Singly Hydrogen-Bridged Borane Anions Derived from the Hydroboration Products of 1,3-Butadiene. An X-Ray Structure Determination of $[N(n\text{-}C_4H_9)_4{}^+][B_2(C_4H_8)_2H_3{}^-]$

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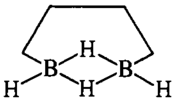
Abstract: Treatment of selected hydroboration products of 1,3-butadiene with potassium hydride results in hydride ion addition to give the singly hydrogen bridged anions μ-hydro-1,2-dihydro-1,2:1,2-bis(tetramethylene)diborate(1−); μ-hydro-1,2-tetramethylene-1,1:2,2-bis(tetramethylene)diborate(1−); μ-butylidene-μ-hydro-1,1:2,2-bis(tetramethylene)diborate(1−); and 1,2-dihydro-1,2-tetramethylene-1,1:2,2-bis(tetramethylene)diborate(2−). Syntheses, reactions, and NMR spectra of these anions are presented. An X-ray structure determination of tetra-*n*-butylammonium μ-hydro-1,2-dihydro-1,2:1,2-bis(tetramethylene)diborate conclusively establishes the existence of a transannular hydrogen bridge.

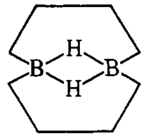
The characterization of organoboranes formed upon hydroborating 1,3-butadiene with B_2H_6 or Lewis base adducts of BH_3 has been of interest for over a decade. Compositions of the products obtained depend upon the ratios of reactants and only relatively recently have the systems been completely elucidated.[1]

When 2 mol of BH_3 (equivalent to 1 mol of B_2H_6) react with 1 mol of 1,3-butadiene, 1,2-tetramethylenediborane(6) (I) is formed.[2,3] The structure of this compound was determined principally through the application of boron-11 and proton NMR spectroscopy.[2,3]



I

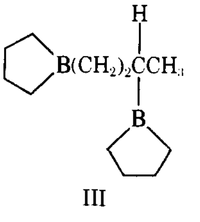
When 2 mol of BH_3 react with 2 mol of 1,3-butadiene, 1,2:1,2-bis(tetramethylene)diborane(6) (II) is formed.[3-5]



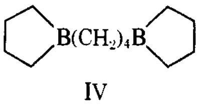
II

This structure which contains a transannular hydrogen bridge system was first championed by Zweifel, Nagase, and Brown.[4] Independent chemical evidence in support of the structure was obtained by Breuer and Brown[5] and Young and Shore.[3]

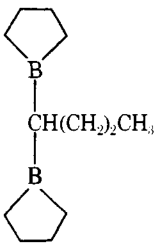
When 2 mol of BH_3 react with 3 mol of 1,3-butadiene, isomeric products of composition $(C_4H_8)_3B_2$ are formed. Using elegant chemical methods to untangle this system, Brown, Negishi, and Gupta[6] showed that the isomers obtained from a hydroboration reaction at 0° are primarily a mixture of 1,3-bis(1-boracyclopentyl)butane (III) and 1,4-bis(1-boracyclopentyl)butane (IV), with isomer III being the predominant product under kinetically controlled conditions. Under conditions which permit thermal rearrangement (140–170°) isomer III disappears and a mixture containing isomer IV and a new isomer, 1,1-bis(1-boracyclopentyl)butane (V), is formed in a 25:75 molar ratio. Isomers IV and V may be isolated in a pure state, but not III.[6]



III



IV

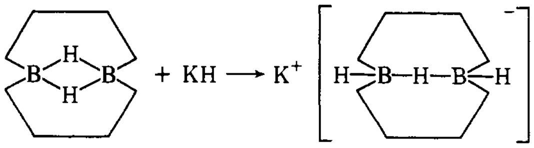


V

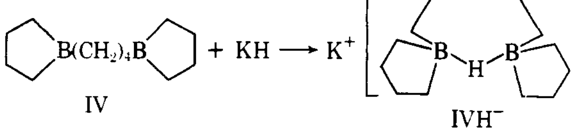
In this article we report the synthesis and characterization of singly hydrogen-bridged anions derived from II, IV, and V by adding hydride ion. NMR spectra of these anions and the parent organoboranes support the structures proposed. The X-ray structure of the anion derived from II verifies the existence of a transannular hydrogen bridge system.[7]

Results and Discussion

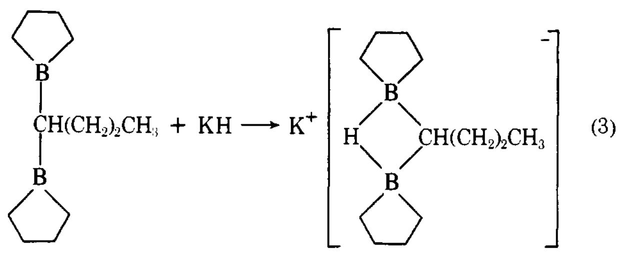
Syntheses of Single Hydrogen Bridged Organoborane Anions. Potassium hydride has major advantages over lithium or sodium hydride in transferring hydride to weak Lewis acids of boron.[8] Accordingly, potassium hydride was utilized as the hydride source. In THF, KH adds rapidly to II, IV, and V according to the reactions 1-3. The reaction be-



II IIH⁻ (1)



IV IVH⁻ (2)



V VH⁻

tween V and KH, unless performed under carefully selected conditions, always produces some $K^+[IVH^-]$ as well as the major product $K^+[VH^-]$, which indicates that structural rearrangement of V can occur during hydride ion addition. A rearrangement product, II, is the major product in the reaction of I with KH.

$$\underset{\text{I}}{B_2(C_4H_8)H_4} + KH \longrightarrow \underset{\text{II}}{\tfrac{1}{2}B_2(C_4H_8)_2H_2} + KBH_4 \qquad (4)$$

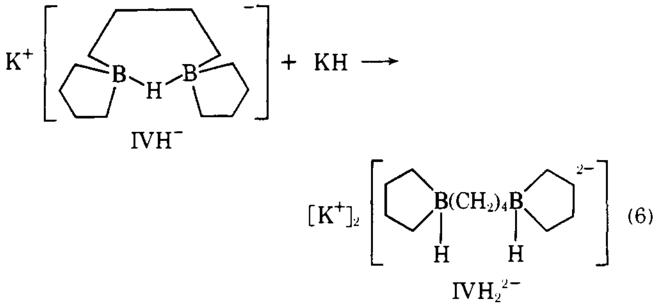
The potassium salts of the anions μ-hydro-1,2-dihydro-1,2:1,2-bis(tetramethylene)diborate(1−) (IIH^-), μ-hydro-1,2-tetramethylene-1,1:2,2-bis(tetramethylene)diborate(1−) (IVH^-), and μ-butylidene-μ-hydro-1,1:2,2-bis(tetramethylene)diborate(1−) (VH^-) are very soluble in etheral solvents and resist crystallization from such solvents. In general these salts yielded viscous, nonvolatile liquids. However, from dioxane solution, it was possible to isolate the crystalline solvate of $K^+[IIH^-]$. The salts $[N(n\text{-}C_4H_9)_4{}^+][IIH^-]$, $[P(C_6H_5)_3(CH_3)^+][IIH^-]$, $[N(n\text{-}C_4H_9)_4{}^+][IVH^-]$, and $[P(C_6H_5)_3(CH_3)^+][IVH^-]$ were prepared and isolated as crystalline solids which could be handled at room temperature in an inert atmosphere. Solid salts of the anion VH^- could not be isolated. The $N(n\text{-}C_4H_9)_4{}^+$ and $P(C_6H_5)_3(CH_3)^+$ salts are very soluble in CH_2Cl_2 and $CHCl_3$ but are only slightly soluble in THF and $(CH_3)_2O$. They were prepared in a mixed THF-CH_2Cl_2 solvent by metathesis reactions, a typical example of which is given below.

$$K^+[IIH^-] + [N(n\text{-}C_4H_9)_4{}^+]I^- \longrightarrow [N(n\text{-}C_4H_9)_4{}^+][IIH^-] + KI \qquad (5)$$

Infrared spectra of the singly hydrogen bridged anions show bands which can be assigned to stretching motions of bonds involving boron and hydrogen. Two broad bands, containing fine structure, at 2230 and 2045 cm^{-1} are assigned to terminal B-H and bridging B-H-B stretching motions, respectively, in the IIH^- ion. Broad bands at 2100 cm^{-1} in the infrared spectra of IVH^- and VH^- are assigned to bridge stretching motions. These values are consistent with the assignments made for the singly hydrogen-bridged anion[9a] $H_3B\text{-}H\text{-}BH_3{}^-$.

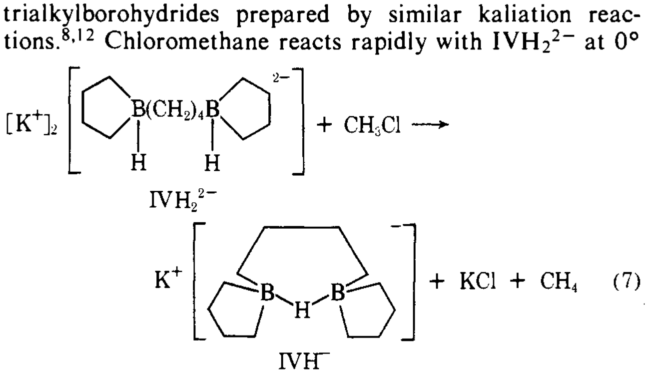
Reactions of Singly Hydrogen-Bridged Organoboranes and Their Derivatives. Each singly hydrogen-bridged anion, IIH^-, IVH^-, and VH^-, reacts with HCl at −78° to form 1 mol of H_2 per mole of anion and the parent organoborane associated with that anion II, IV, and V.

At room temperature in THF solution hydride addition to IVH^- is complete after several hours. Another convenient route to $[K^+]_2[IVH_2{}^{2-}]$ involves the reaction of IV with a large excess of KH in THF at room temperature. This salt can be isolated as a white crystalline solid which is stable at room temperature in the absence of moisture. It is also slowly formed when a metallic potassium mirror is allowed to react with IV in either $(C_2H_5)_2O$ or THF. The source of H^- for this reaction is unreacted IV since reactions in THF-d_8 did not produce B-D bonds. Several other cyclic trialkyl boranes also react with alkali metals to form species which contain boron-hydrogen bonds.[10] The terminal B-H stretching frequency in the infrared spectrum of $IVH_2{}^{2-}$ occurs at 1980 cm^{-1}. This value is consistent with values observed for other trialkylborohydrides.[10,11]

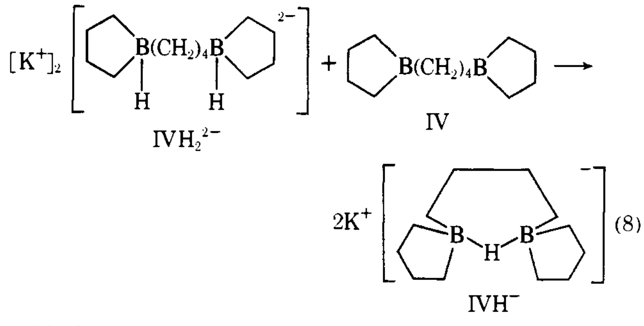


IVH⁻ IVH₂²⁻ (6)

The $IVH_2{}^{2-}$ dianion is an effective nucleophile which would be of interest to compare with some recently reported trialkylborohydrides prepared by similar kaliation reactions.[8,12] Chloromethane reacts rapidly with $IVH_2{}^{2-}$ at 0° to form IVH^-. Hydride ion is readily transferred from $IVH_2{}^{2-}$ to IV to form IVH^-.

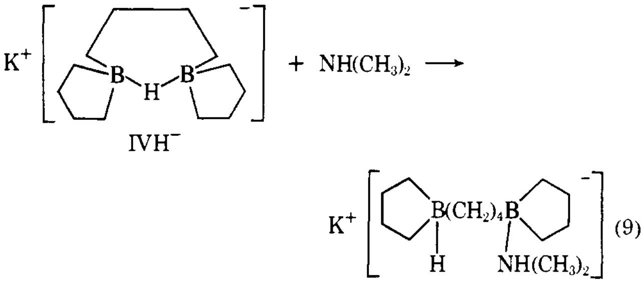


IVH₂²⁻ IVH⁻ (7)



IVH₂²⁻ IV IVH⁻ (8)

Displacement of the single hydrogen-bridge in IVH^- occurs rapidly in liquid $N(CH_3)_2H$ at 0°.



IVH⁻ IVNH(CH₃)₂H⁻ (9)

The anion VH^- reacts very slowly with KH in THF at room temperature. From boron-11 NMR spectra, noticeable reaction is observed in less than 24 hr. However, even after a period of some 45 days a significant amount of starting material $K^+[VH^-]$ (ca. 65 mol %) is present in the reaction mixture. Interestingly, the boron-11 NMR spectrum of the cleavage product strongly resembles that of $IVH_2{}^{2-}$. By the same token the reaction between VH^- and $N(CH_3)_2H$ is also sluggish (ca. 25 mol % VH^- remains unreacted after 2 weeks at room temperature) and the cleavage product has a boron-11 NMR spectrum which strongly resembles that of $IVNH(CH_3)_2H^-$. Thus the cleavage of

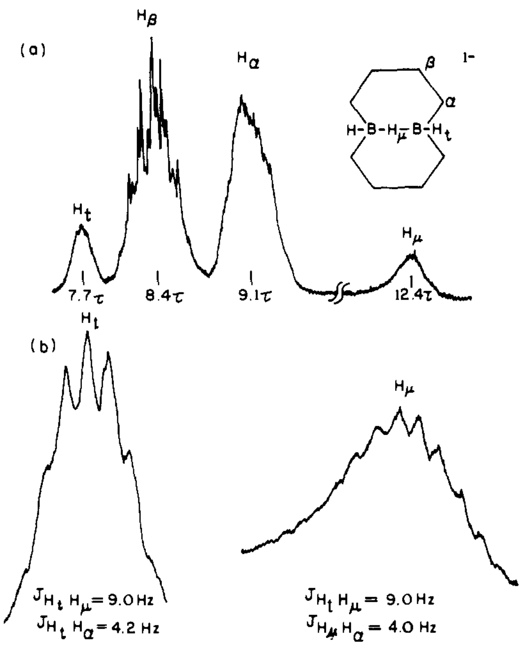


Figure 1. (a) Proton NMR spectrum (100 MHz) with boron-11 spin decoupled of $K^+[IIH^-]$ in THF-d_8. (b) Expanded scans of the terminal and bridge hydrogen resonances.

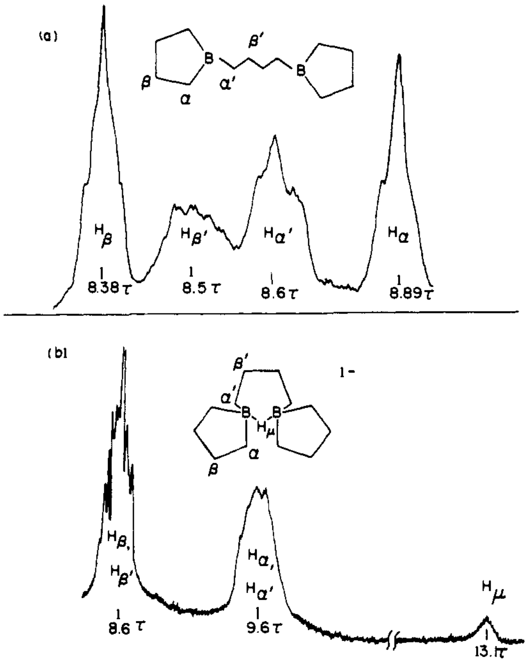


Figure 2. (a) Proton NMR spectrum (220 MHz) of IV in CH_2Cl_2. (b) Proton NMR spectrum (100 MHz) with boron-11 spin decoupled of $[P(C_6H_5)_3CH_3^+][IVH^-]$ in CH_2Cl_2.

VH^- either involves a subsequent rearrangement to adducts of the skeleton of IV or gives products which are based on the skeleton of V but coincidentally produce NMR spectra which strongly resemble adducts based on the skeleton of IV. We believe that the former interpretation of the results is more likely for the following reasons. In the reaction of VH^- if rearrangement does not occur, then cleavage of the bridge by H^- would give two negative centers separated by a single carbon atom, a potentially unstable arrangement. In the reaction of VH^- with $N(CH_3)_2H$ if rearrangement did not occur, molecular models indicate substantial crowding in the vicinity of the boron atoms and the carbon atom to which they are bound.

The IIH^- ion is resistant to nucleophilic attack. There was no apparent reaction when K^+IIH^- was left in contact with liquid $N(CH_3)_2H$ at room temperature. By the same token there was no apparent reaction between K^+IIH^- and KH in THF over a period of 2 weeks at room temperature.

NMR Spectra. A. II and IIH^-. The boron-11 and proton NMR spectra of II have been previously reported.[3] A single boron-11 resonance is observed at −28.5 ppm ($BF_3O(C_2H_5)_2$ = 0 ppm). Spin coupling of boron-11 with bridging hydrogens is not apparent in the NMR spectrum. In the proton NMR spectrum two broad resonances, one at τ 9.1 and one at τ 8.5 (TMS = τ 10) have been assigned to the hydrogens of the α and β methylene groups. The resonance of the bridging protons is not observed. It is probably overlapped by the resonance of the hydrogens of one of the methylene groups.[2]

The boron-11 NMR spectrum of the single hydrogen-bridged anion IIH^- consists of a doublet (δ 4.9 ppm, J = 70 Hz) which arises from a single terminal hydrogen on each boron spin coupling with that boron. That this resonance is indeed a doublet was established by proton spin decoupling. Spin coupling of the bridging proton with boron was not apparent. This is consistent with the case of $H_3B{-}H{-}BH_3^-$ in which spin coupling of only the terminal hydrogens with boron is observed in the boron-11 NMR spectrum.[9a]

Terminal B–H and bridging B–H–B proton resonances are clearly visible in the boron-11 decoupled proton NMR spectrum of IIH^- taken at 100 MHz (Figure 1). The chemical shifts of these resonances are consistent with previously assigned resonances for terminal and bridging protons. By analogy with the assignments made by Lindner and Onak[2b] for several organoboranes containing methylene groups, the α and β methylene protons are assigned in Figure 1a. The negative charge on the anion apparently has not increased the shielding on these types of methylene protons relative to the corresponding ones in the parent organoborane, II. No attempt was made to analyze the complex multiplet character of the α and β methylene proton resonances.

Figure 1b depicts expanded scans of the terminal B–H and bridging B–H–B resonances in the boron-11 spin decoupled proton NMR spectrum of IIH^-. The multiplet character of the terminal hydrogen resonance was treated as first-order spin coupling involving the bridging hydrogen and the four hydrogens of the α carbons which are bound to the same boron atom as each terminal hydrogen. The spectrum is thus expected to be a doublet of quintets, and the coupling constants shown in Figure 1b were determined on this basis. By the same token, the multiplet character of the bridging hydrogen resonance was treated as first-order spin coupling involving both terminal hydrogens and all eight hydrogens of the α carbons. The spectrum is thus expected to be a triplet of a nonet and the coupling constants shown in Figure 1b were determined on this basis. The magnitudes of the coupling constants are consistent with those reported by Lindner and Onak[2b] for several methyl diboranes and alkylpentaboranes.

B. IV and IVH^-. The boron-11 NMR spectrum of IV consists of a single resonance at −90 ppm, while that of the anion of IVH^- consists of a single resonance which occurs at −6.7 ppm. There is no apparent spin coupling between the bridging B–H–B hydrogen and boron atoms in this spectrum.

The boron-11 decoupled ^1H NMR spectrum of IV, taken at 100 MHz, consists of closely spaced partially overlapping resonances. At 220 MHz the four separate, complex, resonances are clearly discernible (Figure 2a), and this spectrum is consistent with the structure of IV which was deduced by chemical methods. Assignments were made on the

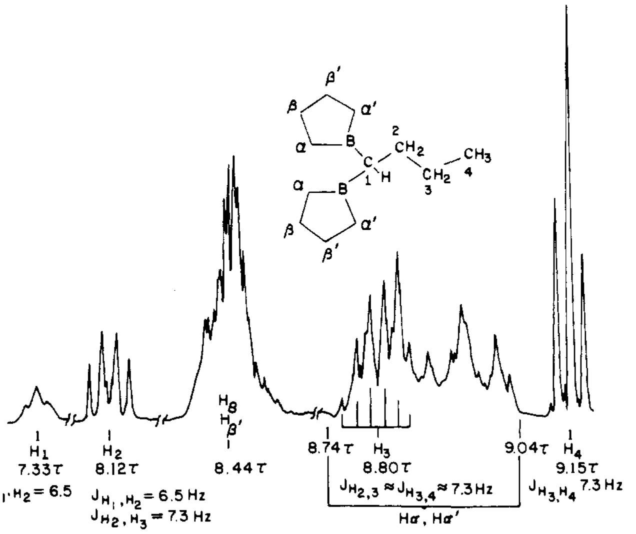


Figure 3. Proton NMR spectrum (300 MHz) of V in CH_2Cl_2.

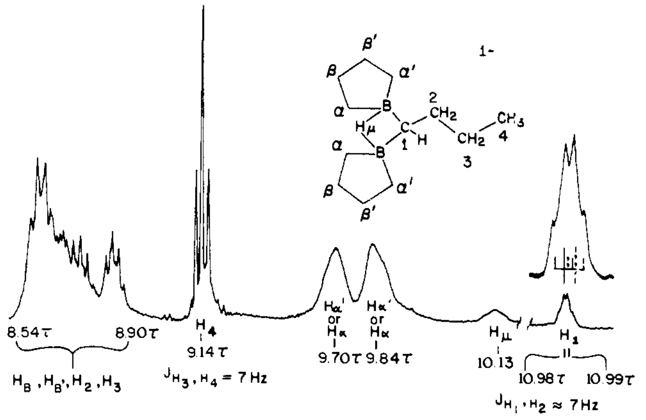


Figure 4. Proton NMR spectrum (300 MHz) of $[P(C_6H_5)_3CH_3^+][VH^-]$ in CH_2Cl_2.

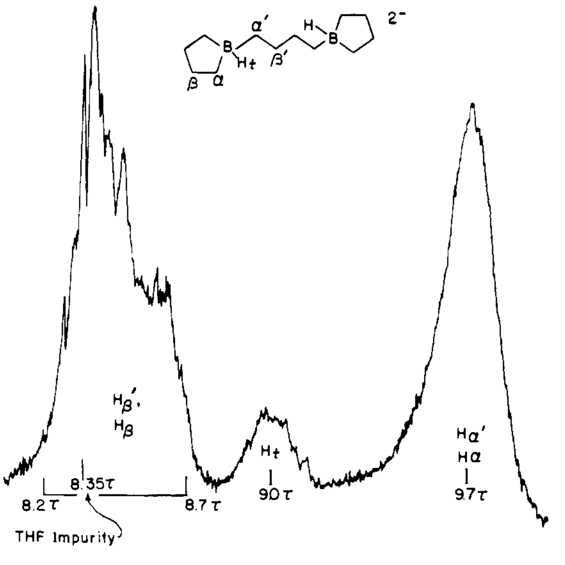


Figure 5. Proton NMR spectrum (100 MHz) of $[K^+]_2[IVH_2^{2-}]$.

basis of the relative areas of the resonances and from a comparison of these resonances with those of similar chemical shifts in the 220-MHz ^1H NMR spectrum of 1-boracyclopentylpropane. In the spectrum of 1-boracyclopentylpropane, $CH_2(CH_2)_3CH_2B(CH_2)_2CH_3$, spin coupling of the hydrogens in the propyl chain is apparently first order. The α' and β' protons in this chain have chemical shifts which are similar to those assigned to the α' and β' protons in the tetramethylene chain of IV.

The boron-11 decoupled ^1H NMR spectrum of IVH^-, taken at 100 MHz (Figure 2b) is much simpler than that of IV at 100 MHz. It is likely that the ^1H NMR spectrum, if observed at higher field strength, would reveal the separate α, α', β, and β' resonances. The B-H-B bridging proton resonance occurs at a value which is consistent for such a hydrogen.[9]

C. V and VH^-. The boron-11 NMR spectrum of V consists of a single resonance at −90 ppm, while that of the VH^- anion consists of a single resonance which occurs at 10.4 ppm. There is no apparent spin coupling between the bridging B-H-B hydrogen and boron atoms in this spectrum.

The ^1H NMR spectrum of V, taken at 300 MHz, is shown in Figure 3. This spectrum is consistent with the structure of V which was deduced by chemical methods.[6] Assignments of H_1, H_2, and H_4 are based on relative areas and first-order spin couplings. The assignment of H_3 is based on six relatively sharp peaks which range in separation from 7.0 to 7.5 Hz. These are believed to arise from first-order spin coupling of H_3 with H_2 and H_4. Since the spectrum was obtained at 300 MHz, the relative shifts of the H_1, H_2, H_3, and H_4 resonances in units of hertz are significantly larger than their coupling constants. Therefore assumption of first-order spin coupling is not unreasonable. Underlying this sextet, there appears to be a very broad resonance. We believe that this resonance probably arises primarily from nonequivalent α and α' methylene hydrogens of the boracyclopentyl rings. From molecular models, hindered rotation of these rings is indicated.

The ^1H NMR spectrum of VH^-, taken at 300 MHz is shown in Figure 4. The broad resonance assigned to the bridging B-H-B proton has a typical appearance when boron-11 is not spin decoupled from the proton.[9a] The rigid structure which arises from the presence of bridging hydrogen results in a clear cut separation of the α and α' resonances. The H_1 resonance of VH^- occurs at markedly higher τ value than the resonance of the corresponding hydrogen in V (τ 10.98 vs. τ 7.33). This resonance appears to be a quartet in the spectrum of VH^- rather than a triplet as observed in the spectrum of V. An expanded scan of this resonance (Figure 4) shows that the relative peak separation in this quartet is not constant. We believe that these four peaks are best described as two overlapping triplets (J = 7 Hz) which are separated by about 4 Hz. (At 100 MHz the H_1 resonance appears as a triplet.) Hindered rotation of the CH_2CH_3 group about the C_2-C_3 bond could give rise to nonequivalent H_1 atoms. Two kinds of H_1 could also arise from the existence of axial and equatorial isomers caused by puckering of the four-membered ring which contains the bridging B-H-B system. A slow rate of inversion could lead to two separate H_1 resonances.

D. IVH_2^{2-}. The boron-11 NMR spectrum of IVH_2^{2-} consists of a doublet (δ 13.7 ppm, J = 70 Hz) which arises from a single terminal hydrogen on each boron spin coupling with that boron. The boron-11 spin decoupled ^1H NMR spectrum of IVH_2^{2-}, taken at 100 MHz (Figure 5), shows terminal B-H resonances as a single peak with a τ value which is in the range observed for such hydrogens.[9]

E. $IVNH(CH_3)_2H^-$. The boron-11 NMR spectrum of this anion which is derived from the addition of $N(CH_3)_2H$ to IVH^- (eq 9) consists of a broad singlet (δ 0.5 ppm) and a doublet (δ 14.5 ppm, J = 65 Hz). This is consistent with the proposed structure which contains $N(CH_3)_2H$ on one boron and a terminal hydrogen on the other boron.

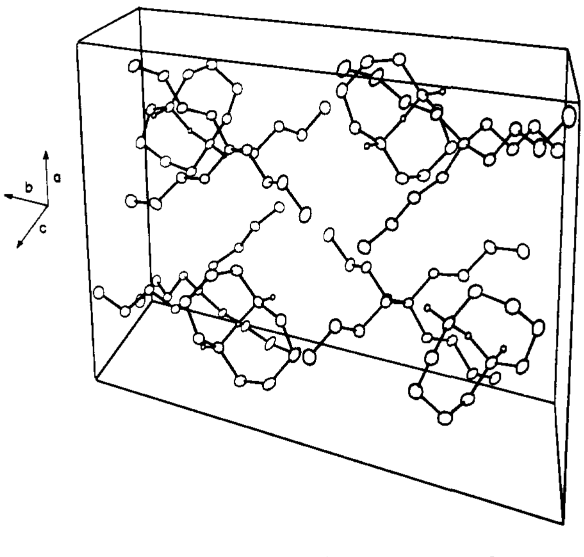


Figure 6. The unit cell of $[N(n\text{-}C_4H_9)_4^+][B_2(C_4H_8)_2H_3^-]$.

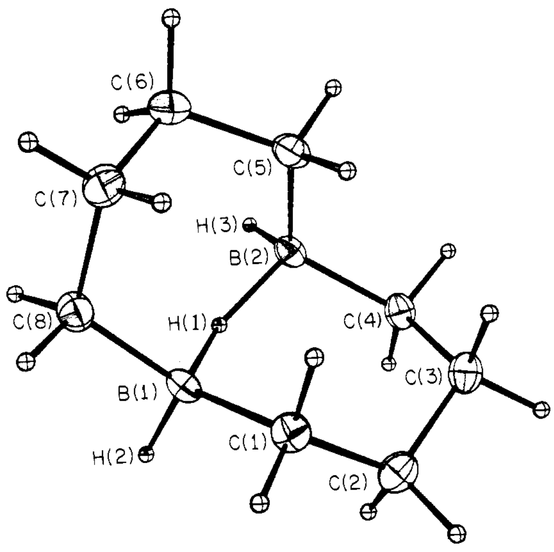


Figure 7. Structure of $B_2(C_4H_8)_2H_3^-$ showing thermal motion ellipsoids.

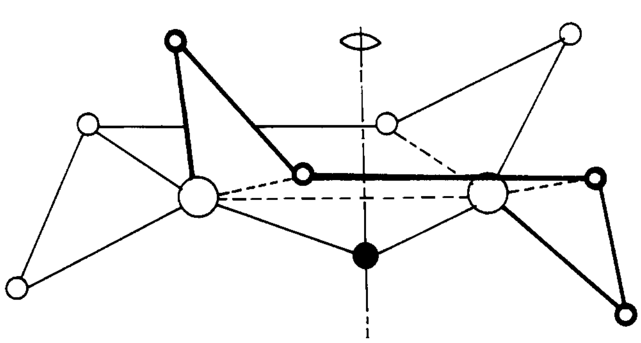


Figure 8. Simplified diagram of topography of $B_2(C_4H_8)_2H_3^-$.

Crystal and Molecular Structure of $[N(n\text{-}C_4H_9)_4^+][B_2(C_4H_8)_2H_3^-]$. From a single-crystal X-ray study, employing automated diffractometry, the crystal and molecular structure of $[N(n\text{-}C_4H_9)_4^+][IIH^-]$ was determined (space group $P2_1/c$; a = 10.65 (6), b = 13.951 (10), c = 21.734 (14) Å; β = 118.48 (3)°; Z = 4; d(calcd) = 0.937 (1) g/cm^3). The unit cell is shown in Figure 6. The structure of IIH^-, showing thermal motion ellipsoids,[13] is depicted in Figure 7. The existence of a transannular hydrogen bridge in this structure implies, to us, the presence of a transannular hydrogen bridge system in the parent hydride II and thus supports the structure of II which was deduced by chemical methods.[3,5]

The anion IIH^- has approximate C_2 symmetry with the rotation axis passing through the bridging hydrogen and being normal to the bc plane. Figure 8 presents a simplified diagram of the anion topography which consists of a double chair conformation and an angle of approximately 120° between the planes of the fused chairs. Table I gives selected bond distances and angles. Small deviations from C_2 symmetry are accounted for by differences in packing around the anion since one branch of the $N(n\text{-}C_4H_9)_4^+$ cation lies in close proximity to the C(1)-C(4) group while the C(5)-C(8) group lies in comparatively free space.

The $B_2H_7^-$ ion is related to IIH^- in that its proton magnetic resonance spectrum indicates the presence of a singly hydrogen bridged structure,[8a] $H_3B\text{-}H\text{-}BH_3^-$. A B-H bridge bond distance of 1.309 Å has been predicted for this anion.[14] This value agrees well, within one standard deviation, with the B-H bridge bond distance in IIH^- of 1.30 Å (Table I). The B-H-B bond angle in IIH^- is 140°. This nonlinearity appears to be imposed by the two tetramethylene groups which link the boron atoms since molecular models indicate that with increasing B-H-B bond angle unreasonable contact distances for hydrogen atoms result.

The cation $N(n\text{-}C_4H_9)_4^+$ is of idealized S_4 symmetry. Each n-butyl branch has a trans conformation in which nearest neighbors lie opposite a line drawn through the C-C bond midpoints. (A review of observed geometries of $N(n\text{-}C_4H_9)_4^+$ has been presented by Snow and Ibers.[15]) Three N-C bonds have identical values of 1.520 (3) Å while the fourth is 1.531 Å. The two angles bisected by the S_4 axis average 111.0 (2)° and the four angles related by S_4^1 and S_4^3 operations have a mean of 108.7 (4)°. The 12 C-C distances range from 1.501 (4) to 1.531 (4) Å with a mean value of 1.513 Å. The angles in the butyl chains have the following mean values: N-C1-C2 = 115.8 (4)°; C1-C2-C3 = 111.0 (3); C2-C3-C4 = 112.4 (5)°.

Table I. Selected Bond Distances (Å) and Bond Angles (deg) in $B_2(C_4H_8)_2H_3^-$

	Bond Distances		
B(1)-C(1)	1.596 (4)	B(2)-C(4)	1.610 (4)
B(1)-C(8)	1.609 (5)	B(2)-C(5)	1.606 (6)
C(1)-C(2)	1.525 (4)	C(5)-C(6)	1.534 (5)
C(2)-C(3)	1.514 (4)	C(6)-C(7)	1.511 (4)
C(3)-C(4)	1.528 (4)	C(7)-C(8)	1.537 (6)
B(1)-H(1)	1.28 (2)	B(2)-H(1)	1.31 (2)
B(1)-H(2)	1.16 (3)	B(2)-H(3)	1.16 (2)
	Bond Angles		
B(1)-H(1)-B(2)	140 (2)		
C(1)-B(1)-C(8)	118.5 (3)	C(4)-B(2)-C(5)	117.3 (3)
B(1)-C(1)-C(2)	116.4 (3)	B(2)-C(5)-C(6)	114.9 (3)
C(1)-C(2)-C(3)	113.8 (3)	C(5)-C(6)-C(7)	113.8 (2)
C(2)-C(3)-C(4)	113.8 (3)	C(6)-C(7)-C(8)	114.3 (3)
C(3)-C(4)-B(1)	117.4 (3)	C(7)-C(8)-B(2)	116.8 (3)

The mean C-H distance for the cation and anion is 0.98 (6) Å as estimated by

$$\bar{x} = \Sigma_i(X_i)/\sigma_i^2/\Sigma_i(1/\sigma_i^2)$$

where σ_i is the estimated standard deviation from the least-squares refinement. This value is in agreement with C-H distances reviewed by Churchill.[16]

Table II presents fractional coordinates and anisotropic thermal parameters for B, C, and N. Table III presents fractional coordinates and isotropic thermal parameters for H.

Table II. Positional Parameters and Anisotropic Temperature Factors of the Nonhydrogen Atoms in $[N(n\text{-}C_4H_9)_4^+][B_2H_3(C_4H_8)_2^-]$

Atom	x/a	y/b	z/c	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
				Anion					
B(1)	0.2389 (4)	0.8658 (2)	0.2857 (2)	149 (5)	59 (5)	31 (1)	19 (3)	41 (2)	13 (1)
B(2)	0.3980 (4)	0.7433 (2)	0.3670 (2)	127 (5)	59 (5)	31 (1)	12 (3)	29 (2)	12 (1)
C(1)	0.0851 (3)	0.8068 (2)	0.2577 (1)	135 (4)	67 (4)	37 (1)	15 (2)	31 (2)	4 (1)
C(2)	0.0831 (3)	0.7075 (2)	0.2280 (2)	148 (5)	77 (5)	41 (1)	0 (3)	34 (2)	−6 (1)
C(3)	0.1643 (3)	0.6317 (2)	0.2833 (2)	162 (5)	63 (5)	47 (1)	−6 (3)	51 (2)	−2 (1)
C(4)	0.3356 (3)	0.6452 (2)	0.3237 (2)	151 (4)	54 (4)	44 (1)	9 (2)	43 (2)	7 (1)
C(5)	0.3475 (4)	0.7678 (2)	0.4250 (2)	225 (6)	72 (6)	32 (1)	6 (3)	46 (2)	10 (1)
C(6)	0.3772 (4)	0.8714 (2)	0.4518 (2)	297 (7)	90 (7)	31 (1)	−4 (3)	55 (2)	0 (1)
C(7)	0.2600 (4)	0.9420 (2)	0.4033 (2)	303 (7)	73 (7)	45 (1)	3 (3)	77 (3)	−8 (1)
C(8)	0.2622 (4)	0.9585 (2)	0.3339 (2)	218 (6)	61 (6)	40 (1)	9 (3)	53 (2)	4 (1)
				Cation					
N(1)	0.5896 (2)	0.8068 (1)	0.1943 (1)	131 (3)	40 (3)	25 (1)	−2 (2)	38 (1)	−1 (1)
C(1A)[b]	0.5989 (3)	0.7150 (2)	0.2339 (1)	151 (4)	40 (4)	29 (1)	−7 (2)	40 (2)	0 (1)
C(2A)	0.7566 (3)	0.6798 (2)	0.2835 (1)	155 (4)	48 (4)	31 (1)	−4 (2)	35 (2)	3 (1)
C(3A)	0.7494 (3)	0.5974 (2)	0.3273 (1)	199 (5)	54 (5)	33 (1)	6 (2)	45 (2)	11 (1)
C(4A)	0.9038 (4)	0.5566 (2)	0.3747 (2)	221 (6)	66 (6)	36 (1)	12 (3)	41 (2)	12 (1)
C(1B)	0.6806 (3)	0.8865 (2)	0.2444 (1)	148 (4)	41 (4)	25 (1)	−8 (2)	37 (1)	−2 (1)
C(2B)	0.6514 (3)	0.9023 (2)	0.3065 (1)	181 (5)	65 (5)	29 (1)	−15 (2)	46 (2)	−8 (1)
C(3B)	0.7634 (4)	0.9716 (2)	0.3579 (2)	297 (7)	89 (7)	37 (1)	−68 (3)	72 (2)	−24 (1)
C(4B)	0.7489 (4)	0.9818 (3)	0.4235 (2)	310 (8)	97 (8)	37 (1)	−30 (4)	58 (3)	−17 (1)
C(1C)	0.4252 (3)	0.8377 (2)	0.1536 (1)	128 (4)	51 (4)	28 (1)	8 (2)	36 (1)	0 (1)
C(2C)	0.3177 (3)	0.7660 (2)	0.1022 (1)	142 (4)	59 (4)	31 (1)	3 (2)	29 (2)	−5 (1)
C(3C)	0.1595 (3)	0.8074 (2)	0.0612 (2)	145 (4)	70 (4)	35 (1)	13 (2)	29 (2)	0 (1)
C(4C)	0.0463 (3)	0.7354 (2)	0.0135 (2)	153 (5)	92 (5)	44 (1)	1 (3)	19 (2)	−2 (1)
C(1D)	0.6561 (3)	0.7871 (2)	0.1452 (1)	129 (4)	50 (4)	28 (1)	3 (2)	41 (1)	−2 (1)
C(2D)	0.6505 (3)	0.8702 (2)	0.0996 (1)	166 (4)	58 (4)	26 (1)	6 (1)	41 (2)	3 (1)
C(3D)	0.7317 (3)	0.8467 (2)	0.0578 (1)	158 (4)	94 (4)	28 (1)	2 (3)	43 (2)	3 (1)
C(4D)	0.7213 (4)	0.9277 (3)	0.0097 (2)	237 (6)	123 (6)	33 (1)	−20 (3)	58 (2)	9 (1)

[a] All β's × 10^5. The anisotropic thermal parameters are of the form: $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. [b] n-Butyl chains are designated as C(ij): i = position in relation to central nitrogen atom; j = label for an individual n-butyl chain.

Experimental Section

Apparatus and Equipment. Standard vacuum line and inert atmosphere techniques were used to handle volatile and moisture and air sensitive compounds.[17] NMR spectra, with the exception of those taken at 220 and 300 MHz, were taken on a Varian HA-100 NMR spectrometer which was equipped with heteronuclear decoupling accessories which are described elsewhere.[17] Internal lock, frequency sweep mode was used routinely for proton NMR spectra. Spin coupling between boron-11 and protons was routinely confirmed by heteronuclear decoupling experiments.

Reagents and Solvents. Spectroquality or reagent grade solvents were refluxed in the presence of drying agents such as $LiAlH_4$ or CaH_2 under an atmosphere of dry N_2 for at least 24 hr. The middle fraction was then distilled into a receiver which was fitted with a Teflon plug high-vacuum needle valve and stored. Diborane(6) was purchased from the Callery Chemical Company of Callery, Pa., and was purified by distilling it from a −140° cooled trap to a −196° trap. The procedure of Young and Shore[3] was used to prepare II. The method of Brown, Negishi, and Gupta[6] was used to prepare and isolate IV and V. Potassium hydride, a 50% suspension in mineral oil, was obtained from ROC/RIC of Sun Valley, Calif. It was isolated by extracting the mineral oil with pentane.

Hydride Ion Addition. A. K^+ [IIH^-]. In a typical synthesis, 9.5 mmol of II in 6 ml of THF was allowed to react with 10.8 mmol of KH for 3 hr. Excess KH was removed by vacuum line filtration and the product obtained as a clear, colorless viscous liquid by distilling away the solvent. Attempts to isolate the potassium salt as a solid by prolonged pumping on the system and also by dissolving the viscous liquid in ether with subsequent precipitation failed. However, a crystalline solid, solvated by dioxane, was obtained. Enough dioxane was added to cover the oil completely. Upon stirring the mixture a homogeneous solution resulted and then white crystals of $KB_2(C_4H_8)_2H_3(\text{dioxane})_x$ slowly precipitated. The crystals are stable at room temperature but they are extremely moisture sensitive. They are slightly soluble in THF, dioxane, and CH_2Cl_2.

B. $K^+[IVH^-]$. The procedure for preparing this salt was the same as preparing $K^+[IIH^-]$ except that a slight deficiency of KH was used in order to avoid formation of $[K^+]_2[IVH_2^{2-}]$. Removal of solvent by distillation at room temperature resulted in the formation of a product which was a soft and sticky solid.

C. $K^+[VH^-]$. The reaction of V with KH under conditions described above always resulted in the formation of significant amounts of $K^+[IVH^-]$ through rearrangement of V. However, formation of $K^+[IVH^-]$ as a side product was minimized to virtually undetectable levels, on the basis of NMR spectra, when the reaction was carried out in $(CH_3)_2O$ at room temperature using the following quantities of materials: 1.7 mmol of KH, 0.41 mmol of V, and 0.5 ml of $(CH_3)_2O$. Upon removal of solvent by distillation, $K^+[IVH^-]$ tends to form an oil.

D. $K^+[IVH_2^{2-}]$. This salt was most conveniently prepared by allowing 2.0 mmol of IV to react with 8.0 mmol of KH in 10 ml of THF with continuous stirring for 24 hr at room temperature. The milky white suspension was filtered on the vacuum line using a medium porosity frit. Distilling the solvent from the filtrate at room temperature left the crude white crystalline product which was then recrystallized by dissolving it in THF at room temperature, cooling it to −78° and then filtering the suspension at this temperature, and recovering the product from the frit. This salt is stable at room temperature, but it is very sensitive to moisture. It is readily soluble in THF, $(CH_3)_2O$, and $(C_2H_5)_2O$ at room temperature. It reacts with chlorinated hydrocarbons as indicated in eq 7. A 0.262 mmol sample of this salt was allowed to react with glacial acetic acid in a sealed tube at 140° for 4 days. The gaseous products and boron were assayed: millimoles found, H_2 = 0.491, C_4H_{10} = 0.793, B = 0.520; millimoles calculated, H_2 = 0.524, C_4H_{10} = 0.786, B = 0.524; X-ray powder pattern d values (in Å) and relative intensities, 8.02 (m), 5.46 (m), 4.72 (vs), 3.72 (s), 3.50 (m), 3.29 (m), 3.138 (s), 2.503 (m). Nine other weaker lines ranging in d value from 4.36 to 1.719 were also observed.

A second method by which $[K^+]_2[IVH_2^{2-}]$ was prepared involved the reaction of KH with $K^+[IVH^-]$. In a typical reaction a 0.3 mmol sample of $K^+[IVH^-]$ was allowed to react with excess KH in 0.5 ml of THF at room temperature. After 4 hr, the boron-11 NMR spectrum of the solution indicated the presence of only $[K^+]_2[IVH_2^-]$. The product was isolated as indicated above and further identified by its X-ray powder pattern.

Tetra-n-butylammonium Salts and Triphenylmethylphosphonium Salts by Metathesis Reactions. A. $[N(n\text{-}C_4H_9)_4^+][IIH^-]$. This salt

Table III. Positional Parameters and Isotropic Temperature Factors of the Hydrogen Atoms in $[N(n\text{-}C_4H_9)_4^+][B_2H_3(C_4H_8)_2^-]$

Atom	x/a	y/b	z/c	B
		Anion		
H(1)	0.3552 (22)	0.8132 (14)	0.3214 (10)	3.3 (5)
H(2)	0.2710 (26)	0.8873 (17)	0.2432 (12)	5.3 (6)
H(3)	0.5276 (25)	0.7533 (16)	0.3896 (12)	4.7 (6)
H(4)	0.0585 (31)	0.8037 (19)	0.3004 (14)	7.4 (8)
H(5)	0.0037 (27)	0.8478 (18)	0.2230 (12)	5.9 (6)
H(6)	0.1377 (26)	0.7097 (17)	0.2000 (12)	5.8 (6)
H(7)	−0.0247 (30)	0.6845 (19)	0.1944 (14)	7.2 (7)
H(8)	0.1259 (29)	0.6360 (18)	0.3189 (13)	6.4 (7)
H(9)	0.1294 (30)	0.5643 (19)	0.2570 (13)	6.9 (7)
H(10)	0.3842 (26)	0.5902 (17)	0.3623 (12)	5.3 (6)
H(11)	0.3778 (27)	0.6327 (17)	0.2876 (12)	5.7 (6)
H(12)	0.2242 (30)	0.7507 (19)	0.4061 (14)	7.1 (7)
H(13)	0.4061 (31)	0.7209 (19)	0.4639 (14)	7.6 (8)
H(14)	0.4832 (31)	0.8926 (21)	0.4564 (14)	8.2 (8)
H(15)	0.3722 (30)	0.8764 (19)	0.4975 (14)	6.9 (7)
H(16)	0.2707 (28)	1.0004 (19)	0.4272 (13)	7.0 (7)
H(17)	0.1540 (31)	0.9153 (20)	0.3885 (15)	7.9 (8)
H(18)	0.3654 (32)	0.9949 (20)	0.3477 (14)	8.1 (8)
H(19)	0.1767 (32)	1.0083 (20)	0.3071 (14)	8.2 (8)
		Cation		
H(1A)	0.5468 (22)	0.6672 (14)	0.1987 (10)	3.3 (5)
H(2A)	0.5454 (23)	0.7282 (15)	0.2592 (11)	3.9 (5)
H(3A)	0.8062 (28)	0.6570 (18)	0.2583 (13)	6.4 (7)
H(4A)	0.8167 (26)	0.7315 (16)	0.3146 (12)	4.9 (6)
H(5A)	0.6868 (34)	0.5448 (22)	0.2969 (16)	9.1 (9)
H(6A)	0.7069 (29)	0.6221 (18)	0.3588 (13)	6.7 (7)
H(7A)	0.9065 (29)	0.5148 (19)	0.4076 (13)	7.1 (7)
H(8A)	0.9426 (30)	0.5252 (18)	0.3476 (14)	6.8 (7)
H(9A)	0.9747 (33)	0.6114 (22)	0.4042 (15)	9.2 (9)
H(1B)	0.6547 (23)	0.9456 (15)	0.2156 (11)	3.9 (5)
H(2B)	0.7913 (24)	0.8714 (15)	0.2663 (11)	4.1 (5)
H(3B)	0.5500 (27)	0.9235 (17)	0.2900 (12)	5.7 (6)
H(4B)	0.6683 (29)	0.8448 (18)	0.3301 (13)	6.7 (7)
H(5B)	0.8796 (30)	0.9551 (19)	0.3802 (14)	7.3 (7)
H(6B)	0.7638 (35)	1.0282 (22)	0.3369 (15)	9.7 (9)
H(7B)	0.7693 (43)	0.9172 (30)	0.4492 (20)	14.0 (13)
H(8B)	0.8363 (39)	1.0195 (26)	0.4636 (17)	11.5 (11)
H(9B)	0.6253 (44)	1.0204 (28)	0.4031 (20)	14.8 (13)
H(1C)	0.4030 (22)	0.8526 (14)	0.1901 (10)	3.1 (5)
H(2C)	0.4254 (22)	0.8999 (14)	0.1293 (10)	3.0 (5)
H(3C)	0.3527 (31)	0.7401 (21)	0.0691 (15)	8.2 (8)
H(4C)	0.3122 (28)	0.7115 (17)	0.1276 (13)	5.8 (6)
H(5C)	0.1261 (28)	0.8290 (18)	0.0899 (13)	6.1 (7)
H(6C)	0.1605 (30)	0.8656 (19)	0.0303 (13)	7.2 (7)
H(7C)	0.0777 (33)	0.7030 (19)	−0.0193 (15)	8.3 (8)
H(8C)	−0.0561 (29)	0.7626 (19)	−0.0147 (14)	6.7 (7)
H(9C)	0.0411 (33)	0.6921 (21)	0.0455 (15)	8.4 (8)
H(1D)	0.5974 (23)	0.7326 (15)	0.1159 (11)	3.9 (5)
H(2D)	0.7615 (22)	0.7664 (14)	0.1740 (10)	3.3 (5)
H(3D)	0.5455 (26)	0.8823 (17)	0.0631 (12)	5.1 (6)
H(4D)	0.6993 (29)	0.9306 (18)	0.1313 (14)	6.7 (7)
H(5D)	0.8299 (29)	0.8422 (18)	0.0883 (13)	6.4 (7)
H(6D)	0.6852 (27)	0.7897 (18)	0.0310 (13)	6.1 (7)
H(7D)	0.6097 (33)	0.9350 (20)	−0.0262 (15)	8.2 (8)
H(8D)	0.7563 (29)	0.9851 (19)	0.0343 (13)	6.9 (7)
H(9D)	0.7735 (30)	0.9191 (21)	−0.0124 (14)	8.1 (8)

was prepared by slowly adding 6.68 mmol of $N(n\text{-}C_4H_9)_4I$ dissolved in 4 ml of CH_2Cl_2 to 6.50 mmol of $K^+[IIH^-]$ dissolved in 4 ml of a 1:1 mixture of THF and CH_2Cl_2. After stirring the milkly mixture for an hour at room temperature, the KI precipitate was separated by vacuum line filtration through a fine porosity frit. The $[N(n\text{-}C_4H_9)_4^+][IIH^-]$ was precipitated from the filtrate by slowly condensing 15 ml of $(C_2H_5)_2O$ into the rapidly stirred solution at −78°. It was recovered by filtering the suspension at room temperature through a medium porosity frit and washing the precipitate with fresh $(C_2H_5)_2O$ and filtering at −78°. Samples of the solid proved to be stable under vacuum at room temperature for a period of over 1 year. This salt is insoluble in liquid NH_3 and $(C_2H_5)_2O$, slightly soluble in THF and glyme, and very soluble in CH_2Cl_2, $CHCl_3$, and $NH(CH_3)_2$. A 0.0941 g sample was heated with 0.5 ml of concentrated HNO_3 at 95° for 24 hr, and the hydridic hydrogen and boron were assayed: millimoles found, H_2 = 0.74, B = 0.47; calculated, H_2 = 0.69, B = 0.49; X-ray powder pattern d values (in Å) and relative intensities, 9.59 (s), 9.05 (m), 7.60 (m), 6.57 (m), 5.53 (vw), 5.10 (m), 4.92 (m), 4.73 (m), 4.48 (m), 4.28 (vs), 4.00 (w), 3.73 (w), 3.37 3.37 (vw), 3.15 (vw), 2.11 (vw), 2.09 (vw), 1.99 (vw).

B. $[P(C_6H_5)_3CH_3^+][IIH^-]$. This compound was prepared by a metathesis reaction between $P(C_6H_5)_3CH_3Br$ and $K^+[IIH^-]$ carried out in the same manner as in the preparation of $[N(n\text{-}C_4H_9)_4^+][IIH^-]$. The reaction mixture was reddish brown while the isolated solid was a light tan which did not change upon recrystallization either from a CH_2Cl_2-$(C_2H_5)_2O$ mixture or repeated washings with fresh $(C_2H_5)_2O$. However, the isolated solid became white in color upon aging it at −78° in an evacuated tube. Methylene chloride solutions of the white solid were colorless at −78°, but on warming slowly turned reddish brown. The solution slowly became colorless again when it was cooled to −78°. Solid $[P(C_6H_5)_3CH_3^+][IIH^-]$ appears to be completely decomposed at room temperature after a period of about a week. In methylene chloride it appears to be stable indefinitely at −78° but appears to be completely decomposed after a period of 1 day at room temperature. A 0.262 mmol sample of the salt was allowed to react with glacial acetic acid in a sealed tube at 80° for 3 days. Boron, hydridic hydrogen, evolved butane, and $P(C_6H_5)_3CH_3^+$ were assayed: millimoles found, $P(C_6H_5)_3CH_3^+$ = 0.79, C_4H_{10} = 1.40, H_2 = 2.05, B = 1.37; calculated, $P(C_6H_5)_3CH_3^+$ = 0.76 C_4H_{10} = 1.52, H_2 = 2.28.

C. $[N(n\text{-}C_4H_9)_4^+][IVH^-]$. This salt was prepared in the same manner as $[N(n\text{-}C_4H_9)_4^+][IIH^-]$. The crude product was recovered by vacuum distilling the solvent from the filtrate after filtering off the KI (identified by its X-ray powder pattern) formed. The salt was purified by taking it up in THF at room temperature, slowly condensing twice as much pentane into the rapidly stirred solution at −78° and filtering out the precipitated salt at low temperature. Crystals isolated in this manner are solvated, becoming powdery on distilling away last traces of solvent at room temperature. This salt appears to be stable at room temperature for several days. It is soluble in THF, glyme, and CH_2Cl_2 and is frequently recovered from these solvents as a paste. At room temperature it is moderately soluble in $(CH_3)_2O$ and slightly soluble in $(C_2H_5)_2O$. Solutions of this salt may be handled at room temperature for approximately 2 days before decomposition can be detected.

D. $[P(C_6H_5)_3CH_3^+][IVH^-]$. This salt was prepared and isolated in the same manner as $[P(C_6H_5)_3CH_3^+][IIH^-]$. The KBr precipitate from the reaction was identified from its X-ray defraction pattern. The isolated salt of IVH^- is white in color and possesses approximately the same solubility characteristics as $[N(n\text{-}C_4H_9)_4^+][IVH^-]$ but appears to be less stable. The solid can, however, be easily handled at room temperature for several hours without noticeable decomposition.

E. $[N(n\text{-}C_4H_9)_4^+][VH^-]$ and $[P(C_6H_5)_3CH_3^+][VH^-]$. The procedures used to prepare these salts were the same as those employed in the preparation of the corresponding salts of IIH^-. The alkali metal halide precipitates produced in the metathesis reactions were separated by filtration and identified by X-ray powder diffraction. The products in the filtrates proved to be viscous liquids when the solvent was distilled away. NMR spectra showed that while the VH^- ion was principally present, some IVH^- was also present. Although these salts of VH^- are stable at −78°, they seem to decompose more rapidly than the corresponding IVH^- salts at room temperature.

Reaction between $[K^+]_2[IVH_2^{2-}]$ and IV. An equimolar mixture of $[K^+]_2[IVH_2^{2-}]$ and IV (0.15 mmol each) was placed in 0.3 ml of THF. At room temperature, after a period of less than an hour, NMR spectra indicated that the reactants were entirely consumed and that $K^+[IVH^-]$ was formed.

Reaction between $[K^+]_2[IVH_2^{2-}]$ and CH_3Cl. A 0.30 mmol sample of $[K^+]_2[IVH_2^{2-}]$ was allowed to react with 1 mmol of CH_3Cl in 3 ml of THF at room temperature. Methane gas was immediately evolved (identified by ir and mass spectra) and a precipitate of KCl formed (identified by its X-ray powder pattern). The NMR spectra of the THF solution revealed that all of the $[K^+]_2[IVH_2^{2-}]$ had been consumed and that $K^+[IVH^-]$ had formed.

Reaction of Metallic Potassium with IV and V. About 2 mmol of IV in 4 ml of $(C_2H_5)_2O$ was allowed to react with about 7 mmol of metallic potassium which had been vapor deposited as a mirror on the sides of a reaction tube. The reaction appeared to be complete within an hour at room temperature. Some of the potassium mirror dissolved and the solution became pale greenish brown. After stirring the mixture at room temperature for an additional 4 hr, it was filtered and extracted with THF. Volatile substances were distilled away, and fresh $(C_2H_5)_2O$ was condensed onto the pasty yellow residue. After stirring the system for a few minutes a small amount of white solid settled out and was isolated from the yellow solution by filtration. The X-ray powder pattern and boron-11 NMR spectrum of this solid identified it as $[K^+]_2[IVH_2^{2-}]$.

When 2.18 mmol of a potassium mirror and 2.02 mmol of IV were allowed to react in 4 ml of THF-d_8, $K^+[IVH^-]$ and a lesser amount of $[K^+]_2[IVH_2^{2-}]$ were formed (identified by boron-11 NMR spectra). Hydrolysis of the reaction mixture gave H_2 (identified by its mass spectrum), thus indicating that the origin of the hydridic hydrogen is not the ethereal solvent but the organoborane itself.

Attempts to react $B(n\text{-}C_3H_8)_3$ with metallic potassium under the conditions described above failed.

X-Ray Structure Determination of $[N(n\text{-}C_4H_9)_4^+][B_2(C_4H_8)_2H_3^-]$. Preliminary Weissenberg and precession photographs of the $(h0l)$, $(h1l)$, and $(hk0)$ zones revealed monoclinic symmetry. The systematic absences, $k = 2n + 1$ for $(0k0)$ and $l = 2n + 1$ for $(h0l)$, are unique for the space group $P2_1/c$. The cell dimensions and an orientation matrix for data collection were determined by a least-squares refinement of the setting angles for 16 reflections, well-centered on a Picker FACS-III four circle diffractometer using Cu Kα radiation.

Intensity data were collected from a crystal with approximate dimensions of 0.5 × 0.3 × 0.4 mm mounted in a sealed glass capillary. Data collection was on the Picker FACS-III diffractometer which was controlled by an EMR 6130 computer. Integrated intensities were obtained by a θ-2θ scan technique, scanning the Kα peaks symmetrically for 2° at a rate of 2°/min. All of the symmetry-nonequivalent reflections were measured in three successive concentric shells with 2θ ranges of 0.02-75°, 75-110°, and 110-128°. Stationary-crystal, stationary-counter background counts of 10 sec for the first shell and 20 sec for the second and third shells were taken at the beginning and end of each scan. The diffracted beams were attenuated with layers of brass foil whenever the count rate exceeded approximately 8000 counts per second.

Six standard reflections were measured periodically and showed no significant variation with time. (The intensity data were corrected for background and standard deviations were assigned as previously described[19] using a value of 0.05 for p.) Lorentz and polarization corrections were also applied. The crystal was measured and a Gaussian absorption correction was applied. The six faces were identified by optical and X-ray means as pairs of the forms $\{100\}$, $\{010\}$, and $\{001\}$. The linear absorption coefficient used was 7.28 cm^{-1} and corrections to F^2 varied from 1.222 to 1.395. All 4168 measured reflections were used in the solution of the structure. The 2293 data for which $F_o^2 \geq 3\sigma(F_o^2)$ were used in the subsequent refinement of the structure.

The structure was solved by direct phasing methods.[20] In the least-squares calculations, $w(|F_o| - |F_c|)^2$ was minimized, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes, and the weights, w, were taken as $1/\sigma^2(F_o)$. The atomic scattering factors for B, C, and N were taken from the tabulation of Cromer and Waber.[21] The hydrogen atomic scattering factors for hydrogen were obtained from the calculations of Stewart, Davidson, and Simpson.[22]

An absolute scale value, isotopic temperature factor, and E values were calculated. Relative phases of the 81 largest E values were reduced to products of three arbitrary phases. This was sufficient to define a unique set of inner phases which, in turn, was used to estimate an additional set of 311 phases for E's > 1.4. The positions of all 27 nonhydrogen atoms were found among the 29 largest peaks from an E map using the 392 phased E's. A difference Fourier map following one cycle of block-diagonal least-squares refinement showed the positions of 45 of the 54 hydrogen locations. An additional cycle of block-diagonal least-squares refinement, followed by a difference Fourier map, revealed the remaining nine hydrogen positions. Final least-squares refinements involving coordinates for all atoms, anisotropic parameters for the heavier atoms, with isotropic thermal parameters for the hydrogen atoms converged with values of

$$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$$

and

$$R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$$

equal to 0.043 and 0.056. See paragraph at end of paper regarding supplementary material.

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Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number JACS-75-6063.

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