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Phosphinopentaboranes[1]

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Phosphine derivatives of the type R_2PCl react with LiB_5H_8 in ether to form 2,3-μ-$(CH_3)_2PB_5H_8$ (mp 17°; bp estd 191°), 2,3-μ-$CH_3CF_3PB_5H_8$-A (mp 14°; 1 mm at 25°) which isomerizes irreversibly by an apparently first-order rate process to 2,3-μ-$CH_3CF_3PB_5H_8$-B (mp −28°; 9 mm at 25°; bp estd 137°), and 1-$(CF_3)_2PB_5H_8$ (mp −42°; bp estd 184°). The bridging *vs.* peak positions of phosphorus are proved by the B, F, and H nmr spectra and understood in terms of different phosphine-base strengths. The phosphorus nmr spectra show an interesting dectet for 1-$(CF_3)_2PB_5H_8$ but no resolution for the B–P–B bridged compounds. Both infrared and nmr results indicate weaker-than-normal terminal B–H bonds (with more than normal B_{2p} character) adjacent to bridging P atoms. The $CH_3CF_3PB_5H_8$ isomers show no discernible B–F coupling, whereas 1-$(CF_3)_2PB_5H_8$ shows $J_{B-F} = 6.0$ cps.

The recent discovery of the compound μ-$(CH_3)_3SiB_5H_8$, in which a three-center B–Si–B bond slowly changes to the more stable situation in 2-$(CH_3)_3SiB_5H_8$,[2] suggested the similar synthesis of μ-$R_2PB_5H_8$ compounds whose properties might contribute to the development of chemical principles. Indeed, LiB_5H_8[3] (in ether at −120 to −78°) reacted easily with $(CH_3)_2PCl$ to produce the fairly stable μ-$(CH_3)_2PB_5H_8$, the B–P–B bridged structure of which was confirmed by a proton nmr spectrum showing different environments for the two methyl groups. The similar CH_3CF_3PCl reaction also led to B–P–B bridging, here proved by the existence of two isomers whose ^{11}B nmr spectra included a characteristic triplet quite similar to that found for μ-$(CH_3)_2PB_5H_8$. These isomers were easily distinguishable by their different melting points, volatility, infrared spectra, and nmr chemical shifts. The initial product was almost entirely the higher melting isomer A, which converts completely to isomer B, about 9 times as volatile as A.

The reaction product of LiB_5H_8 with $(CF_3)_2PCl$ or $(CF_3)_2PI$ was still different, consisting solely of 1-$(CF_3)_2PB_5H_8$, with no evidence found for any B–P–B bridged intermediate. It seems that phosphorus here cannot use its lone-pair electrons for base action toward boron, nor can it develop an electron-deficient bridge in the presence of the lone-pair electrons. This result is curious, for we might have expected the environment of phosphorus in a μ-$(CF_3)_2PB_5H_8$ to be similar to that in the stable trimer $[(CF_3)_2PBH_2]_3$,[4] except for half as many B–H bonds and electron-deficient boron. The absence of μ-$(CF_3)_2PB_5H_8$ would support the idea that the stability of $[(CF_3)_2PBH_2]_3$ depends upon interaction between P and four adjacent B–H bonds.[5] However, this argument would lose force if some special stabilization effect favors 1-$(CF_3)_2PB_5H_8$.

Syntheses and Characterizations

The synthesis of each $R_2PB_5H_8$ compound began with the reaction of B_5H_9 with a 0.1 *M* solution of LiC_4H_9 in diethyl ether at −78°, in a vertical tube leading through a stopcock to the high-vacuum manifold. The resulting solution of LiB_5H_8 (2–3 mmoles) was treated with an amount of the R_2PX compound roughly equimolar to the B_5H_9 (both slightly in excess over the original LiB_5H_8). As the mixture warmed slowly from −120 to −78° (or sometimes to −50°), the occurrence of the desired reaction was indicated by a milky precipitate which redissolved during further standing at a fixed temperature (*e.g.*, 2 hr at −50°). No H_2 was formed. The ether and excess reactants (B_5H_9 and sometimes R_2PCl) were distilled from the tube at −50 to −40° into the vacuum system; then the product $R_2PB_5H_8$ could be delivered similarly as the tube warmed to 25°. Each product was purified by repeated high-vacuum fractional condensation through a series of low-temperature U traps.

Dimethylphosphinopentaborane(9).—The product $(CH_3)_2PB_5H_8$ was made from $(CH_3)_2PCl$,[6] in a yield representing 90% of the original LiC_4H_9. One fractional condensation at −15° was sufficient for its purification. The pure compound melted sharply at 16.8° and showed the normal set of vapor tensions given by Table I. Its vapor-phase decomposition became quite appreciable at 85°; or the liquid might suffer as much as 20% conversion to an amber-brown resin during 1 week at 25°. This resin, like others derived from B_5H_9 with bases, showed a very complex ^{11}B nmr spectrum (Figure 1): boron in many environments.

TABLE I

VOLATILITY OF $(CH_3)_2PB_5H_8$

$\log P = 7.0157 + 1.75 \log T - 0.005T - (3010/T)$

$t_{760} = 191.4°$; Trouton constant = 22.5 eu

Temp, °C	52.0	58.5	61.6	66.0	70.4	80.1
P_{obsd}, mm	3.36	4.93	5.90	7.47	9.43	15.5
P_{calcd}, mm	3.38	4.93	5.89	7.47	9.43	15.4

The vapor-phase molecular weight of $(CH_3)_2PB_5H_8$ was determined in a 627-ml immersible tensimeter. At 84° and 14.25 mm pressure, the result was 122.8; at 78° and 10.7 mm, 123.8; calcd, 123.1. For analysis, a 15.4-mg sample (0.125 mmole) was hydrolyzed in the presence of HCl, requiring 24 hr at 100° for completion. The yield of H_2 was 1.37 mmoles, or 99.6% of the value calculated from the equation

$$(CH_3)_2PB_5H_8 + 15H_2O \longrightarrow 11H_2 + 5B(OH)_3 + (CH_3)_2PH$$

Methyltrifluoromethylphosphinopentaboranes.—The slightly volatile isomer $CH_3CF_3PB_5H_8$-A was the main product of the reac-

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

(3) D. F. Gaines and T. V. Iorns, *ibid.*, **89**, 3375 (1967).

(4) A. B. Burg and G. Brendel, *ibid.*, **80**, 3198 (1958).

(5) A. P. Lane and A. B. Burg, *ibid.*, **89**, 1040 (1967).

(6) A. B. Burg and P. J. Slota, Jr., *ibid.*, **80**, 1107 (1958).

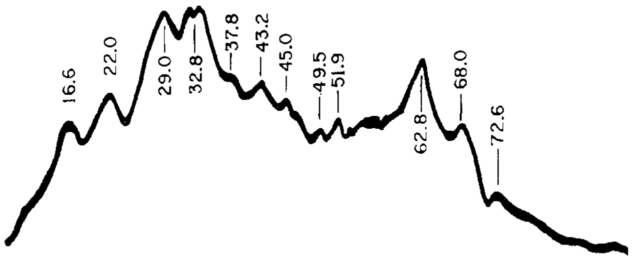

Figure 1.—Boron nmr spectrum of the nonvolatile decomposition product of $(CH_3)_2PB_5H_8$. The line width in each region measures the noise level. The chemical shifts are measured upfield from trimethyl borate.

tion of LiB_5H_8 with CH_3CF_3PCl;[7] the yield represented 91% of the LiC_4H_9. Also found was a 2.8% yield of the more volatile $CH_3CF_3PB_5H_8$-B, probably formed by conversion of isomer A during the processes of isolation and purification. Repeated runs confirmed that the synthesis is quite specific for isomer A. The conversion to B was complete in the liquid phase during 2 hr at 50° or during 48 hr in the vapor phase at 25° (1 mm pressure in a 1-l. bulb). The conversion could be observed by the change in the infrared spectrum in the gas phase at 35° or by the growth of the proton and ^{19}F nmr peaks for isomer B during repeated scans of the "neat" liquid.

Isomer A melted sharply at 13.8° and showed 0.7 mm vapor tension at 20°. It was not feasible to determine the molecular weight in the vapor phase; and in ether solution at 0° the differential pressure method gave 270 at 0.6 *M* or 260 at 0.5 *M* (calcd, 177.1). Under similar conditions the B isomer gave the value 179.9. The mass spectra of both isomers (recorded by West Coast Technical Service, through the kind assistance of Dr. J. F. Ditter, of Space-General Corp.) showed a cutoff peak at 178, corresponding to $CH_3CF_3P(^{11}B)_5H_8$. It was quite clear that isomer A was associated in solution for some structural reason not applicable to isomer B. The results could not be explained on the basis of dimer A in equilibrium with monomer B, for the conversion proved to be irreversible.

The $CH_3CF_3PB_5H_8$ isomer B melted in the range −28.5 to −28.3°. This indication of purity was confirmed by the normal vapor tension data shown in Table II. The vapor-phase molecular weight results at 58–64° were 177.6 and 176.4 (calcd, 177.1).

Table II

Volatility of $CH_3CF_3PB_5H_8$-B

$\log P = 6.3335 + 1.75 \log T - 0.005T - (2450/T)$

$t_{760} = 136.9°$; Trouton constant = 21.45 eu

Temp, °C	24.1	30.0	40.3	45.4	49.7	53.7
P_{obsd}, mm	8.55	11.96	20.82	26.89	33.23	40.12
P_{calcd}, mm	8.57	11.99	20.79	26.93	33.22	40.14

For analysis, 11.0 mg (0.062 mmole) of $CH_3CF_3PB_5H_8$-B, hydrolyzed in 10 ml of water (sealed tube, 48 hr at 100°), gave 0.67 mmole of H_2 (98% of the expected 11 H_2 per molecule). The yield of CH_3CF_3PH was 0.0625 mmole (100.8%); it was identified by its molecular weight (116 as calcd) and infrared spectrum.[7] The boric acid was titrated as 0.312 mmole (100.5% of calcd). Finally, a direct basic hydrolysis of the compound gave 0.97 HCF_3 per mole, after 48 hr at 100°. This full confirmation of the formula $CH_3CF_3PB_5H_8$ for isomer B serves equally well for its precursor, isomer A, since the conversion was quantitative.

Bis(trifluoromethyl)phosphinopentaborane(9).—The compound $(CF_3)_2PB_5H_8$ was made first from 2 mmoles of LiB_5H_8 with 3.21 mmoles of $(CF_3)_2PCl$ in 20 ml of diethyl ether at −78° (15 hr). The ether, removed *in vacuo* at −50°, was not accompanied by any of the expected excess of $(CF_3)_2PCl$, which could have been identified quite easily by its strong infrared spectrum. The slightly volatile product was distilled out *in vacuo* during 5 hr at 24°, leaving a milky oil which apparently included the elements of the missing $(CF_3)_2PCl$. Complete removal of the ether from the product $(CF_3)_2PB_5H_8$ required five-times repeated high-vacuum fractional condensation through a trap at −30°. The yield of the pure product was 266 mg (1.15 mmoles; 57%).

The use of $(CF_3)_2PI$ for this synthesis was essentially the same in all respects.

The sharp melting point of $(CF_3)_2PB_5H_8$ (−42.0°; no range) and the normal character of its vapor tensions (Table III) left no doubt of its purity; no isomerism was observed.

The vapor-phase molecular weight determinations gave 236 and 231; calcd, 231.1. The hydrolytic analysis is described with millimole quantities, as follows.

$$\begin{array}{ccccccccc} (CF_3)_2PB_5H_8 & + & 15HOH & \longrightarrow & 11H_2 & + & 5B(OH)_3 & + & (CF_3)_2PH \\ 0.0837 & & (\text{excess}) & & 0.893 & & 0.410 & & 0.0830 \\ & & & & (97\%) & & (98\%) & & (99\%) \end{array}$$

Table III

Volatility of $(CF_3)_2PB_5H_8$

$\log P = 6.6114 + 1.75 \log T - 0.005T - (2790/T)$

$t_{760} = 184.3°$; Trouton constant = 21.0 eu

Temp, °C	25.0	35.5	45.3	57.0	68.6	74.0	82.0
P_{obsd}, mm	1.20	2.41	4.39	8.29	14.9	19.3	27.7
P_{calcd}, mm	1.24	2.43	4.35	8.28	14.9	19.3	27.7

Nuclear Magnetic Resonance.—The chemical shifts (δ, ppm) and observable coupling constants (*J*, cps), determined by means of the Varian HA-100 instrument (^1H at 100 Mc, ^{19}F at 94.1 Mc, ^{31}P at 40.5 Mc, and ^{11}B at 32.1 Mc) for the four phosphinopentaboranes, are shown in Table IV. Here the δ values for protons relate to tetramethylsilane as a 5% internal standard, and were rechecked by the Varian A-60 instrument. For the other nuclei, the δ values were measured by substitution of tubes containing neat-liquid samples of reference compounds, the side bands of which determined the scale in cps. For boron, trimethyl borate proved convenient for avoiding superposition and was more sharply measurable than the polyborane peaks; for phosphorus, 85% H_3PO_4 was used; and for fluorine, Cl_3CF was used in one case, and the others were corrected from C_6F_6. Since the new compounds and the standards were in tubes of precisely similar bore and wall thickness, the systematic errors due to differences of diamagnetic susceptibility probably did not exceed 0.5 ppm. For consistency, all δ values here are measured upfield from the standards; a minus sign means a downfield shift.

Table IV

Nmr Spectra of Phosphinopentaboranes

			$CH_3CF_3PB_5H_8$					
	$(CH_3)_2PB_5H_8$		Isomer A		Isomer B		$(CF_3)_2PB_5H_8$	
	δ	*J*	δ	*J*	δ	*J*	δ	*J*
1-B	64.8	154	63.7	163	64.2	163	68.8	...
2,3-B	41.3	114	42.1	105	41.1	112	30.4	168
4,5-B	19.1	156	19.8	160	18.6	164		
CH_3	−1.72	12	−1.37	10.0	−1.97	12.6	...	...
	−1.09	10						
P	85[a]	...	33.5[a]	...	47[a]	...	25.1[b]	"73"
F	...	...	59[c]	68	71[c]	61	49.9	P 71.3 B 6.0

[a] Unresolvable peaks, 750–800 cps wide at the base. [b] Dectet; *cf.* Figure 5. [c] Corrected to Cl_3CF reference by adding 165 ppm to the δ measured from C_6F_6, in accord with the measured difference between the two reference tubes actually used.

The ^{11}B spectra of $(CH_3)_2PB_5H_8$ and the $CH_3CF_3PB_5H_8$ isomers all were so very similar that Figure 2 almost could represent any of them. The integration of each showed accurately a 2:2:1 intensity pattern, confirming the B–P–B bridge interpretation. The most interesting feature of this spectral pattern is the central triplet. It cannot be interpreted as a superposed pair of doublets, for a 12.8-Mc spectrum of $CH_3CF_3PB_5H_8$-B (kindly recorded for us by Dr. R. E. Williams) showed the same triplet.

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[7] A. B. Burg, K. K. Joshi, and J. F. Nixon, *J. Am. Chem Soc.*, **88**, 31 (1966).

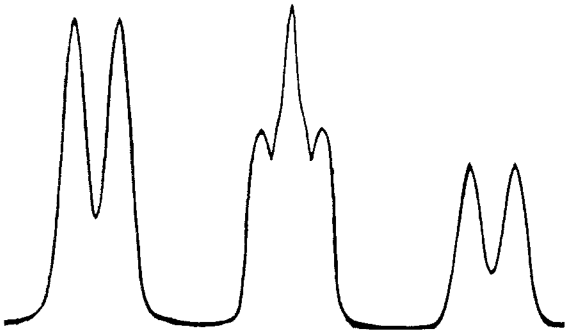

Figure 2.—Boron nmr spectrum of $CH_3CF_3PB_5H_8$-B, typical also of $CH_3CF_3PB_5H_8$-A and $(CH_3)_2PB_5H_8$. The upfield direction is to the right, as usual.

It appears that this triplet is the result of closely similar values of J_{B-H} and J_{B-P} for the 2,3-B atoms, so that one sees a pattern much like that for a quadrupole-blurred BH_2 group. However, slight differences in the width and shape of the central peak for these three compounds would suggest that each has its own small difference between J_{B-H} and J_{B-P}.

Very different is the ^{11}B spectrum for $(CF_3)_2PB_5H_8$, which shows a downfield doublet (basal B–H) and an upfield singlet accurately one-fourth as intense. On this basis alone, the attachment of P to the 1-B atom is beyond doubt.

The proton spectrum of $(CH_3)_2PB_5H_8$ confirms the B–P–B bridge pattern, for the two doublets (well separated and fairly sharp) show two methyl-group environments, due to four-coordinate phosphorus. Similarly, bridging in the $CH_3CF_3PB_5H_8$ isomers correlates with their different methyl-group spectra. Likewise, the fluorine spectra of these isomers show different CF_3 groups. In each case, the F–C–P doublet is so sharp that either peak can be used to establish a field-lock; there is strictly no evidence of coupling to the boron quadrupoles.

The B–H proton spectrum of $CH_3CF_3PB_5H_8$-B at 100 Mc was recorded at high radiofrequency power input in order to saturate the C–H protons while having little effect upon the boron-bonded protons. Figure 3 shows the result of medium suppression of the C–H protons. At still higher power the C–H doublet virtually disappeared, while the main pattern remained essentially the same. A full interpretation was not achieved even by reference to the differently superposed 60-Mc spectrum.

The far simpler 100-Mc proton spectrum of $(CF_3)_2PB_5H_8$ (Figure 4) obviously reconfirms the 1-B position of the $(CF_3)_2P$ group, for the simple 1:1:1:1 quartet corresponds to the equally situated basal B–H protons, and the broad B–H–B spectrum also is undisturbed by proton differences. An obviously similar spectrum has been described for 1-ClB_5H_8.[8]

The phosphorus spectra for $(CH_3)_2PB_5H_8$ and the $CH_3CF_3PB_5H_8$ isomers proved to be quite as featureless as might be expected in view of the effects of two adjacent boron quadrupoles and six half-spin nuclei fairly well coupled to phosphorus; the very broad peaks seem quite unresolvable. For $(CF_3)_2PB_5H_8$, however, the phosphorus spectrum is well resolved (Figure 5). One reason is that J_{P-B} and J_{P-F} are not very different, so that we see four equal $(1 + 1)^6$ septets, superposed to form a dectet

1	6	15	20	15	6	1			
	1	6	15	20	15	6	1		
		1	6	15	20	15	6	1	
			1	6	15	20	15	6	1
1	7	22	42	56	56	42	22	7	1

However, this dectet is somewhat blurred, partly because the two J values are not quite equal. Indeed, the separations of the peaks near the edge of the pattern are lower than in the middle, as though J_{P-F} (71.3 cps as measured by the ^{19}F spectrum; *cf.* Figure 6) were represented at the edges, while a somewhat larger J_{P-B} (perhaps as high as 75 cps) were being described in the central region. Unfortunately, the value of J_{P-B} cannot be measured more directly by means of the boron spectrum, for the 1-B atom there shows only an unresolved singlet, typical of all 1-XB_5H_8 compounds yet observed.

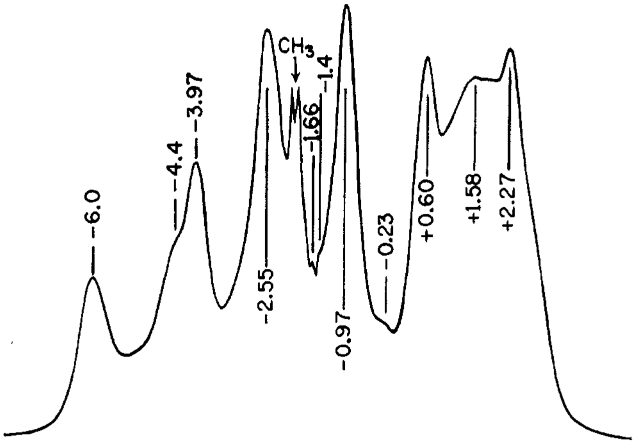

Figure 3.—Proton nmr spectrum of $CH_3CF_3PB_5H_8$-B at 100 Mc, with the CH_3 protons suppressed by saturation.

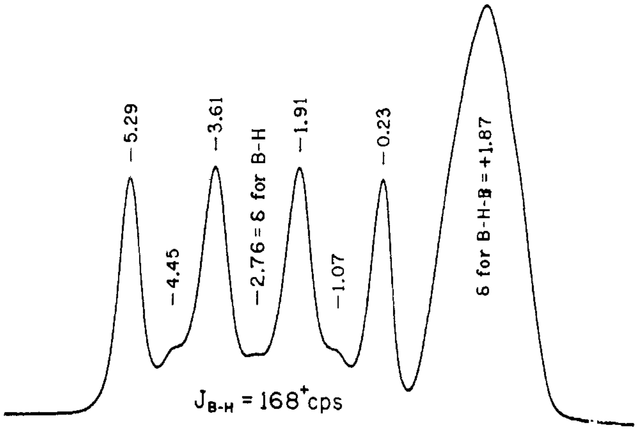

Figure 4.—Proton nmr spectrum of $(CF_3)_2PB_5H_8$ at 100 Mc. The minor features at −4.45, −2.76, and −1.07 ppm (from TMS) are ascribed to the ^{10}B–H septet, which accounts also for the greater height of the −3.61 and −1.91 peaks. The slight undulation in the upper part of the B–H–B peak is real.

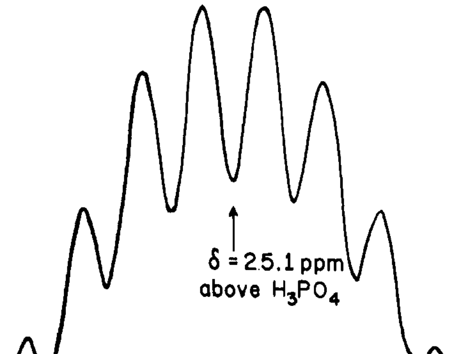

Figure 5.—Phosphorus nmr spectrum of $(CF_3)_2PB_5H_8$ (40.5 Mc).

Infrared Spectra.—The Beckman IR7 instrument was used to record the infrared spectra of the vapors of the four $R_2PB_5H_8$ species, either in a 10-cm cell at the 35° temperature of the cell chamber or at higher temperatures with an 8-cm cell in a transite box with a heater–blower, all in the closed and dry cell chamber.

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[8] D. F. Gaines, *J. Am. Chem. Soc.*, **88**, 4528 (1966).

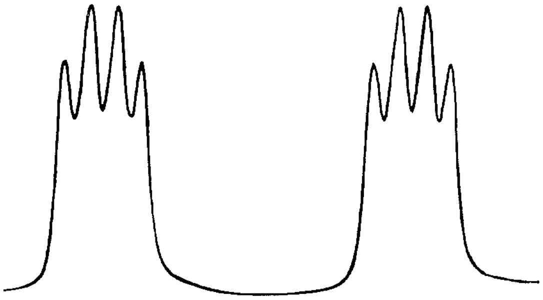

Figure 6.—Fluorine nmr spectrum of $(CF_3)_2PB_5H_8$ at 94.1 Mc.

Where feasible, the relative intensities were determined as $k = (100/PL) \log (I_0/I)$ for path length L and pressure P (reduced to 25°), both in centimeters. These intensities are shown in parentheses after the corresponding frequencies (cm^{-1}) in the following summary of results. The most detailed record was obtained for the relatively volatile isomer $CH_3CF_3PB_5H_8$-B, whereas the results for isomer A were limited by its low volatility and fairly rapid evolution of the vapor of isomer B from the liquid phase during infrared scans. Also the results for $(CH_3)_2PB_5H_8$ were somewhat limited by the possibility of decomposition if one tried to develop a high vapor concentration.

Methyl-group stretching frequencies were recorded for $(CH_3)_2PB_5H_8$ at 2988 (0.8) and 2925 (0.8) and for $CH_3CF_3PB_5H_8$-B at 3017 (0.08) and 2943 (0.08). The higher frequencies and far lower intensities for the latter are in accord with much experience: C–H stretching loses intensity when C–F bonds are in the same molecule; and CF_3 on P induces stronger bonding in adjacent groups. For $(CH_3)_2PB_5H_8$, the methyl-group deformations were normal at 1428 (0.9) and 1395 (0.6), but for $CH_3CF_3PB_5H_8$-B the same region was more confused by the skeletal modes included in the observed peaks 1427 (1.3), 1422 (1.1), 1403 (0.6), 1331 (0.7), 1308 (1.37), 1281 (1.43), and 1229 (0.93). For $(CF_3)_2PB_5H_8$, there was continuous absorption in the same range (1540–1320), with peaks at 1475 (5) and 1443 (6). B–H–B bridging frequencies for $(CF_3)_2PB_5H_8$ appeared at 1867 (5) and 1830 (2); and for the two kinds of B–H–B bridging in $CH_3CF_3PB_5H_8$-B, broad peaks were seen at 1975 (0.3), 1935 (0.3), 1875 (0.3), 1775 (0.2), and 1700 (0.1).

The B–H stretching frequencies correlate well with the structures of the various phosphinopentaboranes. For 1-$(CF_3)_2PB_5H_8$, the four equal B–H bonds show one peak: 2630 (27). Contrastingly, the B–P–B bridged compounds would have 1-B, 2,3-B, and 4,5-B all different. Accordingly, for $CH_3CF_3PB_5H_8$-A we find peaks at 2610 (17), 2606 (17), and 2558 (17), all recorded before isomerization could occur; for $CH_3CF_3PB_5H_8$-B, 2615 (10), 1611 (12), 2609 (11), 2576 (8), and 2556 (13); and for $(CH_3)_2PB_5H_8$, 2607 (12), 2601 (16), 2596 (13), 2565 (7), and 2528 (16). The lowest frequencies here correlate with weaker-than-usual B–H bonding, suggested also by low B–H coupling constants, as will be discussed.

The C–F stretching region shows for $(CF_3)_2PB_5H_8$ the peaks 1197 (45), 1155 (80), 1142 (78), and 1105 (48); for $CH_3CF_3PB_5H_8$-B, 1187 (28) and 1142 (56); and for $CH_3CF_3PB_5H_8$-A, 1208 (18), 1190 (10), 1154 (25), and 1137 (30), some of which may be strongly affected by the presence of the more volatile isomer B.

Most of the remaining peaks are difficult to assign, for they are in regions appropriate for B–H bending, CH_3 rocking and wagging, CF_3 symmetric deformation, and possible skeletal modes. For $(CF_3)_2PB_5H_8$ there is broad absorption from 930 to 850 cm^{-1}, with a maximum at 885 (4), and peaks at 745 (0.9), 685 (2), 560 (1), and 460 (8). The others were not scanned below 600 cm^{-1}. For $(CH_3)_2PB_5H_8$, peaks were found at 947 (8), 865 (1.3), 770 (3.6), and 742 (2); for $CH_3CF_3PB_5H_8$-A, at 976 (2?), 891 (36), and 879 sh (16); and for $CH_3CF_3PB_5H_8$-B, at 1110 (0.9), 1040 (0.9), 1014 (0.6), 971 (1.1), 937 (1.3), 916 R (9.3), 913 Q (10.7), 910 P (8.7), 860 (1.6), 776 (3), 772 (3), 758 (2), and 723 (3).

Rate of Isomerization.—The sharp and well-separated ^{19}F nmr peaks for the $CH_3CF_3PB_5H_8$ isomers were used to explore the rate of the A → B conversion. A sample containing about 90% isomer A and 10% B was thermally equilibrated in the probe at 35.0° during 10 min. For each observation, both doublets were integrated at the same amplification level, usually within the same 40 sec. The mole fraction x of component A was calculated from the heights of both integrals.

In the range 70–23% A the rate was strictly first order: $-\log x = 0.0240 + 0.002270t$ (with t meaning time in minutes and the constant 0.0240 describing the arbitrary starting point). The conformity to this equation, of points taken as regional averages of $\log x$ and t, is shown in Table V.

Table V

Rate Data for A → B Isomerization at 35.0°

Time, min	65.51	88.32	126.05	142.92	189.90	246.25
x, obsd	0.669	0.595	0.492	0.448	0.351	0.259
x, calcd	0.672	0.596	0.490	0.447	0.349	0.261

However, the rate constant for the first 0.5 hr was appreciably lower than for later stages. With every possible allowance for errors such as themal lag and overestimation of the early small integrals for isomer B, the six points in the range 9–32 min determined the equation $-\log x = 0.037 + 0.00220t$. The difference probably is real but not easily explained.

A more extensive kinetic study of this isomerization, perhaps by vapor-phase infrared methods, might be informative.

Structural Discussion

The bridging of two basal boron atoms (numbered 2 and 3) by phosphorus in $(CH_3)_2PB_5H_8$ and $CH_3CF_3PB_5H_8$—in contrast to the 1-B position of the $(CF_3)_2P$ group in $(CF_3)_2PB_5H_8$—is verified beyond doubt by multiple aspects of the nmr spectra. Also, the close correspondence of the nmr spectra of the two $CH_3CF_3PB_5H_8$ species leaves no doubt of their isomeric relationship.

It is interesting that the three B–P–B bridged species all show 2,3-B–H coupling constants about one-third lower than is normal for pentaborane(9) derivatives (*ca.* 110 *vs.* normally 160 cps), suggesting that the B–H bonds adjacent to the B–P–B bridging have less B_{2s} and more B_{2p} character than usual. But hydrogen usually is more firmly bonded by more s character; hence one might expect these B–H bonds to be weaker than normal. In fact, all three of these species show some terminal B–H stretching frequencies decidedly lower than the usual 2600–30-cm^{-1} range observed in most pentaborane(9) derivatives.

Another interesting item is the position—decidedly downfield relative to B_5H_9—of the 4,5-B nmr peaks, despite the expected electron-enriching effect of the electron-donor bridging phosphorus ligands: apparently the cross-ring boron atoms here go opposite to the situation for 4-B in 2-XB_5H_8 compounds, wherein the 4-B moves upfield in proportion to the availability of ligand π electrons.[9] In the present B–P–B bridged compounds, of course, there are no ligand π electrons.

However, a more important problem related to the nmr spectra is the structural decision concerning the $CH_3CF_3PB_5H_8$ isomers. Assuming that the bridging

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

phosphorus atom is roughly tetrahedral and replaces a bridging proton insofar as direction from the B_5 skeleton is concerned, we would recognize that one R group on phosphorus has an "axial" position well below the B_4 plane and extending toward the 4,5-B atoms, while the other R group would be "equatorial," extending outward and almost coplanar with the basal boron atoms. Then space-induction effects might be used to decide which isomer has axial CF_3 and equatorial CH_3, or *vice versa*.

By the simplest argument, a CF_3 group undergoing dipolar interaction with the especially electron-deficient 4,5-B atoms would have ^{19}F peaks more downfield and push the 4,5-B peaks upfield; and methyl groups far from the 4,5-B atoms would show relatively upfield proton peaks. All three expectations are met by the δ values for isomer A. Accordingly, there is a temptation to conclude that isomer A has axial CF_3 with equatorial CH_3 and that isomer B has the opposite situation.

However, this conclusion would lead us to expect isomer A to be stabilized by internal dipolar interaction, whereas in fact it isomerizes quantitatively to isomer B. Also, we must not forget that isomer A is associated; and the only reasonable basis for the assocation would be an intermolecular dipolar interaction between CF_3 of one molecule and the 4,5-B atoms of another. Indeed, the association may amount to more than we have demonstrated, for the 50% too-high molecular weight was determined in solution in ether, which could be expected to work against the postulated dipolar association. Attempts to determine the molecular weight in a more truly inert solvent, such as *n*-pentane, failed for lack of solubility.

Considering, then, that quite high actual molecular weights might prevail in the "neat" liquid isomer A, we may argue that this isomer could connect an equatorial CF_3 to the 4,5-B atoms of an adjacent molecule, with better space-inductive interaction (and more downfield chemical shift) than if an axial CF_3 were less effectively reaching toward 4,5-B in the same molecule. By this argument, isomer A would use equatorial CF_3 to maintain a weak dipolar polymer bonding, while axial CH_3 would be little affected by 4,5-B atoms which are receiving the charge effect of CF_3 from another molecule in a relatively effective manner. Then isomer B could be stabilized as a monomer by a dipolar action of axial CF_3 toward 4,5-B in the same molecule, while the equatorial methyl group would fail to develop effective polymer bonding to an adjacent molecule.

Both of the opposing ideas of the isomer structures have their merits, and we prefer not to choose between them at this time. Possibly the decision can be made later, on the basis of fuller information, including work on analogous compounds and more rigorously studied arguments.

Even less productive would be attempts to explain why isomer A is the exclusive product of the original synthesis.

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The Nuclear Magnetic Resonance Spectra of Aluminum Borohydride–Trimethylamine[1a,b]

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The H^1, B^{11}, and Al^{27} nmr spectra of aluminum borohydride and its trimethylamine adduct have been examined. On the basis of these spectra and cryoscopic data, the adduct is shown to be an undissociated monomer with magnetically equivalent borons and hydridic hydrogens. The adduct is unique in that it has a lower symmetry (C_3 or C_{3v}) than the original aluminum borohydride (D_{3h}) yet the electric field gradient at the Al^{27} nucleus appears to be smaller in the adduct than in the free acceptor.

With their discovery of aluminum borohydride, Schlesinger, Sanderson, and Burg noted that it formed 1:1 adducts with trimethylamine, ammonia, and ether, all of which had some stability at room temperature.[2] Further addition of trimethylamine to its adduct resulted in the cleavage of the aluminum–boron framework to produce $(CH_3)_3NBH_3$. More recently, it has been reported that a total of 4 equiv of amine will react with aluminum borohydride to degrade it to adducts of

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(2) H. I. Schlesinger, R. T. Sanderson, and A. B. Burg, *J. Am. Chem. Soc.*, **62**, 3421 (1940).