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Molecular Structure of 1,5-Dicarba-*closo*-pentaborane(5) and 1,6-Dicarba-*closo*-hexaborane(6), by Gas-Phase Electron Diffraction

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Gas-phase electron diffraction patterns of 1,5-dicarba-*closo*-pentaborane and 1,6-dicarba-*closo*-hexaborane were recorded at room temperature. Least-squares analyses of the reduced intensity data confirmed the D_{3h} and D_{4h} symmetry of the respective carboranes in the gas phase. The carbon atoms are located at apical positions in the polyhedra and may be considered as bonded to a planar girdle of three and four boron atoms, respectively. The bond lengths for the 1,5-dicarba-*closo*-pentaborane(5) with D_{3h} symmetry are B–C = 1.556 Å, B–B = 1.853 Å, C–H = 1.071 Å, and B–H = 1.183 Å. The bond angles are BCC = 73.05°, CBB = 53.48°, and CBC = 93.16°. The distance from the apical carbon atom to the belt is 1.131 Å. The bond lengths for the 1,6-dicarba-*closo*-hexaborane(6) with D_{4h} symmetry are B–C = 1.633 Å, B–B = 1.720 Å, C–H = 1.103 Å, and B–H = 1.244 Å. The bond angles are B_2CB_3 = 63.56°, CBB = 58.22°, CBC = 83.73°, and B_2CB_4 = 96.26°. The distance from the apical carbon atom to the belt of four boron atoms is 1.090 Å. Comparisons were made with related compounds whose structures were determined from microwave spectra or X-ray diffraction data.

Introduction

During the past few years the structures of the small carboranes have been investigated almost exclusively *via* their ^1H and ^{11}B nuclear magnetic resonance spectra. While this technique provides information on the number of equivalent atoms and thus imposes restrictions on the postulated atom connectivities and molecular symmetry, the magnitudes of the geometric parameters and of their vibrational amplitudes must be derived from diffraction and rotation–vibration spectra. Because the necessary crystalline samples are not readily available, X-ray crystal analysis is not generally applicable to the small *closo*-carboranes; however, for several of the carboranes microwave spectra have yielded interesting structural parameters.[1-3]

For the ortho, meta, and para carboranes Bohn[4] reported structures derived from electron diffraction data. In this report we present structural parameters for the two smallest members of the *closo*-carborane series 1,5-$B_3C_2H_5$ and 1,6-$B_4C_2H_6$ deduced from electron diffraction patterns of the gas phase.

Experimental Section

1,5-$B_3C_2H_5$. A sample of 1,5-$B_3C_2H_5$ was obtained from Chemical Systems, Inc.[5] Based on glpc analysis it was found to be at least 98% pure. The sample tube, which was fitted with a high-vacuum Rota-flow needle valve, was connected directly to the nozzle lead tube of the electron diffraction apparatus. The sample remained at room temperature while sectored photographs were taken with the Cornell instrument.[6] The sample to plate distances and wavelengths were established by concurrently recording MgO diffraction patterns[7] [λ 0.052125 and 0.048539 Å at sample to plate distances of 263.8 mm (q = 10–56 Å^{-1}) and 130.3 mm (q = 20–96 Å^{-1}) respectively, where $q = (40/\lambda) \sin \theta/2$]. All patterns were recorded on 4 × 5 in. Kodak Electron Image plates. The radial optical density functions for the diffraction data were obtained with a double-beam Jarrel-Ash densitometer, interfaced with a digital recorder. Three and four data sets were taken for the long and short nozzle to plate distances, respectively. These were converted to relative intensities, interpolated at integral values of q, corrected for nonflatness of the focal plane and averaged.

1,6-$B_4C_2H_6$. The sample of 1,6-$B_4C_2H_6$ was also obtained from Chemical Systems, Inc.,[5] analyzed by glpc, and found to be at least 96% pure. A portion of this sample was purified by gas chromatography on an F & M 700 with 3-ft columns of Apeizon L on Chromosorb P. The sample used for the electron diffraction study was at least 99% pure. Sectored patterns were recorded with a wavelength of 0.058104 and 0.048539 Å at sample to plate distances of 278.4 mm (q = 7–47 Å^{-1}) and 123.4 mm (q = 20–110 Å^{-1}), respectively. MgO patterns taken concurrently established the long nozzle to plate distance at 278.4 mm; the short distance of 123.4 mm was checked with CO_2 diffraction patterns, recorded concurrently with the sample.[8,9] Four data sets for each distance were collected, processed, corrected for the photographic plate saturation,[10] and averaged. The procedure for structural analysis has been described elsewhere.[11-13]

The reduced intensities for 1,5-$B_3C_2H_5$ and 1,6-$B_4C_2H_6$ have been deposited with NAPS.

Results

1,5-$B_3C_2H_5$. The relative scattered intensity as a function of the angle [q(Å^{-1})] has been plotted, along with a refined background, in Figure 1a. The reduced scattered intensity [$qM(q)$] as a function of q is shown in Figure 2a. On the basis of the ^1H nmr and ^{11}B nmr data[14] the molecular configuration of the $B_3C_2H_5$ carborane was assumed to be D_{3h}, a trigonal bipyramid with C-H at the apical positions. If this symmetry is assumed, then by placing the origin of coordinates at the intersection of the C_3 axis and the three C_2 axes, only four parameters are required to specify the coordinates of the atoms: distance from origin to carbon (o–C), distance from origin to boron (o–B), and the C–H and B–H distances.

Twelve vibrational parameters are needed to describe the atom-pair vibrational motions (l_{ij}). Since the long nonbonded l_{ij}'s are less sensitive to the least-squares refinement of the $qM(q)$ curve, they were set at reasonable values (estimated from the radial distribution curve, Figure 3a) and held fixed until the final refinement step. In the final calculation all four of the geometrical parameters and ten of the vibrational parameters were varied, holding only $l(H_7\text{---}H_8)$ and $l(H_6\text{---}$

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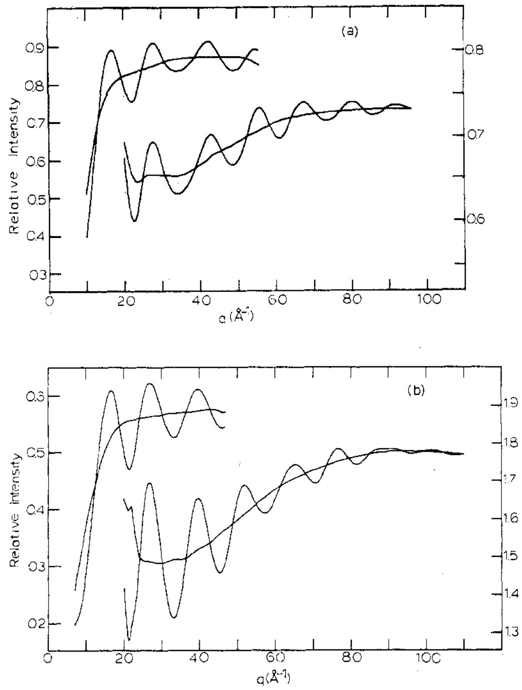

Figure 1. The relative scattered intensity and refined background curves for (a) 1,5-$B_3C_2H_5$ (splice point $q = 46$ Å^{-1}) and (b) 1,6-$B_4C_2H_6$ (splice point $q = 42$ Å^{-1}).

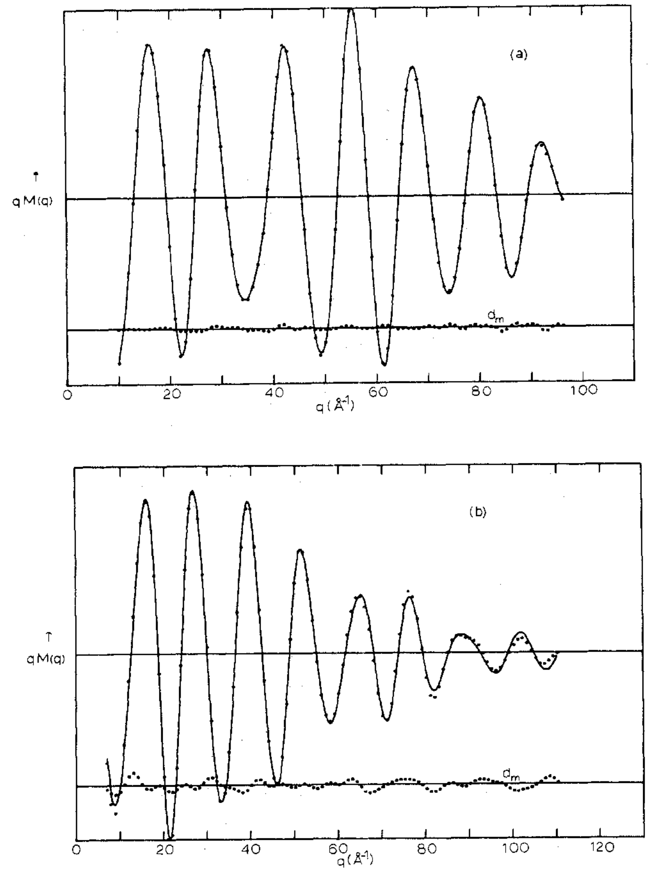

Figure 2. The reduced experimental molecular scattering curves, $qM(q)$ (dots), the theoretical $qM(q)$ (solid line), and the dashed difference curve, d_m (experimental minus theoretical), for (a) 1,5-$B_3C_2H_5$ and (b) 1,6-$B_4C_2H_6$.

H_{10}) fixed. The final standard deviation and R factor were 0.00937 and 0.01633, respectively.[15]

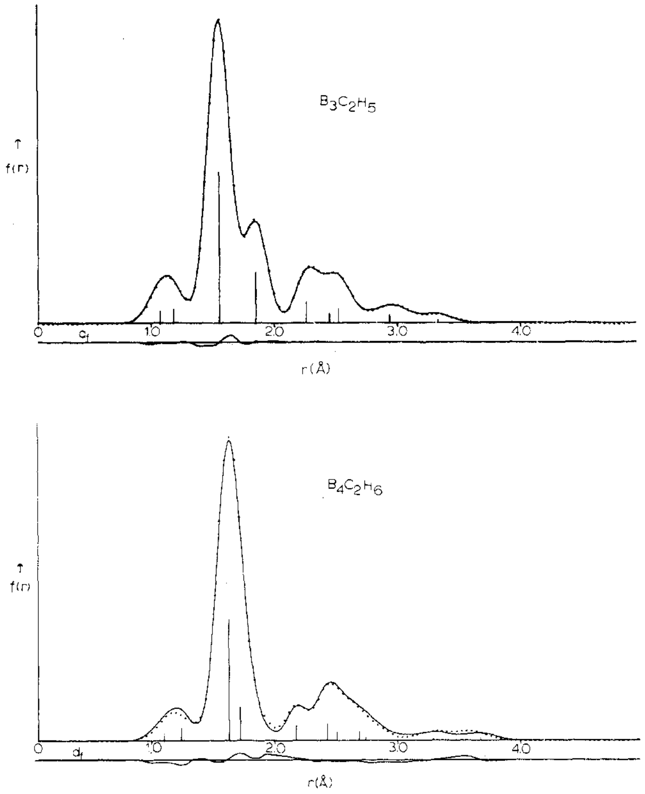

Figure 3. The refined experimental radial distribution curve (dots), the theoretical radial distribution curve (the solid line), and the difference curve, d_f (experimental minus theoretical), for (a) 1,5-$B_3C_2H_5$ and (b) 1,6-$B_4C_2H_6$.

The radial distribution curve shown in Figure 3a was obtained after a series of refinements of the background. The difference between the experimental and "best" model curves, shown in Figure 3a, is denoted by the dashed line, d_f. The first peak is a superposition of the terminal C-H and B-H bonded distances. The second and third peaks at 1.55 and 1.85 Å are clearly resolved and are assigned to the B-C and B-B bonded distances, respectively. The fourth peak at 2.26 Å is due to the C---C nonbonded distance, while B---H_6 and C---H_7 nonbonded distances comprise the fifth peak centered at 2.50 Å. In the radial distribution curve the atom-atom pair distances are indicated by vertical lines; the height of each was made proportional to the theoretical peak height. Values for the geometrical parameters and the root-mean-square amplitudes were refined in a series of least-squares calculations to match the $qM(q)$ curve. The best set of geometric and thermal parameters for the 1,5-$B_3C_2H_5$ is summarized in Table I. The reduced experimental molecular intensity curve and that calculated for the best model are shown in Figure 2a along with the difference curve, d_m.

1,6-$B_4C_2H_6$. The optical density data were evaluated and processed in the manner described for 1,5-$B_3C_2H_5$ and plotted as a function of the scattering angle, along with a refined background in Figure 1b. The $qM(q)$ curve was plotted as a function of the scattering angle in Figure 2b. After the usual refinement procedure a radial distribution curve, shown in Figure 3b, was obtained. The first peak, although not resolved, is due to the C-H and B-H terminal distances. The second peak centered at 1.70 Å is due to the B-B and B-C distances while the third is clearly resolved and attributed to the C---C distance. Here also, the vertical lines indicate the distance of atom-atom pairs. The available ir, ^1H nmr, and ^{11}B nmr spectra[16] indicate that 1,6-$B_4C_2H_6$ has D_{4h} symmetry with the carbon atoms (C_1 and C_6) located at opposite

[15] $R = \Sigma |I_{obsd} - I_{calcd}| / |I_{calcd}|$; I_{obsd} = observed intensity; I_{calcd} = calculated intensity.

Table I. Geometrical and Thermal Parameters (Å)[a]

		$B_3C_2H_5$	
o-C	1.1306 (0.0017)	l(B-C)	0.0570 (0.0004)
o-B	1.0696 (0.0016)	l(B-B)	0.0614 (0.0012)
C-H	1.0713 (0.0069)	l(B-H)	0.071 (0.006)
B-H	1.1831 (0.0063)	l(C-H)	0.074 (0.009)
		l(C---C)	0.050 (0.003)
		l(H_1---B)	0.122 (0.012)
		l(H_7---C)	0.090 (0.006)
		$B_4C_2H_6$	
o-C	1.0896 (0.0036)	l(B-C)	0.0684 (0.0015)
o-B	1.2160 (0.0030)	l(B-B)	0.0922 (0.0098)
C-H	1.1036 (0.0218)	l(B-H)	0.73
B-H	1.2436 (0.0122)	l(C-H)	0.085
		l(C---C)	0.0519 (0.0099)
		l(B---B)	0.0694 (0.0099)
		l(H_1---B)	0.125 (0.039)
		l(H_2---C)	0.120 (0.030)

[a] The calculated uncertainties are given in parentheses. l_{ij} values shown without accompanying uncertainties were estimated from the radial distribution curve and held fixed during the final calculation. These uncertainties are 3 times the least-squares standard deviation or 0.15% of the quantity listed, whichever is greater.[13]

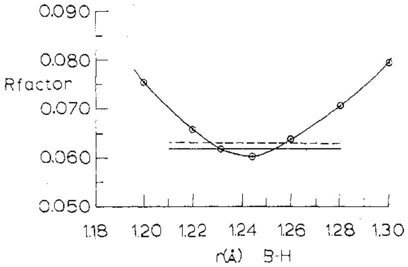

Figure 4. The plot of R factor *vs.* B-H distance where the two horizontal lines refer to the 99.5% (the dashed line) and 95.0% (the solid line) confidence intervals with Hamilton's ratio of R factors ($\mathcal{R}$) corresponding to 1.050 and 1.025, respectively. ($\mathcal{R}$ = R factor/best R factor.)

	Å			
R factor	B-H	C-H	o-B	o-C
0.07551	1.200	1.103	1.217	1.088
0.06570	1.220	1.099	1.217	1.088
0.06020	1.244	1.104	1.216	1.089
0.06364	1.260	1.108	1.215	1.090
0.07057	1.280	1.117	1.215	1.091
0.07934	1.300	1.126	1.214	1.091

The C-H distance was allowed to vary except when the B-H distance was set at 1.160 and 1.180 Å. At these B-H distances, the value of the C-H bond length varied more than 0.1 Å from the best fit value of 1.103 Å. In all other cases deviation from 1.103 Å was less than 0.01 Å.

vertex positions. If the origin is placed at the intersection of the C_4 axis and the four C_2 axes, only four geometrical parameters are required to specify the atom positions. The following four were used: origin to carbon (o-C), origin to boron (o-B), C-H, and B-H. For D_{4h}, CoB = $\pi/2$. Fifteen vibrational parameters are needed to specify the l_{ij}'s. The longer nonbonded l_{ij}'s were held constant in synthesizing the trial radial distribution curves until the final calculation, when only the longest l_{ij}'s were held fixed. In the final calculation all four geometrical parameters and seven vibrational parameters were varied; the l_{ij}'s associated with distances over 3 Å and the l_{ij}'s for the terminal C-H and B-H were held fixed. The final standard deviation and R factor were 0.03327 and 0.06020, respectively.

A second model with D_{2d} symmetry was also tested; the carbon-origin-bond angle (CoB) was introduced as an additional parameter. The least-squares calculation reduced this parameter to 89.89° (0.84) with no substantial improvement in the standard deviation or R factor. The fit obtained from the D_{2d} model indicates that on the basis of the available diffraction data the molecule is well represented by D_{4h} symmetry, with a planar girdle of boron atoms placed equidistant between the two apical carbon atoms. The "best" set of parameters is listed in Table I.

Table II. Atom-Pair Distances[a]

Distance					
Bonded	Value, Å	Nonbonded	Value, Å	Angle	Value, deg
		1,5-$B_3C_2H_5$			
C-H	1.071 (0.007)	C---C	2.261 (0.003)	BCB	73.05 (0.01)
B-H	1.183 (0.006)	H_6---B	2.448 (0.005)	CBB	53.48 (0.01)
C-B	1.556 (0.002)	H_7---C	2.520 (0.007)	CBC	93.16 (0.01)
B-B	1.853 (0.002)	B_2---H_8	2.937 (0.007)		
		1,6-$B_4C_2H_6$			
C-H	1.103 (0.022)	C---C	2.179 (0.007)	B_2CB_3	63.55 (0.02)
B-H	1.244 (0.012)	B---B	2.432 (0.006)	CBB	58.22 (0.02)
C-B	1.633 (0.004)	H_7---B	2.508 (0.023)	CBC	83.73 (0.02)
B-B	1.720 (0.004)	H_8---C	2.690 (0.015)	B_2CB_4	96.26 (0.02)
		H_8---B_3	2.744 (0.021)		

[a] The calculated uncertainties are given in parentheses.

The terminal B-H distance of 1.244 Å was of some concern, since the apical B-H in the 2,3-$B_4C_2H_6$[1] and the terminal B-H length in the 1,5-$B_3C_2H_5$ are 1.183 Å. To determine how sensitive our model was to changes in this parameter, the B-H distance was set at a sequence of values, between 1.160 and 1.300 Å, and the least-squares reduction repeated, in which the same seven l_{ij}'s and the three remaining geometrical parameters were simultaneously varied. Throughout the range of 1.200-1.300 Å, the B-H and C-H bond distances correlate well. The C-H varies by 0.02 Å, while the origin to carbon and origin to boron parameters differ by less than 0.003 Å. However, for any specified B-H distance less than 1.200 Å, the C-H bond length would differ by more than 0.10 Å from the best fit value of 1.103 Å. A plot of the B-H distance *vs.* resulting R factors is shown in Figure 4. On applying Hamilton's ratio of R factors ($\mathcal{R}$) to test the significance of our results,[17] a 95% confidence limit confines the B-H bond length between 1.23 and 1.25 Å. In comparison a 99.5% confidence interval limits the B-H distance between 1.23 and 1.26 Å. From our model the best fit distance is 1.244 Å, which also agrees quite well with the average terminal B-H distance of 1.24 Å derived from preliminary work on the 2,4-$B_5C_2H_7$.[18] The final internuclear distances and bond angles for these molecules are shown in Table II.

Discussion

The symmetry of 1,5-$B_3C_2H_5$ and 1,6-$B_4C_2H_6$ as derived from ^1H nmr and ^{11}B nmr spectra are substantiated by these electron diffraction studies. In both molecules the carbon atoms are located at apical positions in the polyhedron and may be considered as bonded to a planar girdle of three and four borons, respectively. The B-B bond lengths obtained in this study are consistent with those reported in preliminary work by Cheung, Beaudet, and Segal[19] while the B-C distances are in agreement with those reported for 2,3-dicarba-*closo*-hexaborane(1). In the microwave structure of 2,3-$B_4C_2H_6$ the B(1)-B(4) distance of 1.721 Å and B(4)-B(5)

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distance of 1.752 Å compare well with the B–B distance of 1.72 Å in 1,6-$B_4C_2H_6$. The boron–carbon distances are also quite close, being 1.605 Å for B(4)–C(3) in 2,3-$B_4C_2H_6$ and 1.620 Å in 1,6-$B_4C_2H_6$. If one considers the 2,3-$B_4C_2H_6$ and 1,6-$B_4C_2H_6$ to be "near" octahedra, the B----B nonbonded distances between opposite vertices are 2.436 and 2.41 Å, respectively. However, in contrast to the microwave data, which estimated the B–H apex distance to be 1.183 Å, the present electron diffraction data show 1.244 Å for 1,6-$B_4C_2H_6$. As noted above, the latter value compares favorably with preliminary data on the *closo*-2,4-$B_5C_2H_7$[18] and with the electron diffraction data on bis(trifluorophosphine)diborane(4), in which the B–H was reported to be 1.252 Å.[20]

The compound 1,5-$B_3C_2H_5$ differs markedly from either the 1,6- or 2,3-$B_4C_2H_6$. In contrast to the six-membered polyhedra, the B–C is shorter (1.556 Å *vs.* 1.62 Å for the 1,6-$B_4C_2H_6$) and the B–B distance longer (1.85 Å compared to 1.72 Å for the 1,6-$B_4C_2H_6$). The B–H distance is 1.183 Å, in closer agreement with B–H terminal bond lengths as determined in other molecules.[21] The B–B distance of 1.85 Å is long in comparison with comparable separations found in the octahedral carboranes. As noted by Beaudet[19] this suggests the 1,5-$B_3C_2H_5$ may be viewed as a classically bonded structure, in which the trigonal bipyramid is bonded through the C–B–C bonds, but involves no strong B–B overlap.

In this particular case the closer approach of the boron to carbon distance (1.556 Å in 1,5-$B_3C_2H_5$ and 1.62 Å in 1,6-$B_4C_2H_6$) may result in a substantially weakened B–B bond. The more electronegative carbon atoms can drain electron density away from the boron atoms resulting in a decrease in the boron–carbon distance, thus allowing a weakening and substantial lengthening of the boron–boron bond. This effect has been noted previously by Bohn in the electron diffraction structures of the ortho, meta, and para carboranes. The B(2)–B(3) bond in *m*-$B_{10}Br_2H_8C_2H_2$, in which the B(2,3) borons are bonded to two carbon atoms each, has a particularly long distance of 1.89 Å as determined by X-ray diffraction.[22]

Registry No. 1,5-$B_3C_2H_5$, 20693-66-7; 1,6-$B_4C_2H_6$, 20693-67-8.

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Preparation and Lewis Basicity toward Borane of Difluorophosphites

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Ethyl and trifluoroethyl difluorophosphites (PF_2OTfet), as well as the previously reported methyl difluorophosphite, have been prepared directly from the reaction of PF_3, pyridine, and the appropriate alcohol. PF_2OEt and PF_2OTfet combine with B_2H_6 to form adducts which exhibit temperature-dependent ^1H nmr spectra. A series of base displacement reactions established the base strength toward borane as $PF_2OEt > PF_2OMe > PF_2OTfet$. This basicity order is mirrored by the series of values of the J_{PB} coupling constants.

The main synthetic route to difluorophosphites[1,2] has involved a metathetical reaction using a fluorinating agent, mainly SbF_3, and the corresponding chloro compound. The chloro derivative is prepared from the reaction of PCl_3, an alcohol, and a tertiary amine. Difluorophosphites are also produced in the reaction of either PF_5 or PF_3 and $P(OMe)_3$[3] and from the reaction of PF_3, epoxides, and a tertiary amine.[4] The utility of the latter reactions is limited by many side products and low yields. No good single-step syntheses have been reported for the preparation of difluorophosphites.

Recently there has been considerable interest in the basicity toward borane of certain phosphines. Cowley and Damasco[5] have reported an empirical relationship between the J_{PB} coupling constant and the base strength of a series of phosphines; however, in a study by Rudolph and Schultz[6] a correlation between the magnitude of J_{PB} and the dative bond strength for the adducts did not appear to be general except for the case where the phosphine belongs to a series of smoothly varying phosphine ligands [*i.e.*, $PF_2X \cdot BH_3$ (X = F, Cl, Br) or $PF_{3-n}H_n \cdot BH_3$]. Foester and Cohn[7] have reported that a 1:1 correlation between base strength and J_{PB} is not possible in a series of the type PF_2X (X = Me, MeO, Me_2N, MeS). The base strengths of these structurally similar phosphines[8,9] were determined by displacement reactions with the assumptions that the entropy change upon coordination should be fairly constant and any contributions to entropy differences small.

The order of base strengths and of J_{PB} values for a series

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