Journal of Organometallic Chemistry, 349 (1988) 11–22
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Chemistry of 1,1,4,4-tetramethyl-1,4-diazonia-2,5-diboratacyclohexane

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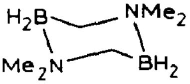
(Received January 21st, 1988)

Abstract

Reactivity of 1,1,4,4-tetramethyl-1,4-diazonia-2,5-diboratacyclohexane toward a variety of substances was surveyed. The halogenation to 2-iodo and 2,5-diiodo derivatives is of particular interest because subsequent iodide displacements allow substitutional elaboration of the ring system. A novel cleavage reaction of esters by the 2-iodo derivative gives stable, neutral, oxygen-bonded derivatives.

Since the discovery of 1,1,4,4-tetramethyl-1,4-diazonia-2,5-diboratacyclohexane (**1**), reported in 1964 [1], information related to structure [2] and syntheses [3] has accumulated. Several substituted systems have also been prepared indirectly, and the study of the chemistry of these has been initiated [4]. Less is known of the chemistry of the parent ring system itself. A survey was made of its reactivity with a range of reagents, and the results are herein reported. New chemistry and derivatives were found in the study of halogenation and halo products, and in the reaction with diborane.



(1)

Discussion

The selection of reagents to survey was to some extent guided by the expectation that ring opening, at least under forcing conditions, would lead to trigonal borane and amine functionalities; **1**, however, was inert to most reagents examined. One striking example is the quantitative recovery of **1** and methyl chloride after heating 19 h in a sealed tube at 240 °C. Other similar results, along with those reactions which were observed, are collected in Table 1. An astonishing stability, first

0022-328X/88/$03.50

Table 1

Reactivity survey of $Me_2\overline{NCH_2BH_2NMe_2CH_2B}H_2$ (**1**)

Reagent/amount (mmol)	Amount **1** (mmol)	Conditions	Observations
Chlorine/excess	1.85	CH_2Cl_2 solvent	Tetrachloro-1 produced, 99% yield
Bromine/excess	0.72	CH_2Cl_2/Na_2CO_3/2 days	Tetrabromo/tribromo-1
Iodine (See Experimental)			
B_2H_6/0.82	0.25	18 h, 70 °C, ampoule	**1**, and uncharacterized residue
B_2H_6/1.78, and Et_3NBH_3/0.3 ml	0.689	18 h, 180 °C 13 ml ampoule	125 mg, 100% yield $(Et_3NH)_2B_{12}H_{12}$
Et_3N/5.9	0.59	11 h, 180 °C	**1**, Et_3N recovered
Me_3B/0.56	0.56	8 h, 165 °C	**1**, BMe_3 recovered
Me_3P/0.66	0.32	3 h, 290 °C, ampoule	**1**, 0.52 mmol Me_3P recovered
CH_3Cl/1.24	0.53	19 h, 240 °C	1.24 mmol CH_3Cl, 0.53 mmol **1** recovered
D_20/1 ml	0.37	few drops 6*M* KOH, EtOH, r.t., 6 days	0.30 mmol **1** recovered
Ethylene/0.684	0.35	19 h, 240 °C	0.67 mmol ethylene, 0.33 mmol **1** recovered
C_5H_6/0.33	0.32	8 h, 300 °C	liquid and black solid, 0.13 mmol **1**, no other BH-containing product
$Me_2NC(O)Cl$/2.33	1.05	13 h, 180 °C	0.4 mmol dichloro- and tri-chloro-**1**
Me_3NBH_2I/0.758	0.418	46 h, 118 °C	no Me_3BH_2I recovered. 36.5 mg mixture **1** and Me_3NBH_3 0.082 mmol 2-iodo-**1** 0.060 mmol 2,5-diiodo-**1**

suggested by thermal study [3c], is confirmed by the survey. The reactions with halogens, diborane, and carbamoyl chloride, may be classified as substitutions.

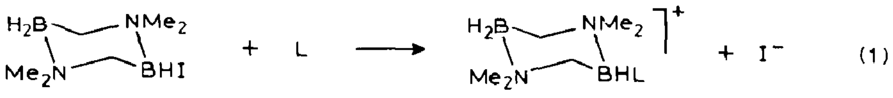
Deuterium/hydrogen exchange with B_2D_6 was effected by contact at 70 °C for 14 h. A 90% recovery of partly deuterated **1** and diborane was observed. The intensity of the BD stretch in the infrared at 1730 cm^{-1} indicated about the same deuterium content as in the charge, suggestive of statistical incorporation. The mechanism for the exchange likely involves hydrogen bridging with borane-d_3 (BD_3).

Reaction of iodine with **1** in chloroform proceeds with gas (assumed to be hydrogen) evolution and formation of the monoiodo **2** or diiodo **3** derivatives, depending on stoichiometry and reaction time. Identification of the 2,5-diiodo derivative is based on its infrared spectrum (a singlet instead of multiplet BH expected for a 2,2-diiodo derivative), and iodide displacement to the 2,5-bis-DMF-$\mathbf{1}^{2+}$ derivative. Either diiodo diastereomer, *cis* or *trans*, would be expected to give a doublet ring *N*-methyl resonance; but the small separation (2.69 and 2.71 ppm) is concordant with the smaller separation of the *trans* isomer of the 2,5-bis(neopentyl) substituted ring [5]. Other halogens lead to more halogenated species. Tetrachloro (**4**) and tetrabromo (**5**) derivatives were characterized.

Displacement reactions of $Me_2\overline{NCH_2BH_2NMe_2CH_2B}HI$ (**2**)

The facile iodide displacement reaction of Me_3NBH_2I [6] does not obtain for **1**. Only unhindered Lewis bases react at room temperature (eq. 1); pyridine (py), pyridine-*N*-oxide (pyO), dimethylformamide (DMF), and *N*,*N*-dimethylacetamide

(DMA) form the corresponding cations **6**, **7**, **8**, and **9**. Me_2NH and Me_3P give some evidence of reaction at room temperature, but NMe_3 does not. Bonding in **8** and **9** is

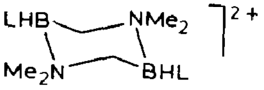


(1)

(**6** L = py ,
7 L = pyO ,
8 L = DMF ,
9 L = DMA)

assigned B–O–C=NMe_2(*R*) because of nonequivalent *N*-methyl resonances, similar to those in the related borane cations $LBH_2NMe_3^+$ [7].

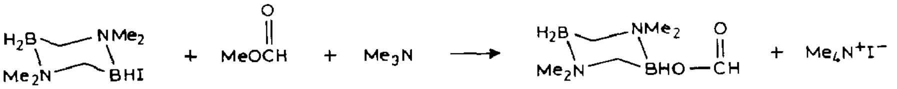
One dication, **10**, was synthesized by iodide displacement from **3** by DMF.



(**10**)

Ester cleavage by **2**

A rather interesting reaction was discovered for the monoiodo derivative, **1**, as a consequence of its lack of reaction with trimethylamine. Heating of **2** in methyl formate in the presence of trimethylamine (to serve as an activator of carbonyl and/or sink for Me^+) gives dealkylation of the ester (eq. 2).

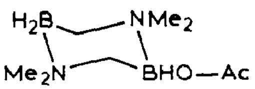


(2)

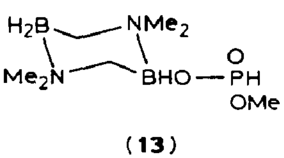
(**11**)

Identity of the formate, **11**, was established by NMR and mass spectral data, and by the synthesis method. Impetus for the investigation of this reaction came from attempts to synthesize **11**, a compound which had been isolated in a one-time, nonreproducible reaction of the 2-dimethylaminomethyl derivative of **1** and methylene chloride. After failure to repeat the latter reaction using various sources of materials and impurities, the alternate synthesis described was undertaken.

Extension of the dealkylation reaction to DMA and dimethyl phosphite gave acetyloxy and methyl phosphite derivatives **12** and **13** as liquids stable in the air.



and



(**12**) (**13**)

Use of ethyl formate instead of methyl formate also led to the 2-formyloxy derivative in fair yield, so a general reaction is implicated.

The mass spectral data for **11**, **12**, and **13** have *P* – 1 high mass clusters expected for the assigned compositions. When these spectra are compared with those of other oxygen-linked derivatives of **1**, structural themes emerge in the fragmentation

Table 2

$Me_2\overline{NCH_2BH_2NMe_2CH_2B}H\text{-}L^+$, L-**1**$^+$, PF_6^- salts

Compound	m.p. (°C)	Yield (%)	Analyses (Found (Calcd.) (%))				^{1}H NMR [a], δ(H) (ppm)		
			C	H	N	B	Solvent		
1-py$^+$ PF_6^-	185–189	60	36.35	6.31	11.80	5.39	CH_2Cl_2	NMe	2.60, 2.63, 2.76
(**6**PF_6^-)			36.20	6.62	11.52	5.92		NC_5H_5	8.0–8.5
1-Opy$^+$ PF_6^-	167–168	72	35.10	6.33	10.76		CH_2Cl_2	NMe	(2.72, 2.76, 2.65) (12)
(7 PF_6^-)			34.68	6.35	11.03			CH_2	2.19 (broad) (3.5)
								NC_5H_5	8.0–8.4 (4.6)
$Me_2\overline{NCH_2BH_2NMe_2CH_2B}HMe_2N{=}CHO^+$ PF_6^-,	109–111	40	29.91	7.37	11.20		CH_2Cl_2	NMe	2.66 (12)
			30.12	7.31	11.72			CH_2	2.15 (broad) (3.8)
1-DMF$^+$ PF_6^- (**8** PF_6^-)								$CH{=}NMe_2$	(3.20, 3.25) (6.3)
								CH	8.03 (0.9)
$Me_2\overline{NCH_2BH_2NMe_2CH_2B}HMe_2N{=}C(CH_3)O^+$ PF_6^-	139	48	32.54	7.53	10.72		CH_2Cl_2	NMe	(2.63, 2.66) (12)
			32.21	7.57	11.27			CH_2	2.02 (broad) (3.8)
1-DMA$^+$ PF_6^- (**9** PF_6^-)								$C{=}NMe_2$	(3.19, 3.30) (6)
								$OC(CH_3){=}N$	2.41 (3.4)
1-NMe_3^+ PF_6^-	168–170	29	31.32	8.35	12.11		CD_3CN	NMe	(2.91, 2.79,
(**14**-PF_6^-)			31.34	8.18	12.18				2.69, 2.61) (13)
								NMe_3	2.12 (9)
1-PMe_3^+ PF_6^-		23	29.87	7.27	7.72				
(**15**-PF_6^-)			29.87	7.80	7.74				

[a] Downfield from internal tetramethylsilane; 60 MHz frequency.

patterns (Table 3). $C_6H_{17}N_2OB_2$ and $C_3H_{10}NOB_2$ fragments are significant for all species studied, suggestive of stable, probably cyclic structures. For **11**, **12**, and **13**, fragment compositions are present that can be reconciled to structures with O–C–O or O–P–O bridges, and this may indicate a common proclivity in the fragmentation of acyloxy species. The intense, common *m/e* 112 peak (and corresponding ^{10}B-containing *m/e* 111 peak) and the similar *m/e* 98 peak have compositions reconcilable with B–O–B-bridged heterocycles. Finally, a *m/e* 113 and corresponding 112 peak (not shown in Table 3 because they contain no oxygen) are present at moderate intensity in all the BCN-sequenced derivatives examined. Its composition as $C_5H_{14}N_2B$ is not as easily rationalized. A conjugated structure, $[Me_2N{=}BHCH{=}NMe_2]^+$, has enormous appeal, if not valence significance, as a plausible structure for this peak. All the formula compositions are confirmed by the correct masses and intensities of isotopic isomers, including (generally) that of the corresponding $^{13}CC_{n-1}$-containing isomer for each C_n cluster.

When the ester cleavage reaction is conducted in toluene instead of neat ester, at 60 °C with near stoichiometric amount of ester and a small excess of amine, the dealkylation product yield diminishes and cation **14** is isolated (eq. 3). In the less polar medium, iodide displacement by trimethylamine becomes dominant.

(3)

(2) (14)

Displacement was also observed under similar conditions with trimethylphosphine to give the corresponding cation $Me_2\overline{NCH_2BH_2NMe_2CH_2B}HPMe_3^+$ (**15**), as the iodide salt. Isolation and characterization of these cations help the long term study of the stereochemistry of the parent ring. Since NMe_3 is sterically analogous to t-butyl, known to be conformationally pure equatorial in cyclohexane [8], it is reasonable to assume that the **2**-NMe_3^+ and **2**-PMe_3^+ cations are similarly locked equatorial derivatives. Study of reactions at the remote BH_2 of these species could then relate to axial/equatorial differences and correlate inversion or retention processes.

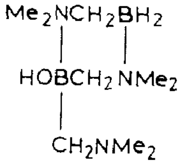
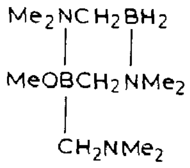
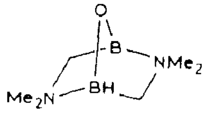
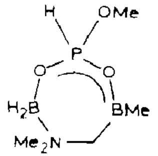
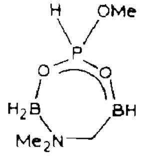
The 2-formyloxy and 2-acetyloxy derivatives of **1** are completely stable at room temperature in the air, a property recently noted in a acetyloxy-substituted derivatives of 2-dimethylaminomethyl-**1** [9].

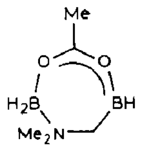
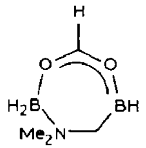
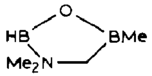
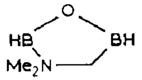
Experimental

Where required, standard vacuum line procedures were employed. A line equipped with Delmar–Urry o-ring joints and Teflon® needle stopcocks, with pumping capability to 10^{-5} mmHg noncondensible gas, provided for reactions, transfer, and sublimations. Melting points (uncorrected) were measured in a Thomas–Hoover capillary melting point apparatus. Analyses were obtained from: Alfred Bernhardt Microanalytical Laboratory, Mülheim, West Germany; Midwest Microlab Inc., Indianopolis; Peninsular Chem Research, Gainesville, FL; and Schwarzkopf Microanalytical Laboratory, Woodside, NY. Low resolution NMR were obtained with a Varian A60-A and a Hitachi/Perkin–Elmer R24B instrument. High resolution NMR and mass spectral data were obtained from regional instrumentation centers

Table 3

Mass spectral fragments of oxygen-linked derivatives of **1**

m/e, calcd.	Composition	Plausible structure	Intensity in spectrum of				
			11 1-O_2CH	**12** 1-O_2CMe	**13** 1-O_2POMe(H)		
155.1527	$C_6H_{17}N_2O^{11}B_2$		11.7	10.9	1.4	29.8	5.5
192.1132	$C_5H_{17}NO_3P^{11}B_2$		–	–	17	–	–
178.0976	$C_4H_{15}NO_3P^{11}B_2$		–	–	61	–	–

142.1211	$C_5H_{14}NO_2{}^{11}B_2$		–	6	–	–	–
128.1054	$C_4H_{12}NO_2{}^{11}B_2$		12.4	–	–	–	–
112.1105	$C_4H_{12}NO^{11}B_2$		10	15	14	95	20
98.0948	$C_3H_{10}NO^{11}B_2$		100	100	13	29	11

(acknowledged later). Infrared spectra were obtained on Perkin–Elmer 237B, Beckman IR12, and Beckman 4240 spectrometers. Infrared spectral data are reported in cm^{-1}, and are for mineral oil mulls; absorptions masked by mulling agent are not reported. Proton NMR chemical shifts are in ppm downfield from internal tetramethylsilane with relative proton areas in parentheses.

Ethereal solvents: tetrahydrofuran (THF), 1,2-dimethoxyethane (glyme), bis[2-(2-methoxyethoxyl)ethyl] ether (tetraglyme) were freed of peroxides by passage through alumina and standing over potassium hydroxide before distillation from lithium aluminium hydride (under vacuum for higher ethers). Other solvents were purified and rendered anhydrous by standard procedures [10]. DMF and DMA were distilled under vacuum from phosphorus pentoxide. Pyridine-oxide was sublimed under vacuum at 70 °C. Trimethylphosphine was prepared from ethereal methylmagnesium bromide and phosphorus trichloride and purified via the silver iodide complex [11]. Cyclopentadiene was thermally cracked from the dimer and used immediately. Other reagents were best available commercial products, used as received. Diborane(6) (Callery Chemical Co.) was essentially free of higher boranes. Diborane-d_6 (0.416 mmol, 63% yield) was prepared from sodium borohydride-d_4 (Alfa; 53.3 mg) in 1.4 ml tetraglyme solution by addition of iodine (167 mg) in 2 ml tetraglyme according to literature procedures [12].

*1,1,4,4-Tetramethyl-1,4-diazonia-2,5-diboratacyclohexane (**1**).* Compound **1** was prepared by reaction of $(Me_3N)_2BH_2^+Cl^-$ [3d] and n-butyllithium in hexane, run in 1/1.1 stoichiometry, using hexane, glyme, or THF solvents. Yields were variable, around 45 to 56%. Typically, to 2 g of salt, slurried in about 8 ml solvent in a 50-ml reactor, n-butyllithium was added under nitrogen atmosphere via syringe over 15 min with some cooling to keep at room temperature. Conducting the reaction with a small amount of added tetramethylethylenediamine did not improve the yield. Product was isolated after 11 h stirring by volatilization from the reaction flask, eventually heating to 100 °C. The white solid caught in a U-trap at −50 °C was dissolved in a small amount of ether and shaken with an equal amount of dilute hydrochloric acid. The acid wash was separated and treated with NH_4^+ PF_6^- to precipitate $Me_3NBH_2CH_2NHMe_2^+$ PF_6^- in small yield (~ 5%), identified by its infrared spectrum [3d]. The ether phase was evaporated and the solid residue recrystallized from absolute ethanol (loading of 1 g per 6 ml) to effect a pure product, identified by its infrared spectrum [3d]. Recovery better than 70% was achieved.

Reactivity survey

Reactions at room temperature (halogens, D_2O) were carried out in small reaction flasks attached via o-ring joints to the vacuum line. Reactions at elevated temperature were carried out in sealed ampoules. A summary is presented in Table 1; details of experiments in which new materials were characterized are discussed in the following.

D/H exchange. B_2D_6 (0.416 mmol) and **1** (90.3 mg, 0.638 mmol) were sealed in an ampoule and heated for 14 h at 70 °C. On work up, 0.006 mmol noncondensible gas (H_2?), 81.6 mg of partly deuterated **1**, and 0.391 mmol of partly deuterated diborane were recovered by fractionation through traps cooled to −40 °C and −196 °C, respectively. B–D stretching infrared absorption of the partly deuterated **1** at 1730 cm^{-1} is a multiplet.

2-Iodo-1,1,4,4-tetramethyl-1,4-diazonia-2,5-diboratacyclohexane (**2**). A stirred solution of 145 mg (1.02 mmol) **1** in 4 ml dry $CHCl_3$ was treated dropwise under nitrogen with a solution of 130 mg (0.51 mmol I_2) in 10 ml $CHCl_3$, over 20 min, during which gas was evolved. After stirring overnight, solvent was removed under vacuum from the now colorless solution, leaving a white, water-insoluble solid. Sublimation at 120–140 ° C under dynamic high vacuum gave the *B*-monoiodo derivative, **2**. Proton NMR (CH_2Cl_2) NMe 2.86, 2.83 (unresolved doublet)(6) 2.66 (6.1); CH_2 2.15–2.55 broad, unresolved (3.5). Infrared: 2480m sharp singlet, 2330s multiplet, 1405m, 1345w, 1300w, 1235w, 1185s doublet, 1120m, 1105m, 1030m, 1005s, 985s, 960w, 925w, 885w doublet, 850m, 820w, 745m.

2,5-Diiodo-1,1,4,4-tetramethyl-1,4-diazonia-2,5-diboratacyclohexane (*3*). A stirred solution of 420 mg (2.96 mmol) of **1** in 4 ml $CHCl_3$ was treated dropwise under nitrogen with 31 ml of $CHCl_3$ solution of 752 mg (2.96 mmol I_2). When 16 ml had been added, the solution became permanently brown-colored. After stirring overnight, the brown-colored precipitate was separated by filtration and washed with a small portion of solvent. Sublimation at 150 ° C under high vacuum gave 633 mg **3**, 55%, as a white solid which did not melt but decomposed at 198–200 ° C. Anal. Found: C, 18.25; H, 4.40; N 6.99. $C_6H_{18}N_2B_2I_2$ calcd.: C, 18.35; H, 4.61; N, 7.12%. Infrared 2480s, 1405m, 1325w, 1300w, 1225w, 1190s, 1140w, 1120m, 1090m, 1015s, 950s, 870s, 830s, 715s.

2,2,5,5-Tetrachloro-1,1,4,4-tetramethyl-1,4-diazonia-2,5-diboratacyclohexane (*4*). For 0.75 h chlorine gas was bubbled slowly through a stirred solution of 263 mg (1.85 mmol) **1** in 15 ml CH_2Cl_2. A white precipitate appeared and the liquid turned yellow. After an additional 2 h stirring, the solvent was removed under vacuum to leave a pale yellow solid which whitened after a wash with a small portion of benzene; 515 mg, 99% of tetrachloro derivative **4**. A purified sample was obtained after sublimation, 120–140 ° C/high vacuum. It did not melt, but yellowed at 223 ° C. Anal. Found: C, 26.46; H, 5.51; N 9.67. $C_6H_{16}N_2B_2Cl_4$ calcd.: C, 25.85; H, 5.77; N, 10.13%. Infrared: 2390vw, 1485s, 1415w, 1395w, 1365m, 1320w, 1270s, 1215w, 1180m, 1125m, 1110m, 1015w, 1045w, 1025s, 990s, 960s, 915s, 845s, 810s doublet, 700s. Mass spectral data at low resolution show a cluster centered at *m/e* 280 that can be rationalized by assuming 80% parent and 20% parent-1 fragments, for $C_6H_{16}N_2B_2Cl_4$. Intensity of the *me* 280 peak is 3% that of the 100% *m/e* 58 = Me_2NCH_2.

2,2,5,5-Tetrabromo-1,1,4,4-tetramethyl-1,4-diazona-2,5-diboratacyclohexane (*5*). A solution of 102 mg (0.72 mmol) of 1 in 10 ml CH_2Cl_2 was stirred with 1 g sodium carbonate under nitrogen and treated slowly with bromine via a syringe until the solution colored, then an additional 0.1 ml of bromine was added. The slurry was stirred 2 days and then filtered. The filtrate was treated with hexane to precipitate 11 mg cream-colored solid. The "sodium carbonate" insolubles were extracted thrice with 8-ml portions of CH_2Cl_2 and the washings evaporated to 10 ml volume under vacuum. About 20 ml of hexane were added, causing precipitation of 64 mg additional of the cream-colored solid for a total yield of 75 mg of product characterized as the tetrabromo derivative of **1**, 23%. Sublimation under high vacuum at 130–150 ° C gave 29 mg of purified product as a cream-white solid. Anal. Found: C, 16.53; H, 3.67; N, 6.22; B, 4.5; Br, 67.91. $C_6H_{16}N_2B_2Br_4$ calcd.: C, 15.76; H, 3.53; N, 6.12; B, 4.7; Br, 69.86%. Mixture of 77% tetrabromo and 23% tribromo calcd: C, 16.52; H, 3.74; N, 6.41; B, 4.9; Br, 68.3%. Infrared: 1415w, 1405w, 1330w, 1300m, 1265w, 1220w, 1180w, 1130w, 1100m, 1040w, 1010m, 990m, 950s, 900s, 825s, 765s doublet.

*$LH\overline{BCH_2NMe_2BH_2CH_2N}Me_2{}^+$. (**6**, L = py; **7**, L = py-0; **8**, L = DMF; **9**, L = DMA; **14**, L = NMe_3, and **15**, L = PMe_3).* Monovalent cations were synthesized by iodide displacement from **2** by two general procedures. For the unhindered ligand (all but trimethylamine and trimethylphosphine), an excess of ligand and iodo derivative were kept at room temperature for 18–24 h. Solvent was removed under vacuum, the residue leached with water, and the solution treated with $NH_4{}^+$ $PF_6{}^-$. The sparingly soluble precipitated salts were collected and recrystallized from hot water. Analyses and proton NMR spectral data are collected in Table 2. For the hindered ligands, a solution of **2** and excess ligand in toluene was heated in a sealed ampoule for 2–7 days at 60 °C. An insoluble, colorless crystalline product slowly formed. Volatiles were removed and the residue worked up as before for the hexafluorophosphate salt. Infrared spectral data: 2-py-1^+ $PF_6{}^-$ (**6**); 2460w, 2340m multiplet, 1625m, 1415w, 1305w, 1225w, 1185s, 1160w, 1120m, 1100w, 1060w, 1010w, 970m, 900m, 845s broad, 800w, 785m; 2-pyO$^-$ 1^+ $PF_6{}^-$ (**7**), 3140m, 2420w, 2350m multiplet, 1410w, 1340w, 1310w, 1185s doublet, 1160m, 1140s, 1130w, 1100w doublet, 1030w, 1015w, 970s, 960w, 935w, 875s, 845s broad, 810m, 785m, 745w; 2-DMF-1^+ $PF_6{}^-$ (**8**), 2420m, 2335m multiplet, 1690s broad, 1420w, 1360m, 1315w, 1255w, 1285m, 1145m, 1130m, 1120m, 1105m, 1065w, 1035w, 1015w, 1000w, 975m, 925w, 890m doublet, 850s broad, 755w; 2-DMA-1^+ $PF_6{}^+$ (**9**), 2440w, 2350m multiplet, 1645s, 1410m, 1360w, 1305w, 1260w, 1185s doublet, 1160m, 1140m, 1130m, 1115w, 1105m, 1030w, 1000m doublet, 975m, 935w, 910w, 850s broad; 2-NMe_3-1^+ $PF_6{}^-$ (**14**), 2440w (2460 shoulder), 2340m (2360sh, 2390sh), 2300w, 1340w, 1305w, 1245w, 1232w, 1190–1185s doublet, 1168w, 1150w, 1130w, 1110/1100/1090w triplet, 1032w, 1005w, 990w, 980w, 968m, 840s (860, 880, 890 sh), 810w. 2-PMe_3-1^+ $PF_6{}^-$ (**15**), 2395w, 2360w, 2330w, 1325w, 1310m, 1260w, 1240w, 1180m (1185, 1195w shoulders), 1160w, 1135w, 1110w (1120vw shoulder), 1090w, 1052–1060w doublet, 1030w, 1005m, 980m, 955–965m doublet, 935w, 905w, 890w, 845s (875w shoulder), 760w multiplet.

*2-Acyloxyl and phosphinyl derivatives, $LH\overline{BCH_2NMe_2BH_2CH_2N}Me_2$. (**11**, L = HCO_2; **12**, L = CH_3CO_2; **13**, L = $HP(OMe)O_2$).* Neutral boron-substituted derivatives of **1** were prepared in a common manner as represented here for 2-formyloxy-**1** (**11**). An ampoule (~ 15 ml) was charged with 2-iodo derivative, **2**, prepared from 78.6 mg **1** (90.55 mmol), purified by sublimation and used without reweighing. About 1.5 ml of methyl formate and 3.0 mmol trimethylamine were condensed into the ampoule under vacuum, and the ampoule was sealed. On warming, the mixture became cloudy, and a fine, white crystalline precipitate formed over 5 d. The ampoule was opened, the fluid contents were transferred to a sublimer and the solvent removed under vacuum. The residue was sublimed, 80 °C/high vacuum, to give 46 mg, 45%. $HCO_2H\overline{BCH_2NMe_2BH_2CH_2N}Me_2$ (**11**), as a white nonhygroscopic solid, stable in air, m.p. 72.5–74 °C/sealed capillary. Anal. Found: C, 46.01; H, 10.81; N, 14.70. $C_7H_{20}N_2O_2B_2$ calcd.: C, 45.23; H, 10.84; N, 15.07%. Proton NMR (360 MHz, $CDCl_3$): NMe 2.579, 2.599, 2.620, 2.667 (12); CHO 8.252 (0.9); CH_2 2.0–2.4 broad (6).

The crystalline, insoluble product in the ampoule, 94 mg, was identified as primarily Me_4N^+ I^- by its infrared spectrum.

12 and **13** are colorless liquids, stable in air at room temperature and distilling at 0 °C and 80 °C, respectively, under high vacuum.

Mass spectral data for **11**, **12**, and **13** are listed: assigned composition, observed *m/e* (mmass deviation, observed-calcd.)[intensity observed/calcd., based on isotopic abundance and normalized to highest peak in cluster].

For **11**, infrared spectrum: 3400w sharp (over a broad absorption), 2740w, 2385m, 2320s, 2280w, 2250w (2210, 2230, vw sh), 1701s, 1670w sharp, 1430w, 1410w. 1335w, 1350w, 1310w, 1295m, 1250s, 1235s, 1200m shoulder, 1185s, 1150m, 1132m, 1120w, 1110m, 1102m, 1030w, 1010m, 995w shoulder, 968m, 952w, 930w, 892w sh, 880m, 858m, 830w, 745m; mass spectral data: $C_7H_{19}N_2O_2B_2$, $p-1$ 186.1683(1.7)[7.8/3.4], 185.1633(0.0)[43.8], 184.1662(−0.7)[20.9/21.6], 183.1687 (−1.8)[3.0/2.7]; $C_6H_{17}N_2OB_2$, $p-1-CH_2O$ 155.1555(2.8)[11.7], 154.1555(−0.8) [9.0/5.7]; $C_4H_{12}NO_2B_2$ 129.1116(2.8)[0.7/0.5], 128.1077(2.3)[12.4], 127.1108(1.8) [6.5/6.1]; $C_5H_{14}N_2B$ 114.1282(−0.1)[1.0/1.0], 113.1246(−0.4)[17.5], 112.1277 (−0.9)[4.2/4.3]; $C_4H_{12}NOB$ 112.1098(0.7)[10.3], 111.1141(1.6)[4.1/5.1]; $C_3H_{10}NOB_2$ 99.1017(3.5)[3.8/3], 98.0945(−0.3)[100], 97.0982(3.4)[48.6/49.3], 96.1030(0.9) [5.3/6.1]; $C_3H_{12}N_2B$ 86.1119(3.3)[0.9/0.4], 85.1060(0.8)[10.7], 84.111(2.3)[2.2/2.6]; $C_4H_{11}NB$ 84.0987(0.2)[17.0], 83.1024(0.2)[4.2/4.2]; C_3H_9NB 71.0865(0.3)[3.3/2.4]; C_3H_9NB 70.0828(0.0)[71.9], 69.0864(0.0)[18.2/17.8].

For **12**, infrared spectrum: (neat) 2990w, 2920s, 2850m, 2320m (2340, 2300 sh), 1700s (1650 sh), 1460s, 1372s, 1295s, 1180s (1165m, 1160m sh), 1120m, 1110m 1028m, 1005m, 975m, 925w, 905w, 870w, 840m, 820w, 765w, 740w; mass spectral data: $C_8H_{21}N_2O_2B_2$, $p-1$ 200.1833(1.1)[1.9/1.5], 199.1800(1.1)[16.9], 198.1830 (0.5)[8.0/8.3], 197.1867(0.5)[0.9/1.0]; $C_6H_{19}N_2OB_2$ 158.1710(−0.7)[0.5/0.5], 157.1687(0.3)[8.0], 156.1700(−2.0)[4.4/3.9]; $C_6H_{17}N_2OB_2$ 155.1531(0.4)[10.9], 154.1560(−0.4)[5.5/5.4], 153.1602(0.2)[0.5/0.6]; $C_5H_{14}NO_2B_2$ 143.1244(0.1) [0.3/0.3], 142.1211(0.0)[5.6], 141.1248(0.1)[2.8/2.8]; $C_5H_{14}N_2B$ 114.1282(0.0) [0.3/0.5], 113.1245(−0.4)[8.5], 112.1286(0.0)[1.9/2.1]; $C_4H_{12}NOB_2$ 113.1140(0.2) [0.8/0.7], 112.1107(0.2)[15], 111.1139(−0.2)[8.0/7.4]; $C_3H_{10}NOB_2$ 99.0982(0.0) [3.5/3.3], 98.0952(0.4)[100], 97.0987(0.2)[48.8/49.3], 96.1024(0.3)[5.7/6.1]; $C_4H_{11}NB$ 84.0997(1.2)[12.3], 83.1033(1.2)[3.0/3.0]; C_3H_9NB 71.0873(1.1)[1.8/1.5], 70.0833 (0.5)[46.8], 69.0865(0.1)[11.5/11.6]; C_3H_8N 58.0678(2.1)[51.6];

For **13** infrared spectrum: (neat) 3000w, 2930m, 2850w, 2400m, 2340m (2280 sh), 1475m (several sh), 1405w, 1300w (1310, 1330w sh), 1240s, 1135s, 1165m sh, 1150–1145m doublet, 1120m, 1100m, 1045s, 1005s (975w sh), 925w, 900w, 840w, 790w (815, 770w sh), 735w. Proton NMR for **13**: (60 MHz , $CDCl_3$) POMe [3.78, 3.58 doublet, *J*(POCH)12 Hz] (3), NMe [2.61, shoulder 2.55] (12), CH_2 2.0 broad (4); mass spectral data: $C_7H_{22}N_2O_3B_2$, $p-1$ 236.1597(0.9)[0.9/1.2], 235.1557(0.3) [15.1], 234.1587(−0.4)[7.6/7.4], 233.1633(0.6)[0.6/0.9]; $C_5H_{17}NO_3PB_2$ 192.1137 (0.5)[7.0], 191.1172(0.4)[3.7/3.4]; $C_4H_{15}NO_3PB_2$ 179.1015(0.6)[2.7/2.7], 178.0979 (0.3)[60.8], 177.1010(−0.2)[32.6/30], 176.1040(−0.9)[4.6/3.6]; $C_4H_{13}NO_3PB_2$ 176.0823(0.4)[8.0], 175.0857(0.2)[4.1/3.9]; $C_5H_{14}N_2B$ 114.1287(0.3)[0.9/1.2], 113.1254(0.4)[22.0], 112.1290(0.4)[5.1/5.4], 112.1111(0.6)[13.5], 111.1143(0.2) [6.7/6.6]; $C_4H_{13}NOB$ 103.1129(0.5)[1.3/1.6], 102.1094(0.4)[35.5], 101.1131(0.4) [9.2/8.8], $C_3H_{12}NOB_2$ 100.1108(0.3)[25.5], 99.1134(−0.7)[13.3/12.6], 98.1174 (−0.4)[1.7/1.6]; $C_4H_{11}NOB$ 100.0935(0.1)[5.3], 99.0970(−0.1)[1.6/1.3]; $C_3H_{10}NOB_2$ 98.0950(0.2)[12.6], 97.0978(−0.6)[8.3/6.2]; $C_3H_{11}NOB$ 88.0939(0.5)[11.9], 87.0976 (0.5)[2.8/2.9]; $C_3H_{11}NB$ 72.0993(0.9)[45.4], 71.1029(0.8)[11.0/11.2]; C_3H_9NB 70.0831(0.3)[72.6], 69.0864(0.0)[18.7/17.9]; C_3H_8N 58.0682(2.1)[100].

Acknowledgment

Support of this research in part from a grant from the University of South Dakota Research Fund is appreciated. Assistance from the Colorado State University Regional NMR Center (NSF grant No. CHE-8208821) in obtaining proton NMR data, and the Midwest Center for Mass spectrometry, University of Nebraska/Lincoln, in the obtaining of mass spectral data is most gratefully acknowledged.

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