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BCN- AND BCP-SEQUENCED BORANES

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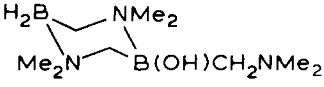
Summary

Study of hydrolytic and cleavage reactions of two BCN-sequenced boranes has led to the characterization of a volatile, hydroxylated tetravalent borane heterocycle and a triborane derivative. Synthesis and characterization of a monohydrogen-bridged phosphonium diborane, $Me_2P(CH_2BH_2)_2H$, and an azoniaphosphoniabisborata heterocycle, $BH_2CH_2Me_2PCH_2BH_2NMe_2$, new BCP-sequenced species, are also reported.

Valence saturated, BCN-sequenced boranes with sterically protected boron, as a class, are stable in air and in aqueous solution [1]. Indeed, the $-BH_2CH_2$-NMe_2- skeletal sequence in cyclic and acyclic compounds such as $H_2BCH_2NMe_2BH_2CH_2NMe_2$ and $Me_3NBH_2CH_2NMe_2$ is sufficiently robust for elaboration of derivative chemistry based on halogenation and displacement reactions, a happy feature for practical applications. Study of this chemistry continues to lead to interesting, sometimes surprising new entities, two of which are reported here: a volatile hydroxylated heterocycle, $Me_2NCH_2BH_2NMe_2CH_2B$-$(OH)CH_2NMe_2$, from controlled hydrolysis of $Me_2NCH_2BH_2CH_2NMe_2BH_2$-$CH_2NMe_2^-$; and a triborane(7) derivative by the cleavage of $Me_2NCH_2BH_2CH_2$ with diborane. Additionally, a study of BCP-sequenced systems was initiated, and two new phosphoniaborata heterocycles were prepared and characterized.

BCN-sequenced heterocycles

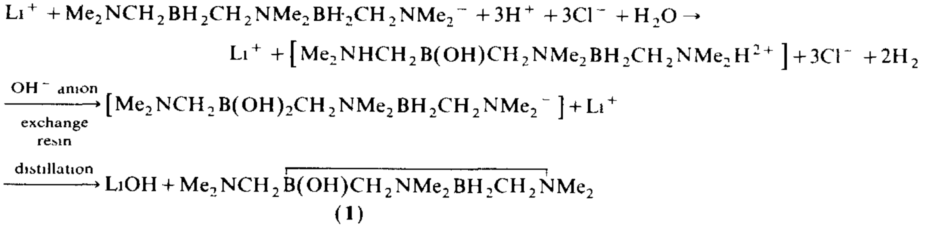
A novel hydroxylated heterocycle, 2-hydroxy-2-(dimethylaminomethyl)-1,1,4,4-tetramethyl-1,4-diazonia-2,5-diboratacyclohexane (**1**) is isolated as a water-clear,



(1)

high-boiling liquid by controlled hydrolysis of the functionally substituted bis-borane borohydride anion $Me_2NCH_2BH_2CH_2NMe_2BH_2CH_2NMe_2^-$ [1]. The preparative procedure (Scheme 1) involves conversion of anions to hydroxide subsequent to acid-catalyzed hydrolysis, finishing with pyrolytic distillation.

SCHEME 1 *



$$Li^+ + Me_2NCH_2BH_2CH_2NMe_2BH_2CH_2NMe_2^- + 3H^+ + 3Cl^- + H_2O \rightarrow$$

$$Li^+ + [Me_2NHCH_2B(OH)CH_2NMe_2BH_2CH_2NMe_2H^{2+}] + 3Cl^- + 2H_2$$

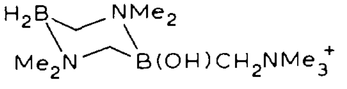
$$\xrightarrow[\text{exchange resin}]{OH^- \text{ anion}} [Me_2NCH_2B(OH)_2CH_2NMe_2BH_2CH_2NMe_2^-] + Li^+$$

$$\xrightarrow{\text{distillation}} LiOH + Me_2NCH_2\overline{B(OH)CH_2NMe_2BH_2CH_2N}Me_2$$

(1)

A hydrogen-bonded condensed state and a monomeric vapor are inferred from the broad infrared OH absorption of the liquid, and the $(P-3)$ molecular ions in the mass spectrum. Inter- as well as intra-molecular hydrogen bonding must obtain to account for the noticeable viscosity.

1 is quaternized at the amine function by methyl iodide to form a water-stable cation (**2**) whose salts have sharp, non-hydrogen-bonded infrared OH stretches.

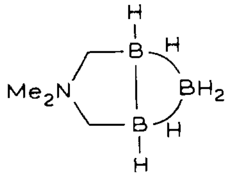


(**2**)

Proton NMR data (non-equivalent ring multiplets) are consonant with a chair configuration and a mixture of equatorial and axial substitution.

Volatility of a quadrivalent hydroxylated borane is an unusual feature, so the integrity of the heterocyclic structure of **1** during volatilization may be questioned. Certainly the enhancement of Lewis acidity of the hydroxylated boron by two dimethylaminomethyl substituents favors an intact ring. One direct, albeit not easy, verification of integrity hinges on a successful resolution of enantiomers developed by the dissymmetric boron site.

Because 1,1-dimethyl-1,3-azoniaboratacyclobutane, $Me_2\overline{NCH_2BH_2C}H_2$ [2], also has a $-CH_2BH_2CH_2-$ function, a similar hydrolytic procedure was explored. Ring cleavage by acid to form tetramethylammonium ion was observed, implicating some ylidic nature to the methylene bridge carbons. Attempts then to cleave the ring with diborane led instead to the isolation of a triborane derivative (**3**) as an air-stable, sublimable white solid. Elemental analyses, parent mass peaks, and BHB infrared absorption observed suggest probable structures:



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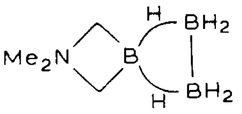

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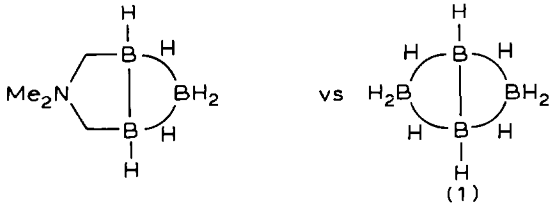
* Non-isolated, proposed intermediates appear in parentheses.

Attempts to cleave a labile B_2H_4 moiety from the triborane failed with ammonia, trimethylphosphine, and triphenylphosphine even under forcing conditions of 90 °C with the later two bases. Moreover the fingerprint region infrared absorption is very different and simpler than that of the precursor azoniaborata-cyclobutane which is a moiety of the spirotriborane structure. Thus neither chemical reactivity nor details of the infrared is as expected for a spirotriborane arrangement. By contrast the ^{11}B and ^{1}H NMR data together support the other possibility which may be viewed as analogous to tetraborane(10), and similar to $Me_3PBH_2CH_2CH_2BH\overset{\frown}{H_2}B_2H_3PMe_3$ [3].

(3)



(3) vs (1)

Methylene proton resonance in **3** is upfield from *N*-methyl as opposed to the peculiar downfield position in the azoniaboratacyclobutane precursor. The ^{11}B resonances at +2.6 and −27.5 ppm for one and two borons, respectively, are in relative positions anticipated for a disubstituted triborane, in that known monosub-

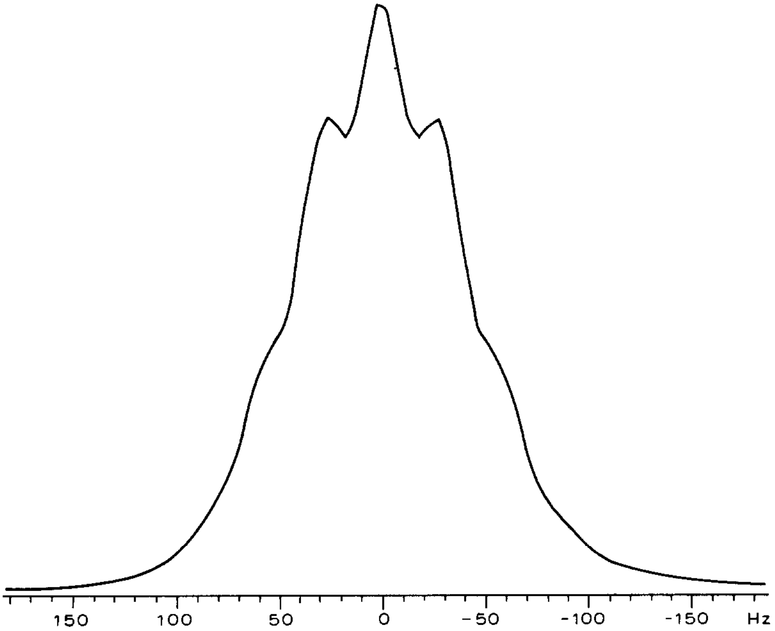


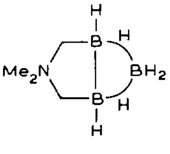
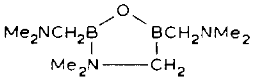
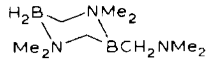
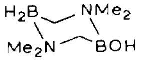
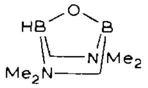
Fig. 1. ^{11}B NMR spectrum (48.14 MHz) of upfield resonance of  .

TABLE 1

MASS DATA FOR $Me_2NCH_2\overline{B(OH)CH_2NMe_2BH_2CH_2N}Me_2$ (1)

Composition assigned	m/e (obs.)	Δ [a] (mmass)	Intensity		Plausible structures
			Obs.	Calcd. [b]	
$C_9H_{24}N_3O^{11}B_2$	212.2111	0.6	4.3	4 7	
$C_9H_{24}N_3O^{11}B^{10}B$	211.2136	−0.6	2 3 [b]		
$C_9H_{26}N_3{}^{11}B_2$	198.2322	0.9	1.4	1.5	
$C_9H_{26}N_3{}^{11}B^{10}B$	197.2346	−0.3	0.7 [b]		
	169.1680		1.2		
	158.1710		4.6		
$C_6H_{19}N_2O^{11}B_2$	157.1678	−0.5	68.3	70.8	
$C_6H_{19}O^{11}B^{10}B$	156.1707	−1.2	34.9 [b]		
$C_6H_{17}N_2O^{11}B_2$	155.1557	3.0	29.8	27.0	
$C_6H_{17}N_2O^{11}B^{10}B$	154.1553	−1.0	13.3 [b]	13.3	
$C_6H_{17}N_2O^{10}B_2$	153.1511	−8.9	3.0	1.6 [c]	
	145.1510		5.6		
	144.1519		2.0		
$(Me_2NCH_2BH_2)_2H$	141.1728	−0.6	0.5		
$C_5H_{15}N_2O^{11}B_2$	141.1362	−0.8	3.1	3.1	
$C_5H_{15}N_2O^{11}B^{10}B$	140.1404	−0.3	1.5 [b]		
	113.1204 [d]		11.5		
$C_4H_{12}NO^{11}B_2$	112.1105	0	94.8	98.3	
$C_4H_{12}NO^{11}B^{10}B$	111.1133	−0.8	48.5 [b]	48.5	
$C_4H_{12}NO^{10}B_2$	110.1102	7.6 [c]	9.3	5.9 [c]	
	99.0950		10.7		
$C_3H_{10}NO^{11}B_2$	98.0939	−1.0	29.0	25.6	
$C_3H_{10}NO^{11}B^{10}B$	97.0983	−0.2	12.6 [b]	12.6	
$C_3H_{10}NO^{10}B_2$	96.1018	−0.3	2.2	1.5	
	86.0781		19.4		
	84.0913		34.1		
	72.0986		11.8		
$Me_2NCH_2{}^{11}BH$	70.0819	−0.9	73.33	91 7	
$Me_2NCH_2{}^{10}BH$	69.0837	−2.7	22.6 [b]		
Me_2NCH_2	58.0674	1.8	100		
	56.0678		32.2		

[a] Observed m/e minus formula mass. [b] Based on abundancies of boron isotopes and normalized to indicated observed intensity. [c] Rather poor match of intensity and mass for $^{10}B_2$ containing fragments is generally observed. Low inherent intensity (6.1% of $^{11}B_2$-containing fragment) and overlap with another fragment of close mass may be responsible. [d] Only fragments of intensity greater than 10% are tabulated below mass 140, generally.

stituted triboranes like $B_3H_7 \cdot THF$ and $B_3H_7 \cdot NMe_3$ have the unique, substituted boron resonance upfield [4]. Both resonances are broad and split by hydrogen. The upfield resonance has the most distinguishable pattern, that of an even number of (at least four but likely six with J(BH) 30 Hz) hydrogens (Fig. 1). Chemical shift of the downfield resonance assigned to the BH_2 moiety of **3** is close to that of the structurally analogous 2,4-borons of tetraborane(10) (+5.2 ppm, [5]) and metal hydride-bridged analogs of tetraborane (+0.3 to +9.0 ppm, [6]). Similarly, the shift of the upfield resonance assigned to the $Me_2\overline{NCH_2(BH)_2C}H_2$ moiety is close to that of the structurally analogous azoniaboratacyclobutane (−28.5 ppm). In the H-

TABLE 2

MASS DATA FOR $Me_2N(CH_2)_2B_3H_6$ (3), $C_4H_{16}NB_3$

Composition assigned	*m/e* obs	Δ[a] (mmass)	Intensity	
			Obs.	Calcd[b]
$C_4H_{15}N^{11}B_3$	110.1471[c]	−1.2	2.84	3.01
$C_4H_{15}N^{11}B_2{}^{10}B$	109.1518	−0.2	2.23[b]	2.23[b]
$C_4H_{14}N^{11}B_3$	109.1408	0.2	13.80	13.84
$C_4H_{14}N^{11}B_2{}^{10}B$	108.1444	0.2	10.24[b]	10.24[b]
$C_4H_{14}N^{11}B^{10}B_2$	107.1481	0.3	1.94	2.52
$C_4H_{12}N^{11}B_3$	107.1247	−0.2	5.90	4.31
$C_4H_{12}N^{11}B_2{}^{10}B$	106.1286	0.1	3.19[b]	3.19[b]
	105.0704		1.8	
$C_4H_{13}N^{11}B_2$	97.1240	0.5	1.6[c]	
$C_4H_{13}N^{11}B^{10}B$	96.1274	0.4	0.7	0.4
$C_4H_{12}N^{11}B_2$	96.1156	0.02	2.4[b]	
$C_4H_{12}N^{11}B^{10}B$	92.1010	0.7	1.1	0.6
$C_4H_{11}{}^{11}BN$	84.0987	0.3	4.4	
$C_3H_{10}N^{11}B\,(CH_3)_2NCH_2BH_2$	71.0905	−0.1	7.6	
$C_3H_9N^{11}B\,(CH_3)_2NCH_2BH$	70.0827	−0.06	10.4[b]	
	69.9985		13.1	
$C_3H_9N^{10}B$	69.0873	0.9	0.9	2.6
	68.9789		1.1	
	65.0219		2.6	
	59.0771		2.6	
$(CH_3)_2NCH_2$	58.0681	2.4	58.3	
	56.0697		11.8	
	51.0068		100	

[a] Observed *m/e* minus formula mass. [b] Based on abundancies of boron isotopes and normalized to indicated intensity. [c] Chemical ionization at low resolution had a 110 *m/e* base peak and a high mass envelope at 110, 109, 108 with 100%, 75%, and 21% intensities, respectively, versus 100% [b], 74%, and 18% calculated for $C_4H_{15}NB_3$.

decoupled spectrum, the observed broader width of the unique boron is inexplicable by quadrapolar broadening in view of its apparently more symmetrical electrical field.

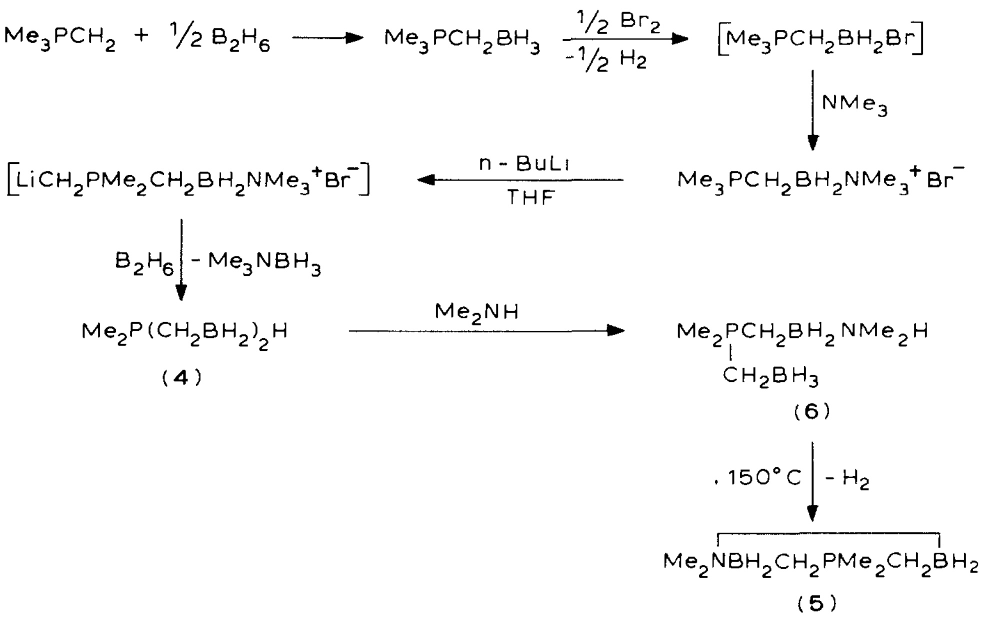
Mass spectral data for **1** and **3**, collected in Tables 1 and 2, show parent molecular weight envelopes and the presence of 2- and 3-borons, respectively. Tentative assignments of fragment formulas are based on deductions of the number of boron atoms. Knowledge of the parent compound chemistry and the likelihood of cyclic structures for the fragments allows some speculation about the fragments.

Absence of the $(P-1)$ ion for **1** is unusual for BCN-sequenced compounds. Loss of a hydrogen molecule from the protonic hydrogen on the hydroxyl and the hydridic proton on the $(P-1)$ fragment could account for $(P-3)$ as highest significant mass fragment. Loss of the Me_2NCH_2 substituent would give the $C_6H_{19}N_2OB_2$ fragment which was observed as a very abundant ion. The intense (second only to $Me_2NCH_2{}^+$) 112.1105 fragment with assumed composition $C_4H_{12}NOB_2$ is more speculative. A structure similar to **4** with an oxide bridge and trigonal borons would be consistent with the formula and would be obtainable from the $C_6H_{19}N_2OB_2$ fragment by loss of Me_2N followed by rearrangement.

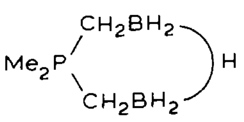
BCP-sequenced heterocycles

Two new heterocycles, $\mathrm{Me_2P(CH_2BH_2)_2H}$ (**4**) and $\mathrm{Me_2\overline{NBH_2CH_2PMe_2CH_2BH_2}}$ (**5**) having BCP sequences were isolated using the preparative reactions shown, (Scheme 2) wherein non-isolated intermediates appear in parentheses.

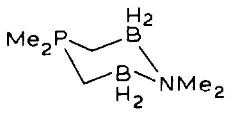
SCHEME 2



μ-(Methylenedimethylphosphinomethyl)diborane(6) (**4**) and 1,1,4,4-tetramethyl-1-azonia-4-phosphonia-2,6-diboratacyclohexane (**5**) are white, sublimable crystalline

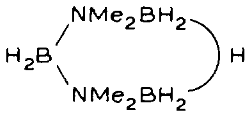


(4)



(5)

solids. Both are thermally stable, but **4** is moisture-sensitive. **4** is one of few monohydrogen-bridged species and is nominally analogous to the borane adduct of dimethylaminoborane dimer reported by Keller [7]:



It differs from this molecule in that the bridge may be cleaved without loss of the skeletal framework. The dimethylamine adduct, **6**, can be sublimed without decomposition, and, does not lose $\mathrm{Me_2NHBH_3}$ nor $\mathrm{(Me_2NBH_2)_2}$ and hydrogen to form the phosphonia analogue of $\mathrm{Me_2\overline{NCH_2BH_2CH_2}}$. The structure of **5**, is a permutation montage of two previously reported heterocycles, $\mathrm{Me_2\overline{PCH_2BH_2CH_2BH_2}}$ [8]

TABLE 3

MASS DATA FOR $Me_2P(CH_2BH_2)_2H$ (4), $C_4H_{15}PB_2$

Composition assigned	*m/e* obs.	Δ[a] (mmass)	Intensity	
			Obs.	Calcd[b]
$C_4H_{14}P^{11}B_2$	115.1016	−0.3	34.75	24.84
$C_4H_{14}P^{11}B^{10}B$	114.1056	0.0	12.25[b]	
$C_4H_{13}P^{11}B_2$	114.0942	0.1	26.90	20.79
$C_4H_{13}P^{11}B^{10}B$	113.0976	−0.1	10.25[b]	
$C_4H_{12}P^{11}B_2$	113.0863	0.0	31.76	33.89
$C_4H_{12}P^{11}B^{10}B$	112.0900	0.0	16.71[b]	
$C_4H_{11}P^{11}B_2$	112.0785	0.1	39.81	35.10
$C_4H_{11}P^{11}B^{10}B$	111.0823	0.2	17.31[b]	
$C_4H_{10}P^{11}B_2$	111.0705	−0.1	28.96	28.49
$C_4H_{10}P^{11}B^{10}B$	110.0742	0.0	14.05[b]	
	102.0774		16.11	
	80.9907		6.7	
C_3H_9P	76.0446	0.4	19.2	
C_3H_3P	69.9986	1.4	100	
$C_2H_3P^{11}B$	69.0084	1.9	9.5	
	68.9654		7.3	
	68.9619		6.2	

[a] Observed *m/e* minus formula mass. [b] Based on abundancies of boron isotopes, normalized to indicated intensity.

TABLE 4

MASS DATA FOR $Me_2P(CH_2BH_2)_2NMe_2$ (5), $C_6H_{20}NPB_2$

Composition assigned	*m/e* obs.	Δ[a] (mmass)	Intensity	
			Obs.	Calcd[b]
$C_6H_{20}NP^{11}B_2$	159.1482	−2.7	5.6	
$C_6H_{19}NP^{11}B_2$	158.1436	−0.6	66.4[b]	
$C_6H_{19}NP^{11}B^{10}B$	157.1440	−3.8	41.4	32.7
$C_6H_{17}NP^{11}B_2$	156.1289	0.4	100[b]	
$C_6H_{17}NP^{11}B^{10}B$	155.1308	−1.3	47.3	49.3
$C_6H_{15}NP^{11}B_2$	154.1201	−7.3	19.7	
$C_6H_{15}NP^{11}B^{10}B$	153.1161	−0.4	6.7	
	152.1206		1.1	
	146.1260		2.4	
	145.1196		15.2	
	144.1178		23.2	
	143.1322		3.0	
	144.1156		4.9	
$C_5H_{15}NP^{11}B_2$	142.1130	0.2	24.0[b]	
$C_5H_{15}NP^{11}B^{10}B$	141.1144	−2.0	14.6	11.8
	102.0782		20.3	
	101.0711		31.2	
	94.1002		10.7	
$C_3H_9P(Me_3P)$	76.0447	0.5	20.2	
C_3H_9P	75.0307	0.43	4.3	
$C_3H_9N^{11}B(Me_2NCH_2BH)$	70.0826	−0.2	12.2[b]	
	69.9987		4.0	
$C_3H_9N^{10}B$	69.0866	−2.5	2.8	3.0
	69.0718		4.8	

[a] Observed *m/e* minus formula mass. [b] Based on boron isotope abundancies, normalized to indicated intensity.

and $\mathrm{Me_2\overline{NCH_2BH_2NMe_2B}H_2}$ [9]. Mass spectral data for **4** and **5** are collected in Tables 3 and 4.

Examination of the structures and reactivity of BCN- and BCP-sequenced species shows many similarities and one notable difference. All structures have alternating polarity, some with fixed charges (as opposed to dative bonds), and kinetic stability toward hydrolysis and oxidation when the borane function has bulky substituents. There is a difference in stability toward hydrolysis of the $\mathrm{-CH_2BH_2CH_2-}$ function in BCN- vs. BCP-sequenced derivatives. $\mathrm{Me_2\overline{PBH_2PMe_2CH_2BH_2}CH_2}$ is reported to be very stable [8]; $\mathrm{Me_3PCH_2BH_3}$ [10], $\mathrm{Me_2\overline{NCH_2BH_2C}H_2}$, and $\mathrm{Me_2NCH_2BH_2CH_2NMe_2BH_2CH_2NMe_2^-}$ are decreasingly so. A net positive charge for the $\mathrm{CH_2\overset{+}{P}Me_2\overset{-}{B}H_2\overset{+}{P}Me_2CH_2}$ moiety in the first mentioned diphosphoniadiboratacyclohexane was suggested as responsible for decreased hydridic nature and lability of a chelated $\mathrm{\overset{-}{B}H_2}$ moiety, and a similar argument would obtain for $\mathrm{Me_2\overline{N^+CH_2BH_2^-C}H_2}$.

Experimental details

Reagent grade solvents were employed. 1,2-Dimethoxyethane (glyme) and tetrahydrofuran (THF) were purified by reflux with lithium aluminum hydride prior to distillation. Hexane was freed from olefin with sulfuric acid, washed, dried, and distilled from calcium hydride. Trimethylphosphine and trimethylphosphinemethylene were prepared using published methods (respectively, [11] and [12]). Diborane (Callery Chemical) was essentially free of higher boron hydrides. $\mathrm{Me_3PCH_2BH_2NMe_3^+\ Br^-}$ was prepared from the borane adduct of trimethylphosphinemethylene in chloroform by addition of 0.5 mol equivalent bromine followed by 1 mol equivalent trimethylamine. Product salt, after solvent removal under vacuum, was used without further purification. All other reagents were commercially obtained and were used without further purification. Infrared and proton NMR data were obtained on Beckman 4240 and Hitachi/Perkin–Elmer R24B instruments. Microanalytical data are from Schwarzkopf Microanalytical Laboratory, Woodside, NY, and Mic Anal., Tucson, AZ. Mass data are obtained from the Midwest Center for Mass Spectrometry, Lincoln, NE.

2-Hydroxy-2-(dimethylaminomethyl)-1,1,4,4-tetramethyl-1,4-diazonia-2,5-diboratacyclohexane (1)

A solution of 286 mg (1.3 mmol) $\mathrm{Li^+\ Me_2NCH_2BH_2CH_2NMe_2BH_2CH_2NMe_2^-}$ [1] in 15 ml deoxygenated water was treated with 2.7 ml 1 *M* hydrochloric acid. After gas evolution ceased, the solution was evaporated, the white solid residue was heated to 80 °C under dynamic high vacuum pumping, and product was collected in a U-trap. The clear, viscous, oily product was warmed to room temperature and intermittantly pumped until the vapor pressure fell to less than 1 mmHg to remove water traces; 150 mg, 50% yield. A portion dissolved in hexane was methylated with methyl iodide and metathesized to the hexafluorophosphate. The product salt could not be recrystallized from hot water; it was recrystallized from 1/1 acetonitrile/methylene chloride by addition of a three-times portion of hexane to obtain white crystals, m.p. 203–204 °C. Anal. Found: C, 31.1; H, 8.0; N, 10.4. $\mathrm{Me_3NCH_2\overline{B(OH)CH_2NMe_2BH_2CH_2N}Me_2^+\ PF_6^-}$ calcd.: C, 32.0; H, 8.1; N, 11.2%. 0.75 hydrate calcd. : C, 31.2; H, 8.4; N, 10.8%.

IR absorptions (neat) [13] for $Me_2NCH_2B(OH)CH_2NMe_2BH_2CH_2NMe_2$ 3480bd m, 2990m, 2940 s, 2900sh, 2870sh, 2840vw, 2820m, 2770s, 2400w, 2330s, 2260w, 1480-1465-1455tp s, 1420vw, 1405w, 1320m, 1300–1290db m, 1280w, 1250-db w, 1230vw, 1190bd m, 1170s, 1135m, 1105m, 1080m, 1030vw, 1010m, 980m, 950w, 925w, 870s, 840w, 800m, 755w, 735m.

IR absorptions (mull) [13] for $Me_3NCH_2B(OH)CH_2NMe_2BH_2CH_2NMe_2^+$ PF_6^- 3680s sharp, 2405w, 2325 s, 2260w, 1420w, 1415vw, 1410w, 1360vw, 1350w, 1320w, 1300w, 1240w, 1230w, 1230w, 1190m, 1180s, 1165m, 1140m, 1125vw, 1115w, 1110m, 1095m, 1075m, 1035w, 1010m, 980s, 970m, 920s, 905m, 840s, 765w, 750w.

^1H NMR [14] for $Me_3NCH_2B(OH)CH_2NMe_2BH_2CH_2NMe_2^+$ I^- (D_2O): 3.04(9) NMe_3; 2.72, 2.67(5) unequal doublet, ring NMe_2; 2.54, 2.47, 2.43(8) triplet, ring NMe_2.

μ-(Methylidodimethylammoniomethyl)triborane(7) (3)

A 40 mg-portion (0.5 mmol) $Me_2NCH_2BH_2CH_2$ [2] was sealed in an ampoule with 3 ml glyme and 0.5 mmol diborane. After heating overnight at 80 °C, the ampoule was opened to vent generated gas. Solvent was removed under vacuum, and the product collected as a white solid by sublimation at 50–100 °C/high vacuum; yield 20 mg. Purification by contact with trimethylphosphine followed by sublimation gave white crystals, m.p. 84–85 °C. No reaction with ammonia to 40 °C, trimethylphosphine to 60 °C, and triphenylphosphine in xylene to 85 °C was observed. Anal. Found: C, 43.8; H, 15.0; N, 12.6. $C_4H_{16}BN$ calcd.: C, 43.4; H, 14.7; N, 12.7%.

IR absorptions (mull) [13]: 2390m, 2320s, 2200vw, 2150vw, 2090w, 2060–2070db w, 1355w, 1340vw, 1305vw, 1295vw, 1265w, 1160m, 1140m, 1105m, 1085m, 1055vw, 1025vw, 1010w, 980s, 950s, 930w, 910vw, 890w, 835w, 770w, 720w.

^1H NMR [14] in $CDCl_3$: 2.95 (3) with shoulder NMe_2; 2.50 broad 18 Hz at half-height (2) $N(CH_2)_2$. H-decoupled ^{11}B NMR in $CHCl_3$ [15]; +2.6 (1); −27.45 (2).

μ-(Methylenedimethylphosphinomethyl)diborane(6) (4)

A stirred mixture of 660 mg (2.8 mmol) $Me_3PCH_2BH_2NMe_3^+$ Br^- in about 5 ml THF was treated dropwise with 0.5 ml 1.6 *M* n-butyllithium in hexane (syringe) keeping pot temperature at −25 °C for 15 min. Most solid had dissolved at this time, and 2.7 mmol (measured as a gas) diborane were added. After stirring briefly at room temperature, solvent was removed and the residue sublimed to pot temperature of 80 °C to give 118 mg product and 77 mg Me_3NBH_3 which collected in cold trap. Two resublimations of another preparation below 80 °C gave white crystals in 60% recovery; m.p. 68–72 °C. Product was sensitive to moisture.

IR absorptions (mull) [13]: 2420sh, s, 2390s, 2310m, 2210bd w, 1935bd s, 1420-1415-1410 tp m, 1305m, 1295s, 1265bd w, 1175s, 1140bd m, 1100bd w, 1080bd w, 1060w, 1050vw, 990db bd s, 955s, 945sh, 930sh, 905w, 840w, 890–880db w, 770m, 760m.

^1H NMR in CH_2Cl_2 [14]: 1.71, 1.49 doublet, J(PCH) 13.2 Hz (6) PMe_2; 0.95, 0.75 broad doublet, J(PCH) 12 Hz $P(CH_2)_2$. ^{11}B NMR in $CHCl_3$ [15] 1/2/1 doublet −13.1 ppm, J(HB) 109 Hz. Splitting from the bridge hydrogen was not distinguishable.

1,1,4,4-Tetramethyl-1-azonia-4-phosphonia-2,6-diboratacyclohexane (5)

To 118 mg **4** was added 1.8 mmol Me_2NH (measured as a gas) and 0.75 ml THF. After stirring 5 min, solvent and volatile reagents were removed under vacuum, and the inferred product adduct, $H_3BCH_2PCH_2BH_2NMe_2H$, was sublimed at 80 °C as a white solid, 130 mg, 80%. Heating product under 0.75 atm. nitrogen in ampoule for 1 h gave 93 mg white sublimate, 70 °C/high vacuum. A resublimed sample was analyzed, m.p. 136–138 °C/under nitrogen in sealed capillary. Anal. Found: C, 45.5; H, 12.2; N, 8.6. $C_6H_{20}B_2NP$ calcd.: C, 45.4; H, 12.7; N, 8.8%.

IR absorptions (mull) [13]: 3000m, 2380w, 2290–2310db s, 2240–2250db s, 2120vw, 2050vw, 1470m, 1450w, 1425vw, 1410vw, 1395vw, 1310vw, 1295m, 1230w, 1185s, 1150w, 1135–1125db s, 1100m, 1075s, 1045m, 1010m, 980m, 955s, 935s, 905m, 830–825db vw, 795m, 770m, 755m.

^1H NMR resonances in $CHCl_3$ [14]: 2.25 (5.7) NMe_2; 1.70, 1.50 doublet, $J(PCH)$ 12 Hz (6) PMe_2; 0.85, 0.70 doublet, $J(PCH)$ 9 Hz (3.8) $P(CH_2)_2$.

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14 Chemical shift in ppm downfield from reference tetramethylsilane or a trimethylsilyl-substituted sulfonate salt. Relative intensity in parentheses.

15 Relative to BF_3·etherate, at 48.14 MHz, run by the Colorado State University Regional NMR Center.