Derivatives of the Hypho Class of Boron Hydrides. I. The Molecular Structure and Nuclear Magnetic Resonance Spectra of Stereochemically Nonrigid $B_6H_{10}[P(CH_3)_3]_2$

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Abstract: The reaction of $P(CH_3)_3$ with B_6H_{10} in THF or in a hydrocarbon produces $B_6H_{10}[P(CH_3)_3]_2$ which can be isolated as a crystalline solid; it is stable at room temperature for several days under vacuum. An x-ray structure determination shows that the boron structure of $B_6H_{10}[P(CH_3)_3]_2$ is not a pentagonal pyramid as in B_6H_{10} but more closely resembles a fragment of the equatorial belt of an icosahedron. Based upon the molecular structure, the skeletal electron count of 20 electrons reveals that $B_6H_{10}[P(CH_3)_3]_2$ is a derivative of the hypho class of boron hydrides in which the number of skeletal electrons is given by $2n + 8$ where n = number of boron vertices in the polyhedral structure. Variable temperature ^1H NMR spectra reveal that the molecule is stereochemically nonrigid with bridging hydrogens exchanging positions with terminal BH_2 hydrogens.

In the presence of strongly basic anions such as H^- or in the presence of the molecular base ammonia, the boron hydrides B_5H_9 and B_6H_{10} function as Brönsted acids[1] each yielding a proton to form the conjugate bases $B_5H_8^-$ and $B_6H_9^-$. On the other hand these boron hydrides form readily discernible bis-ligand adducts with the molecular bases $N(CH_3)_3$ and $P(CH_3)_3$.[2]

It has been recently shown that the bis-ligand adducts of pentaborane(9), $B_5H_9L_2$, are members of a class of previously unrecognized polyhedral structures which contain $2n + 8$ skeletal electrons, where n is the number of vertices occupied by boron atoms.[3] This class has been assigned the name hypho (Greek for net),[4,5a] and represents an extension of the previously recognized classes closo, nido, and arachno[5b] which can be shown to contain $2n + 2$, $2n + 4$, and $2n + 6$ skeletal electrons, respectively.[6,7] In principle, $B_6H_{10}L_2$ adducts should belong to the hypho class. In the present study we verify this point from the determination of the molecular structure of $B_6H_{10}[P(CH_3)_3]_2$ which in turn permits a skeletal electron count as defined by Wade,[6] and by Rudolph.[7] We also show in the present study that the adduct $B_6H_{10}[P(CH_3)_3]_2$ is stereochemically nonrigid on the proton NMR time scale.

Experimental Section

Apparatus and NMR Equipment. Standard vacuum line and inert atmosphere techniques were used to handle volatile, moisture-, and air-sensitive materials. ^1H NMR and boron-11 NMR spectra were obtained using a Varian HA-100 high-resolution spectrometer at 100 and at 32.1 MHz, respectively. All ^1H NMR chemical shifts are given in τ units relative to $(CH_3)_4Si = \tau$ 10.00, using $CH_2Cl_2 = \tau$ 4.65 as the internal standard. Boron-11 NMR shifts were obtained relative to $BF_3O(C_2H_5)_2$, δ 0.00 ppm. The NMR spectrometer was equipped with heteronuclear decoupling accessories which are described elsewhere.[8]

Materials. All solvents were dried over $LiAlH_4$ and stored in glass vessels having Teflon valves. Hexaborane(10) was prepared from $1\text{-}BrB_5H_8$ and B_2H_6 by the method of Johnson, Brice, and Shore:[9] it was stored at −78° until used. Trimethylphosphine was prepared from CH_3MgI and PCl_3 in ether and was stored as the silver iodide complex. It was regenerated by heating the complex to 150°.[10] Trimethylphosphine-d_9 was prepared in the same way with the Grignard being prepared from CD_3I.

Preparation and Properties of $B_6H_{10}[P(CH_3)_3]_2$. In a typical preparation, 2.0 mmol of B_6H_{10} and 4.0 mmol of $P(CH_3)_3$ were dissolved in n-heptane and stirred at room temperature for 30 min. Solvent was pumped away from the system at room temperature leaving a white crystalline product which is stable at room temperature under vacuum for several days. It melts with decomposition at 125°. Anal. Calcd for $B_6H_{10}[P(CH_3)_3]_2$: B, 28.5; hydridic H, 4.44. Found: B, 26.8; hydridic H, 4.40.

The prominent infrared frequencies of $B_6H_{10}[P(CH_3)_3]_2$ in a Nujol mull are, cm^{-1} (intensity): 2440 (vs) 2390 (s), 2380 (sh), 2370 (m), 2295 (sh), 1885 (vw), 1410 (m), 1308 (w), 1298 (s), 1153 (m), 1059 (m), 955 (s), 945 (s), 902 (m), 860 (w), 840 (w), 820 (m), 750 (m), 735 (m), 620 (m).

The following lines appeared in the x-ray powder diffraction pattern of $B_6H_{10}[P(CH_3)_3]_2$, dÅ (intensity): 4.11 (vw), 3.92 (m), 3.05 (w), 2.88 (vw), 2.80 (vs), 2.66 (vs), 2.39 (m), 2.24 (w), 2.17 (m), 2.06 (s), 1.92 (w), 1.79 (w), 1.72 (v), 1.67 (vw), 1.62 (vw), 1.56 (w), 1.52 (m), 1.48 (w), 1.41 (m), 1.28 (w), 1.28 (m).

A tensimetric titration at 0° in which small increments of $P(CH_3)_3$ were added to 2 ml of 0.5 M B_6H_{10} in n-heptane further established the reaction stoichiometry at 2 mol of $P(CH_3)_3$ per mole of B_6H_{10}. The titration curve gave no indication of a 1:1 stoichiometric reaction. The adduct $B_6H_{10}[P(CH_3)_3]_2$ is essentially insoluble in methylcyclohexane and n-heptane, but shows significant solubility in methylene chloride and THF. Whereas B_6H_{10} is readily deprotonated by KH, the adduct does not appear to react with KH in THF.

X Ray Structure Determination of $B_6H_{10}[P(CH_3)_3]_2$. Single crystals of $B_6H_{10}[P(CH_3)_3]_2$ were grown from ethyl ether at 0° and sealed under dry N_2 in thin-walled glass capillaries. Preliminary precession photographs showed the unit cell to be monoclinic. Systematic extinctions ($h0l$, $l \neq 2n$; $0k0$, $k \neq 2n$) uniquely defined the space group as $P2_1/c$. From single-crystal diffractometry, cell dimensions were obtained: $a = 12.145$ (3), $b = 12.051$ (4), $c = 12.231$ (3) Å; $\beta = 114.65$ (2)°. An assumed $Z = 4$ gave $d_{\text{calcd}} = 0.930$. Cell dimensions and an orientation matrix for data collection were obtained by a least-squares refinement of the setting angles for 15 reflections, well-centered, on a Syntex $P\bar{1}$ automated diffractometer (using Mo Kα radiation) ($\lambda = 0.7107$ Å). The crystal was plate-like of approximate dimensions 0.3 × 0.2 × 0.1 mm. Intensities were collected by scanning in 2θ (scan rate = 4°/min, scan range = 3°, 2θ max = 50°) (using Mo Kα radiation), monochromatized by reflection from the (004) plane of an oriented graphite monochromator (2θ mon = 11.69°). A rapid scan rate was chosen because of the tendency for the compound to decompose at room temperature. Data collection at a lower temperature did not appear to be feasible because of a phase change which appears to occur several degrees below 0° which resulted in shattered crystals. Of the 3853 reflections which were measured, 2199 were greater than $3\sigma(I)$ and were regarded as observed. Corrections for Lorentz and polarization effects were applied. Three standard reflections were measured periodically; they showed a decrease in intensity of about 4% over the course of data collection.

The structure was solved by direct methods and Fourier techniques.[11] The 163 reflections having $E_{\text{obsd}} \geq 1.20$ were used to calculate an E map from which the positions of the phosphorus and

Table I. Fractional Coordinates and Thermal Parameters for $B_6H_{10}[P(CH_3)_3]_2$[a]

Atom	10^4x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}.
P(1)	5225 (1)	4014 (1)	2577 (1)	504 (7)	514 (7)	711 (8)	−35 (6)	292 (6)	−42 (6)
P(2)	319 (1)	2774 (1)	1883 (1)	389 (6)	587 (7)	464 (6)	−2 (5)	185 (5)	−27 (6)
B(1)	1964 (5)	4446 (7)	3739 (6)	538 (34)	1034 (54)	727 (42)	−41 (35)	270 (31)	−324 (40)
B(2)	2898 (4)	3829 (5)	3067 (5)	405 (25)	511 (30)	459 (26)	−41 (22)	155 (21)	−71 (22)
B(3)	3748 (5)	4662 (4)	2418 (5)	559 (30)	358 (25)	583 (31)	−17 (23)	235 (25)	−50 (23)
B(4)	2882 (7)	5236 (7)	961 (7)	701 (41)	918 (56)	893 (51)	−134 (38)	145 (37)	425 (44)
B(5)	2400 (5)	4012 (5)	1481 (5)	471 (27)	539 (31)	442 (27)	−63 (24)	123 (22)	72 (24)
B(6)	1330 (5)	4027 (5)	2184 (5)	426 (26)	518 (30)	569 (31)	65 (23)	163 (24)	−50 (25)
C(1)	995 (5)	1608 (5)	2839 (6)	643 (33)	645 (36)	1047 (48)	−10 (28)	329 (33)	114 (33)
C(2)	−213 (5)	2254 (6)	375 (5)	630 (32)	1086 (48)	723 (35)	−302 (33)	343 (28)	−305 (35)
C(3)	−1046 (4)	3078 (5)	2072 (5)	496 (27)	923 (41)	632 (31)	85 (26)	277 (24)	24 (28)
C(4)	6300 (6)	5054 (6)	2582 (7)	862 (42)	934 (48)	1468 (54)	−84 (38)	765 (45)	2 (46)
C(5)	5993 (6)	3261 (6)	3975 (6)	670 (36)	985 (49)	980 (49)	98 (35)	189 (34)	196 (39)
C(6)	5104 (7)	3045 (6)	1415 (7)	1136 (55)	990 (55)	1095 (54)	243 (44)	544 (45)	−259 (43)

[a] The complete temperature factor expression is $\exp\{-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl)\}$.

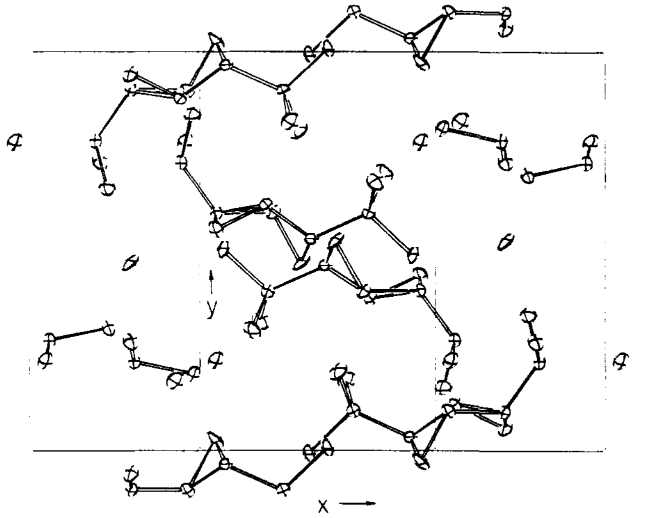


Figure 1. Packing diagram of non-hydrogen atoms.

carbon atoms were located. Least-squares refinement of coordinates and isotropic temperature factors gave a conventional R of 0.340. A Fourier map was then calculated which established the location of the boron atoms. After five cycles of least-squares refinement in which isotropic temperature factors were used for all atoms, R decreased to 0.240. Conversion to anisotropic temperature factors reduced R to 0.140.

Initial attempts to refine carbon atoms anisotropically gave unsatisfactory P-C distances, as well as extremely large temperature factors. In order to obtain a better model, the carbon atoms were removed, and a difference electron density synthesis was calculated. Although the carbon atoms were apparently disordered, it is possible that large thermal motions cause overlapping of atom pairs to produce a single peak. Since all attempts to resolve the disorder were unsuccessful, the approximate model was retained. A difference electron density synthesis was calculated which revealed the sites of all hydrogen atoms and contained no prominent peaks other than those attributable to hydrogen.

Full-matrix least-squares refinements with anisotropic temperature factors for phosphorus, carbon, and boron, and isotropic temperature factors for hydrogens gave a final conventional R of 0.070 and a final weighted R of 0.074. For the final least-squares refinements, data were weighted by the function $w = 1/\sigma^2$ where $\sigma^2 = 10.36 + |F_o| - 0.0085|F_o|^2 + 0.00015|F_o|^3$, and corrections for anomalous dispersion were included.[12] The error in an observation of unit weight Σ was $\Sigma = 0.86$. Refinement was terminated when the shifts in all parameters were less than one-fourth of the estimated standard deviations. The atomic scattering factors for B, C, and N were taken from the tabulation of Cromer and Waber.[13] The hydrogen atomic scattering factors were obtained from the calculations of Stewart, Davidson, and Simpson.[14,15]

Results and Discussion

Crystal and Molecular Structure of $B_6H_{10}[P(CH_3)_3]_2$. Positional and anisotropic thermal parameters of non-hydrogen atoms are listed in Table I. Positional and isotropic thermal parameters of hydrogen atoms are listed in Table II. Figure 1 is a packing diagram. There are no abnormally short nonbonded contact distances between different molecules in the structure.

Table II. Fractional Coordinates and Thermal Parameters for the Hydrogen Atoms

Atom	10^3x	y	z	U
H(1)	181 (10)	391 (9)	448 (9)	0.075
H (11)	189 (10)	530 (9)	386 (10)	0.075
H(12)	305 (8)	430 (8)	402 (8)	0.051
H(2)	314 (8)	294 (8)	336 (8)	0.051
H(3)	394 (9)	529 (8)	299 (8)	0.053
H(4)	325 (11)	514 (9)	32 (11)	0.085
H(44)	270 (9)	604 (8)	93 (8)	0.085
H(45)	203 (10)	473 (9)	63 (10)	0.073
H(5)	259 (8)	322 (9)	112 (8)	0.054
H(6)	81 (9)	474 (8)	177 (8)	0.054
H(111)	154 (10)	133 (9)	262 (10)	0.073
H(112)	53 (10)	107 (9)	270 (10)	0.073
H(113)	135 (10)	180 (9)	366 (10)	0.073
H(21)	−72 (10)	169 (9)	22 (9)	0.073
H(22)	−53 (9)	282 (9)	−11 (9)	0.073
H(23)	41 (9)	207 (9)	28 (9)	0.073
H(31)	−152 (10)	243 (10)	194 (10)	0.073
H(32)	−92 (10)	337 (9)	269 (9)	0.073
H(33)	−149 (10)	366 (9)	152 (10)	0.073
H(41)	686 (11)	471 (10)	260 (11)	0.094
H(42)	600 (11)	545 (10)	183 (11)	0.094
H(43)	645 (11)	553 (10)	332 (11)	0.094
H(51)	547 (11)	264 (10)	391 (10)	0.088
H(52)	602 (11)	363 (10)	445 (10)	0.088
H(53)	703 (11)	303 (10)	430 (10)	0.088
H(61)	468 (11)	343 (11)	63 (11)	0.097
H(62)	578 (11)	277 (11)	149 (11)	0.097
H(63)	477 (11)	250 (11)	152 (11)	0.097

Figures 2 and 3 provide two different views of the molecular structure, showing thermal motion ellipsoids.[16] The molecule has approximate C_2 symmetry. Selected bond distances and bond angles are provided in Tables III and IV, respectively. Within the B_6H_{10} moiety, distances compare well with those normally found in boron hydrides. The range of boron-boron distances is 1.745 (7) to 1.841 (9) Å. Within the triangular faces, B-B-B angles vary from 57.4 (3) to 62.8 (3)° with an average value of 61.6°. The boron-hydrogen bonds range from 0.99 (5) to 1.19 (6) Å. One bridge is symmetric with B-H (bridge) distances of 1.23 (5) Å, while the other is asymmetric with B-H (bridge) distances of 1.05 (7) and 1.29 (5) Å. The P(2)-B(6) and the P(1)-B(3) distances are 1.884 (6) and 1.890 (6) Å compared to B-P distances of 1.90 (1) and 1.98 (1) Å which involve the apically and basally coordinated trimethylphosphines in the pyramidal $B_5H_9[P(CH_3)_3]_2$ molecule.[3] The trimethylphosphines show normal tetrahedral geometry.

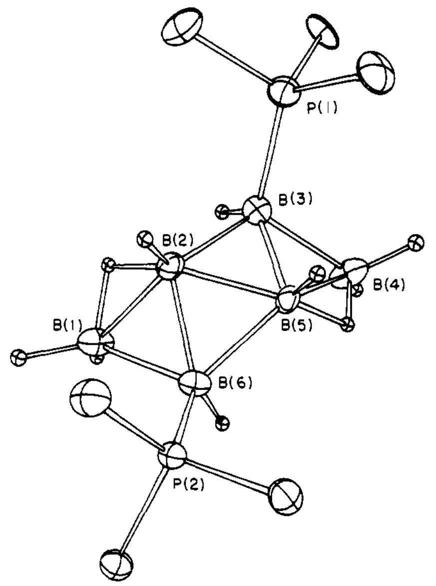


Figure 2. Structure of $B_6H_{10}[P(CH_3)_3]_2$ showing thermal motion ellipsoids.

Table III. Bond Distances (Å) of $B_6H_{10}[P(CH_3)_3]_2$[a]

P(2)–B(6)	1.883 (6)	B(5)–B(4)	1.798 (11)
P(1)–B(3)	1.890 (6)	B(2)–B(1)	1.814 (11)
P(2)–C(1)	1.792 (6)	B(6)–H(6)	1.06 (4)
P(2)–C(2)	1.794 (6)	B(3)–H(3)	0.99 (5)
P(2)–C(3)	1.805 (6)	B(5)–H(5)	1.12 (5)
P(1)–C(4)	1.808 (8)	B(5)–H(45)	1.29 (5)
P(1)–C(5)	1.812 (7)	B(2)–H(2)	1.14 (4)
P(1)–C(6)	1.798 (9)	B(2)–H(12)	1.24 (5)
B(5)–B(6)	1.833 (10)	B(1)–H(1)	1.19 (6)
B(2)–B(6)	1.770 (7)	B(1)–H(11)	1.04 (5)
B(6)–B(1)	1.801 (9)	B(1)–H(12)	1.23 (5)
B(3)–B(5)	1.745 (7)	B(4)–H(44)	0.99 (5)
B(3)–B(2)	1.841 (9)	B(4)–H(4)	1.05 (7)
B(3)–B(4)	1.788 (9)	B(4)–H(45)	1.11 (6)
B(5)–B(2)	1.788 (8)		

[a] The average C–H distance is 0.90 (6) Å.

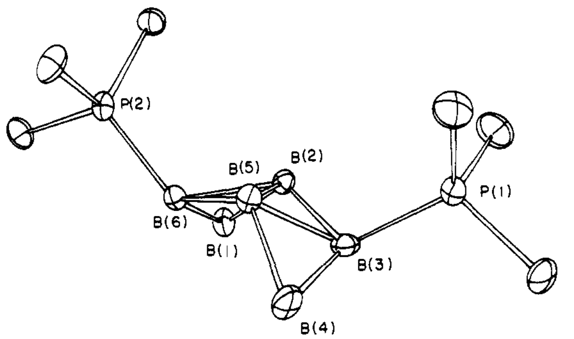


Figure 3. Conformation of the B_6 framework in $B_6H_{10}[P(CH_3)_3]_2$.

Table IV. Bond Angles (deg) in $B_6H_{10}[P(CH_3)_3]_2$[a]

C(1)–P(2)–C(2)	105.5 (3)	B(1)–B(6)–H(6)	101 (3)
C(1)–P(2)–C(3)	105.7 (3)	B(2)–B(6)–H(6)	132 (2)
C(2)–P(2)–C(3)	104.3 (3)	B(5)–B(6)–H(6)	100 (3)
C(1)–P(2)–B(6)	114.7 (2)	P(2)–B(6)–H(6)	110 (2)
C(2)–P(2)–B(6)	114.0 (3)	B(5)–B(3)–H(3)	134 (3)
C(3)–P(2)–B(6)	111.8 (3)	B(2)–B(3)–H(3)	97 (3)
C(4)–P(1)–C(5)	104.9 (3)	B(4)–B(3)–H(3)	106 (2)
C(4)–P(1)–C(6)	105.9 (4)	P(1)–B(3)–H(3)	108 (3)
C(5)–P(1)–C(6)	105.2 (3)	B(6)–B(5)–H(5)	120 (3)
C(4)–P(1)–B(3)	111.5 (3)	B(3)–B(5)–H(5)	111 (2)
C(5)–P(1)–B(3)	113.3 (3)	B(2)–B(5)–H(5)	107 (2)
C(6)–P(1)–B(3)	115.2 (3)	B(4)–B(5)–H(5)	114 (3)
B(5)–B(6)–P(2)	115.6 (4)	B(6)–B(5)–H(45)	108 (3)
B(2)–B(6)–P(2)	117.3 (3)	B(3)–B(5)–H(45)	98 (2)
B(1)–B(6)–P(2)	112.8 (4)	B(2)–B(5)–H(45)	144 (3)
B(5)–B(6)–B(2)	59.5 (3)	B(4)–B(5)–H(45)	38 (2)
B(5)–B(6)–B(1)	115.0 (4)	B(6)–B(2)–H(2)	113 (2)
B(5)–B(3)–P(1)	118.4 (3)	B(3)–B(2)–H(2)	123 (3)
B(2)–B(3)–P(1)	114.2 (3)	B(5)–B(2)–H(2)	113 (2)
B(4)–B(3)–P(1)	113.6 (5)	B(1)–B(2)–H(2)	112 (3)
B(5)–B(3)–B(4)	61.2 (4)	B(6)–B(2)–H(12)	102 (2)
B(2)–B(3)–B(4)	116.0 (4)	B(3)–B(2)–H(12)	106 (2)
B(5)–B(3)–B(2)	59.8 (3)	B(5)–B(2)–H(12)	145 (2)
B(3)–B(5)–B(4)	60.6 (3)	B(3)–B(2)–H(12)	42 (2)
B(6)–B(5)–B(4)	123.8 (5)	B(6)–B(1)–H(1)	121 (2)
B(6)–B(5)–B(2)	58.5 (3)	B(2)–B(1)–H(1)	116 (3)
B(2)–B(5)–B(4)	118.2 (4)	B(6)–B(1)–H(11)	114 (3)
B(3)–B(5)–B(2)	62.8 (3)	B(2)–B(1)–H(11)	125 (4)
B(6)–B(5)–B(3)	110.0 (4)	B(3)–B(4)–H(44)	117 (3)
B(6)–B(2)–B(5)	62.0 (3)	B(5)–B(4)–H(44)	134 (3)
B(6)–B(2)–B(1)	60.3 (3)	B(3)–B(4)–H(4)	116 (3)
B(6)–B(2)–B(3)	108.5 (4)	B(5)–B(4)–H(4)	118 (3)
B(3)–B(2)–B(5)	57.4 (3)	H(5)–B(5)–H(45)	108 (4)
B(3)–B(2)–B(1)	122.8 (4)	H(2)–B(2)–H(12)	103 (3)
B(5)–B(2)–B(1)	116.6 (4)	H(1)–B(1)–H(11)	112 (4)
B(6)–B(1)–B(2)	58.6 (4)	H(44)–B(4)–H(4)	103 (4)
B(3)–B(4)–B(5)	58.2 (4)		

[a] The average H–C–H bond angle is 110 (6)°.

The range of the P-C bond lengths is 1.792 (6) to 1.812 (6) Å. The normal range of P-C bonds in aliphatic phosphines is 1.81-1.85 Å.[17]

The boron framework in $B_6H_{10}[P(CH_3)_3]_2$ closely resembles the equatorial belt of an icosahedron. This is the first demonstrated example of such a structure. However, this arrangement has been proposed for B_6H_{12} on the basis of boron-11 and ^1H NMR spectra.[18]

Figure 3 shows the conformation of the B_6 framework in $B_6H_{10}[P(CH_3)_3]_2$. The relationship of this structure to the pentagonal pyramidal boron arrangement in B_6H_{10} can be visualized by placing B(1) between B(4) and B(6) to form a pentagonal plane.

It has long been recognized that the neutral boron hydrides form two homologous series B_nH_{n+4} and B_nH_{n+6}.[19] These have more recently been termed nido and arachno boron hydrides.[5b] By a method of electron counting stated by Wade[6,20] and Rudolph,[7] the number of so-called "skeletal" electrons can be determined. It can be shown that for the nido series it is $2n + 4$ and for the arachno series it is $2n + 6$, where n is the number of boron atoms at vertices in the polyhedral skeleton. It is seen that the number of skeletal electrons is implied by the formula of the neutral binary hydride. The adduct $B_6H_{10}[P(CH_3)_3]_2$ is isoelectronic with the hypothetical dianion $B_6H_{12}^{2-}$ which in turn is isoelectronic with the hypothetical neutral hydride B_6H_{14}. Thus from the foregoing considerations, B_6H_{14} and its isoelectronic counterpart $B_6H_{10}[P(CH_3)_3]_2$ are expected to belong to a homologous series which contains $2n + 8$ skeletal electrons (20 electrons). Such a series has been recently recognized and established in the case of $B_5H_9[P(CH_3)_3]_2$ where the structure has been determined and the skeletal electron count can be made.[3] Furthermore, the $B_5H_{12}^-$ ion is in principle a member of this series,[21] being isoelectronic with the hypothetical B_5H_{13}. Members of this series are expected to have relatively open and flat frameworks. Indeed, in going from closo to nido to arachno structures in which the number of vertices is constant, the structure becomes more open as the number of skeletal electrons is increased.[4-7,20]

The method for counting skeletal electrons was developed independently by Wade[6] and by Rudolph and Pretzer.[7] We note that these rules can be rationalized in terms of an observation made by Lipscomb.[22] That is: *"In each of the boron hydrides based upon a single polyhedral fragment there are two surfaces, the surface of the terminal H atoms [exo], and a smaller nearly spherical surface containing the B atoms, H bridges, and the extra H atoms [endo] of*

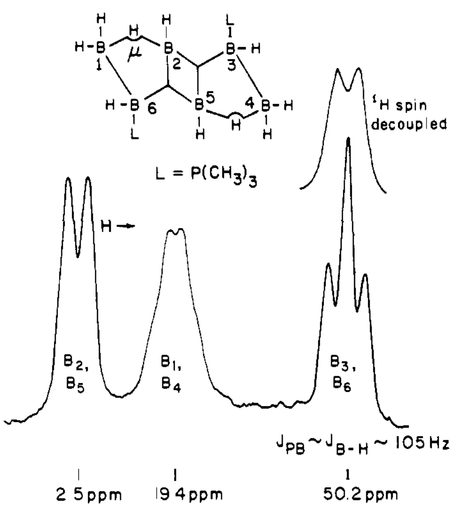
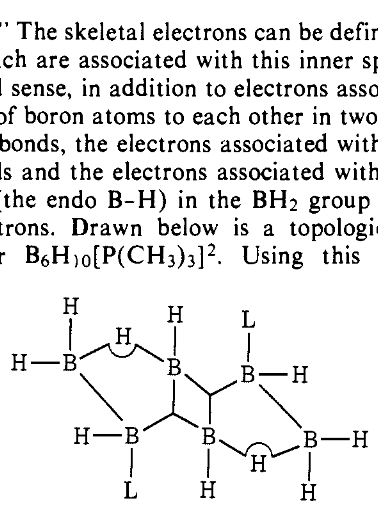


Figure 4. Boron-11 NMR spectrum of $B_6H_{10}[P(CH_3)_3]_2$ in CH_2Cl_2 at 55°.

BH_2 groups." The skeletal electrons can be defined as those electrons which are associated with this inner sphere. Thus in a localized sense, in addition to electrons associated with the bonding of boron atoms to each other in two-center and three-center bonds, the electrons associated with one of the B-H-B bonds and the electrons associated with one of the B-H bonds (the endo B-H) in the BH_2 group are termed skeletal electrons. Drawn below is a topological valence structure for $B_6H_{10}[P(CH_3)_3]^2$. Using this method of counting electrons we obtain 20 skeletal electrons, in agreement with the $2n + 8$ rule.



By successive removal of vertices while retaining the same number of skeletal electrons, the relationship between closo, nido, and arachno structures has been illustrated.[5,7,20] A hypho structure would be derived from a closo structure by removing three vertices. Thus $B_6H_{10}[P(CH_3)_3]_2$ can be considered to be derived from a nine-vertex polyhedron (tricapped prism) which contains 20 skeletal electrons (e.g., $B_9H_9^{2-}$) from which three vertices have been removed to give a boron arrangement which resembles the B_6 structure in this compound.

NMR Spectra. The boron-11 NMR spectrum of $B_6H_{10}[P(CH_3)_3]_2$ taken at 55° in methylene chloride is shown in Figure 4. Assignment of the low field resonance to B_2 and B_5 is based upon the doublet character of the resonance. The high field resonance which is a triplet in the normal spectrum collapses to a doublet when proton decoupling is employed (see inset in Figure 4). This indicates that a single phosphorus-31 and a single proton are bound to a boron atom and spin couple with it with approximately the same coupling constant. Boron atoms B_3 and B_6 are therefore assigned to this resonance. The resonance assigned to B_1 and B_4 is believed to be a poorly resolved quartet which arises from the two terminal hydrogens and the bridging hydrogen associated with each of these boron atoms. The three hydrogens appear to be exchanging on the basis of the proton spectra described below. If it had been possible to observe this spectrum at higher temperature (the compound decomposes in solution above 60°) the spectrum probably would have been better resolved. At about 30° this resonance appears as a broad single peak.

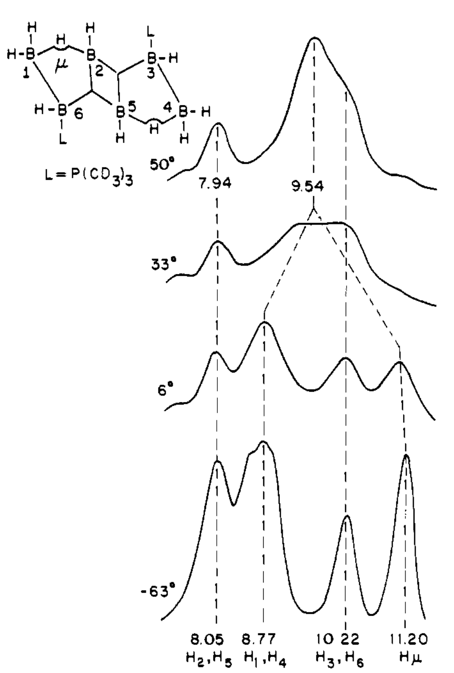


Figure 5. Variable temperature boron-11 spin decoupled ¹H NMR spectra of $B_6H_{10}[P(CH_3)_3]_2$ in CH_2Cl_2.

The proton NMR spectrum of $B_6H_{10}[P(CH_3)_3]_2$ taken at normal rf transmitter power shows just a doublet (τ 8.72), which arises from spin coupling of the phosphorus-31 with the methyl protons ($J_{P\text{-}H}$ = 11.5 Hz). At higher power settings under conditions of boron-11 spin decoupling the resonances of protons attached to boron are observed, but there is some overlap with the doublet due to the methyl protons. Therefore spectra of protons attached to boron were taken of $B_6H_{10}[P(CD_3)_3]_2$.

¹H NMR spectra of $B_6H_{10}[P(CD_3)_3]_2$ with boron-11 spin decoupling were obtained over the temperature range of 50 to −90°. Spectra in which broad band (ca. 1500 Hz) boron-11 decoupling was employed are shown in Figure 5. Positions of proton resonances are essentially constant below 6°. Assignments of resonances are based upon selective narrow band decoupling of boron-11 at frequencies which can be correlated to the individual boron resonances observed in Figure 4. The peak assigned to the H_1 and H_4 protons is given a relative area of 4. (The remaining peaks are all assigned relative areas of 2.) The discontinuity in this peak probably arises from slightly different chemical shifts of the exo and endo hydrogens plus the fact that there was a small amount of protium impurity (ca. 1 atom % protium in the $P(CD_3)_3$). The peak assigned to the H_3 and H_6 protons is somewhat attenuated when broad band decoupling of boron-11 is employed because at the optimum average frequency for decoupling all of the resonances insufficient power is distributed to completely decouple H_3 and H_6. However, when narrow line decoupling is employed this peak is markedly enhanced and is therefore assigned a relative area of two. The peak assigned to the bridge protons has a τ value which falls in the range which is usually observed for bridging protons.[23] This resonance is not especially sensitive to spin decoupling of boron-11 which is also consistent for bridging protons since they generally couple weakly with boron-11.[23] However, some enhancement of this peak did occur when a narrow band boron-11 decoupling frequency was employed which was between the boron-11 frequency which was required to decouple the H_1,

H_4 protons and the frequency which was required to decouple H_2, H_5 protons.

Above 6° the bridging hydrogens and the H_1 and H_4 hydrogens undergo noticeable exchange averaging on the NMR time scale. Exchange appears to be complete at about 50° giving an experimental averaged resonance of τ 9.54. This is in good agreement with the weighted average (τ 9.50) of the individual resonances observed in the limiting spectrum at −63°. The exchange process could occur by means of twisting motions of the BH_2 groups to break hydrogen bridge bonds and place terminal hydrogens in bridging positions while bridging hydrogens move to terminal positions.[3] The essential invariance of the resonances assigned to H_2, H_5, H_3, and H_6 suggests that these hydrogens do not exchange rapidly on the ^1H NMR time scale.

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Supplementary Material Available: structure factors of $B_6H_{10}[P(CH_3)_3]_2$ (18 pages). Ordering information is given on any current masthead page.

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On the Stereochemistry of Polar 2 + 2 Cycloadditions

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Abstract: Quantum mechanical calculations of the restricted Hartree-Fock (RHF) type on model polar 2 + 2 cycloaddition systems predict a transoid approach of the two cycloaddends. This contrasts with the results of experimental studies of polar 2 + 2 cycloadditions, all of which indicate a preferred cisoid approach of the two cycloaddends. These findings suggest that either the *overall* reaction sequence involving a transoid "approach" has a higher barrier than the reaction sequence involving a cisoid approach, forbidden in the Woodward–Hoffmann sense, or that a RHF level of theory is inadequate for the treatment of such reactions.

Polar 2 + 2 cycloadditions have been extensively studied in the past 20 years.[2] These reactions constitute a simple way of constructing functionalized four-member rings which can be further manipulated toward the desired end in the course of a synthesis. Mechanistic interest in these reactions has resurfaced very recently.[3a] At this point, there is sufficient experimental data available so that one can attempt an integration of the known facts into a coherent pattern that will constitute a good approximation of the mechanism of these reactions. In this paper we use theoretical arguments coupled with quantitative calculations at various levels of sophistication in order to interpret the available experimental data and gain insights into the mechanism of 2 + 2 cycloadditions. The calculations which have been employed include Mulliken-Wolfsberg-Helmholtz, abbreviated MWH, calculations,[3b] SCF-MO-CNDO/2 calculations,[4] and ab initio calculations using an STO-4G basis set.[5] These calculations are single determinant calculations of the restricted Hartree-Fock (RHF) type.

The Woodward-Hoffmann rules regarding the stereochemistry of pericyclic reactions stipulate that a thermal 2 + 2 cycloadditions will occur in a 2s + 2a fashion. Now, this stereochemical mode of union is sterically unfavorable, and, as a result, many chemists have reasoned that 2 + 2 cycloadditions will occur in a "stepwise" manner involving a diradical or dipolar intermediate wherein pericyclic bonding is absent. Herein lies the first important point which we wish to emphasize: *the initial hypotheses of many experimentalists who attempted to study the mechanism of 2 + 2 cycloadditions are based upon the one-determinantal*

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