(75 mmol) of methyl (methylthio)methyl sulfoxide in 60 mL of THF was added 35.7 mL (75 mmol) of 2.1 M *n*-butyllithium in hexane at 10–15 °C. After 15 min a solution of 10.9 g (60 mmol) of **13** in 20 mL of THF was added at 0–10 °C, and the solution was stirred at 25 °C overnight. The solvents were removed under vacuum to give a yellow foam. TLC indicated no **13** was present.

This intermediate was dissolved in 120 mL of Me_2SO and treated while cooling with 34 mL of 48% HBr. The resulting solution was heated at 55 °C for 2 h and then worked up in the usual way to give the crude **4**. Recrystallization from aqueous acetone gave 11.4 g (78%) of material with single spot on TLC.

Acknowledgment. We thank L. M. Brancone, Dr. R. T. Hargreaves, and their associates for microanalytical data and Dr. W. E. Gore and associates for spectral data. We thank Dr. J. D. Albright for helpful discussions.

Registry No. **1**, 92-91-1; **2**, 135-73-9; **3**, 37166-61-3; **4**, 1145-04-6; **5**, 99114-41-7; **6**, 5449-21-8; **8**, 28179-30-8; **9**, 5697-41-6; **10**, 46817-48-5; **12**, 99114-42-8; **13**, 3218-36-8; **15**, 99114-45-1; 4-$H_3COC_6H_4COCH_3$, 100-06-1; 4-$O_2NC_6H_4COCH_3$, 100-19-6; 4-$BrC_6H_4COCH_3$, 99-90-1; 4-$C_6H_5NHC_6H_4COCH_3$, 23600-83-1; $C_6H_5COCH_2C_6H_5$, 451-40-1; $C_6H_5COCH(OH)C_6H_5$, 119-53-9; $C_6H_5COCH_2COC_6H_5$, 120-46-7; 2-$C_6H_5C_6H_4COCH_3$, 2142-66-7; 4-$H_3COC_6H_4COCH(OH)_2$, 16208-17-6; 4-$O_2NC_6H_4COCHO$, 4974-57-6; 4-$BrC_6H_4COCH(OH)_2$, 80352-42-7; 4-$BrC_6H_4NHC_6H_4$-4-$COCH_3$, 99114-43-9; $C_6H_5COCOC_6H_5$, 134-81-6; $C_6H_5COC(OH)_2COC_6H_5$, 29574-75-2; $C_6H_5CO_2H$, 76-93-7; 4-$C_6H_5C_6H_4CH_2CN$, 31603-77-7; $H_3CSCH_2SOCH_3$, 33577-16-1; 4-$C_6H_5C_6H_4C(=NH)CH(SCH_3)SOCH_3$, 99114-44-0; H_3CSH, 74-93-1; 9,10-phenanthrenedione, 84-11-7.

Hydride Sponge: Complexation of 1,8-Naphthalenediylbis(dimethylborane) with Hydride, Fluoride, and Hydroxide

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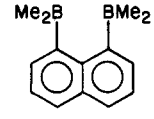
The syntheses of 1,8-naphthalenediylbis(dimethylborane) (**1**) (hydride sponge) and dimethyl-1-naphthylborane (**2**) are described. In solution, **1** abstracts hydride from KH and from a variety of other borohydrides, including **2**·KH, to give a complex, **1**·KH, that is unreactive toward moderately strong acids, benzaldehyde, and free **1**. The crystal structure of **1**·KH·(dioxane)$_3$ reveals the bridged hydride linkage that is primarily responsible for the kinetic and thermodynamic stability of **1**·KH. The complexes **1**·$F^-(NMe_2)_3S^+$ and **1**·$OH{\cdot}PPh_4^+$ are also characterized. These are the first hexaorgano $R_3BXBR_3^-$ species (X = F, OH) to be isolated as pure compounds. Thus, **1** is shown to be a neutral bidentate receptor for small anions.

The design of neutral, geometrically defined receptors for ions is an important goal of modern organic chemistry.[1] Enormous progress has been made in the study of rigid and semirigid polyethers[2] and polyaza compounds[3] interacting with positively charged metal ions and ammonium salts. In contrast, there have been only a few examples of multidentate complexation of anions reported. The best developed systems have been protonated[4] or alkylated[5] polycyclic bases forming inclusion complexes with complementarily sized counterions. The hosts in these systems are actually positively charged analogues of the kinds of compounds that are generally associated with cation complexation, while the "guests" are ions that would be paired with their hosts electrostatically even in the absence of inclusion phenomena.

Very few attempts have been made to arrange *neutral* Lewis acidic functionalities on an organic framework to cooperatively bind anions. One promising effort along these lines is that of M. Newcomb and his co-workers,[6] who have prepared cyclic polystannanes that are potential antipodes of crown ethers. A second group[7] has isolated and characterized complexes of bridging halide ions with *o*-phenylenedimercurials. Oligoboranes have not been extensively pursued in this regard, although 1,2-bis(difluoroboryl)ethane was reported[8] to be a chelating agent for oxygen bases on the basis of low-temperature vapor pressure measurements and precipitation experiments. A recent paper[9] from this laboratory proposed 1,8-diborylnaphthalenes as stereoelectronically defined "ligands" for anions and presented some preliminary data on the prototypical compound **1**.



1

Herein we report the full details of our experiments on **1** and the interaction of **1** with hydride, fluoride, and hydroxide.

Experimental Section

General Procedures. All manipulations of air-sensitive liquids were performed by using standard syringe or vacuum line techniques. Air-sensitive solids were transferred in a nitrogen-filled glovebag. Solvents were distilled from the usual drying agents: ethers from Na or sodium benzophenone; hydrocarbons from sodium; CH_2Cl_2 and CD_3CN from P_2O_5. Acetonitrile and CD_2Cl_2

(1) Weber, E.; Vögtle, F. *Top. Curr. Chem.* **1981**, *98*, 1–41.
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0022-3263/85/1950-5027$01.50/0

Table I. Chemical Shifts of Boranes and Borohydrides in the Presence and Absence of 1[a]

borane	nucleus	δ free	δ KH adduct	δ KH adduct + 1[b]
1	^{1}H (CH_3)	1.02	0.02	1.02
	^{11}B	79	5	79
Et_3B	^{11}B	77	-12.5	75
2	^{1}H (CH_3)	0.59	-0.1 (br)	0.54
	^{1}H (ArH)	7.2–7.8, 8.3 (1 H)	7.1–7.9, 8.8 (1 H)	7.2–7.8, 8.3
	^{11}B	36	-19	33
3	^{11}B	83	8	82
Ph_3B	^{1}H (ArH)	6.8–7.6 (m)	6.6–7.6 (m)	6.8–7.6 (m)
	^{11}B	60[c]		60
BH_3	^{11}B	-1[c]	-42[c,d]	0

[a] Determined in $(CD_2)_4O$ at 30 °C vs. Me_4Si (^{1}H) or BF_3OEt (^{11}B). [b] 1 ± 0.1 equiv of 1 added to KH adduct. ^{1}H and ^{11}B spectra of 1·KH are also observed. [c] Nöth, H.; Wrackmeyer, B. "*Nuclear Magnetic Resonance Spectroscopy of Boron Compounds*"; Springer-Verlag: New York, 1978. [d] LiH adduct used.

(Aldrich Gold Label) were used as received. Butyllithium (in hexane) was standardized by titration. Potassium hydride dispersed in mineral oil was washed with hexane under Ar. Tetraphenylphosphonium chloride and bromide were dried at 110 °C under vacuum. All other reagents were used as received.

Nuclear magnetic resonance spectra were recorded on a JEOL FX-90Q spectrometer containing a variable-temperature probe. Chemical shifts are in ppm vs. Me_4Si (^{1}H and ^{13}C), BF_3·OEt_2 (^{11}B), or $CFCl_3$ (^{19}F). Some ^{1}H and ^{13}C spectra were referenced to residual protons or carbon nuclei in the deuterated solvents.

Infrared spectra were measured with a Nicolet 5DX FT-IR spectrometer. High-resolution mass spectra were obtained on a Nicolet FT/MS-1000 Fourier transform mass spectrometer, with a magnetic field strength of 3.0 T. Electrochemical experiments were performed on a Princeton Applied Research Model 174A polarographic analyzer. Elemental analyses were determined by Galbraith Laboratories, Knoxville, TN.

Ethyl Dimethylborinate.[10] A flask containing 16.1 g (0.077 mol) of $Si(OEt)_4$ was cooled with liquid N_2 under a stream of N_2. An ampule containing 10 g (0.083 mol) of Me_2BBr (*Danger! Pyrophoric*) was cooled to -78 °C and opened, and the contents were poured onto the frozen $Si(OEt)_4$, maintaining a slow current of N_2 over the mixture. A distillation apparatus was attached to the flask and flushed with N_2, and the reactants were allowed to warm to ambient temperature over 20 min. Distillation under N_2 gave 6.8 g (97%) of product, bp 50–55 °C, which was stored at -15 °C under Ar.

1,8-Naphthalenediylbis(dimethylborane) (1). A solution of 1,8-dilithionaphthalene was prepared by treating 10.3 g (0.027 mol) of 1,8-diiodonaphthalene[11] dissolved in 200 mL of Et_2O with 0.060 mol of *n*-BuLi for 10 min at 0 °C. The solution was cooled to -78 °C, added to a second solution containing 6.5 g (0.076 mol) of Me_2BOEt in 40 mL of Et_2O, and stirred at -78 °C. The combined solution was allowed to warm to +10 °C and then was recooled to -78 °C. Boron trifluoride etherate (8.49 g, 7.38 mL, 0.060 mol) was added, the mixture was again allowed to warm to +10 °C, and the solvents were removed in vacuo. The residue was extracted with 40 mL of hexane under a current of Ar, using a spatula to scrape and grind the solids. The suspension was cooled to -78 °C and filtered and the filtrate concentrated at reduced pressure. The resulting oil was distilled twice at 130–140 °C (0.1 torr), yielding 2.65 g of 1 (47%), whose analytical data have been previously reported. Some samples solidified when stored in the freezer, remelting at ca. 35 °C.

Dimethyl-1-naphthylborane (2). A solution of 1-lithionaphthalene was prepared by treating 1-bromonaphthalene (1.2 g, 0.81 mL, 5.8 mmol) with 6.4 mmol of *n*-BuLi in 35 mL of Et_2O at ambient temperature for 30 min. The resulting solution was added slowly to a stirred solution of Me_2BOEt (0.71 g, 8.3 mmol) in 20 mL of Et_2O at -78 °C. The mixture was allowed to warm to +10 °C, recooled to -78 °C, treated with BF_3OEt_2 (0.89 g, 6.3 mmol), and worked up with hexane as described for 1, leaving a pale yellow oil. Distillation of this oil at 105 °C (0.2 torr) gave 0.61 g of 2 (63%), 80–90% pure by NMR, with naphthalene, methylnaphthalene, and butylnaphthalene as the major contaminants: ^{1}H NMR [$(CD_2)_4O$] 0.59[12] (s, 6 H, CH_3), 7.3–7.8 (m, 6 H, ArH), 8.3 (m, 1 H, ArH); ^{11}B NMR [$(CD_2)_4O$] δ + 36;[12] ^{13}C NMR [$(CD_2)_4O$] δ 10 (b, CH_3), 124.9, 125.1, 125.8, 128.2, 129.2, 129.3, 130.5 (tertiary carbons only); high-resolution mass spectrum, calcd for $^{12}C_{12}{}^1H_{13}{}^{11}B$ 168.1105, found 168.1081. A solution of 2·KH was obtained by treating 2 dissolved in $(CD_2)_4O$ with excess KH, either for 18 h at ambient temperature or for 5 min at reflux. The NMR spectra of 2·KH are given in Table I. A solution of 2 in CD_3CN formed a complex with $(NMe_2)_3S$·Me_3SiF_2 as well.

Potassium μ-Hydrido-μ-(1,8-naphthalenediyl)tetramethyldiborate. An aliquot of 1 (0.30 g) dissolved in 20 mL of $(CH_2)_4O$ was treated with excess KH. After 2 h at ambient temperature, the solution was decanted away from the solid KH and concentrated. The residue was triturated with hexane and crystallized from CH_2Cl_2–C_6H_6. The yield was 0.31 g (87%) of a white, somewhat air-sensitive powder. Crystals suitable for X-ray diffraction[9] were obtained by slowly cooling a dilute solution of the powder in hot dioxane: IR (KBr) 2917 (CH), 2087 (BHB), 1476, 1314, 1286, 1272, 1166, 1054, 1025, 977, 899, 836, 815, 794, 695, 484 cm^{-1}; ^{1}H NMR [$(CD_2CD_2O)_2$, 35 °C] δ 0.02 (d, 12 H, $J_{MeH-\mu-H}$ = 2.0 Hz, CH_3), 7.3 (m, 6 H, Ar); ^{11}B NMR [$(CD_2)_4O$] δ +5; ^{13}C NMR [$(CD_2CD_2O)_2$, 35 °C] δ 10 (b, CH_3), 122.6, 124.4, and 125.1 (tertiary), 133.3 and 142.9 (quarternary). Anal. Calcd for $C_{14}H_{19}B_2K$: C, H, B, K.[9] There was no evidence of a signal for the bridging hydride in the ^{1}H NMR spectrum, even when the Me frequencies were decoupled.

Tris(dimethylamino)sulfonium μ-Fluoro-μ-(1,8-naphthalenediyl)tetramethyldiborate. A pure sample of 1 (46 mg, 0.22 mmol) and a deficiency of freshly opened $(NMe_2)_3S^+$-$Me_3SiF_2^-$[13] (Aldrich; 44 mg, 0.16 mmol) were dissolved in 1 mL of CH_3CN. Most of the solvent, as well as the Me_3SiF byproduct, was evaporated, and the residue was triturated with Et_2O. The remaining solid was dried under vacuum, yielding 35 mg (56%): ^{1}H NMR (CD_3CN) δ 0.05 (d, 12 H, J_{FH} = 19.5 Hz, CH_3B), 2.77 (s, 18 H, CH_3N), 7.0–7.5 (m, 6 H, ArH); ^{11}B NMR (CD_3CN) δ +15.5; ^{13}C NMR (CD_3CN) δ 13 (b, CH_3B), 38.7 (CH_3N), 124.5 ($C_{4,5}$), 124.9 (d, J_{CF} = 2.6 Hz, $C_{3,6}$), 125.8 (d, J_{CF} = 8.5 Hz, $C_{2,7}$), 133.7 (C_{4a}), 137.1 (d, J_{CF} = 3.4 Hz, C_{8a}). Anal. Calcd for $C_{20}H_{36}B_2FN_3S$: C, 61.40; H, 9.28; B, 5.53; F, 4.86; N, 10.74. Found: C, 61.31; H, 9.18; B, 5.64; F, 5.28; N, 10.85.

Tetraphenylphosphonium μ-Hydroxy-μ-(1,8-naphthalenediyl)tetramethyldiborate. Aliquots of 1 (55 mg, 0.26 mmol), NEt_3 (distilled from BaO; 27 mg, 37 μL, 0.26 mmol) and H_2O (5 μL, 0.3 mmol) were added to 5 mL of Et_2O under Ar. An oil separated but redissolved upon the addition of PPh_4Cl (97 mg, 0.26 mmol). The solvents were evaporated, and $HNEt_3^+Cl^-$ was precipitated from the residue by adding CH_2Cl_2, C_6H_6, and $(CH_2)_4O$ and partially evaporating the solvents. The supernatant solution was reconcentrated and the residue crystallized from CH_2Cl_2–Et_2O, yielding 80 mg of pale yellow rhomboidal prisms (54%) that became increasingly opaque upon drying: mp 163–165;

(10) Gerrard, W.; Mooney, E. F.; Rees, R. G. *J. Chem. Soc.* **1964**, 740–745.

(11) House, H. O.; Koepsell, D. G.; Campbell, W. J. *J. Org. Chem.* **1972**, *37*, 1003–1011.

(12) In CD_2Cl_2, δ(CH_3) = 1.37 and δ(^{11}B) = 80. Thus, 2 is coordinated by $(CD_2)_4O$ in solution.

(13) Farnham, W. B.; Haslow, R. L. *J. Am. Chem. Soc.* **1981**, *103*, 4608–4610.

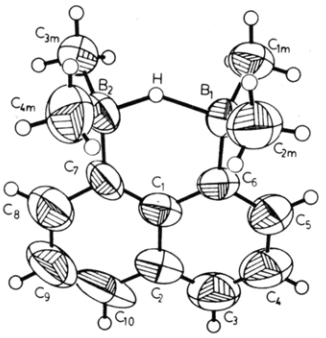
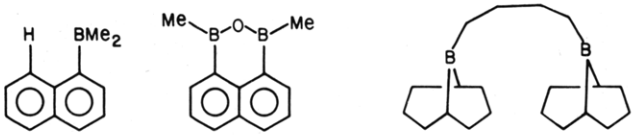


Figure 1. Perspective ORTEP drawing of 1·H⁻ in crystalline 1·KH·(dioxane)$_3$ with non-hydrogen atoms represented by thermal vibration ellipsoids encompassing 50% of their electron density.

IR (CH_2Cl_2) 3619 (OH), 3034, 2917, 1441, 1268 (BO), 1108 cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ −0.06 (s, 12 H, CH_3), 1.69[14] (s 1 H, OH), 7.2 (m, 6 H, Np H), 7.7 (m, 20 H, PPh_4); ^{11}B NMR (CD_2Cl_2) δ +1.5. Anal. Calcd for $C_{38}H_{39}B_2PO$: C, 80.87; H, 6.97; B, 3.83; P, 5.49 Found: C, 81.00; H, 7.12; B, 3.86; P, 5.57.

Results

Boranes **1** and **2** were synthesized from the corresponding lithionaphthalenes by condensation with ethyl dimethylborinate, followed by removal of the ethoxy groups with BF_3·OEt_2 and isolation of the products. Compound **1** is somewhat air-sensitive, decomposing to **3**[15] on overnight exposure to the atmosphere. On the other hand, **2** is highly air-sensitive and yellows markedly in minutes when exposed to oxygen.



2 3 4

A titration of **1** with KEt_3BH, monitored by ^{11}B NMR, showed that exactly 1 equiv of hydride was abstracted per equiv of **1** (eq 1) with the concomitant formation of 1 equiv

$$1 + KEt_3BH \rightarrow 1\cdot KH + BEt_3 \quad (1)$$

$$BEt_3 + KEt_3BH \rightarrow KEt_3BHBEt_3 \quad (2)$$

$$1\cdot KH + KEt_3BH \not\rightarrow 1\cdot 2KH + BEt_3 \quad (3)$$

of BEt_3 ($\delta(^{11}B)$ = 77). Additional KEt_3BH gave an equilibrating mixture of BEt_3 and KB_2Et_6H (eq 2) whose ^{11}B NMR signal was shifted well upfield from 77 ppm. When a second full equivalent of KEt_3BH had been introduced, this signal appeared at +10 ppm, in agreement with the previously reported[16] value for KEt_6B_2H. There was no evidence for the conversion of 1·KH ($\delta(^{11}B)$ = 5) to 1·2KH (eq 3) during this experiment.

In addition to KEt_3BH, a number of other borohydrides acted as hydride donors to **1**, including **2**·KH, 4·KH,[17] KPh_3BH,[18] and $LiBH_4$. In all cases, the donation of hydride to **1** was irreversible according to NMR data listed in Table I. Interestingly, **2** rapidly abstracted hydride from KEt_3BH, irreversibly forming first the hydride dimer $\mathbf{2}_2$·KH ($\delta(^{11}B)$ = 5) (eq 4) and then almost irreversibly forming **2**·KH ($\delta(^{11}B)$ = −19) (eq 5). Compound **2** did not abstract hydride from **4**·KH.

$$2(\mathbf{2}) + KEt_3BH \rightarrow \mathbf{2}_2\cdot KH + BEt_3 \quad (4)$$

$$\mathbf{2}_2\cdot KH + KEt_3BHBEt_3 \rightleftarrows 2(\mathbf{2}\cdot KH) + 2BEt_3 \quad (5)$$

Solutions of 1·KH at 60 °C were stable to treatment with weak to moderately strong acids (CH_3COOH, $HNEt_3Cl$, **5**·HBF_4[19]) and with benzaldehyde and slowly decomposed in the presence of $Ph_3C^+PF_6^-$. No equilibration was observed between **1** and 1·KH at 85 °C in $(CD_2CD_2O)_2$ on the 90-MHz NMR time scale. Abstraction of hydride from Ph_3CH or Et_3SiH by **1** in CD_3CN did not occur.

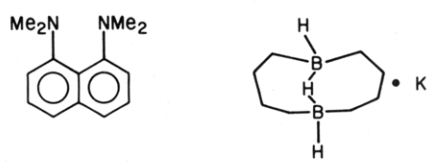


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Table II. Selected Bond Lengths in Crystalline 1·KH·(dioxane)$_3$[a]

type[b]	length, Å	type	length, Å
B_1–H	1.49 (5)	C_1–C_6	1.420 (9)
B_2–H	1.20 (5)	C_1–C_7	1.401 (9)
B_1–C_6	1.605 (10)	C_6–C_5	1.376 (10)
B_2–C_7	1.586 (10)	C_7–C_8	1.380 (10)
B_1–C_{1m}	1.619 (10)	C_5–C_4	1.387 (10)
B_1–C_{2m}	1.592 (10)	C_8–C_9	1.435 (14)
B_2–C_{3m}	1.605 (10)	C_4–C_3	1.331 (13)
B_2–C_{4m}	1.636 (11)	C_9–C_{10}	1.355 (14)
K–O_{2a}	2.723 (7)	C_3–C_2	1.406 (12)
K–O_{1b}	2.812 (5)	C_{10}–C_2	1.361 (13)
K–O_{2c}	2.801 (5)	C_1–C_2	1.464 (9)
K–$O_{1c'}$	2.780 (6)	(B_1–B_2)	(2.544)[c]

[a] The number in parentheses are the estimated standard deviations in the last significant digit(s). [b] Atoms are labeled in agreement with Figures 2–4. [c] Nonbonded distance.

Table III. Selected Bond Angles in Crystalline 1·KH·(dioxane)$_3$[a]

type	angle, deg	type	angle, deg
B_1HB_2	142 (4)	$C_5C_6B_1$	120.2 (6)
C_6B_1H	105 (2)	$C_5C_6C_1$	118.8 (6)
C_7B_2H	108 (2)	$C_1C_6B_1$	120.9 (5)
$C_{1m}B_1H$	100 (2)	$C_6C_1C_2$	119.5 (6)
$C_{2m}B_1H$	106 (2)	$C_7C_1C_2$	121.0 (6)
$C_{1m}B_1C_{2m}$	116.3 (6)	$C_1C_7B_2$	123.4 (6)
$C_6B_1C_{1m}$	114.2 (6)	$C_1C_7C_8$	117.9 (6)
$C_6B_1C_{2m}$	113.0 (6)	$C_8C_7B_2$	118.7 (6)
$C_{3m}B_2H$	99 (2)	$O_{1b}KO_{2c}$	80.1 (2)
$C_{4m}B_2H$	101 (2)	$O_{1b}KO_{2a}$	110.0 (2)
$C_{3m}B_2C_{4m}$	115.7 (6)	$O_{1b}KO_{1c'}$	76.4 (2)
$C_7B_2C_{3m}$	115.9 (6)	$O_{2c}KO_{2a}$	83.4 (2)
$C_7B_2C_{4m}$	114.1 (6)	$O_{2c}KO_{1c'}$	151.5 (2)
$C_6C_1C_7$	119.5 (5)	$O_{1c'}KO_{2a}$	89.6 (2)

[a] See notes *a* and *b* of Table II.

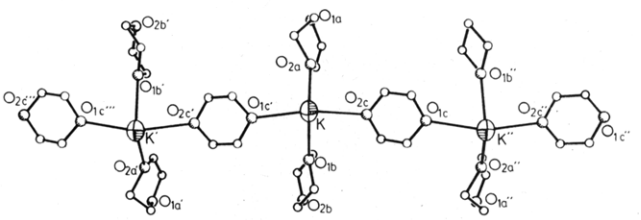

Figure 2. Perspective drawing of a segment of the K^+–dioxane polymer in crystalline 1·KH·(dioxane)$_3$.

(14) This signal appears at 2.6 ppm in CD_3CN and disappears entirely when D_2O is added.
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Table IV. Selected Torsion Angles in Crystalline 1•KH•(dioxane)$_3$[a]

type	angle, deg	type	angle, deg
$C_1C_6B_1H$	5.1 (21)	$C_1C_7B_2H$	0.4 (26)
$C_5C_6B_1H$	177.5 (20)	$C_8C_7B_2H$	179.3 (25)
$C_1C_6B_1C_{1m}$	114.1 (7)	$C_1C_7B_2C_{3m}$	110.5 (7)
$C_5C_6B_1C_{1m}$	68.6 (8)	$C_8C_7B_2C_{3m}$	69.2 (9)
$C_1C_6B_1C_{2m}$	110.0 (7)	$C_1C_7B_2C_{4m}$	111.3 (7)
$C_5C_6B_1C_{2m}$	67.4 (8)	$C_8C_7B_2C_{4m}$	68.9 (9)
$B_1C_6C_1C_7$	0.2 (9)	$B_2C_7C_1C_6$	2.9 (10)

[a] See notes *a* and *b* of Table II.

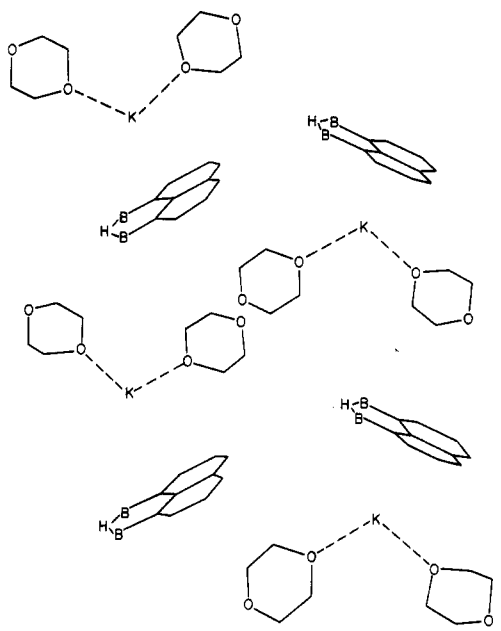
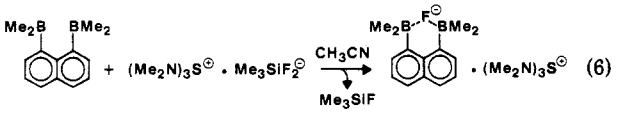


Figure 3. Spatial arrangement of 1·H$^-$, K$^+$, and *nonbridging* dioxanes in crystalline 1·KH·(dioxane)$_3$. The *bridging* dioxanes (not shown) are roughly perpendicular to the plane of the figure and coordinated to K$^+$ (see Figure 2).

The preparation of pure 1·KH was accomplished by reaction of 1 with KH in $(CH_2)_4O$ at ambient temperature. The reaction was complete in <1 h; in contrast, the reaction of 2 with KH required either heating or much longer reaction time to proceed to completion. Precipitation of 1·KH with nonpolar solvents gave analytically pure material. Solvated crystals suitable for X-ray diffraction were grown from dioxane solution, and the structure of 1·KH·(dioxane)$_3$ was determined[9] (Figures 1–3; Tables II–IV).

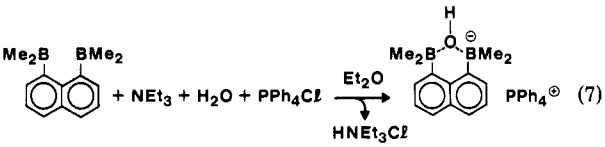
The complex of 1 with fluoride was prepared employing $Me_3SiF_2^-$ as the fluoride donor (eq 6). Although com-



(6)

plexation also occurred when 1 was treated with CsF or Bu_4NF (but not $Bu_4N^+BF_4^-$), only $(NMe_2)_3S^+Me_3SiF_2^-$ gave a clean, isolable adduct. The adduct was characterized especially by ^{19}F–^1H and ^{19}F–^{13}C coupling in its NMR spectra, with the large ^{19}F–$^1H_{Me}$ coupling verified on a 60-MHz spectrometer. The proton resonances and couplings of 1·F$^-$ were unchanged in the presence of free 1, while on the other hand Et_3B and Et_3BF^- formed a rapidly equilibrating mixture. Fluoride was completely removed from 2·F$^-$ by 1.

The hydroxide complex of 1 was generated from 1 and either H_2O/MeLi in $(CD_2)_4O$ or, more reliably, NEt_3/H_2O in CD_3CN or Et_2O (eq 7). The salt PPh_4^+·1·OH$^-$ was obtained by metathesis. Its NMR spectrum was little affected by the addition of $(i\text{-Pr})_2NLi$.



(7)

Attempts at generating a radical anion from 1 electrochemically in an ESR spectrometer probe did not produce a meaningful ESR spectrum while cyclic voltammetry showed that 1 is reduced irreversibly in CH_3CN or in $(CH_2)_4O$, 0.1 M in n-$Bu_4N^+PF_6^-$, at about −0.9 V vs. SCE. No photoelectron transfer reaction was observed between 1 and the potential electron donors *p*-dimethoxybenzene, 1,4-diazabicyclo[2.2.2]octane, triphenylamine, or *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine, using CIDNP as a probe. Compound 1 interacted weakly, if at all, with tetraphenylphosphonium chloride and bromide, as evidenced by ^1H NMR. The reaction of 1 with primary amines led to decomposition.

Discussion

The syntheses of 1 and 2 illustrate one of the few[20] reliable methods of synthesizing triorganoboranes that are not obtainable via hydroboration of alkenes. A previous synthesis of a dimethylarylborane[21] required the inconvenient prior formation of a diarylmercury intermediate. The key to the present method is the in situ formation of triorganoboron ethoxide complexes, which are resistant to undesired nucleophilic attack by unreacted lithiates that lead to tetraorganoborate oligomers. Organoboron bromides do not give clean condensation products with organolithium reagents because no stable bromoborate complex is formed.

Although the relative stabilities of borohydrides have frequently been inferred from their relative reactivities toward substrates,[22] direct competitive studies of organoborane hydride affinity in solution have not generally been reported. Here, ^1H and ^{11}B NMR provided complementary data indicating the direction of the hydride transfers examined in Table I. The hydride affinity of 1 was greater than the hydride affinities of all the other boranes examined here. This behavior is reminiscent of the reactivity of 5[23] (Proton Sponge) with weak proton acids; hence the trivial name Hydride Sponge for 1.

In particular, the abstraction of H$^-$ from 2·H$^-$ by 1 demonstrates a thermodynamic chelate effect in the binding of H$^-$ by boranes. This chelate effect is also manifested by the relative reactivities of 1 and 2 toward solid KH. Of secondary importance is the electron-withdrawing nature of the naphthyl group at the boron atoms, illustrated by the abstraction of H$^-$ from KEt_3BH by 2. However, the failure of 2 to remove H$^-$ from 4 is evidence that the chelate effect is dominant.

Because of the strength of the B–H–B bond and the steric inaccessibility of the complexed hydride, 1·KH is unreactive toward reagents that would destroy other borohydrides. Furthermore, the barrier to disproportionation of 1 and 1·KH is at least 17 kcal/mol, based on the tem-

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perature-dependent NMR studies. Thus, 1 may be useful as a reagent to remove H^- from a reactive medium.

Several features of the crystal structure of 1·KH·(dioxane)$_3$ (Figures 1–3) are worthy of note. The naphthalene nucleus is very slightly distorted. The naphthalene–boron bonds are equal in length (within experimental error), although the B2–C7–C8 and B2–C7–C1 angles differ significantly from 120°, while the B1–C6–C5 and B1–C6–C1 angles do not. The C–B–C angles are all of similar magnitude, exceeding the 109° expected for an ideal tetrahedron at boron. On the other hand, the H–B–C angles are less than 109°. While the B–H–B angle is unremarkable, the B–H lengths differ by ~6 standard deviations.

Some consistencies may be pointed out between the structures of 1·KH and 6,[24] even though the molecules are only partially analogous. The average length of the bond between boron and the bridging hydride (1.3 Å) is similar in each of them, as are the angles at the bridging hydride (140°), the B–C lengths (1.61 Å), and the C–B–C angles (113–118°). The bridged hydride in 6 is not positioned unsymmetrically between the borons as it is in 1·KH. However, B–H–B asymmetry in diborohydrides is not unprecedented, having been observed[25] in the crystal structure of $KB_2H_7{\cdot}CH_2Cl_2$. Theoretical calculations[26] predict very small energy differences among various alternative geometries about the bridging hydride in isolated $B_2H_7^-$, so in general the observed geometries of bridged borohydrides in the solid state may be determined primarily by subtle crystal packing forces, rather than by the energetics inherent in the B–H–B linkage. The K–B2 distance (3.97 Å) is considerably shorter than the K–B1 distance (4.86 Å) in 1·KH·(dioxane)$_3$; perhaps the K^+ is influential in drawing the H^- toward B2.

The repeating structure of 1·KH·(dioxane)$_3$ (Figure 3) consists of channels of naphthalenediborohydride units alternating with rows of dioxane-solvated potassium ions. The oxygen–potassium lengths are 2.7–2.8 Å while the K–H distance is 4.4 Å. Thus, the hydride anion is relatively sequestered from its counterion.

There is a fundamental difference between 1·KH and previously characterized diborohydrides, including 6. The hydride adduct is formed uniquely from 1 without appreciably straining the diborane precursor (which would be enthalpically unfavorable) or selecting one out of many conformations (which would be entropically disfavored). Both of these factors contribute to the extraordinary stability of 1·H^-.

Fluoroborates and μ-fluorodiborates have been discussed in the literature to a limited extent. Theoretical studies of the parent species BH_3F^-[27] and $H_3BFBH_3^-$[28] have recently appeared, and the geometry of the latter is a matter of disagreement. Actual observation of fluoroborates has been confined to the gas phase,[29] while the only μ-fluorodiborate to be at all characterized[30] is $B_2F_7^-$ in solution at low temperature by NMR. It was claimed that $B_2F_7^-$ was "the only known example of a halogen atom bridging two boron atoms" and that it dissociates rapidly above −100 °C.[30]

The fluoride donor $(NMe_2)_3S^+{\cdot}Me_3SiF_2^-$ was the most reliable source of pure, dry F^- for the preparation of the 1·F^- complex. The drying of alkali-metal[31] and tetraalkylammonium[32] fluorides has recently been shown to be problematical, and the material obtained from an attempt to prepare $(PPh_3)_2NF$[33] was unsuitable.

The complex 1·F^-·$(NMe_2)_3S^+$ is the first μ-fluorodiborate to be isolated and characterized. Although a crystal structure was not obtained, the bridged fluoride structural assignment is supported by several pieces of evidence. Unlike mixtures of Et_3B–Et_3BF^- at 25 °C, or BF_3–BF_4^-[30] at −100 °C, solutions of 1 and 1·F^- did not exchange F^- on the NMR time scale even at 80 °C. A chelate effect was observed when 1 was added to a solution of 2·F^-·$(Me_2N)_3S^+$, all of the F^- instantly associating with 1. The ^{13}C and ^1H NMR spectra of 1·F^- were indicative of a symmetrical complex and superficially resembled those of the bridging complex 1·KH. One would expect analogous structures of 1·H^- and 1·F^- since the ionic radii of H^- and F^- are comparable.[34]

Although a limited number of μ-oxo- and μ-hydroxydiboron fluorides[35] and esters[36] have been reported, no examples of $R_3BOBR_3^{2-}$ or $R_3B(OH)BR_3^-$ species (R = carbon substituent) have been previously characterized. Thus, 1·OH^-·PPh_4^+ is the first such complex to be isolated. Among its spectroscopic features are NMR and IR peaks assigned to a non-hydrogen-bonded OH group. Treatment of the complex with strong bases seemed to remove the OH proton, but the invariance of the ArH and CH_3 bands in the ^1H NMR spectrum under these conditions suggests that the O–M bond in 1·OM^-·PPh_4^+ (M = Li, Na) is quite strong. The ^1H and ^{11}B NMR and also the IR data are consistent with a symmetrically bridged B(OH)B structural designation, as is the fact that the monohydroxide was formed in the presence of excess H_2O.

Investigation of the electron-acceptor properties of 1 was inspired by several illustrations[37] of the enhanced electron-donor abilities of proximate diamines. It was hoped that the interacting vacant orbitals on the borons of 1 would display a special single-electron affinity in a manner analogous to the enhanced single-electron-donating ability of the various diamines. The target species, 1–, would have been an interesting case of the $B_2R_6^-$ radical anion, of which two others (R = H,[38] OMe[39]) have been described. Unfortunately, the generation of 1^- has not yet been achieved.

Compound 1 is the newest addition to the set of compounds that may be termed 1,8-bis(permethylelement)-

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naphthalenes.[40] Other such species that have been reported ("element" = C, Si[41] Ge, Sn, P[42]) are of interest because of the crowding of the "peri" substituents and the resulting distortions of their structures.

In summary, a rigid bidentate Lewis acidic receptor for small anions has been synthesized, and its complexes with hydride, fluoride, and hydroxide have been characterized by a variety of methods. The hydride complex was extraordinarily stable both kinetically and thermodynamically. The fluoride and hydroxide complexes are the first hexaorgano $R_3BXBR_3^-$ species (X = F, OH) to be isolated as pure compounds. Further work on multidentate Lewis acids is in progress.

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Supplementary Material Available: Tables of atomic coordinates, thermal parameters, bond lengths, and bond angles for $[K][C_{14}H_{19}B_2][C_4H_8O_2]_3$ (1·KH·(dioxane)$_3$) (11 pages). Ordering information is given on any current masthead page.

Influence of Pseudoallylic Strain on the Conformational Preference of 4-Methyl-4-phenylpipecolic Acid Derivatives

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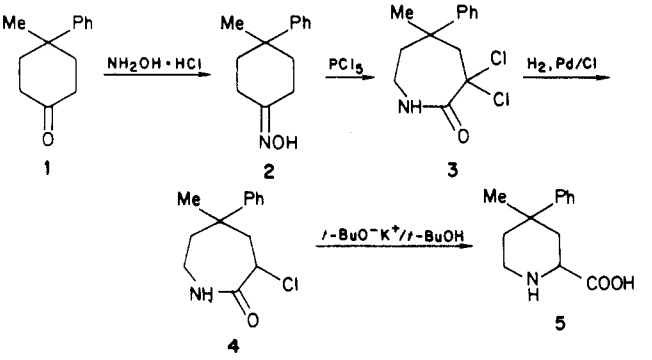
The synthesis of diastereomeric 4-methyl-4-phenylpipecolic acids and their derivatives is described. Investigation by double resonance proton spectroscopy revealed that the conformational preference of substituents attached to the piperidine ring depends upon the hybridization of the piperidine nitrogen. In the free amino acids or leucinamide dipeptides, the C-2 carboxyl group is equatorial. Introduction of a carbamyl moiety on the piperidine nitrogen induces a change in the piperidine ring conformation such that the C-2 carboxyl group is axial, despite a cis-diaxial interaction with the C-4 substituent. The inverted conformational preference of the C-2 and C-4 groups in the *tert*-butyloxycarbonyl and unprotected derivatives is attributed to a severe steric interaction between the partially sp^2 hybridized NCO moiety in the carbamate group and an equatorial C-2 carboxyl group. The X-ray crystal structures of both *cis*- and *trans*-*N*-[(*tert*-butyloxy)carbonyl]-4-methyl-4-phenylpipecolic acids corroborate the solution spectroscopic studies and the concept of pseudoallylic strain in substituted piperidine carbamates. In addition, comparison of the two crystallographically determined structures indicates that hydrogen bonding to the carbonyl of the carbamate produces delocalization into the N–C bond resulting in a shorter bond and more planar piperidyl nitrogen. The conformational preference afforded by pseudoallylic strain indicates that substituted pipecolic acids can be employed in the design of conformationally restricted peptide analogues.

The flexibility of peptide hormones precludes convenient determination of their bioactive conformation by standard spectroscopic techniques. This has necessitated the use of molecular modifications that restrict the conformational freedom of the peptide backbone or amino acid side chains.[1,2] Few convenient approaches are available for side chain restriction of individual amino acid residues. The substitution of α,β-dehydroamino acids[3] fixes the side chain torsion angle but eliminates chirality. A few cyclic amino acids have been incorporated into peptide analogues, including derivatives of aminoindane[4] and aminotetralin,[5] but no conformational information has been reported on such analogues.

A more generalized approach involving the utilization of cyclic amino acids that produce predictable restriction of side chain conformation would be quite useful. The large body of spectroscopic literature on six-membered ring systems makes pipecolic acid derivatives attractive for incuding side chain restriction as an approach to studying the relationship between the conformation of peptides and biological activity.

Scheme I



Here we report on a convenient synthesis for the preparation of C-4 disubstituted pipecolic acids and on the effect of pseudoallylic strain[6] in stabilizing a cis-diaxial

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