Inorg. Chem. **1993**, *32*, 5889–5893 **5889**

Synthesis and Chemistry of 1,1,4,4-Tetramethyl-1-azonia-4-phosphonia-2,5-diboratacyclohexane, a Novel Multipolar Framework Heterocycle

Scott W. Dougherty and Norman E. Miller*

Chemistry Department, University of South Dakota,
Vermillion, South Dakota 57069

Received April 29, 1993

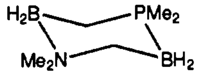
Introduction

A number of saturated valency heterocycles with boryl and methylene moieties have been characterized, beginning with $Me_2NCH_2BH_2NMe_2CH_2BH_2$, reported in 1964.[1] Rings of four, five, and six members are known, for example the following: $Me_2N(CH_2)_2BH_2$;[2] $Me_2NBH_2CH_2NMe_2BH_2$;[3] $MeGaCH_2NMe_2BH_2CH_2EMe_2$[4] (E = P, N); $Me_2AlCH_2NMe_2BH_2CH_2NMe_2$;[4a] $H_2B(PMe_2CH_2)_2ER_n$ (ER_2 = BH_2, $AlMe_2$, $GaMe_2$, $AuMe_2$).[5] They are part of a larger class of cyclic and acyclic compounds with alternating polar sites arising generally from dative bonds. A more generic name of multipolar framework compounds has been applied[4b] to highlight the molecular architecture of saturated, single-bonded valency and multiple polar sites. As many as seven poles have been incorporated in a single species such as $[(Me_3PBH_2CH_2NMe_2)_2BH_2]^+$,[6] but an upward limit has not been probed.

Several six-membered multipolar framework heterocycles are nominally diadducts of biphilic cyclopropane-like monomers such as $Me_2NCH_2BH_2$. There is no evidence, however, for these monomers except in mass spectral plasmas. Two types of rings are known, those composed of like monomers as for $(MeSCH_2BH_2)_2$[7] and $(Me_2NCH_2BH_2)_2$[1] and those composed of different monomers as for $Me_2GaCH_2PMe_2BH_2CH_2NMe_2$.[4b] In principle, heterocycles of the latter type could disproportionate in part into dimers of the component monomers, presumably via ring dissociation at one adduct bond. Such a disproportionation has yet to be observed, which fact is indicative of considerable structural integrity toward ring opening for these heterocycles.

Results and Discussion

1,1,4,4-Tetramethyl-1-azonia-4-phosphonia-2,5-diboratacyclohexane. A new example of the mixed-monomer, six-membered heterocycles, having N and P basic sites, has been characterized and is reported here. 1,1,4,4-Tetramethyl-1-azonia-4-phosphonia-2,5-diboratacyclohexane, **1**, is prepared by cyclization using a lithiated, borane-substituted tertiary amine of yet undetermined association (Scheme I).



1

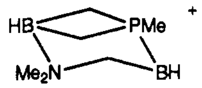
Scheme I

$$Me_3PBH_2CH_2NMe_2 \xrightarrow[\text{hexane}]{t\text{-BuLi}} [LiCH_2PMe_2CH_2NMe_2] \xrightarrow[\text{hexane}]{Me_2SBH_2Cl} \mathbf{1}$$

Nominally an adduct of $(Me_2NCH_2BH_2)$ and $(Me_2PCH_2BH_2)$ monomers, **1** is a transparent colorless crystalline solid (of white appearance in the aggregate), mp 90–91 °C, soluble in organic solvents, and insoluble in water. It sublimes easily under high vacuum slightly above room temperature and is stable in moist air with no deterioration over long (>half-year) periods in screw-capped vials. Its physical properties (mp, IR spectrum, solubility, appearance, ...) are more similar to those of its analogue $(Me_2NCH_2BH_2)_2$ than are its chemical properties (*vide infra*). It may be recrystallized from methanol/water (30%) and can be sublimed. It has a camphor-like odor characteristic of its $(Me_2NCH_2BH_2)_2$ analogue but with an overtone of phosphine stench.

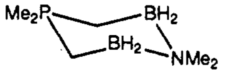
Isolation of **1** was complicated by $(Me_2NCH_2BH_2)_2$ contaminant carried along with the $Me_3PBH_2CH_2NMe_2$[6] starting material. Clean separation was effected on an analytical scale GC capillary column coated with methylsilicone gum. Separation by HPLC on an analytical scale was also observed but was difficult to scale to preparative level owing to the lack of a suitably sensitive detection system and because of close retention times. Neither **1** nor $(Me_2NCH_2BH_2)_2$ has much low-frequency UV absorbance. A 15 mg-sample of 98% purity (by GC/MS) was obtained from a 80% preparation by multiple sublimations. Larger samples purified to about 90% level were achievable after two or three sublimations.

A monomeric form for **1** in the vapor phase was substantiated by mass spectral data (Table I), which show a strong (parent − 3H)$^+$ envelope. The compositions of **1** and many of its fragmentation parts in the MS plasma were affirmed by high-resolution mass data (Table II). The presence of a (parent − 3H)$^+$ cluster in multipolar framework heterocycles is unusual since the most intense peak of multipolar heterocycles is seldom near the parent mass. The difference may arise because phosphorus readily stabilizes ylidic methylene, $P{=}CH_2$. Negative hydrogen on boron could favor loss of H_2 to form the ylide. This, along with loss of hydrogen ($H^•$) and methyl ($CH_3^•$) could account for the two 100% envelopes at *m/e* 156/155 and 142/141, respectively. Cyclization of the ylidic structure could lead to a bicyclic cation,



(M − 3H)$^+$

The new mixed monomer heterocycle **1** is a permutation of a known heterocycle bearing a fixed positive center and a *μ*-dimethylamino bridge,[8]



This latter heterocycle melts and sublimes at much higher temperatures and has different IR and NMR spectra. Its mass spectral fragmentation pattern, however, is very similar[8] to that for **1** except that the *m/e* 142/141 envelope is about one-fourth as intense.

---

(1) Miller, N. E.; Muetterties, E. L. *Inorg. Chem.* **1964**, *3*, 1196.
(2) Warnock, G. F.; Miller, N. E. *Inorg. Chem.* **1979**, *18*, 3620.
(3) Gragg, B. R.; Ryschkewitsch, G. E. *Inorg. Chem.* **1976**, *15*, 1209.
(4) (a) Miller, N. E. *J. Organomet. Chem.* **1977**, *137*, 131. (b) Webb, K. M.; Miller, N. E. *J. Organomet. Chem.*, in press.
(5) (a) Schmidbaur, H.; Füller, H. J.; Müller, G.; Frank, A. *Chem. Ber.* **1979**, *112*, 1448. (b) Schmidbaur, H. *J. Organomet. Chem.* **1980**, *200*, 287.
(6) Byrne, M. J.; Miller, N. E. *Inorg. Chem.* **1981**, *20*, 1328.
(7) Nöth, H.; Sedlak, D. *Chem. Ber.* **1983**, *116*, 1479.
(8) Miller, N. E. *J. Organomet. Chem.* **1984**, *269*, 123.

0020-1669/93/1332-5889$04.00/0

Table I. Low-Resolution Mass Spectral Data[a]

1					2				
m/e	intensity, %	calcd[b]	formula	assgnt	*m/e*	intensity, %	calcd[b]	formula	assgnt
					159	5		$^{13}CC_6H_{19}NP^{11}B_2$ or $C_8H_{20}NP^{11}B_2$	$(M - CO_2 - H)^+$ or $(M - CO_2)^+$
158	16		$C_6H_{19}NP^{11}B_2$	$(M - H)^+$?	158	58	58*	$C_6H_{19}NP^{11}B_2$	$(M - CO_2 - H)^+$
157	14		$C_6H_{19}NP^{11}B^{10}B$	$(M - H)^+$	157	36	21	$C_6H_{19}NP^{11}B^{10}B$	$(M - CO_2 - H)^+$
156	97	97*	$C_6H_{17}NP^{11}B_2$	$(M - 3H)^+$	156	100	100*	$C_6H_{17}NP^{11}B_2$	$(M - CO_2 - 3H)^+$
155	55	48	$C_6H_{17}NP^{11}B^{10}B$	$(M - 3H)^+$	155	45	49	$C_6H_{17}NP^{11}B^{10}B$	$(M - CO_2 - 3H)^+$
154	33	6	$C_6H_{17}NP^{10}B_2$	$(M - 3H)^+$	154	19	6	$C_6H_{17}NP^{10}B_2$	$(M - CO_2 - 3H)^+$
153	12				153	10			
142	100		$C_5H_{15}NP^{11}B_2$?						
141	51		$C_5H_{15}NP^{11}B^{10}B$						

[a] High mass portion of fragmentation under EI with Hewlett Packard 5890 GC/MS. [b] Calculated for boron isotope abundances, normalized to peak marked with an asterisk in the cluster.

Table II. High-Resolution Mass Spectral Data[a]

1						2					
m/e	formula	Δ,[b] mmass	intensity[c]	calcd[d]	assgnt	*m/e*	formula	Δ, mmass	intensity	calcd[d]	assgnt
						202.1344	$C_7H_{19}NPO_2{}^{11}B_2$	0.4	1.6	*	$(M - H)^+$
						201.1369	$C_7H_{19}NPO_2{}^{11}B^{10}B$	0.7	0.6	0.8	$(M - H)^+$
						158.1445	$C_6H_{19}NP^{11}B_2$	0.5	99	99*	$(M - CO_2 - H)^+$
						157.1475	$C_6H_{19}NP^{11}B^{10}B$	−0.3	48	49	$(M - CO_2 - H)^+$
156.1287	$C_6H_{17}NP^{11}B_2$	0.2	2.2		$(M - 3H)^+$	156.1284	$C_6H_{17}NP^{11}B_2$	−0.1	100	100*	$(M - CO_2 - 3H)^+$
155.1317	$C_6H_{17}NP^{11}B^{10}B$	−0.3	1.1	1.1	$(M - 3H)^+$	155.1319	$C_6H_{17}NP^{11}B^{10}B$	−0.2	51	49	$(M - CO_2 - 3H)^+$
						154.1348	$C_6H_{17}NP^{10}B_2$	−1.0	7	6	$(M - CO_2 - 3H)^+$
85.9511	$CH_2{}^{37}Cl^{35}Cl$	0.7	67		sampling solvent						
83.9542	$CH_2{}^{35}Cl_2$	0.8	100								
70.0825	$C_3H_9N^{11}B$	−0.3	87	87*		70.0828	$C_3H_9N^{11}B$	0.0	87	87*	$Me_2NCH_2{}^{11}BH$
69.0862	$C_3H_9N^{10}B$	−0.3	22	42		69.0866	$C_3H_9N^{10}B$	0.0	22	22	$Me_2NCH_2{}^{10}BH$

[a] EI spectrum from Midwest Center for Mass Spectrometry. [b] Observed − calculated. [c] Intensity for **1** suppressed by the presence of CH_2Cl_2 traces arising from solvent used in injection. [d] Based on B isotope abundances, normalized to peak marked with an asterisk.

Table III. NMR Data (δ, ppm)[a]

	assgnt	1	$Me_2\overline{NCH_2BH_2NMe_2CH_2B}H_2$[b]	2
^1H	$N(CH_3)_2$	2.54 (6)	2.51 (6)	2.73, 2.71 (6) doublet
	NCH_2	2.35 (2) broad	2.01 (2)	2.45–2.35 (2), broad unequal resonances
	$P(CH_3)_2$	1.30 (6) doublet, J_{PCH} = 11 Hz		1.39/1.35 doublet, 1.30/1.26 doublet [both (6)]
	PCH_2	0.6–0.64 (2) multiplet		0.89, 0.84, 0.79, 0.76 (2) unequal, broad
^{11}B	NBH_2	−7.5 (1) 1:2:1 triplet, J_{HB} = 96 Hz, H-decoupled singlet	−9.2 1:2:1 triplet, J_{HB} = 98 Hz, H-decoupled singlet	−8.1, −9.1 (1) equal doublet, H-decoupled singlet −8.6, J_{HB} = 97 Hz
	PBH_2	−30.7, −31.4 (1) doublet of triplets, H decoupled to equal doublet, J_{HB} = 91 Hz, J_{PB} = 73 Hz		−30.0, −31.0, −31.8, −32.7 overlapping triplets, H-decoupled equal doublet, −31.0, −31.7, J_{PB} = 71 Hz
^{31}P (H-decoupled)		−10.99 equal quartet, J_{BP} = 72 Hz		−8.30 approx equal quartet, J_{BP} = 70 Hz

[a] Chemical shift downfield (+), in $CDCl_3$ solution. Referenced to TMSi, external boron trifluoride etherate, and external 85% H_3PO_4 for ^1H, B, and P.

Multinuclear NMR data (Table III) support a chair conformation as known[9] for the $(Me_2NCH_2BH_2)_2$ analogue. A rapid inversion ring motion is presumed because PMe and NMe hydrogens are *not* diastereotopic. Although inversion has not been frozen out in **1** or its analogue, it has been with the *cis*-2,5-dineopentyl derivative of the latter ring.[10]

A stability toward disproportionation is inferred from the absence of any evidence for the dimer of $Me_2PCH_2BH_2$ during GC/MS analysis, mass spectral analysis, purification, storage, and melting. This stability is like that observed for other six-membered multipolar framework heterocycles of mixed monomers. It is not intuitively apparent why this should be so, since adducts normally equilibrate fairly readily. Although disproportionation would not favor the dimers by entropy of mixing, a mixture containing dimers would be anticipated since there is no net difference in number and general type of adduct bonds. It is assumed then, that the rate step for disproportionation (ring opening) is not accessible to temperatures up to 150 °C.

There is no noticeable difference in the stability of **1** and its $(Me_2NCH_2BH_2)_2$ analogue in ambient air. The molecular difference between these two (a change of one nitrogen by phosphorus), however, leads to a noticeable lability toward ambient conditions of $Me_2\overline{GaCH_2PMe_2BH_2CH_2N}Me_2$ as compared to $Me_2\overline{GaCH_2NMe_2BH_2CH_2N}Me_2$.[4b] Consequently, the gallium site is likely involved in a cooperative fashion with phosphorus to cause labilization.

Halogenation of 1. A monoiodo derivative was sought to be used as a precursor to a carboxylic acid derivative of **1**. However, the reaction with iodine in chloroform solution did not proceed as it does for $(Me_2NCH_2BH_2)_2$. Reaction with a deficient amount of iodine did not affect the ratio of **1**/$(Me_2NCH_2BH_2)_2$ remaining, so it must proceed at the same rate for both heterocycles. The iodinated product was sublimed in low (30%) yield presumably

---

(9) Hseu, T. H.; Larsen, L. A. *Inorg. Chem.* **1975**, *14*, 330.
(10) Miller, N. E. *Inorg. Chem.* **1988**, *27*, 2196.

because of its sensitivity to traces of water. It dissolves readily in water to give a neutral solution (with gas evolution). Evaporation of the solvent gave a solid whose IR spectrum showed attenuated BH absorption as well as absorbances characteristic of OH, NH, and borate moieties. A ring opening on hydrolysis of the monoiodide of **1** is assumed, resulting in a nonvolatile species with $-CH_2NMe_2H^+$ and $-CH_2B(OH)_3^-$ moieties. This is remarkably different from the iodination of $(Me_2NCH_2BH_2)_2$, which produces the monoiodo derivative along with a small amount of the 2,5-diiodo derivative,[11] both of which are water-insoluble and unreactive with water.

The reaction of **1** with bromine (in less than 1 equiv amount) in chloroform solution rapidly gave a product that was primarily 2-bromo-**1**, along with small amounts of di-, tri-, and tetrabromo derivatives. ^{11}B NMR data established the site of monobromination in that the triplet of N-bonded boron changed to a doublet on bromination, whereas the multiplet of P-bonded boron was unchanged. The reaction was not only regioselective at the 2-boron site but also selective for **1** over $(Me_2NCH_2BH_2)_2$. Since the bromo derivatives are so much less volatile, purification from unreacted contaminant was readily effected.

Two tribromo-**1** isomers were observed by GC/MS, and a tentative assignment of 2,2,5- and 2,5,5-isomers to the earlier/later eluting isomers, respectively, was made assuming bromine only attaches to boron and that a smaller $Me_2NCH_2BH^+$ fragment would be evidenced by the 2,5,5-isomer. Mass spectrum fragmentation patterns for the mono-, di-, tri-, and tetrabromo products (Table IV) graphically show that electron impact leads to loss of one Br to form the 100% peak envelope, as is also true for the fragmentation of the 2-bromo and 2,5-dibromo derivatives of $(Me_2NCH_2BH_2)_2$ (found in small amounts in bromination products). A small amount of monochloro-**1**, assumed to be the 2-isomer, found in the brominated products was present also in samples of unpurified **1**. It undoubtedly comes by ring closure involving the Me_2SBHCl_2 impurity in the Me_2SBH_2Cl reactant. Surprisingly, mass spectral fragmentation of polybromo derivatives of **1** does not lead to consecutive loss of Br atoms after the first.

Carboxylation of 1. Brominated product from **1**, subliming at 55–60 °C, was determined to be 80–90% 2-Br-**1**, $Me_2NCH_2BH_2PMe_2CH_2BHBr$. It was employed to synthesize the 2-carboxylic acid, **2**, by a recently reported methodology,[12] Scheme II. **2** is a white (transparent crystalline) solid, mp 170 °C (sinter 167–8 °C), with decomposition in an N_2-filled capillary. An overall yield as high as 43% was achieved, based on consumed 2-Br-**1**. When recrystallized from methanol/water (30/70), **2** has no phosphine stench, which fact signals significant aqueous and ambient stability.

A chair-form conformation for **2** is assumed and confirmed by diastereotopic N-methyl and P-methyl hydrogen resonances (Table III). ^{11}B data permit assignment as the 2-HO_2C derivative. The N-bound boron resonance was a doublet (for BH) whereas the P-bound boron resonance was the unchanged doublet of triplets found for **1**.

Clearly, the 2-carboxylic acid derivative is stable and readily synthesized, a significant finding in its own right since the carboxylic acid functionality allows conjugation of this heterocyclic ring to other structures. A second generation of derivatives based on **2**, similar to that being developed for $Me_2NCH_2BH_2NMe_2CH_2BHCO_2H$[12] may be anticipated, but with some chemical differences arising from the presence of phosphorus in the ring. The synthesis of **2** furthermore provides evidence of the general applicability of the new carboxylation method for intact boranes.

Table IV. Mass Spectral Data[a] for Brominated Products of **1**

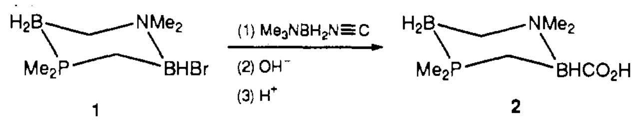
2-bromo-1				dibromo-1				(2,2,5)[b]-tribromo-1				(2,5,5)[b]-tribromo-1				tetrabromo-1			
m/e	intensity, %	calcd[c]	assgnt	me	intensity, %	calcd[c]	assgn	m/e	intensity, %	calcd[c]	assgnt	m/e	intensity, %	calcd[c]	assgnt	m/e	intensity, %	calcd[c]	assgnt
239	2			239	6			319	4			319	4						
238	8	*	$C_6H_{18}NP^{11}B_2{}^{81}Br$ $(M-H)^+$	238	88	99	$C_6H_{18}NP^{11}B_2{}^{81}Br$ $(M-Br)^+$	318	50	48	$C_6H_{17}NP^{11}B_2{}^{81}Br_2$ $(M-Br)^+$	318	50	48	$(M-Br)^+$	398	25	30	$C_6H_{16}NP^{11}B_2{}^{81}Br_3$ $(M-Br)^+$
237	4	4	$(M-H)^+$	237	48	46	$(M-Br)^+$	317	30	23	$(M-Br)^+$	317	30	23	$(M-Br)^+$	397	27	15	$(M-Br)^+$
236	11	*	$(M-2H)^+$	236	100	100	$(M-Br)^+$	316	100	100	$(M-Br)^+$	316	100	100	$(M-Br)^+$	396	98	94	$(M-Br)^+$
235	5	5	$(M-2H)^+$	235	45	47	$(M-Br)^+$	315	59	48	$(M-Br)^+$	315	59	48	$(M-Br)^+$	395	54	46	$(M-Br)^+$
234	3	*	$(M-3H)^+$	234	14	6	$(M-Br)^+$	314	53	56	$(M-Br)^+$	314	53	56	$(M-Br)^+$	394	100	100	$(M-Br)^+$
233	1	1.5	$(M-3H)^+$	233	4			313	24	24	$(M-Br)^+$	313	24	24	$(M-Br)^+$	393	50	47	$(M-Br)^+$
158	97	97*	$C_6H_{19}NP^{11}B_2$ $(M-Br)^+$													391	16	16	$(M-Br)^+$
157	54	45	$(M-Br)^+$																
156	100	100*	$(M-Br-2H)^+$																
155	44	49	$(M-Br-2H)^+$																
154	19	6	$(M-Br-2H)^+$																
142	8																		
141	5																		
70	49		$C_3H_9N^{11}B$ $(Me_2NCH_2BH)^+$	70	56			70	64			70	37			70	0		
69	13		$(Me_2NCH_2BH)^+$	69	14			69	15			69	11			69	0		

[a] GC/MS Hewlett Packard 5890 EI data. Intensity normalized to largest peak. [b] Tentative assignment of bromine positions. [c] Based on relative abundances of ^{11}B, ^{10}B, ^{81}Br, and ^{79}Br, normalized to largest peak or peak marked with an asterisk in the cluster.

---

(11) Miller, N. E.; Reznicek, D. L. *J. Organomet. Chem.* **1988**, *349*, 11.
(12) Miller, N. E. *Inorg. Chem.* **1991**, *30*, 2228.

Scheme II



Experimental Section

Where required, standard high-vacuum-line procedures were employed.[12] Melting points were measured with a Thomas-Hoover capillary melting point apparatus and are uncorrected for emergent stem. Analyses were obtained from Schwarzkopf Microanalytical Laboratory, Woodside, NY. NMR, IR, and GC/MS data were obtained on Bruker AC300, Biorad Digilab FTS-40, and Hewlett-Packard 5988A instrumentation, respectively. High-resolution mass spectral data were obtained from the Midwest Center for Mass Spectrometry, Department of Chemistry, University of Nebraska, Lincoln, NE. Chloroform was freed of ethanol by repeated water extraction followed by drying over sodium sulfate and distillation from P_4O_{10}. Hexane was purified from olefin and oxidation products by repeated extraction with concentrated sulfuric acid, followed by washing with water, drying, and distillation from calcium hydride. Dimethyl sulfide–chloroborane was a commercial sample (Aldrich) containing 1–5% $Cl_2BH–SMe_2$. Other commerically available reagents and solvents were reagent grade and used as received. NMR data are reported as chemical shifts, δ (ppm), referenced to TMSi (based on solvent residual proton), external boron trifluoride etherate, and external 85% phosphoric acid, respectively, for H, B, and P.

1,1,4,4-Tetramethyl-1-azonia-4-phosphonia-2,5-diboratacyclohexane, 1. In a nitrogen-filled 50-mL round-bottomed reaction flask 3.3 mL of 1.58 M *tert*-butyllithium (5.2 mmol) in pentane was added via syringe to a stirred solution of 5.2 mmol of trimethylphosphine–((dimethylamino)methyl)borane[6] in 40 mL of dry hexane at –25 °C. The resulting solution was allowed to warm to room temperature and stand overnight. To this was added 0.57 mL (0.52 mmol) of dimethyl sulfide–chloroborane dropwise from a syringe while stirring, whereupon a white precipitate formed which turned into a yellow-tinged semisolid on long stirring. After 2 days the mixture was treated with an equal amount of distilled water under stirring. The organic phase was separated and washed again with water before drying over magnesium sulfate. Solvent was removed under vacuum, and the remaining residue was sublimed to 50 °C under high vacuum to produce a white solid, 371 mg, shown to be a mixture primarily of **1** and $(Me_2NCH_2BH_2)_2$ along with a trace of monochloro-**1** by GC/MS, yield 33% (1.74 mmol) of **1**, based on GC/MS data. Purification to 80–90% was effected by one to three sublimations at room temperature using a cold finger cooled at 14–18 °C while dynamic high-vacuum pumping was maintained. A 150-mg sample of 80% purity was subjected to ten consecutive sublimations in an 8-mm tube under high vacuum to an 1-in.-long cold section maintained near 0–10 °C by means of a tight-fitting copper jacket cooled by circulating cooled tap water. The final sublimate, 15 mg, was used for analyses, melting point, and spectral data. GC/MS showed 98+% purity, but elemental analyses comported better to 94%, mp 90–91 °C, sealed capillary under nitrogen. Anal. Calcd for $C_6H_{20}NPB_2$: C, 45.37; H, 12.69; N, 8.82; P, 19.50. Found: C, 45.84; H, 13.05; N, 9.97; P, 18.25. Calcd for 94% **1** and 6% $(Me_2NCH_2BH_2)_2$: C, 45.71; H, 12.79; N, 9.51; P, 18.27. IR data (exclusive of absorption masked by mineral oil): 2338 s, 2266 m shoulder, 1477 m, 1306/1288 w doublet, 1232 w, 1191 m, 1164 s, 1147 vw, 1134 m, 1050 s, 1023 w, 1000 m, 972 w, 956/944 m doublet, 926 s, 898 w, 798 w, 780 m, 758 w, 738 cm^{-1} m. NMR and mass spectral data are collected in Tables I–III.

Reaction of 1 with Halogens. Iodination. In a nitrogen-filled 50-mL round-bottomed reactor attached to vacuum line and pressure relief manometer, 97 mg of sample [80% **1**, 20% $(Me_2NCH_2BH_2)_2$] containing 0.61 mmol of **1** was dissolved in 2 mL of dry chloroform. To this was added with stirring via syringe dropwise a solution of 77.0 mg (0.61 mmol of I) of iodine in 4 mL of dry chloroform. Reaction (as monitored by color fading) was initially rapid but nearly stopped when addition was $^3/_4$ complete. After 3 days the solution was colorless, and solvent was removed under vacuum to leave an off-white residue. Sublimation at 100 °C under high vacuum gave only 63 mg of white sublimate in 2 h. It was a hygroscopic material that dissolved mostly in water with gas evolution to produce a neutral-pH solution. Evaporation of water from the solution left a soft solid whose IR was related to the initial sublimate. Both had sharp BH absorption at 2378 cm^{-1} as well as bands as 3200, 3355, and 1400 cm^{-1} normally associated with OH, NH, and borate.

Bromination. A solution of a 57.2-mg sample (87% **1**; 0.31 mmol) in about 3 mL of chloroform was treated dropwise with a chloroform solution containing 18 mg (0.225 mmol of Br) of bromine over $1^1/_2$ h, giving a clear solution. Solvent was removed under vacuum to leave a white solid residue. Sublimation of the residue at 80–90 °C for 4 h gave 61 mg of white sublimate on the cold finger and 6.5 mg of solid in the attached cold trap cooled to –196 °C. The latter material analyzed by GC/MS as 25% **1** and 75% $(MeNCH_2BH_2)_2$, corresponding to 5 mg of $(Me_2NCH_2BH_2)_2$ or 72% of that originally charged, establishing preferential bromination of **1**. The sublimate analyzed as 83% monobromo-**1** and 16% dibromo-**1**. A small amount of residue in the sublimer analyzed by GC/MS as mostly dibromo-**1** and $(Me_2NCH_2BHBr)_2$ with traces of tribromo-**1**.

In a larger run using a 173-mg sample (87% **1**, 0.95 mmol) and 1.02 mmol of bromine (atom), 114 mg of product subliming at 55–60 °C was isolated, analyzing by GC/MS as 85% monobromo-**1**, 0.9% $Me_2NCH_2BH_2NMe_2CH_2BHBr$, and 12% as a mixture of 2-monochloro-**1** and $(Me_2NCH_2BHBr)_2$. An additional 42 mg of product subliming to 70 °C was found by GC/MS to be 0.4% $Me_2NCH_2BH_2NMe_2CH_2BHBr$, 17% monobromo-**1**, 11% $(Me_2NCH_2BHBr)_2$, 53% dibromo-**1**, 12% tribromo-**1** (in two isomeric forms), and 4% tetrabromo-**1** (Table IV). Bromine in products was about 53 mg, or 67% of that charged. Retention times (min) observed [temperature profile: 35 °C for 2 min, temperature ramp 15°/min, final temperature 250 °C for 5 min, 21.33 min total] were as follows: 10.1, $(Me_2NCH_2BH_2NMe_2CH_2BHBr)$; 10.2, 2-chloro-**1**; 11.1, 2-bromo-**1**; 13.8, dibromo-**1**; 15.2 and 15.4, two isomers of tribromo-**1**; 16.8, tetrabromo-**1**. Mass spectral data are collected in Table IV. NMR (δ, ppm) data for an 88% pure sample of 2-bromo-**1** are as follows. ^{11}B: N–B, 1.43, 0.25 doublet, J_{HB} = 113 Hz, decouples to shouldered singlet at 0.76; P–B, –31.02 1:2:1 triplet, –31.74 1:2:1 triplet, J_{HB} = 94 Hz, J_{PB} = 69 Hz, decouples to shouldered doublet at –31.0, –31.7, J_{PB} = 67 Hz. ^{31}P (H-decoupled): –61.0, –6.67, –7.25, –7.82 quartet, J_{BP} = 69 Hz. ^1H: 19 peaks from 2.5 to 2.87; major peaks 2.77, 2.65; four broad peaks 1.3–1.4.

1,1,4,4-Tetramethyl-1-azonia-4-phosphonia-2,5-diboratacyclohexane-2-carboxylic Acid, 2. A sample of monobrominated **1** from three preparations estimated to contain 395 mg (1.66 mmol) of 2-bromo-**1** and 162 mg (1.65 mmol) of $Me_3NBH_2N{\equiv}C$[12] in 1.2 mL of dry chloroform was stirred in the dark for 3 days. Solvent and unreacted $Me_3NBH_2N{\equiv}C$ were removed under high-vacuum pumping, and the remaining residue was treated with 8.4 mL of deoxygenated distilled water. An insoluble solid was removed by filtration and dried. It analyzed by IR to be unreacted 2-bromo-**1**, 124 mg (31% recovery). The aqueous solution was mixed with 9.6 mL of deoxygenated 1 M NaOH. Gas (assumed to be hydrogen), evolved over a 1-day period, amounted to 40 mL (ambient) compared to 46 mL expected (based on consumed 2-bromo-**1**). No additional gas was evolved when an additional 2 mL of 6 M NaOH was added in 2 mL of water. To the resulting solution was added 1.3 mL of 6 M HCl and 5 mL of 1 M HCl, followed by incremental amounts of 1 M HCl to maintain pH at 3.8 (8 mL of 1 M HCl total). Crystalline solid was removed by filtration and recrystallized from 30/70% methanol/water to give 78 mg, first crop, and 24 mg, second crop, of 2-HO_2C-**1** as a white-appearing solid composed of transparent crystals, mp 170 °C with decomposition (sintering 167–168 °C) in nitrogen-filled capillary.

Anal. Calcd for $C_7H_{20}NPB_2O_2$: C, 41.45; H, 9.94; N, 6.90; P, 15.27. Found: C, 41.76; H, 9.33; N, 7.06; P, 13.39. A satisfactory P value was not achievable but is believed an analytical difficulty even though two independent laboratories gave values 13.32 and 13.39. NMR ^1H areas for NMe_2 and PMe_2 resonances were equivalent, ^{11}B resonances were very symmetrical, and careful high-resolution mass spectrum and IR comparisons rule out possible contamination by $Me_2NCH_2BH_2NMe_2CH_2BHCO_2H$, the likely contaminant to produce low phosphorus analysis.

NMR data are tabulated (Table III). IR data for mineral oil mull (exclusive of masked bands): 3060 s broad (OH), 2723 m, 2616 w (2374 m, 2330 s, 2266 m BH), 1648 s broad C=O, 1479 m, 1441 m, 1421 m, 1403 m, 1300 m, 1290 m, 1242 s, 1195 w, 1170 m, 1150 m, 1123 s, 1112 s, 1056 s, 1006 m, 943/929 s doublet, 860 w, 830 w, 799 w, 782 w, 755 w, 725 cm^{-1} w.

Mass spectral data, Table I, establish facile loss of CO_2H on electron impact. FAB data using a 3-NBA matrix evidence a cluster at *m/e*

202.1, and the high-resolution peak at $m/e = 201.1376$ is +4.5 ppm from $C_7H_{19}O_2NP^{11}B^{10}B = (M-2H+H^+) = (M-H)^+$, assuming protonation of the carboxylic acid group.

Acknowledgment. Support for this research by a Cottrell College Science Grant (No. C-2595) from the Research Corp. and an in part matching grant from the Future Fund of the State of South Dakota is gratefully acknowledged. NSF grants and matching South Dakota Future Fund grants for GC/MS, NMR, and FTIR instrumentation at the University of South Dakota are also acknowledged. High-resolution mass spectral data were obtained from the Midwest Center for Mass Spectrometry at the Department of Chemistry, University of Nebraska/Lincoln.