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Multipolar framework chemistry. Gallium- and phosphorus-containing heterocycles

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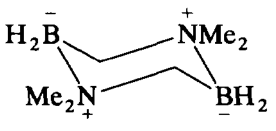
Abstract

A novel six-membered heterocycle with B, Ga, N, and P heteroatoms, $Me_2\overline{GaCH_2PMe_2BH_2CH_2N}Me_2$, is synthesized from a lithiated borane base. Its reaction with anhydrous acids leads to Ga–Me bond cleavage and formation of monosubstituted derivatives. A similar derivative chemistry pertains for the analogous heterocycle, $Me_2\overline{GaCH_2NMe_2BH_2CH_2N}Me_2$. Two related six-membered heterocycles with phosphonia atoms are also characterized, one with a thionia ring atom and one a spiroheterocycle with piperidine: $Me_2P(CH_2BH_2)_2SMe$ and $Me_2P(CH_2BH_2)_2N(CH_2)_2CH_2$.

1. Introduction

Characterization of an increasing number of new compounds with the common molecular features of saturated valency and multiple polar sites arising from dative bonding encourages a classification of this type of molecular architecture as multipolar framework chemistry. 1,1,4,4-Tetramethyl-1,4-diazonia-2,5-diboratacyclohexane [1]



is such a compound, and it has sufficient thermal stability to presume skeletal integrity in chemical processing [2]. The alternating polarity contributes to the stability of this compound, and to its crystalline orientation [3]. Also a critical feature, particularly because of its N–B dative bonding, is the steric buttressing of the borane moiety by the methyl groups on nitrogen, a feature demonstrated to be important for the stability of the cation $(Me_3N)_2BH_2^+$ [4]. In those molecules with P–B dative bonding, the polarity contributes more significantly. In the heterocycle $H_2B(PMe_2CH_2)_2BH_2$ [5], even the sterically unprotected borane has ambient stability.

In this laboratory multipolar framework examples with acyclic and heterocyclic structure have been characterized. A few examples of each type show something of the scope possible:

$Me_3\overset{+}{N}\overset{-}{B}H_2CH_2\overset{+}{N}Me_2\overset{-}{B}H_3$,

$[(Me_3\overset{+}{N}\overset{-}{B}H_2CH_2\overset{+}{N}Me_2)_2\overset{-}{B}H_2]^+$ [6],

$Me_2\overset{+}{N}(CH_2)_2\overset{-}{B}H_2$ [7],

$Me_2\overset{+}{P}(CH_2\overset{-}{B}H_2)_2\overset{+}{N}Me_2$ [8].

Recent success in bringing about substitution at the boron site(s) with anionic and neutral ligands [9], but more importantly with transformable groups such as $-CO_2H$ [10], is an encouraging development. Substitution reactions will allow the conjugation of multipolar framework moieties to a variety of organic structures and give access to their unique polarity features for practical applications.

Continuing exploration of heterocycles in the multipolar framework category has led to the isolation of a new six-membered ring with B, Ga, N, and P heteroatom polar sites. Study of its chemistry and the method of synthesis was undertaken and is reported here. Additionally, other heterocycles with phosphonia replacement of carbon have been made with B, P, N and B, P, S heteroatom polar sites.

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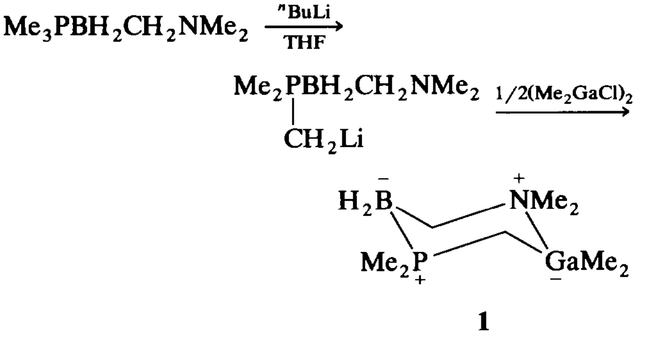
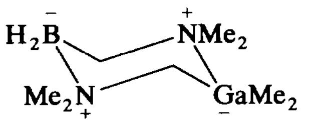
2. Results and discussion

Synthesis of a new heterocycle, 1,1,3,3,4,4-hexamethyl-1-azonia-2-gallata-4-phosphonia-5-boratacyclohexane (**1**) was achieved using a lithiated linear base $Me_3PBH_2CH_2NMe_2$ (Scheme 1).



Scheme 1.

The heterocycle **1** is a distillable clear liquid at room temperature, soluble in organic solvents, with a phosphine-like odor. Toward air oxidation, it is not as robust as its BCNGaCN-sequenced analogue, **2** [11].



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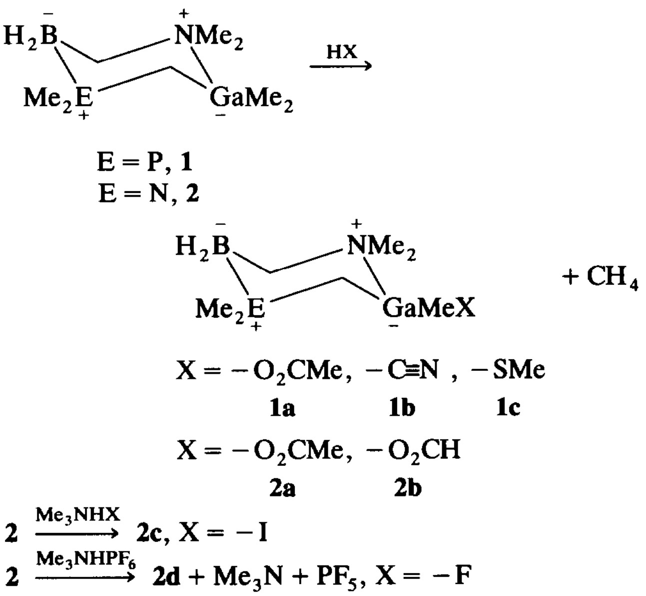
The structural assignment of **1** was supported by analyses, mass spectral and infrared data, and multinuclear NMR (^{31}P, ^{1}H, ^{11}B). High resolution mass spectral data show an intense high mass envelope (as compared to low intensity parent mass peaks for BCNBCN-sequenced heterocycles), a general feature for the gallium-containing heterocycles examined. A 50% peak at m/e 232.0753 agrees to 0.4 ppm with expected exact mass for $C_7H_{21}NP^{11}B^{71}Ga$, the parent minus CH_3 mass. Furthermore, the intensity pattern for the 232.0753, 231.0799, 230.0769, and 229.0804 (50, 20, 94, 22%) envelope agrees with that expected for the $^{11}B^{71}Ga$, $^{10}B^{71}Ga$, $^{11}B^{69}Ga$, $^{10}B^{69}Ga$ abundance (62, 15, 94*, 23%) normalizing on the 94% peak. The facile loss of CH_3 corresponds to the facile loss of H from the BCNBCN-sequenced heterocycles. Thus, a monomeric formula in the gas phase is established. ^{11}B NMR also establishes B–P bonding by shift ($\delta = -29.8$ ppm) and splitting, the approximate 1:3:3:1 signal ($J \approx 90$ Hz) arising from similar BP and BH coupling constants. On proton decoupling a clean doublet, $J_{BP} = 73$ Hz, is observed.

Both gallium-containing heterocycles, **1** and **2**, were found to react with protonic acids in the absence of solvent to substitute methyl on gallium by the anion form of the acid (Scheme 2).



Scheme 2.

The regiospecificity clearly reflects a more negative methyl on gallium than hydrogen on boron. Reaction in the presence of chloroform solvent was not observed.

Characterization of the cyano derivative **1b** was made difficult because a cyanide stretch could not be distinguished in the infrared spectrum. The composition of **1b** was supported by mass spectral data and the physical state as a solid *versus* liquid **1**. It is known that the C≡N stretch in the $-BH_2-C{\equiv}N$ moiety is weak compared to isonitrile-linked moiety $-BH_2-N{\equiv}C$ [12]. Likely, a weak absorption on the low frequency side of the BH stretching absorption is in fact a cyanide stretch. High resolution mass spectral data show significant parent$-Me^+$ and parent$-CN^+$ envelopes of roughly the correct intensity ratios expected. Formulation as a cyanide rather than an isonitrile derivative is based on the absence of a strong isonitrile infrared stretch.

The oxyanion substituents in **1a**, **2a** and **2b** are formulated as Ga–O bonded, analogous to similar substituents on $Me_2\overline{NCH_2BH_2NMe_2CH_2B}H_2$.

In sharp contrast to many multipolar framework compounds, **1** and **2** do not react smoothly with halogens, and no characterizable compound was isolated. The production of $Me_3NH^+I^-$ and $Me_4N^+I^-$ in the iodination of **2** suggests that there is no selectivity for Ga with the more aggressive electrophiles. Derivatives with GaI (**2c**) and GaF (**2d**) bonds were isolated from reactions using Me_3NHI and Me_3NHPF_6 above room temperature. **2c** is very reactive in air.

TABLE 1. Reaction $Me_2NCH_2BH_2NMe_2CH_2Li$ and $H_2BX\text{-}L \rightarrow Me_2\overline{NCH_2BH_2NMe_2CH_2B}H_2$

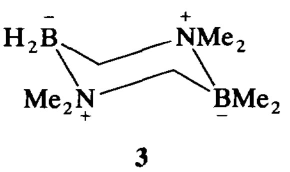
X	L	Solvent	% Yield
–	–	Ether	– [a]
Cl	SMe_2	Hexane	11.1, 2.4
Cl	SMe_2	Benzene	–
Cl	SMe_2	Ether	15.2, 14.5, 10.6
Cl	SMe_2	$CH_3OCH_2CH_2OCH_3$	–
Cl	OEt_2	Ether	1.4, 7.8
Br	SMe_2	Hexane	–
Br	SMe_2	Ether	–
Br	SMe_2	$CHCl_3$	–

[a] Blank run using only lithium chelate to estimate amount of $Me_2\overline{NCH_2BH_2NMe_2CH_2B}H_2$ contaminant present. No entry means yield was not measurably significant.

2.1. *Ring closure with lithiated bases and boron halides*

Both **1** and **2** were obtained in reasonable yields by a ring closure involving a lithiated multipolar base and the Me_2GaCl moiety. An interesting extension of this method using haloboranes might be suited to obtaining BCN-sequenced heterocycles with monosubstituted boron not readily accessible otherwise. A systematic investigation was therefore undertaken to find conditions appropriate for ring closure using $LiCH_2NMe_2BH_2CH_2NMe_2$ with $XBH_2\text{–}L$ adducts, wherein the product would be the highly stable, known multipolar heterocycle $Me_2\overline{NCH_2BH_2NMe_2CH_2B}H_2$ (Table 1). In no case was more than 15% yield observed, and more often than not no yield was observed. In all cases a polymeric, gummy semisolid was the main product. Attempts to reduce polymerization by slow addition of one or both reagents and/or dilution by five-fold also failed. These results, though disappointing are not significantly different than the low yield reported by Schmidbaur's group for the synthesis of the very stable heterocycle $H_2\overline{BPMe_2CH_2BH_2CH_2P}Me_2$ [5].

Surprisingly, the highest yield (15%) resulted by rapid combination at low temperature (−78°C) followed by warming to room temperature and long stirring. Me_2SBH_2Cl gave the better yield when ether was the solvent. The only new heterocycle attempted using the conditions giving the best yield was the B-dimethyl derivative (**3**).



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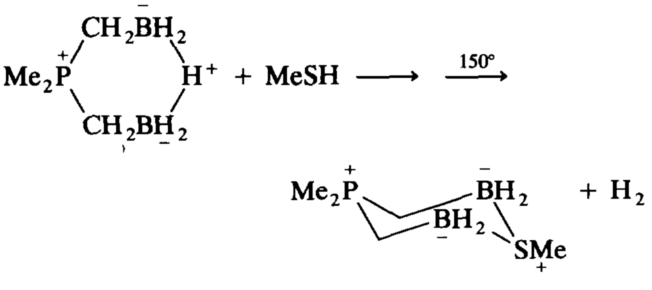
2.2. *Phosphonia heterocycles with μ-ligand diborane linkage*

A new multipolar heterocycle **4** with B, P, and S polar heteroatoms was made by a reported method [8].



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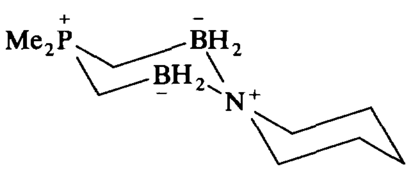
With a "1,3" disposition of two BH_2 moieties, this heterocycle resembles diborane with both bridges replaced by μ-ligands. Its structure is presumed to be a chair form of a cyclohexane-like ring which is the basis of its replacement name, 1,4,4-trimethyl-1-thionia-4-phosphonia-3,5-diboratacyclohexane.

It is a white sublimable solid with significant stability under ambient conditions. This stability is likely related to the electron releasing ability of the $\text{–}SMeBH_2\text{–}$ moiety toward the other BH_2 group. Similar enhanced stability obtains for $Me_3NBH_2SMeBH_2NMe_3^+$ and $(Me_3NBH_2SMe)_2BH_2^+$ [14] as compared to $(Me_2S)_2BH_2^+$ [4]. The ^1H NMR revealed diastereotopic PCH_3 by its resonances (1:2:1 triplet of overlapping doublets) consistent with a chair conformation of the ring, whether rapidly inverting or not.



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In a similar manner a spiroheterocycle, **5**, was synthesized using piperidine instead of MeSH. Like the analogous heterocycle $Me_2P(CH_2BH_2)_2NMe_2$, made from dimethylamine, **5** is an air-stable, sublimable white solid. The magnitude of this stability is established by unchanged infrared and NMR spectra for samples stored in screw-capped vials for six years.

3. Experimental details

Where required, a standard vacuum line capable of pumping to 10^{-5} Torr noncondensible gas was used. Melting points, uncorrected for emergent steam, were measured with a Thomas-Hoover capillary melting point apparatus. High resolution mass data were obtained from the Midwest Center for Mass Spectrometry, Chemistry Department, University of Nebraska/Lincoln. Elemental analyses were obtained from Schwarzkopf Microanalytical Lab, Woodside, New York. Chloroform was freed of ethanol by repeated water extraction followed by drying over sodium sulfate and distillation from phosphoric anhydride. Hexane was freed of olefin traces by repeated extraction with concentrated sulfuric acid followed by water washing, drying, and distillation from calcium hydride. Ether, tetrahydrofuran, and glyme (ethylene glycol dimethyl ether) were dried over KOH and distilled from lithium aluminum hydride and/or sodium ketyl. Other reagents, including n- and t-butyllithium were commercially obtained and used without additional purification. NMR chemical shifts, δ, ppm for ^{1}H, ^{11}B, and ^{31}P were referenced to tetramethylsilane (or residual $CHCl_3$), external BF_3-etherate, and external 85% aqueous H_3PO_4, respectively. NMR data were obtained on a Bruker AC300 (300 MHz, 96.3 MHz, and 121.5 MHz, respectively, for ^{1}H, ^{11}B, ^{31}P). Infrared (IR) data were obtained on a Digilab FTS-40 or Beckman 4240 spectrometer.

3.1. $Me_2\overline{GaCH_2PMe_2BH_2CH_2N}Me_2$ (1)

$Me_3PBH_2CH_2NMe_2$, 150 mg (1.0 mmol), prepared similarly to a literature method [6], dissolved in 3 ml of THF was treated in one portion with 0.6 ml of 1.7 M (1.02 mmol) t-butyllithium in pentane at −30°C, and allowed to stir for 30 min at −30°C. To the resulting bright yellow solution was added 1.0 ml of a solution containing dimethylgallium chloride (1.02 mmol Ga equivalent) in benzene, discharging the color. A white crystalline precipitate formed slowly after warming to room temperature. After an additional 12 h stirring, solvent was removed under vacuum. The volatile product passed a −20°C trap and was stopped in a −78°C trap; mp 18–23°C. In a larger run, using 6.46 mmol starting material, a yield of 41% was achieved. Analysis calculated for $C_8H_{24}NPBGa$: C, 39.09; H, 9.84; N, 5.70. Found: C, 39.87; H, 9.11; N, 6.32%.

High resolution mass spectrum, *m/e*, % intensity, formula, Δ(*m/e* observed − *m/e* calculated, ppm), assignment: 232.0753, 50, $C_7H_{21}NP^{11}B^{71}Ga$, 0.4, (parent − $CH_3)^+$; 231.0799, 20, $C_7H_{21}NP^{10}B^{71}Ga$, 4.6, (parent − $CH_3)^+$; 230.0769, 94, $C_7H_{21}NP^{11}B^{69}Ga$, 3.9, (parent − $CH_3)^+$; 229.0804, 71, $C_7H_{21}NP^{10}B^{69}Ga$, 3.3; 185.0172, 58.0650, 100, C_3H_8N, −11.6, $(CH_3)_2N{=}CH_2^+$

NMR data (nucleus, multiplet (area), δ, coupling constant): ^{11}B (H decoupled), doublet, −29.8, J_{BP} 74 Hz; ^{31}P (H decoupled) quartet, −3.97, J_{PB} 74 Hz; ^{1}H, Me_2N singlet (6), 2.29; PMe_2 doublet (6), 1.227; PCH_2 doublet (2), 0.276; $GaMe_2$ singlet (6), −0.58.

IR data (cm^{-1}; abbreviations, s strong, m medium, w weak): 2889 s (structured), 2338s, 2266w, 1460m (structured), 1420w (structured), 1370w, 1300w, 1285m, 1194m, 1142m, 1100s, 1069w, 1010/1000 doublet m, 975m, 940m, 918m, 891m, 841m, 790m, 746m, 715s.

3.2. $Me_2\overline{NCH_2BH_2PMe_2CH_2Ga}MeX$ (1a–c)

Reactants were charged into small ampoules equipped with breakoff capillaries for reintroduction into the vacuum line, using standard vacuum line techniques. On warming and stirring at reaction temperature gas evolution was observable. After the reaction period the ampoules were connected to vacuum line, and the noncondensible gas was measured. The residue was transferred to a sublimer and heated under high vacuum dynamic pumping (Table 2).

Anal. calcd. for **1a**, $C_9H_{24}NPO_2GaB$: C, 37.30; H, 8.34; N, 4.83. Found: C, 37.69; H, 8.27; N, 3.95%. Calcd. for **1b**, $C_8H_{21}N_2PGaB$: C, 37.42; H, 8.24; N, 10.91. Found: C, 38.31; H, 8.79; N, 10.06%. Calcd. for **1c**, $C_8H_{24}NPSGaB$: C, 34.58; H, 8.71; N, 5.04. Found: C, 35.69; H, 8.43; N, 4.84%.

High resolution mass spectral data, assignment, *m/e*, Δ mmass, % intensity (calculated, based on ⋆ peak): **1a** (parent − $CH_3)^+$, $C_8H_{21}NO_2P^{11}B^{71}Ga$, 276.0662, 1.1, 37% (32%); $C_8H_{21}NO_2P^{10}B^{11}B^{71}Ga$, 275.0692, 0.4, 12% (8%); $C_8H_{21}NO_2P^{11}B^{69}Ga$, 274.0665, 0.5, 48% (⋆); $C_8H_{21}NO_2P^{10}B^{69}Ga$, 273.0713, 1.7, 13% (12%); $(CH_3)_2NCH_2^+$ C_3H_8N, 58.0678, 2, 100%. **1b** (parent − $CH_3)^+$, $C_7H_{18}N_2P^{11}B^{71}Ga$, 243.0553, 0.5, 8% (12%); $C_7H_{18}N_2P^{10}B^{71}Ga$, 242.0513, 7.2, 3% (3%); $C_7H_{18}N_2P^{11}B^{69}Ga$, 241.0560, 0.3, 18% (⋆); $(CH_3)_2N{=}CH_2^+$ C_3H_8N, 58.0680, 2.3, 100%. **1c** (parent − $CH_3)^+$, $C_7H_{21}NPS^{11}B^{71}Ga$, 264.0485, 1.1, 19% (18%); $C_7H_{21}NPS^{10}B^{71}Ga$, 263.0522, 1.2, 7% (4%); $C_7H_{21}NP^{11}B^{69}Ga$, 262.0493, 1.1, 2.8% (⋆); $C_7H_{21}NPS^{10}B^{69}Ga$, 261.0543, 2.4, 6% (7%); $(CH_3)_2N{=}CH_2^+$, 58.0681, 2.4, 100%.

IR data: **1a**, 2961/2471s broad (structured), 2347m, 2276w, 1614s, 1383s, 1321m, 1191w, 1161w, 1044m, 947m, 925m, 718m. **1b** (mineral oil mull), 2368w, 2344m, 2273w, 1311w, 1290w, 1209w, 1142m, 1072w, 1046m,

TABLE 2. Synthesis of $Me_2\overline{NCH_2BH_2PMe_2CH_2Ga}MeX$. All runs were with 0.218 mmol of **1**

Product	Reactant, mmol	Temp/Time	CH_4, mmol	
1a	glacial HOAc, 0.35	RT, 24 h	0.17	clear viscous liquid; distills 65–70°C/ high vacuum
1b	HCN, 0.34	100°, *ca.* 15 h	0.12	38 mg (70%) white solid; sublimes 60–70°C/ high vacuum; mp 96–100°C
1c	MeSH, 0.24	100°, 17 h	0.22	16 mg (30%) viscous liquid; distills 60–70°C/ high vacuum

1026m, 1012w, 968m, 955m, 922m, 895m, 852m, 787m, 751m, 716s. **1c**, 2918s (structured), 2338s, 2275w, 1470m, 1420w, 1287m, 1142m, 1022s, 972s, 945s, 920s, 893w, 787m, 750m, 714s.

3.3. $Me_2\overline{NCH_2BH_2NMe_2CH_2Ga}MeX$. (2a–d)

$Me_2\overline{NCH_2BH_2NMe_2CH_2Ga}Me_2$ [11] was prepared from 1.258 g (9.25 mmol) of $LiCH_2NMe_2BH_2CH_2NMe_2$ and 4.6 mmol of $(Me_2GaCl)_2$ in 18 ml benzene, and the product on workup was caught at −78°C by trap-to-trap distillation under dynamic pumping. The 5-0-acetyloxy-derivative (**2a**) was prepared by combining reagents neat in a small ampoule under vacuum and then heating the mixture to 60°C for 1 h. On opening, the gas was vented and the ampoule placed in a sublimer for heating under dynamic vacuum (10^{-5} Torr) at 60°C. In a typical run, 37 mg (0.14 mmol) of product was obtained as white crystals, beginning with 39 mg (0.17 mmol) of heterocycle and 0.17 mmole (10.2 μl) of acetic acid; yield, 80%; mp 55–57°C. Anal. calcd. for **2a**, $C_9H_{24}N_2O_2Ga$: C, 39.62; H, 8.87; N, 10.27. Found: C, 39.82; H, 9.19; N, 10.30%. Mass data (FAB), *m/e* 271.1101; calculated for $C_9H_{24}N_2{}^{11}B^{69}GaO_2$, 271.11094.

In a similar manner the 5-formyloxy-derivative (**2b**) was isolated as a clear liquid. Anal. calcd. for **2b**, $C_8H_{23}N_2O_2BGa$: C, 37.13; H, 8.57; N, 10.82. Found: C, 37.40; H, 8.89; N, 10.62%. Mass data (FAB), *m/e* 259.1120; calculated for $C_8H_{23}N_2O_2BGa$, 259.11094.

The 5-iodo-derivative (**2c**) was obtained by heating a mixture of 31 mg (0.14 mmol) of **2** and 25 mg (0.14 mmol) of $Me_3NH^+I^-$ in an ampoule for 4 days at 100°C. On opening, 0.32 mole total of gas was vented and the remaining residue was extracted with methylene chloride. The solution was transferred to a sublimer and solvent removed under vacuum. Heating at 60°C/high vacuum gave a white solid product reacting readily with water and air. High resolution mass spectral data: $(Parent-H)^+$ $C_7H_{20}N_2{}^{11}B^{71}GaI$, 341.0068, 5.8, 1.1% (0.9%); $C_7H_{20}N_2{}^{10}B^{71}GaI$, 340.0072, 2.5, 0.36% (0.22%); $C_7H_{20}N_2{}^{11}B^{69}GaI$, 339.0036, 1.7, 1.4% (⋆); $C_7H_{20}N_2{}^{10}B^{69}GaI$, 338.0042, −1.3, 0.37% (0.35%); $(Parent-I^-)$ $C_7H_{21}N_2{}^{11}B^{71}Ga$, 215.1051, 0.6, 25.4% (23.7%); $C_7H_{21}N_2{}^{10}B^{71}Ga$, 214.1082, 0.1, 9.5% (5.8%); $C_7H_{21}N_2{}^{11}B^{69}Ga$, 213.1051, −0.2, 36.1% (⋆); $C_7H_{21}N_2{}^{10}B^{69}Ga$, 212.1089, −0.1, 9.3% (9.0%); $(CH_3)_2N{=}CH_2{}^+$ C_3H_8N, 58.0616, 0.4, 100%.

The 5-fluoro-derivative (**2d**) was prepared by heating 28 mg (0.12 mmol) of **1** and 25 mg (0.12 mmol) of $NMe_3H^+PF_6{}^-$ for 48 h at 95°C. IR examination of the condensible gas product showed bonds assignable to Me_3N and PF_5. Remaining product soluble in methylene chloride was sublimed to give a white solid. Mass spectral data (FAB) *m/e* 232.1157, calculated for $M-H^+$ $C_7H_{22}N_2{}^{10}B^{69}Ga$, 232.1153; low resolution FAB has $M-F^+$ *m/e* 215, 213 peaks (75 and 100%).

IR data: **2a**, 2382w shoulder, 2328m broad (structured), 2253w shoulder, 1640s, 1609w shoulder, 1383s, 1321s, 1288m, 1259vw, 1204w, 1102m, 1159s, 1115w, 1105m, 1038vw, 1005m, 982m, 926w, 880m, 740m, 721w. **2b** (neat), 2993vw shoulder, 2920m, 2855m, 2342m, 2363w shoulder, 1651s, 1466m, 1277s, 1184m, 1161s, 1113w, 1099w, 1003m, 984m, 882m, 735m. **2c**, 2332m (structured), 2249w, 1293w, 1209w, 1183w, 1159s, 1128vw, 1117w, 1099m, 1059m, 1036w, 1007m, 984w, 947w, 935vw, 882w, 864w, 729m. **2d** (neat), 2909–2854s (structured), 2855vw shoulder, 2820w shoulder, 2363s (structured), 2262m shoulder, 1464s (structured), 1420vw, 1404w, 1315w, 1285m, 1258vw, 1231w, 1184s, 1177s, 1138w, 1111–1098m doublet, 1086w, 1017vw shoulder, 1003m, 978m, 922w, 879m, 860w shoulder, 754s, 723s.

3.4. $Me_2\overline{BCH_2NMe_2BH_2CH_2N}Me_2$ (3)

A solution of 126 mg (0.93 mmol) of $LiCH_2NMe_2BH_2CH_2NMe_2$ and 1.06 mmol of Me_2BCl (prepared from Me_3B and HCl) in 10 ml dry ether was sealed in an ampoule under vacuum. Upon warming to room temperature and stirring for 12 h, the mixture was fractionated through cold traps. The semi-solid trapped at −55°C was identified as title compound by high resolution mass spectral data (assignment, *m/e*, *Δ* (mmass), intensity): $(Parent-CH_3)^+$ $C_7H_{21}N_2{}^{11}B_2$, 155.1896, 3.1, 2.1%; $C_7H_{21}N_2{}^{11}B^{10}B$, 154.1922, −3.6, 1.0%; $(Parent-C_2H_5)^+$ $C_6H_{19}N_2{}^{11}B_2$, 1.6, 5.1%; $C_6H_{19}N_2{}^{11}B^{10}B$, −11.3, 2.6%; $Me_2N{=}CH_2{}^+$ C_3H_8N, 58.0678, +2.1, 100%. The IR spectrum excluded admixture with $H_2\overline{BCH_2NMe_2BH_2CH_2N}Me_2$ impurity in the sample by absence of the latter's strong absorption at 915 and 1335 cm^{-1}, and an attenuated BH stretching absorption: (exclusive of absorption masked by mineral oil) 2340w (structured), 1400w, 1290s, 1240m (multiplet), 1110s (multiplet), 1065s, 985s, 910/890vw doublet, 870s.

3.5. $Me_2P(CH_2BH_2)_2SMe$ (4)

$Me_2P(CH_2BH_2)_2H$ [8], 48.7 mg (0.42 mmol), 0.42 mmol MeSH, and 2 ml benzene were combined under vacuum in a 50 ml reaction flask attached to the vacuum line. Gas evolution commenced on warming to room temperature and continued briskly for about 15 min. After an additional stirring period of several h the total yield of noncondensible gas was 0.42 mmole. Solvent was removed under vacuum to leave a white solid which sublimed at 75°/high vacuum. A sample exposed to air for one day had an unchanged IR spectrum.

High resolution mass spectral data: (Parent − H)$^+$ $C_5H_{16}P^{11}B_2S$, 161.0896, 0, 2.5%; $C_5H_{16}P^{11}B^{10}B$, 160.0907, −1.0, 0.8%; (Parent − 3H)$^+$ $C_5H_{14}P^{11}B_2S$, 159.0743, 0.3, 8.2%; $C_5H_{14}P^{11}B^{10}BS$, 158.0779, 0.3, 4.2%; (Parent − 5H)$^+$ $C_5H_{12}P^{11}B_2$, 0.5, 2.2%; $C_5H_{12}P^{11}B^{10}B$, −0.2, 1.2%; $[Me_2P(CH_2BH_2)_2]^+$ $C_4H_{14}P^{11}B_2$, 0.8, 36.9%; $C_4H_{14}P^{11}B^{10}B$, 114.1052, −0.3, 19.7%; $C_4H_{14}P^{10}B_2$, 113.1093, 0.1, 1.6%; 57.0730, 100%; 56.0650, 27%.

IR data: 2365s, 2296s, 1420m, 1302/1291m doublet, 1164m, 1155m, 1132m, 1085m, 1057m, 1037m, 988/982m doublet, 960/953m doublet, 911w, 880w, 768m, 752w, 722w.

NMR data: ^{11}B, δ 19.0 (1:2:1 triplet), J_{HB} 103 Hz; ^{31}P, δ 25.0 (H decoupled). ^1H, SMe 1.69 (3), PMe_2 1.64, 1.59, 1.54 (*ca.* 1:2:1 triplet) PMe_2 (6); CH_2 1.0 and −0.82 broad multiplets (4).

3.6. $Me_2P(CH_2BH_2)_2N(CH_2CH_2)_2CH_2$ (5)

A mixture of 71 mg (0.61 mmol) of $Me_2P(CH_2BH_2)_2H$ and 0.67 mmole of piperidine (dried over CaH_2) in 1 ml of dry THF produced a white insoluble solid judged to be $H_3BCH_2(Me_2)P(CH_2BH_2)_2NH(CH_2CH_2)_2CH_2$ from presence of an NH IR absorption. Solvent was removed and the remaining solid was heated at 155°C for 4 h in a closed system. Sublimation and resublimation at 70°C/high vacuum of the pyrolyzed product gave 65 mg of title compound; mp 141–148°C, sealed cap. under N_2; yield 54%. Anal. calcd. for $C_9H_{24}NPB_2$: C, 54.35; H, 12.16; N, 7.04. Found: C, 54.00; H, 13.10; N, 7.03%.

IR data: 2403–2216s broad and structured BH, 1444m complex multiplet, 1308m, 1292m, 1209m, 1195s, 1174s, 1092s, 1058w, 1037/1043s doublet, 962/952s doublet, 942s, 874/870m doublet, 766m.

NMR data: ^{11}B, −11.7 (1:2:1 triplet); ^1H PMe_2 (6) 1.57 (doublet) J_{PCH} 12 Hz, $N(CH_2CH_2)_2CH_2$ (4, 3.6, 2.6) 2.59, 1.65, 1.48 structured multiplets; PCH_2 (3.4) 0.70–0.66 structured multiplet.

High resolution mass spectral data: (Parent − H)$^+$ $^{13}CC_8H_{23}NP^{11}B_2$, 199.1780, −0.7, 3.6%; $C_9H_{23}NP^{11}B_2$, 198.1751, −0.3, 36%, $C_9H_{23}NP^{11}B^{10}B$, 197.1728, 6.2, 28%; (Parent − 3H)$^+$ $C_9H_{21}NP^{11}B_2$, 196.1600, 0.2, 100%; $C_8H_{21}NP^{11}B^{10}B$, 195.1625, −0.9, 49%.

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