H–C(2)	9.60				
2,3-Dimethylpentaborane	H–B(1)	9.55	168	B(1)–H	50.0 (50.1)	168
	H–B(4, 5)	7.84	160	B(2, 3)–CH$_3$	−0.4 (−0.8)	
	H$_\mu$(2)	11.03 (11.1)		B(4, 5)–H	19.5 (18.8)	160
	H$_\mu$(3, 5)	11.70 (11.7)				
	H$_\mu$(4)	12.50 (12.5)				
	H–C	9.69				
1-Chloropentaborane	H–B(2, 3, 4, 5)	7.22	168	B(1)–Cl	28.7 (29.5)	
	H$_\mu$(2, 3, 4, 5)	11.65 (11.6)	30	B(2, 3 ,4, 5)–H	11.9 (12.3)	164
2-Chloropentaborane	H–B(1)	9.27	175	B(1)–H	52.2 (51.9)	176
	H–B(3, 5)	7.41	167	B(2)–Cl	1.1 (1.1)	
	H–B(4)	7.68	160	B(3, 5)–H	13.7 (13.4)	171
	H$_\mu$(2, 5)	10.50 (10.5)		B(4)–H	23.4 (23.1)	169
	H$_\mu$(3, 4)	12.08 (12.1)				
1-Bromopentaborane	H–B(2, 3, 4, 5)	7.17	166	B(1)–Br	37.3 (37.0)	165
	H$_\mu$(2, 3, 4,5)	11.55 (11.6)		B(2, 3, 4, 5)–H	12.4 (12.3)	
2-Bromopentaborane	H–B(1)	9.29	179	B(1)–H	50.8 (51.0)	173
	H–B(3, 4, 5)	7.42[d]	167	B(2)–Br	8.7 (9.8)	
	H$_\mu$(2, 5)	10.77 (10.7)		B(3,5)–H	12.5 (12.9)	181
	H$_\mu$(3, 4)	12.08 (12.0)		B(4)–H	19.6 (19.4)	166
2-Methyl-1-bromopentaborane	H–B(3, 5)	⎰ 7.50[d]	159	B(1)–Br	35.1 (35.5)	
	H–B(4)	⎱		B(2)–CH$_3$	−1.7 (−2.1)	
	H$_\mu$(2, 5)	11.19 (11.0)		B(3, 5)–H	12.1 (12.5)	158
	H$_\mu$(3, 4)	11.68 (11.7)		B(4)–H	16.9 (17.5)	152
	H–C	9.68				
3-Methyl-2-bromopentaborane	H–B(1)	9.23	174	B(1)–H	49.6 (49.5)	175
	H–B(4, 5)	7.44[d]	162	B(2)–Br	10.9 (10.0)	
	H$_\mu$(2)	9.97 (10.1)		B(3)–CH$_3$	−2.2 (−1.5)	
	H$_\mu$(3)	11.25 (11.4)		B(4)–H	19.3[e] (19.6)	170
	H$_\mu$(4)	12.02 (12.1)		B(5)–H	19.3[e] (18.1)	170
	H$_\mu$(5)	10.73 (10.8)				
	H–C	9.53				
1-Chloro-2-methylpentaborane	H–B(3, 5)	⎰ 7.36[d]	161	B(1)–Cl	27.6 (28.0)	
	H–B(4)	⎱		B(2)–CH$_3$	−1.5 (−2.1)	
	H$_\mu$(2, 5)	11.0$'$ (11.0)		B(3, 5)–H	12.4 (12.5)	156
	H$_\mu$(3, 4)	11.5$'$ (11.7)		B(4)–H	17.4 (17.5)	151
	H–C	9.51				
2-Chloro-1-methylpentaborane	H–B(3, 5)	7.55	166	B(1)–CH$_3$	43.7 (43.6)	
	H–B(4)	7.63[g]	166	B(2)–Cl	0.8 (0.2)	
	H$_\mu$(2, 5)	10.32 (10.3)		B(3, 5)–H	12.9 (12.3)	162
	H$_\mu$(3, 4)	11.81 (11.9)		B(4)–H	22.0 (22.2)	173
	H–C	9.93				
2-Chloro-3-methylpentaborane	H–B(1)	9.28	174	B(1)–H	50.6 (50.4)	173
	H–B(4, 5)	7.75[d]	160	B(2)–Cl	2.2 (1.3)	
	H$_\mu$(2)	9.87 (9.9)		B(3)–CH$_3$	−1.0 (−1.0)	
	H$_\mu$(3)	11.37 (11.5)		B(4)–H	24.0 (23.2)	148
	H$_\mu$(4)	12.14 (12.2)		B(5)–H	19.4 (18.6)	152
	H$_\mu$(5)	10.56 (10.6)				
	H–C	9.60				

TABLE II (*Continued*)

Compound	Proton environment	τ_{exptl} (τ_{calcd}),[b] ppm	J, cps	Boron environment	δ_{exptl} (δ_{calcd}),[c] ppm	J, cps
2-Chloro-4-methylpentaborane	H–B(1)	9.23	174	B(1)–H	50.9 (50.4)	171
	H–B(3, 5)	7.56	165	B(2)–Cl	6.6 (6.3)	
	H$_\mu$(2, 5)	10.49 (10.6)		B(3, 5)–H	14.1 (13.6)	191
	H$_\mu$(3, 4)	11.28 (11.5)		B(4)–CH$_3$	9.6 (8.7)	
	H–C	9.67				
1,2,3-Trimethylpentaborane	H–B(4, 5)	7.81	157	B(1)–CH$_3$	42.5 (41.8)	
	H$_\mu$(2)	11.2 (10.9)		B(2, 3)–CH$_3$	−0.3 (1.7)	
	H$_\mu$(3, 5)	11.6 (11.6)		B(4, 5)–H	18.2 (17.9)	156
	H$_\mu$(4)	12.0 (12.3)				
	H–C(1)	10.06				
	H–C(2, 3)	9.72				
2,3,4-Trimethylpentaborane	H–B(1)	9.58	166	B(1)–H	48.3 (48.6)	166
	H–B(5)	7.87	156	B(2, 4)–CH$_3$	5.2 (4.4)	
	H$_\mu$(2, 3)	11.2 (11.2)		B(3)–CH$_3$	0.3 (−0.6)	
	H$_\mu$(4, 5)	11.54 (11.9)		B(5)–H	19.3 (19.0)	156
	H–C(2, 4)	9.70[i]				
	H–C(3)	9.70[i]				
1-Chloro-2,3-dimethylpentaborane	H–B(4, 5)	7.47	158	B(1)–Cl	27.4 (26.8)	
	H$_\mu$(2)	10.6 (10.4)		B(2, 3)–CH$_3$	−0.8 (−1.8)	
	H$_\mu$(3, 5)	11.1 (11.1)		B(4, 5)–H	17.6 (17.7)	160
	H$_\mu$(4)	11.7 (11.7)				
	H–C(2, 3)	7.47				
2-Chloro-1,3-dimethylpentaborane	H–B(4, 5)	7.60[d]	165	B(1)–CH$_3$	42.7 (42.1)	
	H$_\mu$(2)	(10.0)[h] (9.7)		B(2)–Cl	1.8 (0.4)	
	H$_\mu$(3)	11.3 (11.3)		B(3)–CH$_3$	−0.8 (−1.9)	
	H$_\mu$(4)	12.0 (12.0)		B(4)–H	22.9 (22.4)	138
	H$_\mu$(5)	10.5 (10.4)		B(5)–H	18.3 (17.7)	144
	H–C(1)	9.94				
	H–C(3)	9.57				
2-Chloro-1,4-dimethylpentaborane	H–B(3, 5)	7.63	163	B(1)–CH$_3$	41.7 (42.1)	
	H$_\mu$(2, 5)	10.4 (10.4)		B(2)–Cl	4.3 (5.4)	
	H$_\mu$(3, 4)	11.3 (11.3)		B(3, 5)–H	12.2 (12.7)	172
	H–C(1)	10.0		B(4)–CH$_3$	7.4 (7.8)	
	H–C(4)	9.73				
2-Chloro-3,4-dimethylpentaborane	H–B(1)	9.23	170	B(1)–H	48.4 (48.9)	163
	H–B(5)	7.67	163	B(2)–Cl	6.3 (6.3)	
	H$_\mu$(3)	(10.0) (10.0)		B(3)–CH$_3$	−1.2 (−0.8)	
	H$_\mu$(3)	10.7 (10.9)		B(4)–CH$_3$	9.0 (8.9)	
	H$_\mu$(4)	11.7 (11.6)		B(5)–H	19.1 (18.8)	160
	H$_\mu$(5)	10.7 (10.7)				
	H–C(3)[i]	9.67				
	H–C(4)[i]					
3-Chloro-2,4-dimethylpentaborane	H–B(1)	9.27	170	B(1)–H	48.9 (48.9)	168
	H–B(5)	7.76	152	B(2, 4)–CH$_3$	4.2 (4.5)	
	H$_\mu$(2, 3)	(10.0) (10.0)		B(3)–Cl	4.2 (1.5)	
	H$_\mu$(4, 5)	11.7 (11.6)		B(5)–H	23.9 (23.5)	161
	H–C(2, 4)	9.64				

[a] All samples neat, except 1-chloro- and 1-chloro-2,3-dimethylpentaborane, which were recorded in BCl$_3$ solution. Hydrogen-1 resonances relative to TMS internal standard; τ 10.0 used rather than δ to avoid negative values. δ values for ^{11}B resonances relative to BF$_3 \cdot$O(C$_2$H$_5$)$_2$ = 0.0. Only ^{1}H–^{11}B coupling considered. B(1) is apex; B(2, 3, 4, 5) are basal boron atoms. H–B(1) indicates proton terminally attached to boron atom (1), etc.; H$_\mu$(2) indicates bridge proton between boron atoms (2) and (3), etc. Proton shifts are an average of values obtained at 60, 100, and 220 MHz in most cases. Bridge proton–boron couplings obtained from 220-MHz spectra, where recorded. In some cases decoupled spectra exhibited slight alterations in chemical shift of ±0.2 ppm, or less. Where this occurred, averages were again taken. [b] The τ_μ values in parentheses are calculated from eq 3. [c] The ^{11}B values in parentheses are calculated from eq 1 or 2. [d] No resolution apparent between the nonequivalent protons. Broad peaks. [e] Overlap of B(4) and B(5) resonances. Decoupling boron ratio 1:1:2:1 aided assignment. [f] Hydrogen-1 resonances estimated from decoupling experiments at 100 MHz only; very broad ambiguous 220-MHz spectra. [g] H–B(4) resonance occurs as a shoulder. [h] H$_\mu$(2) not resolved. Occurs as shoulder on H–C(1) resonance in decoupled 100-MHz spectrum. [i] No resolution between methyl groups at 100 MHz.

ethyl etherate (Table II). All spectra were run on neat liquids sealed in 5-mm medium-wall nmr tubes, except where noted otherwise.

The reinvestigation of some of the compounds previously reported[1] was necessitated by some anomalies that became apparent when spectra of new derivatives were measured. The explanation lies in the fact that many of the derivatives reported before[1] were investigated in aromatic solvents, such as benzene or 2,6-lutidine. These compounds have been shown to have a substantial effect upon the internal shift differences in pentaborane derivatives. To determine the nature of this effect several measurements were made at 220 MHz. To determine whether the primary effect was a shift of pentaborane resonances by the benzene solvent, or *vice versa*, three samples were used (C$_6$H$_6$–TMS, B$_5$H$_9$–TMS, and C$_6$H$_6$–B$_5$H$_9$–TMS)[14] together with neat B$_5$H$_9$. Using neat pentaborane and pentaborane–tetra-

(14) A complete dilution study was beyond the scope of this work.

methylsilane samples it was possible to establish that no internal shift of the B_5H_9 resonances was caused by the TMS standard. Thus, the ratio

[difference ($\Delta\tau$) between bridge and base $^1H-^{11}B$ resonance]
[difference ($\Delta\tau$) between bridge and apex $^1H-^{11}B$ resonance]

remains constant, regardless of the presence of the TMS. Similarly, the chemical shift of benzene in TMS is unmodified by the presence of pentaborane. However, a significant internal shift in the various pentaborane resonances is caused by the benzene. By comparing two tubes containing, respectively, B_5H_9–TMS and C_6H_6–B_5H_9–TMS, it was found that the presence of benzene caused: (a) a downfield shift in the apex $H-^{11}B$ resonance, (b) an upfield shift in the base terminal $H-^{11}B$ resonance, and (c) an upfield shift in the bridge proton resonance. Consequently, most of the compounds previously investigated were reexamined using neat samples and were then calibrated with TMS (internal standard), in an effort to obtain consistent data.

Mass spectra were run on a CEC 20-620 instrument. Many spectra were also run on a Hitachi RMU-6D instrument, this being essential in the case of the materials of higher molecular weight. The quoted cutoff points are the highest peaks in the parent ion group envelopes.

Preparations were of three types—methylation, halogenation, and rearrangement—and were in essence simple extensions of known reaction sequences.[1,4,15] Methylations were carried out in sealed ampoules incorporating attached nmr tubes for monitoring the course of the reactions. Chlorinations, carried out in boron trichloride solutions in a manner similar to that described by Gaines and Martens,[4] employed a reaction vessel connected to a vacuum line *via* stopcocks lubricated with Kel-F grease. Also employed was a detachable external manometer (for easy cleaning) which was waxed into the reaction vessel, thus enabling the pressure to be constantly monitored during the warming up–reaction phase. Judicious use of cooling baths during this phase and occasional removal of HCl (by brief pumping while holding the reagents at $-80°$) enabled trouble-free chlorinations to be accomplished. For the base-catalysis rearrangements hexamethylenetetramine was found to be most convenient; although, in common with Burg,[5] we have found haloboranes, *e.g.*, bromo- and chloropentaboranes, to react *explosively* with this base at temperatures in excess of $90-100°$. For each rearrangement the base was sublimed into the ampoule, as described above, from a reservoir which was then sealed off. The substrate was then condensed in and the ampoule was sealed off. An attached nmr tube allowed for monitoring the rearrangement process. As usual, a break-seal was incorporated for subsequent removal and purification of products.

2-Chloro-1-methylpentaborane(9) (I).—A reaction ampoule (50 ml) fitted with an nmr tube and break-seal, *vide supra*, was flamed out on the vacuum line and then charged with aluminum chloride (anhydrous; 0.5 g), 2-chloropentaborane(9) (3.1 mmol), methyl chloride (3.4 mmol), and boron trichloride (3 ml). After sealing off and warming to room temperature the vessel was placed in an oven ($50°$) for 30 hr. Afterward, the products were introduced to the vacuum line. Fractionation of the products on the low-temperature, high-vacuum distillation column yielded high-volatility by-products ($HBCl_2$, excess CH_3Cl, etc.) at $-100°$. The product, I, distilled from the column at $-50°$; yield 2.3 mmol (73%). The pure compound, produced after a second fractionation, had a melting point of -48 to $-49°$ and exhibited the expected cutoff in the mass spectrum at m/e 114.

1-Chloro-2-methylpentaborane(9) (II).—The dried reaction flask was charged with aluminum chloride (anhydrous; 1.5 g) and attached to the vacuum line. Boron trichloride (10 ml) and 2-methylpentaborane(9) (27 mmol) were condensed in, and then this mixture was warmed to $-80°$ and stirred to ensure dissolution of the 2-methylpentaborane(9) in the boron trichloride. The mixture was then frozen, chlorine (13 mmol) was condensed in, using an external manometer to avoid contaminating the vacuum-line manometers, and the mixture was warmed

to $-80°$ and stirred for 10 min. The mixture was then allowed to warm slowly by lowering the $-80°$ bath cautiously. Pressure rose rapidly and at $-30°$ the yellow color became discharged. Cooling intermittently to $-80°$ and pumping very briefly removed the excess HCl. After stirring at $-30°$ for several minutes, the solution was maintained at $0°$ for 0.5 hr, stirring continually. After this period of time all volatile materials were removed for fractionation. Fractionation was accomplished on the distillation column. Equilibration of products to the column from a $-80°$ trap allowed the high-volatility materials to be removed more efficiently and at a column temperature of $-110°$, HCl, unreacted Cl_2, and traces of other impurities were rapidly removed. BCl_3 was recovered at -105 through $-97°$. After removal of the bulk of the contaminants the products were allowed to distil to the column by removing the $-80°$ bath. Excess 2-$CH_3B_5H_8$ was removed at -75 through $-61°$ (15.5 mmol was recovered). Traces of oily impurities were discarded and pure 1-Cl-2-$CH_3B_5H_7$ was recovered at -30 through $-25°$; yield 10.5 mmol (91.5% based on consumed 2-$CH_3B_5H_8$). This compound was considerably less volatile than I but exhibited an almost identical mass spectrum. The expected cutoff was noted at m/e 114.

2-Chloro-3-methylpentaborane(9) (III).—This compound was conveniently prepared by the base-catalyzed rearrangement of I or II. Most conveniently hexamethylenetetramine was used, but diethyl ether also accomplished these isomerizations. However, at ambient temperature the ether-catalyzed rearrangements were very slow; for I only about a 10% conversion was attained within a time period of 2–3 hr. Hydrogen-1 nmr monitoring showed that on hexamethylenetetramine both compounds isomerize over a period of 2–3 hr, with the rate observed for I being a little slower than for II. Both compounds were essentially totally rearranged, but a side reaction led to yellow oils that somewhat inhibited the complete recovery of products. Only moderate warming ($60-70°$) of these oils is recommended to preclude the possibility of explosion (*vide supra*). In a representative reaction, I (0.9 mmol) was sealed off in contact with hexamethylenetetramine (0.15 g) sublimed as described above in the section on materials. Subsequent fractionation of volatile materials yielded small quantities of high volatility impurities including some hydrogen, 1-$CH_3B_5H_8$, and 2-$CH_3B_5H_8$ indicating that some reduction of the B–Cl bond also occurred. At higher column temperatures the lower volatility products were recovered; small traces of oily fractions were discarded and pure III was distilled from the fractionating column at $-40°$. Yield of pure material was 50%.

Similarly, II rearranged on the base, yielding, after brief effervescence, a clear yellow solution. Distillation of volatile products yielded, as before, some 2-$CH_3B_5H_8$ together with traces of other unidentified materials. Pure III again distilled at $-40°$ and the yield in this case was 60%. In common with I and II, III exhibited air and moisture sensitivity characteristic of all these compounds.

2-Chloro-4-methylpentaborane(9) (IV).—In the above preparations of III small amounts (10% of the volatile product) of a second material were recovered in the fractionations, and this was shown to be IV. This material was very slightly less volatile than III and was separated by long careful fractionations over periods of many hours. Compound III distilled slowly at $-41°$ and was followed at $-39°$ by IV. Careful monitoring by infrared spectroscopy was essential to the success of this separation. Only small amounts could be obtained pure, and a small sample yielded a mass spectrum very similar to those of I and II, again exhibiting the expected parent m/e at 114; in contrast, of course, the infrared (Table I) and nmr spectra (Table II) were markedly different. This compound melted at $-40°$.

2-Bromo-3-methylpentaborane(9) (V).—In a manner analogous to the preparation of III, 1-bromo-2-methylpentaborane(9) (1.0 mmol) was equilibrated at ambient temperature for 3 hr on hexamethylenetetramine (0.2 g). Fractionation of products was hampered by their very similar volatilities. As in other rearrangements, small amounts of high volatility side products

(15) A. B. Burg and J. S. Sandhu, *J. Am. Chem. Soc.*, **87**, 3787 (1965).

were produced, together with 2-CH$_3$B$_5$H$_8$ (0.15 mmol) resulting from reduction of the B–Br bond. Pure V was distilled from the column at −26°. However, at the latter stages of distillation, a second product (obtained impure in only small amounts) began to contaminate the main product, and this in turn became contaminated by the distillation of unchanged 1-Br-2-CH$_3$B$_5$H$_7$. The yield of pure III was only 30% based on 1-Br-2-CH$_3$B$_5$H$_7$ taken, but 0.5 mmol of the precursor was recovered, unchanged. Although never obtained pure, despite repeated fractionations, the second product was strongly suspected to be 2-Br-4-CH$_3$B$_5$H$_7$, by analogy with the behavior and infrared spectrum of IV. The infrared spectrum of V shows a surprising similarity to the chloro compound III.

2-Chloro-1,3-dimethylpentaborane(9) (VI).—Into a dried 50-ml reaction bulb, fitted with an nmr tube for monitoring and a break-seal for recovery, was placed anhydrous aluminum chloride (0.3 g). After pumping to high vacuum, boron trichloride (1 ml), 2-chloro-3-methylpentaborane(9) (III) (1.2 mmol), and methyl chloride (1.5 mmol) were condensed in and the bulb sealed off. Heating to 45° for 3 hr eliminated the apex hydrogen resonance quartet from the ¹H nmr spectrum, indicating that the reaction was complete. Fractionation of product yielded the excess CH$_3$Cl, BCl$_3$ solvent, and the usual traces of a by-product. Pure VI distilled from the column at −40 through −35°. Traces of lower volatility oils were discarded; yield 60% pure material. The mass spectrum of the compound exhibited the expected cutoff at *m/e* 128. This product was also formed in appreciable quantities in the preparation of 1,2-(CH$_3$)$_2$B$_5$H$_7$ from 2-CH$_3$B$_5$H$_8$ and CH$_3$Cl (*vide infra*).

2-Chloro-1,4-dimethylpentaborane(9) (VII).—This material was produced, in small quantities, in the preparation of 1,2-(CH$_3$)$_2$B$_5$H$_7$, *vide infra*.

2-Chloro-3,4-dimethylpentaborane(9) (VIII), 3-Chloro-2,4-dimethylpentaborane(9) (IX), and 1-Chloro-2,3-dimethylpentaborane (X).—These materials are produced in the base-catalyzed rearrangement of VI. 2-Chloro-1,3-dimethylpentaborane(9) (3.0 mmol) was equilibrated at 25° for 6 hr on freshly sublimed hexamethylenetetramine, after which time the apex:base H–¹¹B resonance intensity ratio was nearly unity.

Fractionation of the volatile products on the low-temperature column yielded trace quantities of 2-CH$_3$B$_5$H$_8$ and 2-Cl-3-CH$_3$-B$_5$H$_7$ at low temperature. Compound IX distilled from the column in the range −40 to −32° and was immediately followed by VIII in the range −32 to −26°. A solid material of lower volatility remained on the column at this point and this was removed at −18° and shown to be X. All three compounds exhibited very similar mass spectra, with the cutoff at *m/e* 128. In each case, the most intense peak in the parent ion envelope occurred at *m/e* 126, corresponding to ¹²C$_2$¹¹B$_5$¹H$_{12}$³⁶Cl. Compounds VIII and IX are liquid at room temperatures; X is solid, and thus nmr spectra were recorded in BCl$_3$ solution. Infrared spectra of VIII and IX are reported in Table I; the low vapor pressure of X prevented a detailed infrared analysis. Yields of materials were: VIII, 30%; IX, 25%; X, 8%. Present in a mixture containing X was 1-chloro-2,4-dimethylpentaborane (2% yield).

Preparation of 1,2-Dimethylpentaborane(9).—Earlier reports[1] indicate that yields of 50% may be obtained in the reaction between 2-methylpentaborane(9) and methyl chloride in the presence of a catalytic amount of aluminum chloride. In a reinvestigation of this reaction we have found that the lower volatility side products contain various chlorinated materials. The characterization of these materials was facilitated by the comparison of spectra in the known compounds and the use of decoupling experiments. Using conditions established previously,[1] a 1-l. reaction bulb was charged with aluminum chloride (0.5 g), 2-methylpentaborane(9) (23 mmol), and methyl chloride (23 mmol) and heated to 55° for 18 hr, yielding a yellow oily product. Fractionation of the products of this reaction yielded the following: at low temperatures, −110°, traces of HCl and HBCl$_2$ were collected; warming the column to −90° yielded CH$_3$BCl$_2$, unreacted CH$_3$Cl, and traces of BCl$_3$. These materials were

followed at −80 to −70° by unreacted 2-CH$_3$B$_5$H$_8$. The total amounts of these high volatility impurities were small. At −62°, 1,2-(CH$_3$)$_2$B$_5$H$_7$ (13 mmol, 55%) was collected, leaving behind about 25% of the initial liquid product mixture. This lower volatility material was shown to contain the chlorinated side products. Careful fractionation, monitored by infrared analysis and ¹H and ¹¹B nmr spectra, yielded (a) 2-Cl-3-CH$_3$B$_5$H$_7$ (III) (1.5 mmol, 6%) collected at −42°, (b) 2-Cl-1,3-(CH$_3$)$_2$B$_5$H$_6$ (VI) (2.5 mmol, 12%) collected between −37 and −30°, and (c) 2-Cl-1,4-(CH$_3$)$_2$B$_5$H$_6$ (VII) (0.9 mmol, 4%) collected between −25 and −18°.

Preparation of 1,2,3-Trimethylpentaborane(9).—This was prepared as previously reported[1] and subjected to low-temperature fractionation under vacuum. A mass spectrum showed the expected broad parent ion envelope with cutoff at *m/e* 106. The derivative obtained was not pure 1,2,3-(CH$_3$)$_3$B$_5$H$_6$ but contained 20% of 1,2,4-(CH$_3$)$_3$B$_5$H$_6$;[16] yield *ca.* 40%.

Preparation of 2,3,4-Trimethylpentaborane(9) (XI).—A catalytic amount of hexamethylenetetramine was sublimed into a reaction ampoule, to which was attached an nmr tube side arm fitted with a break-seal at its upper end. The 1,2,3- and 1,2,4-(CH$_3$)$_3$B$_5$H$_6$ mixture (1.58 mmol) obtained previously was condensed into the ampoule which was then sealed. The ampoule and contents were heated in an oven at 55–60° for 40 hr, the products being monitored occasionally by ¹H nmr. It was probable that the yield of 2,3,4-(CH$_3$)$_3$B$_5$H$_6$ was not increased by the last 20 hr of heating.

The volatile products were removed from the ampoule under vacuum using the break-seal and fractionated under high vacuum on a low-temperature fractionation column. Pure 2,3,4-(CH$_3$)$_3$-B$_5$H$_6$ distilled from the column at −49.5 to −45°. The yield was *ca.* 25% based on the amount of 1,2,3- and 1,2,4-(CH$_3$)$_3$B$_5$H$_6$ isomers used, but 25% of the reactants were recovered and it was noticed that qualitatively this appeared to be enriched in the 1,2,4 isomer. A mass spectrum showed the expected broad parent envelope with cutoff at *m/e* 106. In addition, a more volatile product was obtained and shown to contain boron carbon and hydrogen but was not identified.

Use of Hexamethylenetetramine for the Rearrangement of 1-Methylpentaborane and 1,2-Dimethylpentaborane.—The successful use of this base in the rearrangement of apex-polysubstituted derivatives prompted its use for the rearrangement of simpler materials. It has thus been possible to rearrange quantities of 20 mmol of 1-methylpentaborane(9) in 2 hr at 55°. The resulting purification is considerably more facile than that using pyridine bases[1] due to the low volatility of the hexamethylenetetramine. The rearrangement is simply carried out in a sealed bulb with sublimed base and is conveniently monitored by using an attached nmr tube. Similarly, it was found that 4.5 mmol of 1,2-dimethylpentaborane could be readily rearranged at room temperature overnight using hexamethylenetetramine as a catalyst. An infrared comparison showed samples of 2,3-dimethylpentaborane prepared by rearrangement of 1,2-dimethylpentaborane with chloropyridine and hexamethylenetetramine to be identical. It is therefore considered that both rearrangements gave rise to small quantities of the 2,4-dimethylpentaborane isomer, a fact which has been shown here by ¹¹B nmr for the sample from rearrangement on 2-chloropyridine.

Discussion

A schematic diagram which summarizes the preparation of methyl and chloro derivatives of pentaborane is shown in Figure 1. Although the preparative methods utilized are for the most part extensions of previously reported reaction paths, some rather surprising results are obtained in several cases. Thus, the Friedel–Crafts methylation of 2-methylpentaborane gives, in addition to the expected 1,2-dimethylpentaborane, several chlorinated derivatives, III, VI, and VII. This

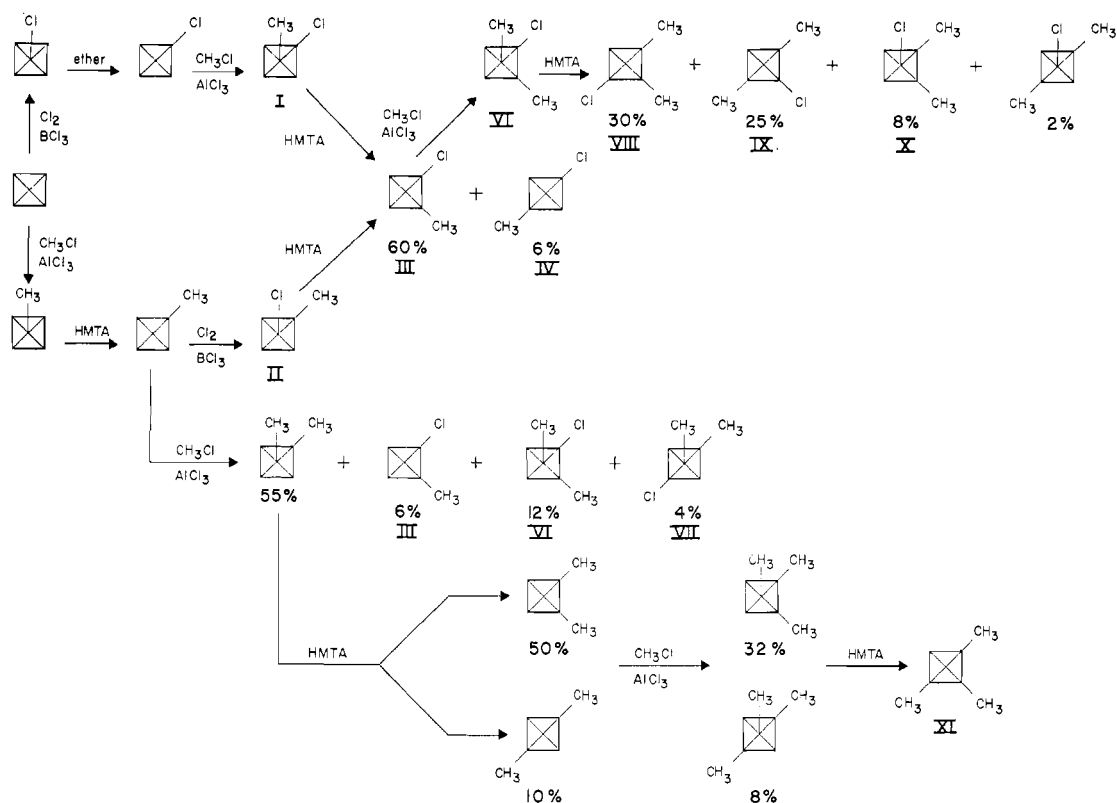(16) As estimated and identified by the ¹¹B nmr spectrum.

Figure 1.—Schematic diagram outlining the preparation of methyl and chloro derivatives of pentaborane.

promises to provide a convenient method of preparing these compounds. Although they are formed in small yields, alternative methods involving the more conventional methylation, chlorination, and rearrangement scheme are obviously more tedious. A good illustration of this is the alternate procedures by which 2-chloro-1,4-dimethylpentaborane can be prepared. Either the direct preparation of VII from 2-methylpentaborane can be realized in small yield or alternatively a three-step chlorination–rearrangement–methylation sequence can be used. The overall yield of the product from the three-step sequence is somewhat higher than the one-step synthesis but obviously requires considerably more effort.

No apically chlorinated derivatives are found from the reaction of methyl chloride with 2-methylpentaborane using aluminum chloride as a catalyst. This observation, coupled with the not insignificant overall yield of basal chlorinated derivatives (ca. 22%), may have mechanistic implications. Since electrophilic attack generally occurs at the negatively charged apex boron, perhaps it is plausible to expect nucleophilic attack by chloride ion at the base of the pyramid as a possibility. Unfortunately, a detailed mechanistic study of this reaction was beyond the scope of the present work and therefore this question will have to be deferred to the future.

Almost exclusively, hexamethylenetetramine[15] was used as a catalyst in the rearrangements. This was found convenient in that the subsequent purification of rearranged materials was unhampered by the

presence of low-volatility bases, such as the 2,6-lutidine used in prior initial experiments.[1,17]

In an early work on the rearrangement of the 1,2-dimethylpentaborane in 2,6-lutidine as a catalyst the 2,3-dimethyl isomer was found as the sole product.[17] A new investigation of this rearrangement using HMTA as a catalyst indicated that a small amount of the 2,4 isomer is formed along with the expected 2,3 isomer. In the present study an examination of the rearrangement products of the apex-substituted chloromethylpentaboranes, I and II, indicates that although the 2,3 product, III, is favored some of the 2,4 isomer, IV, is also formed. Furthermore, a mixture of 1,2,3- and 1,2,4-$(CH_3)_3B_5H_6$ recovered from the base-catalyzed rearrangement of these materials to the 2,3,4 isomer, upon careful fractionation could be partially enriched in the 1,2,4 isomer to approximately a 1:1 mixture. Increase in the amount of the 1,2,4 isomer present could be monitored best by observing the increase in intensity of the infrared vibrations, 1310–1450 (vs), 1235 (m), 973 (m), 854 (s), and 782 cm^{-1} (vw). The ^{11}B nmr spectrum was, however, the most significant piece of information for the identification of the compound as is discussed below. The exact stage at which the 2,4 isomer was produced is not known with certainty but probably occurred at the rearrangement of the 1,2-$(CH_3)_2B_5H_7$ to the 2,3-$(CH_3)_2B_5H_7$ isomer in the preparation of the precursor. In this respect it

(17) T. Onak, L. B. Friedman, J. A. Hartsuck, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **88**, 3439 (1966); L. B. Friedman and W. N. Liscomb, *Inorg. Chem.*, **5**, 1752 (1966).

was of further interest to note that a reinvestigation of a sample of 2,3-$(CH_3)_2B_5H_7$ indicated that it contained *ca.* 20% of the 2,4 isomer, and by careful fractionation a sample enriched to *ca.* 50% of the latter was obtained.[16] Similarly, samples of 1-Cl-2,3-$(CH_3)_2B_5H_6$ and 2-Br-3-$CH_3B_5H_7$ indicated the presence of 17 and 14%, respectively, of the 1-Cl-2,4-$(CH_3)_2B_5H_7$ and 2-Br-4-$(CH_3)B_5H_7$ isomers.[16]

The rearrangement of VI gave a mixture of chlorodimethyl products. One surprising product, 1-chloro-2,3-dimethylpentaborane, appears to be the net result of a 1,2 exchange. Noticeably, the structural isomer 2-chloro-1,4-dimethylpentaborane (VII) is not present in an isolable amount and another isomer, 1-chloro-2,4-dimethylpentaborane, is found only in very small yield. It is tempting to comment on this and on the nature of the products found in higher yield with respect to a plausible mechanism proposed earlier for the related 1,2-dimethylpentaborane rearrangement.[17] In this mechanistic consideration the potentially mobile bridge hydrogens and the boron atoms are involved in a minimum atomic motion (MAM) scheme. Thus, with minor boron skeletal movement, the migration of adjacent bridge hydrogens at a particular basal boron (incipient apex) to positions between the apical (incipient basal) boron and the 3,5-borons can account for the observed rearrangement. For compound VI, four MAM routes are possible (Figure 2). One of these, in which the bridge hydrogens migrate from B(3) to positions about B(1) (pathway 3 → 1) produces the optical isomer of the starting material. In the remaining three routes three of the four obtained product isomers are justified. It is not surprising to find VIII and IX produced in greater yield than X, for a basal preference of methyl and chloro substituents has already been observed in the monosubstituted series. Markedly, not one of the pathways in Figure 2 allows for the production of the 1-chloro-2,4-dimethyl- (2% yield) and 2-chloro-1,4-dimethylpentaborane (VII) isomers (0%). If this mechanistic scheme is hypothetically extended to include further rearrangement of VI, VIII, IX, and X, it is interesting to note that these isomers cannot be directly produced from X. Compound VIII, however, is a potential precursor to one of the isomers and IX is a precursor to the other. The latter two rearrangements involve a net uphill energy change based on the substituent positional preference for the base of the pyramid and thus are unlikely to occur and would account for the very small yield of 1-chloro-2,4-dimethylpentaborane and the absence of VII.

Nuclear Magnetic Resonance. Boron-11 Chemical Shift Correlations.—The ^{11}B nmr spectra are given in Table II. Assignments of resonances to structural units were possible for most compounds using the method outlined in an earlier communication.[8] In the middle stages of this study it became clear that the chemical shifts were largely dictated by contiguous and *trans* substituent effects in the polysubstituted derivatives. Assuming additivity of these two effects alone, it is possible roughly to predict the positions of every
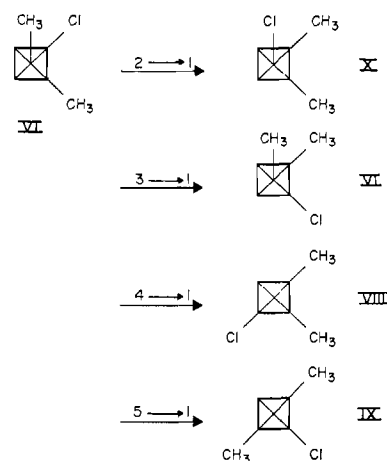

Figure 2.—The four possible "minimum atomic motion" rearrangement reactions for 2-chloro-1,3-dimethylpentaborane. The designation 2 → 1 implies that boron atom in the 2 position of VI becomes the apex in the product.

boron in a pentaborane derivative. A more thorough approach, however, takes into account all possible positional substituent effects. For basal and apical borons this can be expressed by the relationships

$$\delta(^{11}B \text{ apex}) = 53.1 + \sigma_{ac} + \Sigma\sigma_{ab} \qquad (1)$$

$$\delta(^{11}B \text{ base}) = 13.4 + \sigma_{bc} + \sigma_{bt} + \Sigma\sigma_{bn} + \sigma_{ba} \qquad (2)$$

where σ_{ac} is the contiguous substituent effect, apical position, σ_{ab} is the effect of basal substituent on apical position, σ_{bc} is the contiguous substituent effect, basal position, σ_{bt} is the *trans* substituent effect, basal borons, σ_{bn} is the effect of basal substituent on the neighboring basal boron, and σ_{ba} is the effect of apical substituent on the basal boron.
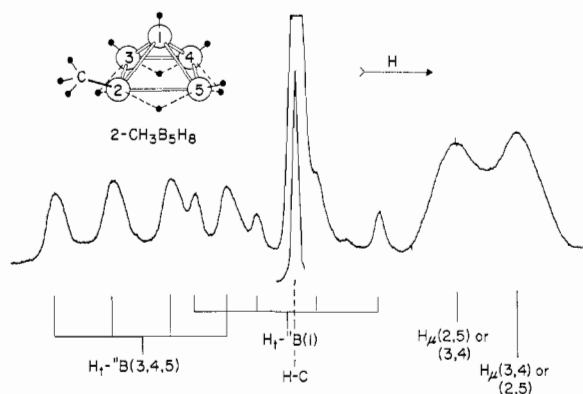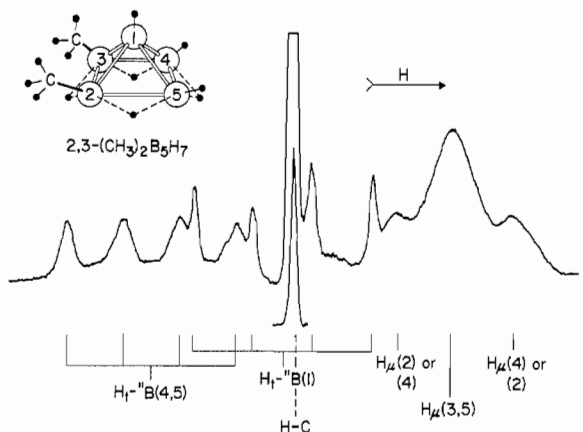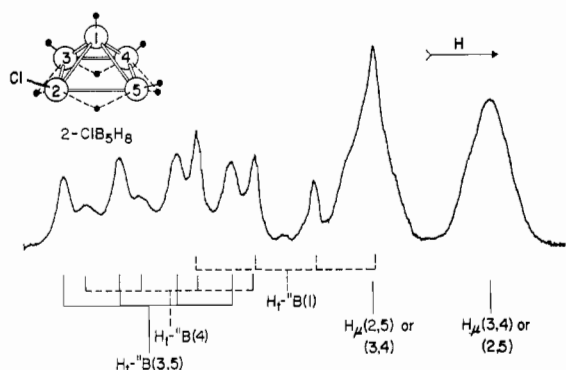
TABLE III

SUBSTITUENT EFFECTS ON THE ^{11}B NMR CHEMICAL SHIFTS

Substituent	σ_{ac}	σ_{ab}	σ_{bc}	σ_{bt}	σ_{bn}	σ_{ba}
Methyl	-8.3	-1.5	-14.4	$+5.2$	$+0.2$	-0.9
	$(5)^a$	(14)	(14)	(17)	(27)	(20)
Chlorine	-23.6	-1.2	-12.3	$+9.7$	0.0	-1.1
	(3)	(7)	(7)	(7)	(14)	(9)
Bromine	-16.1	-2.1	-3.6	$+6.0$	-0.5	-1.1
	(2)	(2)	(2)	(2)	(4)	(8)

^{a} The number of determinations used to calculate the average value of the cited σ.

In Table III values for each of the contributions are given. These are determined by averaging as many comparison chemical shifts as is possible from the number of prepared derivatives. For example, σ_{bt} for a methyl group can be found in a number of ways, *i.e.*, (a) the chemical shift difference between B(4) of 2-methylpentaborane and a basal boron of the unsubstituted pentaborane, (b) a comparison between B(4) of 2,3-dimethylpentaborane and B(3) of 2-methylpentaborane, (c) the chemical shift difference between B(5) of 2-chloro-3-methylpentaborane and B(3) of 2-chloropentaborane, etc. The total number of such comparisons used to determine an average σ is given in Table III along with the value itself. The validity of the assumed additivity of the various σ effects is readily

Figure 3.—Proton nmr spectrum of 2-CH$_3$B$_5$H$_8$; 220 MHz.

Figure 4.—Proton nmr spectrum of 2,3-(CH$_3$)$_2$B$_5$H$_7$; 220 MHz.

Figure 5.—Proton nmr spectrum of 2-ClB$_5$H$_8$; 220 MHz.

seen by a comparison of δ_{exptl} and δ_{calcd} values in Table II. The small average difference (*ca.* 0.5 ppm) between these two values can be attributed, for the most part, to the error in measurement. The boron resonances are usually rather broad and are difficult to measure to an accuracy much greater than this. Also, it is perhaps unwarranted to propose that these additivity rules will hold to any substantially greater degree of accuracy when other effects are considered, for example, steric distortions of the pyramidal framework of pentaborane in the polysubstituted derivatives and its effect on the chemical shifts.

Since the above additivity rule holds fairly well for the methyl, chloro, and bromo derivatives of pentaborane reported in this study, it was of interest to use

the σ values found for chlorine to calculate the ^{11}B chemical shifts for the dichloropentaboranes reported by Gaines and Martens.[4] In Table IV this comparison is made and there appears to be fairly good agreement between calculated and the previously obtained experimental δ values. The one exception is the B(2, 4) resonance in 2,4-dichloropentaborane. The reported shifts for this compound, however, were deduced from the spectrum of a mixture and therefore subject to a degree of uncertainty.

TABLE IV

DICHLOROPENTABORANES:
^{11}B NMR CHEMICAL SHIFT CORRELATIONS

Compound[4]	Boron environment	δ_{exptl},[4] ppm	δ_{calcd}, ppm
1,2-Dichloropentaborane	B(1)–Cl	30.3	28.3
	B(2)–Cl	1.0	0.0
	B(3, 5)–H	13.0	12.3
	B(4)–H	22.1	22.0
2,3-Dichloropentaborane	B(1)–H	49.8	50.7
	B(2, 3)–Cl	1.0	0.9
	B(4, 5)–H	23.3	23.1
2,4-Dichloropentaborane	B(1)–H	49.8	50.7
	B(2, 4)–Cl	1.0	10.8
	B(3, 5)–H	12.4	13.4

Bridge Hydrogen Resonances as a Structural Indicator.—It became apparent early in the study of pentaborane derivative chemistry that as further substitution was accomplished a method would have to be found that would allow for rapid determination of geometry. Thus, for example, the structure of the isomer formed from the base-catalyzed rearrangement of 1,2-(CH$_3$)$_2$B$_5$H$_7$ was in doubt until X-ray analysis[17] showed that the compound was 2,3-(CH$_3$)$_2$B$_5$H$_7$. This uncertainty was a result of ambiguous ^{11}B and ^{1}H nmr spectra. Obviously, many other such instances would be forthcoming as the number of substituents increased. We were particularly interested, therefore, in ascertaining whether, under improved experimental conditions, much more structural information could be obtained from a study of bridge hydrogen resonances. The positions of the methyl substituents of 2,3-(CH$_3$)$_2$B$_5$H$_7$ would have been rapidly determined had it been possible to resolve the pattern of the bridge hydrogen nmr resonances. Very little information has been gathered concerning these and other bridge hydrogen resonances and this is due, no doubt, to the fact that, under normal circumstances, they are broad and, moreover, are usually found to overlap with one or more of the H–^{11}B quartets or alkyl-substituent resonances, when these are present. Some success has been obtained[1] in decoupling experiments with 2-Cl- and 2-BrB$_5$H$_8$, but this was rather limited and provided no absolute assignment.

Initially, to test whether structural information could be obtained from bridge proton resonances, simple compounds were investigated at high field strength using 220 MHz (Figures 3–5), and good resolution was obtained. Thus, for example, Figure 3 shows the proton spectrum of 2-CH$_3$B$_5$H$_8$ recorded at 220 MHz. It is
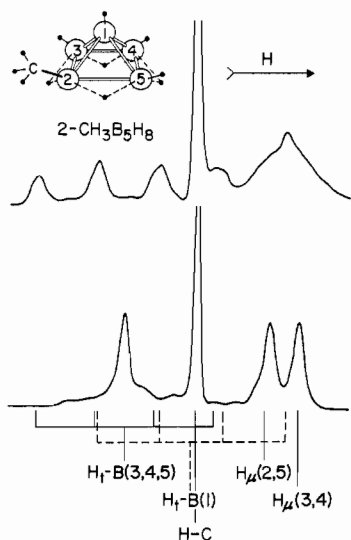
Figure 6.—Proton nmr spectra, undecoupled (above), and boron-11 spectra, decoupled (below), of $2\text{-}CH_3B_5H_8$; 100 MHz.

immediately obvious that at these high-field strengths the increased resolution enables rapid geometrical conclusions to be drawn. Comparison with Figure 6 (undecoupled trace at top of figure), which shows the 100-MHz spectrum, makes this obvious; whereas at 100 MHz the bridge region is broad and diffuse, at the higher field strength the two equal-area bridge resonances appear well resolved, together with the clearly defined apex and basal terminal resonances. Since these initial experimental spectra were run on known compounds to test the possibility of using the bridge resonances as a structural tool, $2,3\text{-}(CH_3)_2B_5H_7$ was of special interest, for reasons outlined above. As is apparent in Figure 4, the three different kinds of bridge hydrogen resonance are well resolved in almost the expected $1:2:1$ ratio, and as in the case of $2\text{-}CH_3B_5H_8$, the apex and base $H\text{-}^{11}B$ quartets are also well resolved. Figure 5 shows the 220-MHz spectrum of $2\text{-}ClB_5H_8$, and this is also of interest because as well as exhibiting the expected two resonances in the bridge region, it is apparent that the basal terminal proton resonance contribution is split into two multiplets. Only in the case of chlorine derivatives has this distinction between the different types of basal terminal hydrogens been observed. In other compounds where this is expected severe broadening is often noted, but no distinct resolution is found.

Having thus shown, by these and other observations, that the bridge hydrogen resonance could be of great use in structure determination, we were led to investigate the possibility of using an available 100-MHz spectrometer with boron-decoupling capability to make similar conclusions. This has now proved to be possible, and the results are in fact more useful because careful observation of partially decoupled spectra has enabled these spectra to be totally assigned;[8] for, although the undecoupled 220-MHz spectra with the superior resolution indicate geometry, they will not of themselves enable assignments to be made when there are several equal-area resonances present. Thus the bridge reso-

nances in Figures 3–5 are not assignable from the undecoupled 220-MHz spectrum, except for the center peak due to $H_\mu(3, 5)$ in Figure 4.

Decoupling Experiments.—As previously described,[8] assignment of complex spectra resulting from polysubstituted materials is possible by selectively decoupling parts of the proton spectrum and observing
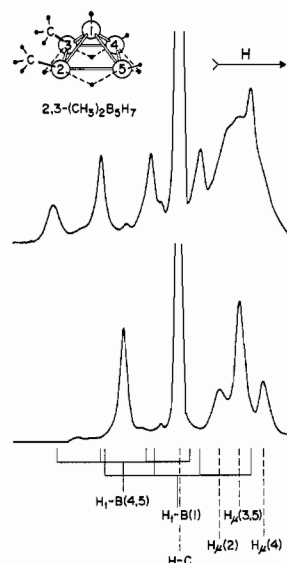

Figure 7.—Proton nmr spectra, undecoupled (above), and boron-11 spectra, decoupled (below), of $2,3\text{-}(CH_3)_2B_5H_7$; 100 MHz.
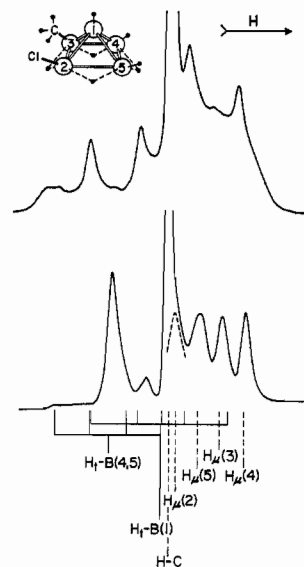

Figure 8.—Proton nmr spectra, undecoupled (above), and boron-11 spectra, decoupled (below), of $2\text{-}Cl\text{-}3\text{-}CH_3B_5H_7$; 100 MHz.

interrelated effects. A similar technique applies also in the case of boron spectra when irradiating the protons. Using these techniques it has been possible to make a total assignment of all the resonances for the compounds listed in Table II. By using several oscillators in each case, totally decoupled boron and proton spectra have also been obtained. Some representative data are reproduced in Figures 6–9, but only the totally decoupled spectrum is reproduced in each case. Figure 8 shows the spectra derived from 2-Cl-3-
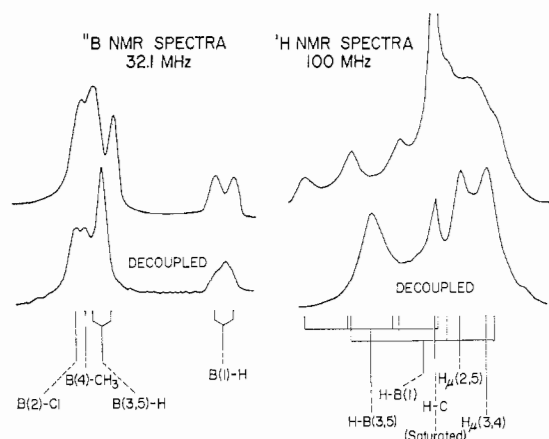
Figure 9.—Proton and boron-11 nmr spectra, undecoupled (above) and decoupled (below), of 2-Cl-4-CH₃B₅H₇.

$CH_3B_5H_7$. Three of the four separate bridge hydrogen resonances are well resolved and the fourth is observable as a shoulder on the methyl resonance. In common with most spectra recorded at 100 MHz the decoupled apex proton resonance falls beneath the methyl peak. Although all four bridge resonances are not completely resolved, it is very apparent that there are indeed four peaks, and this fixes the positions of the substituents within the pentaborane framework. (It was difficult to decouple the apex boron completely while decoupling all of the various basal borons. This accounts for the peak observed between the methyl and base-terminal hydrogen resonances in the bottom spectrum of Figure 8.) The other dibasal isomer of this compound, 2-Cl-4-$CH_3B_5H_7$, exhibits a [11]B and ^{1}H nmr pattern which is shown in Figure 9. Since this spectrum was obtained with a small quantity of material requiring quite high radiofrequency power, especially during the decoupling process, the methyl resonance rapidly became saturated. This premature saturation of alkyl resonances appears to be a rather common occurrence.[18] The [11]B spectrum which is rather ambiguous on its own, becomes readily explicable in terms of the structure deduced from the decoupled-proton spectrum.

Although the primary purpose of decoupling the bridge resonances was to provide geometrical conclusions about the substituted products, a second important function was to provide chemical shift data for the correlation of substituent effects.

Bridge Hydrogen Correlation.—A rough comparison of the chemical shifts for the three types of bridge hydrogens of 2,3-dimethylpentaborane (Table II) indicates that the effect of neighboring methyl groups is roughly additive. Bridge hydrogens adjacent to one methyl group shift downfield from those in pentaborane about 0.6 ppm, whereas those bridge hydrogens with two methyl neighbors shift downfield around 1.3 ppm. By using a more thorough approach whereby distant substituent effects in the base and also apical

(18) The difference in radiofrequency power needed to give good spectra for hydrocarbon moieties is usually approximately 10–50% of that required for [1]H–B spectra. See, for example, G. R. Eaton and W. N. Lipscomb, "NMR Studies of Boron Hydrides and Related Compounds," W. A. Benjamin, Inc., New York, N. Y., 1969, p 563.

TABLE V
Substituent Contributions to the Bridge
Proton Nmr Chemical Shifts

Substituent	σ_n	σ_f	σ_a
CH₃	-0.6 ± 0.2	$+0.1 \pm 0.1$	-0.2 ± 0.1
	(22)[a]	(22)	(20)
Cl	-1.8 ± 0.1	-0.2 ± 0.1	-0.7 ± 0.2
	(14)	(14)	(12)
Br	-1.6	-0.3	-0.7
	(4)	(4)	(8)

[a] The number of comparison determinations used to calculate the average value of the cited σ.

effects are considered, a series of constants (Table V) can be derived which allow an additive relationship (eq 3) to be developed, where σ_n is the near substituent

$$\tau_\mu = 12.3 + \Sigma\sigma_n + \Sigma\sigma_f + \sigma_a \qquad (3)$$

effect, basal position, σ_f is the far substituent effect, basal position, and σ_a is the apical substituent effect. The substituent-effect constants are determined by averaging as many comparison bridge chemical shifts as is possible from the number of prepared derivatives. The use of these and contributions in eq 3 allows τ_{calcd} to be determined for each compound prepared. These calculated values are given in parentheses in Table II. Agreement between the calculated and experimentally obtained values is quite good considering that τ_{exptl} in a number of instances is good to only ±0.05 ppm. This error is largely attributed to the broadness of the resonances, even in the decoupled spectra.

Aside from those compounds mentioned in Table II the only chloro derivative of pentaborane for which bridge resonances have been determined is 1,2-dichloropentaborane. This compound has two chemically different bridge resonances of equal area at τ 9.77 and 11.29.[4] Using eq 3 and the chloro substituent contributions given in Table V calculated values are $\tau_\mu(2, 5)$ 9.8 and $\tau_\mu(3, 4)$ 11.4 for 1,2-dichloropentaborane. This is in sufficiently good agreement with the experimentally obtained values to suggest that the structural assignments of the resonances used for the purpose of the calculations are indeed correct.

Nmr Indications of the 2,4 Isomer Present as Impurities in Some Corresponding 2,3 Derivatives.—It has been previously mentioned that 2,4-$(CH_3)_2B_5H_7$, 1,2,4-$(CH_3)_3B_5H_6$, 1-Cl-2,4-$(CH_3)_2B_5H_6$, and 2-Br-4-$CH_3B_5H_7$ have been identified in mixtures of the corresponding 2,3-base-substituted isomers. Table VI summarizes the chemical shifts and coupling constants observed, together with the theoretically predicted values using the previously derived empirical eq 1–3, for the 2,4-base-substituted pentaborane derivatives. The experimental values have in some cases been assigned from only very small "impurity" resonances observed in otherwise 2,3-base-substituted derivatives. The figures obtained are therefore somewhat tentative, particularly for 1-Cl-2,4-$(CH_3)_2B_5H_6$ and 2-Br-4-$CH_3B_5H_7$, but the closeness of agreement with predicted values leads us to believe that these assignments are correct.

Long-Range Coupling in Apex Methyl Derivatives.—

TABLE VI

NMR DATA FOR 2,4 DERIVATIVES

Compound	Boron environment	δ, ppm Calcd	δ, ppm Exptl[a]	J, Hz	Proton environment	τ, ppm Calcd	τ, ppm Exptl[a]	J, Hz
2,4-Dimethylpentaborane	B(1)–H	50.1	(50.0)	(168)	H–B(1)		(9.55)	(168)
	B(2, 4)–CH₃	4.2	**4.7**	...	H–B(3, 5)		(7.84)	(160)
	B(3, 5)–H	13.8	14.2		$H_\mu(2, 3, 4, 5)$	11.8	(11.7)	...
					H–C(2, 4)		(9.69)	...
1,2,4-Trimethylpentaborane	B(1)–CH₃	41.8	(42.5)	...	H–B(3, 5)		(7.81)	(157)
	B(2, 4)–CH₃	3.3	**4.3**	...	$H_\mu(2, 3, 4, 5)$	11.6	(11.6)	...
	B(3, 5)–H	12.9	13.4	(152)	H–C(1)		(10.06)	...
					H–C(2, 4)		(9.72)	...
1-Chloro-2,4-dimethylpentaborane	B(1)–Cl	26.5	(27.4)	...	H–B(3, 5)		(7.47)	(158)
	B(2, 4)–CH₃	3.1	**3.9**	...	$H_\mu(2, 3, 4, 5)$	11.1	(11.10)	...
	B(3, 5)–H	12.7	13.0	(163)	H–C(2, 4)		(9.70)	...
2-Bromo-4-methylpentaborane	B(1)–H	49.5	(49.4)	(175)	H–B(1)		b	
	B(2)–Br	15.0	b	...	H–B(3, 5)			
	B(3, 5)–H	13.1	b	...	H–C(4)			
	B(4)–CH₃	5.0	**5.1**	...	$H_\mu(2, 5)$	10.8		
					$H_\mu(3, 4)$	11.4		

[a] Bold type indicates that the experimental value was obtained by measuring the entire resonance. Light type indicates that only half of the resonance doublet is directly observed; the remaining half overlaps with the 2,3 isomer in the mixture. Parentheses indicate that the resonance and J values are assumed to overlap almost exactly with the 2,3 isomer. In all cases this could be justified by appropriate area increases over and above the area expected for the pure 2,3 isomer. Obviously, the exact positions of the resonances are subject to minor revision should these 2,4 isomers be obtained pure at a later time. [b] Overlap with resonances assigned to the 2,3 isomer precludes an assignment.

Another interesting feature is the long-range heteronuclear coupling observed in the ¹H nmr of apex-methyl-substituted pentaboranes. Coupling between a boron nucleus and proton nuclei separated by at least one other nucleus has been reported on only rare occasions, for example, in diborane, H–B--H--B–H[19] ($J_{^{11}B-H} = 4$ Hz), and in amine adducts of boron halides, H–C–N–B–X[20] ($J_{^{11}B-H} = 2.7$ Hz).

TABLE VII

COUPLING CONSTANTS FOR APEX METHYLPENTABORANES

Compound	$J[^{11}B_1-H_{CH_3}]$ coupling obsd,[a] Hz
1-CH₃B₅H₈	6.8
1,2-(CH₃)₂B₅H₇	6.1
2-Cl-1-CH₃B₅H₇	6.1
2-Cl-1,4-(CH₃)₂B₅H₆	6.1
1,2,3-(CH₃)₃B₅H₆	6.5

[a] The quoted values are accurate to within ±0.4 Hz.

Table VII shows a list of the pentaborane derivatives having apex methyl groups, which were investigated, and their observed coupling constants $J_{B-H_{CH_3}}$.

Figure 10c shows a typical example of the coupling observed for 2-chloro-1-methylpentaborane (¹H 220 MHz). Also shown for the same compound in Figures 10b and 10a are the spectra observed with and without irradiation to decouple the apex boron atom, respectively (¹H 100 MHz). The quartet observed in the undecoupled spectrum collapsed completely for all the compounds investigated, and a very marked sharpening of all the resonances occurred. It should be noted that when the pentaborane derivative contained a base
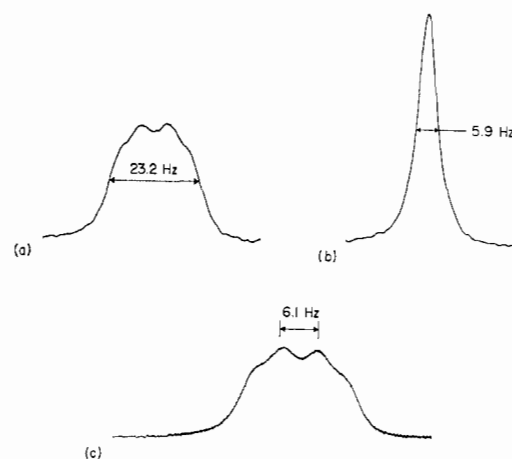

Figure 10.—Proton nmr of the apex methyl group in 2-Cl-1-CH₃B₅H₇: (a) 100 MHz, undecoupled; (b) 100 MHz, boron-11 decoupled; (c) 220 MHz, undecoupled.

methyl substituent, the quartet observed in the undecoupled ¹H nmr was not always symmetrical on account of phasing difficulties associated with the closeness of the methyl resonances.

The converse coupling of the methyl protons to the apex boron nucleus was not detected in the broad ¹¹B nmr resonance observed.

Attempts to observe similar coupling in base-methyl-substituted pentaborane derivatives, which are observed as much narrower resonances, have so far been unsuccessful possibly due to the inherent broadness of each member of the quartet attributable to the quadrupole moment of the boron nucleus.

(19) T. C. Farrar, R. B. Johannesen, and T. D. Coyle, *J. Chem. Phys.*, **49**, 281 (1968).

(20) G. E. Ryschkewitsch and W. J. Rademaker, *J. Magn. Resonance*, **1**, 584 (1969).