4.73 (d, J = 1.7 Hz, 1 H), 1.98 (m, 1 H), 1.74 (m, 3 H), 1.48 (m, 1 H), 1.23 (s, 3 H), 1.50 (m, 2 H), 1.08 (s, 3 H), 0.77 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 164.0, 161.1, 158.1, 148.2, 139.2, 136.6, 122.5, 121.2, 113.1, 110.0, 86.7, 75.3, 48.9, 48.8, 41.5, 39.7, 30.0, 26.7, 25.9, 20.5, 19.8. Anal. Calcd for $C_{21}H_{26}N_2O_2$: C, 74.45; H, 7.68. Found: C, 74.52; H, 7.75.

Preparation of {[2-(6-((*1R,2R,4S*)-1,3,3-Trimethyl-2-norborneoxy)pyridyl)](2-pyridyl)methanol}palladium(II) Chloride (18). A CH_2Cl_2 (20 mL) solution containing **17** (0.40 g, 1.2 mmol) and $(CH_3CN)_2PdCl_2$ (0.36 g, 1.4 mmol) were allowed to react with stirring for 1 h. The palladium complex was precipitated with cold pentane (60 mL), filtered, and then washed with cold pentane. The product was dried under reduced pressure to afford **18** as a light brown powder in quantitative yield. **18(i)**: ^{1}H NMR ($CDCl_3$) δ 8.66 (dd, J = 4.9, 0.9 Hz, 1 H), 7.93 (dt, J = 6.4, 0.8 Hz, 1 H), 7.77 (m, 2 H), 7.70 (t, J = 6.5 Hz, 1 H), 7.54 (d, J = 7.7 Hz, 1 H), 7.16 (m, 1 H), 6.66 (d, J = 8.1 Hz, 1 H), 5.91 (d, J = 8.1 Hz, 1 H), 4.20 (s, 1 H), 2.91 (m, 1 H), 2.00 (m, 1 H), 1.75 (t, J = 3.2 Hz, 2 H), 1.61 (m, 1 H), 1.30 (s, 3 H), 1.35–1.25 (m, 2 H), 1.05, 0.99, 0.88, 0.85 (s, s, s, s, 6 H); ^{13}C NMR ($CDCl_3$) δ 165.5, 159.5, 158.2, 151.7, 142.2, 139.3, 123.9, 123.0, 114.4, 107.6, 93.0, 75.3, 49.8, 48.8, 41.7, 41.0, 30.7, 26.7, 26.0, 21.3, 20.1. **18(ii)**: ^{1}H NMR ($CDCl_3$) δ 8.62 (d, J = 5.9 Hz, 1 H), 7.94 (d, J = 7.5 Hz, 1 H), 7.73 (m, 2 H), 7.85 (m, 1 H), 7.56 (d, J = 7.7 Hz, 1 H), 7.13 (dt, J = 5.8, 1.5 Hz, 1 H), 6.55 (d, J = 7.9 Hz, 1 H), 5.97 (m, 1 H), 3.83 (s, 1 H), 3.10 (m, 1 H), 1.97 (m, 1 H), 1.81 (m, 1 H), 1.56 (m, 2 H), 1.31 (m, 2 H), 1.24 (s, 3 H), 1.19 (s, 3 H), 0.97 (s, 3 H); ^{13}C NMR ($CDCl_3$): δ 165.7, 159.7, 158.1, 151.7, 142.3, 139.1, 123.8, 123.1, 114.5, 108.0, 95.0, 75.3, 50.1, 49.5, 41.3, 40.4, 30.5, 27.6, 25.5, 21.0, 20.2. Anal. Calcd for $C_{21}H_{26}Cl_2N_2O_2Pd$: C, 48.86; H, 5.04. Found: C, 48.41; H, 5.12.

Hydrosilation of Acetophenone. A Schlenk tube was charged with acetophenone (0.6 g, 5 mmol), $[(COD)RhCl]_2$ (12.3 mg, for 100/1 substrate/Rh mol ratio), the appropriate ligand **4**, **5**, or **8**, and dichloromethane (3 mL). The mixture was degassed by three consecutive freeze–pump–thaw cycles. A separate Schlenk tube was changed with diphenylsilane (1.3 mL, 7 mmol) and dichloromethane (1 mL) and degassed as above. The latter solution was cannulated into the acetophenone mixture and allowed to react at −15 °C until the carbonyl band in the infrared spectrum (1685 cm^{-1}) disappeared. The mixture was then diluted with acetone (5 mL) and 10% hydrochloric acid (10 mL) and stirred vigorously for 4 h. The mixture was extracted with ether and the organic layer dried over K_2CO_3. The ether was removed and the crude product purified by bulb–bulb distillation. Contamination by acetophenone in the samples was taken into account and calculated by using the proton NMR spectrum for the purified product. The spectroscopically determined weight of acetophenone in each sample was subtracted out for optical yield calculations.

Asymmetric Cyclopropanation Reactions. To a cool (5 °C) THF (1 mL) solution of 2,5-dimethyl-2,4-hexadiene (3.0 g, 27.2 mmol) was slowly added ethyl diazoacetate (1.0 g, 8.8 mmol) in the presence of catalyst **19(i)** (1 mol %). After nitrogen gas evolution had ceased, the mixture was fractionally distilled under reduced pressure to afford (−)-ethyl chrysanthemate (cis and trans mixture, $[\alpha] = -1.5°$, neat, dm = 1) in 59% chemical yield. A comparison of these data with that of Aratani and co-workers[11c] (Table I, entry 6, 50% optical yield) affords an estimated optical yield of 8.5%. This is based on the assumption that we are observing approximately the same asymmetric induction in the cis and trans isomers as Aratani.

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Synthesis of the Monomeric $HBTrip_2$ (Trip = 2,4,6-*i*-$Pr_3C_6H_2$) and the X-ray Crystal Structures of $[HBMes_2]_2$ (Mes = 2,4,6-$Me_3C_6H_2$) and $HBTrip_2$

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The synthesis and spectroscopic properties of $HBTrip_2$ (**1**) and the X-ray crystal structures of **1** and the dimeric species $[HBMes_2]_2$ (**2**) are described. The synthesis of **1** was carried out by treatment of $Me_2S\cdot BHCl_2$ with 2 equiv of TripMgBr in THF solution. Standard workup gave **1** as a colorless crystalline material that exhibited a broad singlet at 73.5 ppm downfield in the ^{11}B NMR spectrum. X-ray data confirmed a monomeric structure with a planar boron center and a wide CBC angle of 128.0 (4)°. The less sterically encumbered **2** was prepared according to a literature procedure. The X-ray crystal structure reveals a dimeric structure with the expected bridging hydrogens. The compounds of **1** and **2** are the first diorganoboranes to be structurally characterized by X-ray crystallography. In addition, the structure of **1** represents the first structural characterization of a monomeric diorganoborane. Crystal data at 225 K for **1** or 140 K for **2**, with Mo Kα (λ = 0.710 69 Å) radiation: **1**, monoclinic, a = 11.116 (4) Å, b = 14.869 (5) Å, c = 17.321 (6) Å, β = 100.19 (3)°, Z = 4, space group $P2_1/c$, R = 0.093; **2**, monoclinic, a = 12.254 (6) Å, b = 7.768 (2) Å, c = 16.785 (6) Å, β = 109.43 (3)°, Z = 2, space group $P2/n$, R = 0.047.

Introduction

The use of steric effects in order to achieve regiospecificity in the reactions of organoboranes has been a feature of organoboron chemistry for many years.[1] For example, crowded HBR_2 species such as dicyclohexylborane[2] and 9-borabicyclo[3.3.1]nonane (9-BBN)[3] are extremely useful reagents for the hydroboration of less hindered alkenes. In addition, dimesitylborane[4] has proved an especially selective reagent for the hydroboration of alkynes.[5] For

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example, it is capable of distinguishing between the methyl and propyl groups in hex-2-yne with 90% selectivity, whereas 9-BBN is only 65% selective.[5] In spite of the presence of crowding substituents on boron, the structures of diorganoboranes are, for the most part, dimeric. Only one monomeric diorganoborane has been previously reported. The species HB(thexyl)$_2$ was synthesized by the reaction of tetramethylethylene with borane and shown to be monomeric by IR spectroscopy and osmometry.[6]

In the context of main-group chemistry the employment of bulky substituents at the boron center has allowed the isolation of a considerable number of compounds that are interesting because of their unusual bonding, their oxidation state, or their structure.[7] A significant portion of the recent work has concentrated on the versatility of the –BMes$_2$ group. For example, its use has allowed the synthesis of carbanions stabilized by the presence of an α-boryl substituent.[8,9] Such carbanions have found significant utility as, inter alia, boron-Wittig reagents in organic chemistry.[9] More recently, the –BMes$_2$ group has allowed the synthesis of compounds with multiple boron–phosphorus bonds.[10] In addition, it has found use in derivatized amide ligands that allow the synthesis of rare, open-shell, two-coordinate, transition-metal compounds.[11] On the other hand, the chemistry of the bulkier –BTrip$_2$ group has hardly been explored. Only one structure of a compound involving this group has been reported[10b] so far, although there are a number of compounds that are now known that bear at least one Trip (or the related 2,6-i-$Pr_2C_6H_3$– = Dipp) substituent.[12]

In this paper we report a comparison of the steric effects on the structure of the two diorganoboranes HBTrip$_2$ (1) and [HBMes$_2$]$_2$, including a synthesis for 1. To our knowledge these are the only X-ray structures of diorganoboranes and the structure of 1 represents the first demonstration of a terminal B–H bond involving three-coordinate boron in the solid state.

Experimental Section

All manipulations were carried out under an N_2 atmosphere with use of standard Schlenk-tube techniques. All solvents were distilled from drying agents and degassed twice before use. TripBr was purchased from Lancaster Synthesis, and $Me_2S{\cdot}BHCl_2$ was purchased from Aldrich and used as received. ^{1}H and ^{11}B NMR spectra were recorded on a General Electric QE-300 spectrometer operating at 300 or 96.25 MHz.

Table I. Crystallographic Data and Summary of Data Collection and Structure Refinement Parameters for 1 and 2

	1	**2**
formula	$C_{30}H_{47}B$	$C_{36}H_{46}B_2$
fw	418.52	500.39
color and habit	colorless parallelepipeds	colorless parallelepipeds
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2/n$
a, Å	11.116 (4)	12.254 (6)
b, Å	14.869 (5)	7.768 (2)
c, Å	17.321 (6)	16.785 (6)
β, deg	100.19 (3)	109.43 (3)
V, Å^3	2818 (2)	1507 (1)
T, K	225	140
Z	4	2
cryst dimens, mm	0.38 × 0.45 × 1.38	0.20 × 0.50 × 0.62
d_{calcd}, g cm^{-3}	0.99	1.1
radiation (λ, Å)	Mo Kα (0.71069)	Mo Kα (0.71069)
μ(Mo Kα), cm^{-1}	0.50	0.56
range of transmission factors	0.97–0.98	0.96–0.99
diffractometer	P2$_1$, graphite monochromator	P2$_1$, graphite monochromator
scan method; range, bkgd offset, deg	ω; 0.9, 1.0	ω; 1.0, 1.0
scan speed, deg min^{-1}	8	30
2θ range, deg	0–55	0–55
octants collected	$h,k,\pm l$	$h,k,\pm l$
no. of data collected	7198	3896
no. of unique data	6485	3606
no. of data used in refinement	2954 [$I > 3\sigma(I)$]	2245 [$I > 3\sigma(I)$]
no. of params refined	304	270
R	0.098	0.045
R_w[a]	0.093	0.047

[a] $w = 1/\sigma^2(F_o) + 0.00017F_o^2$.

HBTrip$_2$ (1). TripBr (7 g, 24.8 mmol) in THF (10 mL) was added dropwise to Mg turnings (0.65 g, 27 mmol) suspended in THF (5 mL). Prior to this addition, the metal turnings had been ground with a mortar and pestle and placed in a flask, which was then heated and degassed. A crystal of iodine was used to initate the reaction. After the addition was completed, the mixture was refluxed for 1 h and cooled to ambient temperature. It was then added dropwise to $Me_2S{\cdot}BHCl_2$ (1.68 g, 11.6 mmol) in THF (10 mL) in an ice bath. The solution was allowed to come to room temperature and was stirred for another 12 h. The solvents were removed under reduced pressure to give a pale yellow-green viscous material. Extraction into warm (ca. 40 °C) hexane (30 mL) followed by reduction of the volume to ~10 mL under reduced pressure and cooling in a dry-ice–acetone bath gave the product HBTrip$_2$ (1) as colorless crystals; mp 96–98 °C; yield 34% (not optimized). Anal. Calcd for $C_{30}H_{47}B$: C, 86.1; H, 11.32. Found: C, 85.6; H, 11.6. ^{1}H NMR (C_6D_6): δ 1.23 (2 d, CH_3), 2.81 (sept, p-CH), 3.42 (sept, o-CH), 7.16 (s, m-H), 8.5 (br s, BH). ^{11}B NMR (C_6D_6): δ 73.5.

[HBMes$_2$]$_2$ (2) was synthesized as described in the literature.[4] Crystals suitable for X-ray crystallography were grown from pentane at ca. –20 °C.

X-ray Crystallographic Studies

Structure Determination and Refinement. Crystals of the title compounds were coated with a hydrocarbon oil to retard decomposition and mounted in the cold stream of a Syntex P2$_1$ diffractometer equipped with a locally modified Syntex LT-1 low-tempertature device. No decay in the intensity was observed in 2. In the data collection for 1 the intensities of two standard reflections fluctuated by 6%, introducing a systematic error. We believe this fluctuation resulted from insufficient hardening, at 225 K, of the grease used to mount the crystal. Attempted data collection at lower temperature gave much broader peaks and ultimately resulted in shattering the crystal.

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Table II. Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters (Å² × 10³) for $Trip_2BH$

	x	y	z	U^a
B	2525 (5)	634 (4)	409 (3)	41 (2)*
C(1)	3233 (4)	551 (3)	1274 (2)	33 (1)*
C(2)	2889 (4)	-115 (3)	1771 (2)	36 (2)*
C(3)	3476 (4)	-168 (3)	2541 (2)	36 (2)*
C(4)	4444 (4)	397 (3)	2850 (2)	35 (2)*
C(5)	4791 (4)	1034 (3)	2361 (2)	40 (2)*
C(6)	4210 (4)	1135 (3)	1584 (2)	37 (2)*
C(7)	1886 (4)	-794 (3)	1468 (3)	43 (2)*
C(8)	2398 (5)	-1668 (3)	1244 (4)	74 (2)*
C(9)	998 (5)	-957 (5)	2033 (4)	93 (3)*
C(10)	5091 (4)	292 (3)	3697 (2)	44 (2)*
C(11)	6412 (5)	5 (5)	3723 (3)	81 (3)*
C(12)	5023 (6)	1140 (4)	4177 (3)	76 (3)*
C(13)	4688 (4)	1835 (3)	1055 (3)	44 (2)*
C(14A)	6080 (10)	1660 (7)	1009 (6)	52 (3)
C(14B)	5650 (10)	1424 (7)	613 (6)	59 (3)
C(15A)	4419 (10)	2779 (6)	1301 (5)	48 (3)
C(15B)	5341 (12)	2691 (8)	1554 (7)	80 (4)
C(16)	2038 (4)	1508 (3)	-45 (2)	34 (1)*
C(17)	1302 (4)	2143 (3)	252 (2)	39 (2)*
C(18)	922 (4)	2914 (3)	-185 (2)	43 (2)*
C(19)	1273 (4)	3088 (3)	-890 (2)	38 (2)*
C(20)	2005 (4)	2466 (3)	-1177 (2)	37 (2)*
C(21)	2371 (4)	1675 (3)	-774 (2)	33 (1)*
C(22)	857 (4)	1966 (3)	1032 (3)	50 (2)*
C(23A)	638 (12)	2867 (8)	1487 (7)	59 (3)
C(23B)	-632 (11)	1860 (8)	836 (6)	62 (3)
C(24A)	-262 (11)	1372 (8)	920 (6)	64 (3)
C(24B)	1244 (13)	2749 (8)	1609 (7)	65 (4)
C(25)	887 (5)	3955 (3)	-1343 (3)	50 (2)*
C(26)	1349 (6)	4783 (3)	-869 (3)	78 (3)*
C(27)	-476 (5)	3978 (4)	-1622 (4)	90 (3)*
C(28)	3148 (4)	996 (3)	-1136 (2)	44 (2)*
C(29)	4198 (5)	1421 (4)	-1459 (4)	77 (3)*
C(30)	2345 (5)	428 (3)	-1753 (3)	58 (2)*
H	2356 (36)	-14 (27)	71 (22)	51 (12)

[a] Asterisks denote equivalent isotropic *U* values, defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Solution of both structures was accomplished by using direct methods. All crystallographic computing was carried out by using SHELXTL, Version 5, programs installed on a Data General Eclipse S/230 computer. Atomic scattering factors and anomalous dispersion corrections were from common sources.[13] In the case of 1 there is disorder on an ortho *i*-Pr group on each phenyl ring, which can be described as an approximate 35° rotation about C(13) and a 30° rotation around C(22). The affected methyl carbons were refined at 50% occupancy. H atoms were omitted in the disordered groups. Final refinement was carried out with anisotropic thermal parameters for non-hydrogen atoms except for the disordered carbons. The refinement for 2 proceeded smoothly with all non-hydrogen atoms assigned anisotropic thermal parameters. For both structures hydrogen atoms were refined by using a riding model in which an idealized C–H vector of 0.96-Å length was recalculated with each cycle of refinement. Isotropic hydrogen thermal parameters were fixed at 1.2 times the equivalent isotropic thermal parameter of the bonded carbon. Final blocked-cascade least-squares refinement (based on F) converged at $R = 0.098$ and $R_w = 0.093$ for 1 and $R = 0.045$ and $R_w = 0.063$ for 2. The relatively high value for 1 is probably due to the systematic fluctuation in data intensity and the disorder already described. Atomic coordinates for 1 and 2 are provided in Tables II and III, respectively.

Structural Descriptions

$HBTrip_2$ (1). The asymmetric unit contains an essentially isolated molecule of 1 with no imposed symmetry restrictions as shown in Figure 1. Selected bond distances and angles are provided in Table IV. There are no close contacts between either boron or hydrogen and any other groups. There is a relatively short (2.78-Å) contact between C(15a), one of the disordered methyl groups, and H(11a) at $1 - x, {}^1/_2 + y, {}^1/_2 - z$. However, this does not affect the monomeric formulation of 1. The geometry at boron is essentially planar within the limits allowed by the accuracy to which the position of the hydrogen is known. The C–B–C angle is 128.0 (4)°, and the B–C bonds average 1.567 (6) Å in length. the B–H bond length is 1.13 (4) Å. The dihedral angles between the C(1) and C(16) rings and the C(1)C(16)BH plane are 46.0 and 52.9°, respectively.

$[HBMes_2]_2$ (2). The structure consists of dimers with 2-fold symmetry as illustrated in Figure 2. The 2-fold axis passes through the two bridging hydrogen atoms. There

Table III. Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters (Å² × 10³) for $[HBMes_2]_2$

	x	y	z	U^a
B	2994 (2)	7567 (2)	3054 (1)	20 (1)*
C(1)	4360 (1)	7638 (2)	3223 (1)	20 (1)*
C(2)	4979 (1)	9085 (2)	3666 (1)	21 (1)*
C(3)	6163 (2)	9243 (2)	3817 (1)	25 (1)*
C(4)	6780 (1)	8012 (2)	3549 (1)	25 (1)*
C(5)	6179 (1)	6587 (2)	3121 (1)	24 (1)*
C(6)	4988 (1)	6375 (2)	2953 (1)	21 (1)*
C(7)	4376 (2)	10545 (2)	3946 (1)	27 (1)*
C(8)	8065 (2)	8211 (3)	3717 (1)	35 (1)*
C(9)	4464 (2)	4750 (2)	2485 (1)	27 (1)*
C(10)	2446 (1)	7501 (2)	3796 (1)	20 (1)*
C(11)	2726 (1)	6071 (2)	4353 (1)	23 (1)*
C(12)	2233 (2)	5896 (2)	4987 (1)	26 (1)*
C(13)	1452 (2)	7087 (2)	5099 (1)	27 (1)*
C(14)	1188 (1)	8491 (2)	4558 (1)	24 (1)*
C(15)	1671 (1)	8735 (2)	3922 (1)	21 (1)*
C(16)	3497 (2)	4635 (2)	4257 (1)	29 (1)*
C(17)	915 (2)	6852 (3)	5783 (1)	38 (1)*
C(18)	1318 (2)	10367 (2)	3411 (1)	27 (1)*
H(1)	2500	8722 (29)	2500	20 (6)
H(2)	2500	6428 (31)	2500	24 (6)

[a] Asterisks denote equivalent isotropic *U* values, defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table IV. Selected Bond Distances (Å) and Angles (deg) for $HBTrip_2$ (1) and $[HBMes_2]_2$ (2)

Compound 1			
B–H	1.13 (4)	B–C(16)	1.564 (6)
B–C(1)	1.570 (6)		
C(1)–B–C(16)	128.0 (4)	C(16)–B–H	116 (2)
C(1)–B–H	116 (2)		
Compound 2			
B–H(1)	1.29 (2)	B–C(10)	1.601 (3)
B–H(2)	1.28 (2)	B···B′	1.851 (3)
B–C(1)	1.603 (3)		
C(1)–B–C(10)	123.2 (1)	C(1)–B–H(1)	108.4 (3)
H(1)–B–H(2)	88 (1)	C(1)–B–H(2)	111.5 (3)
B–H(1)–B′	92 (2)	C(10)–B–H(1)	111.4 (3)
B–H(2)–B′	93 (2)	C(10)–B–H(2)	108.9 (3)

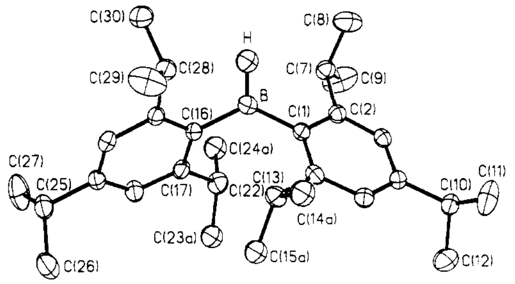

Figure 1. Computer-generated drawing of $[HBTrip_2]_2$ (1). Hydrogen atoms are omitted for clarity with exception of the B hydrogen.

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[13] *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 55–66 99–101.

Table V. Important Bond Lengths (Å) and Angles (deg) for Dimeric Organoboranes

	$B_2H_2Mes_4$[a] (2)	B_2H_6[b]	B_2H_6[c]	$B_2H_2Me_4$[d]	*trans*-$B_2H_4Me_2$[e]	*cis*-$B_2H_4Me_2$[e]
B-C	1.602 (3)			1.590 (3)	1.581 (3)	1.579 (2)
B-H_b	1.285 (20)	1.339 (4)	1.245 (20)	1.36 (4)	1.365 (8)	1.358 (6)
B-H_t		1.196 (7)	1.075 (20)		1.241 (10)	1.239 (8)
C-B-C	123.2 (1)			120.0 (13)		
H_b-B-H_b	88 (1)	97.0 (3)	90 (1)	95 (3)	97.6 (7)	97.1 (6)
B···B	1.851 (3)	1.775 (4)	1.76 (1)	1.840 (10)	1.799 (8)	1.798 (7)

[a] This work. [b] Reference 19 (electron diffraction data). [c] Reference 21 (X-ray data). [d] Reference 22. [e] Reference 23.

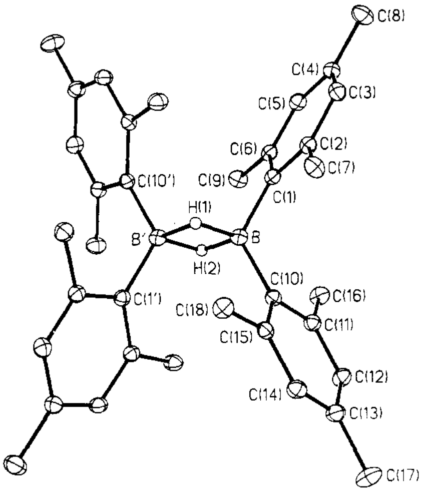

Figure 2. Computer-generated drawing of [HBMes$_2$]$_2$ (2). Hydrogen atoms are omitted for clarity with exception of the B hydrogens.

are no short intermolecular contacts. Selected bond distances and angles are provided in Table IV. The nearly square (internal angles 88 (1)° at B and 92.2 (1.5)° at H) central B_2H_2 array is characterized by almost equal B-H bond distances of 1.28 (2) and 1.29 (2) Å. The boron atoms are 1.851 (3) Å apart. The B-C bonds average 1.602 (3) Å in length, and the C(1)-B-C(10) angle is 123.2 (1)°.

Discussion

Trip$_2$BH was synthesized in a relatively straightforward manner by treatment of the readily available $Me_2S{\cdot}BHCl_2$ starting material with the Grignard reagent TripMgBr in THF solution.[14] This route was chosen over the more conventional pathway,[15] involving LAH reduction of Trip$_2$BX (X = halide), because of difficulties encountered in obtaining a pure product by this method.[14] The colorless crystals of 1 are only mildly air sensitive. Furtheremore, 1 reacts only slowly with moisture to give a mixture of Trip$_2$BOH and probably Trip$_2$B(OH)$_2^-$ (^{11}B NMR, δ 50.1 and 29.8, respectively).[16,17] In this respect, it bears considerable similarity to the dimeric [Mes$_2$BH]$_2$, which also has low air and moisture sensitivity. The ^{1}H NMR spectrum of 1 has, in addition to the peaks that can be attributed to the Trip groups, a broad singlet at δ 8.5. The relative intensity and the position of this peak lead us to assign it to the terminal B-H hydrogen. In addition, the ^{11}B NMR spectrum displayed a broad peak at δ 73.5 consistent with three- rather than four-coordination for the boron center.

The monomeric nature of 1 was confirmed by an X-ray crystal structure. Its unassociated structure represents another example of the kinetic stabilization of an unusual coordination number by steric effects. In this case B-H-B briding is prevented by the large size of the Trip groups. Calculations[18] on B_2H_6 itself show that the association process normally results in about a 35-kcal stabilization. As expected, the C-B-C angle is considerably wider than the purely trigonal value. Both the B-C and the B-H bonds are relatively short. The average B-C length, 1.567 (6) Å, is somewhat less than the B-C bond lengths in many Mes$_2$B derivatives involving three-coordinate boron. It is also considerably shorter than the B-C bonds in Li(Et$_2$O)$_2$P(*t*-Bu)BTrip$_2$, 1.616 (3) Å, which is currently the only other published structure involving in -BTrip$_2$ group.[10b] Presumably, this molecule has longer B-C bonds owing to its greater steric congestion, its negative charge, and a weakening of the B-C bonds due to interaction of the phosphorus lone pair with the empty p orbital on boron.

The B-H bond length in 1 is 1.13 (4) Å, and it is shorter than the bridging B-H distance in 2. Information on terminal B-H bonds involving three-coordinate boron is quite scarce. However, the bond appears to be shorter than the experimentally determined terminal B-H bonds in B_2H_6 (~1.19 Å).[19] It is also shorter than the terminal B-H bond lengths in borohydrides, higher boranes, and related compounds, which average about 1.2 Å.[20] In all of these compounds, however, the boron center is at least four-coordinate. The necessarily high standard deviation for the B-H value in 1 does not, of course, allow a definitive statement on the significance of the 1.13 (4) Å value in relation to the other bond lengths. However, it is notable that the shorter distance in 1 is consistent with the approximate sp^2 hybridization at boron. Changing the relative percentages of s and p character in a particular bonding hybrid orbital has a considerable effect on the bond length, a principle most thoroughly established for carbon compounds. This hybridization argument is also consistent with the shorter B-C distances in 1 compared with those in 2, 1.568 (6) Å vs 1.602 (3) Å.

An alternative explanation[21] of the short B-H bond lengths arises from the inadequacy of the spherical atom model commonly used for data interpretation. Using densities obtained from self-consistent-field molecular wave functions, it is possible to calculate that B-H lengths determined by using the spherical atom model are about 0.05 Å too short. This correction would explain about two-thirds of the discrepancy between the values deter-

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(14) We are grateful to Professor Pelter for helpful advice and discussions. He has informed us that the reduction of Trip$_2$BF with LAH gave an impure sample of Trip$_2$BH.

(15) Singaram, B.; Cole, T. E.; Brown, H. C. *Organometallics* **1984**, *3*, 774.

(16) Dias, H. V. R.; Power, P. P. Unpublished results. The X-ray crystal structure of Trip$_2$BOH reveals a monomeric formulation, whereas Mes$_2$BOH[17a] is tetrameric in the solid state.[17b]

(17) (a) Brown, H. C.; Dodson, V. H. *J. Am. Chem. Soc.* **1957**, *79*, 2302. (b) Power, P. P.; Bartlett, R. A.; Murray, B. D.; Olmstead, M. M.; Power, P. P. *Inorg. Chem.* **1987**, *26*, 2409.

(18) Garabedian, M. E.; Benson, S. W. *J. Am. Chem. Soc.* **1964**, *86*, 176. Fehlner, T. P.; Koski, W. S. *J. Am. Chem. Soc.* **1965**, *87*, 409.

(19) Bartell, L. S.; Carroll, B. L. *J. Am. Chem. Soc.* **1965**, *42*, 1135.

(20) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: Oxford, England, 1984.

(21) Jones, D. S.; Lipscomb, W. N. *Acta Crystallogr.* **1970**, *A26*, 196 and references therein.

mined by X-ray and electron diffraction data (see Table V).

The empty p orbital on boron appears to be essentially unavailable for σ bonding. Although **1** reacts slowly with water, a process that may involve prior association of H_2O, it shows no tendency to coordinate Lewis bases such as SMe_2, Et_2O, THF, or pyridine. Inspection of the illustration in Figure 1 shows that the four ortho *i*-Pr groups protect the boron p orbital from attack by all but the smallest molecules. However, the p orbital may, apparently, be used in π bonding if the hydrogen is replaced by a suitable π donor. This is illustrated by the structure of $Li(Et_2O)_2P(t\text{-}Bu)BTrip_2$, which displays short B–P bonds and a planar phosphorus center.[10b]

The dimeric structure of **2** is in sharp contrast to that of **1** and serves to emphasize that, indeed, extremely large substituents are required to avoid the large stabilization gain upon association. It is notable that in a number of other systems the $-BMes_2$ group has been used as a substituent that may interact in a π but not a σ fashion. Its behavior as a σ-bonded species in **2** is due, no doubt, to the small size of hydrogen and the unique nature of the boron–hydrogen bridge bonding. The configuration of the boron centers in **2**, in fact, closely resembles that seen in the borate species $[Mes_2BH_2Li(DME)_2]$, whose B–H and B–C bond lengths are 1.14 (3) and 1.640 (5) Å, respectively.[4]

Some details of the structure of **2** merit comment. The longer B–C bonds in **2** compared to those in **1** may be attributed to the rehybridization at the boron center. The B–H bonds are, in addition, electron deficient so that the much longer B–H distances are to be expected. Its structure may be compared to some other known structures of diboranes. Inspection of the data[19,22,23] in Table V reveals some differences in the structure of **2**. For example, the B–C bonds are somewhat longer than the values in the other three substituted diboranes. In addition the H_b–B–H_b angle in **2** is significantly smaller (~9°) than those observed in other compounds. The B–H_b distances in **2** are also the shortest observed in any of the structures. The acute H_b–B–H_b angle is manifested in a long···B distance of 1.851 (3) Å. This is similar to that observed in $B_2H_2Me_4$, which, however, has a wider H_b–B–H_b angle of 95.2 (35)°. Apparently, the difference in B–H_b bond lengths between the two compounds almost exactly compensates for the expected difference in the angles so that a similar B···B distance results. There does not appear to be an obvious reason for the relatively short B–H_b bonds in **2**. As in **1**, it could be argued that these differences may be attributable to the inadequacies of the spherical atom model. However, it is difficult to account for the longer B···B separation in **2** in terms of this argument. The presence of four bulky mesityl groups in the molecule may explain why the B–C bonds are somewhat long and also why the B···B separation increases. The wide C–B–C angle in **2**, 123.2 (1)°, may also lead to the expectation that the H_b–B–H_b angle should be closed down somewhat. These changes in hybridization may be consistent with the shorter B–H and longer B–C bonds observed. However, the data currently available in Table V is insufficient to warrant a correlation between the above structural parameters.

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Supplementary Material Available: Tables of anisotropic thermal parameters, bond distances and angles, and hydrogen coordinates (8 pages); tables of structure factors (32 pages). Ordering information is given on any current masthead page.

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