FULL PAPER

Reactivity of the dimesityl-1,8-naphthalenediylborate anion: isolation of the borataalkene isomer and synthesis of 1,8-diborylnaphthalenes

James D. Hoefelmeyer, Stéphane Solé and François P. Gabbaï*

Chemistry TAMU 3255, Texas A&M University, College Station, Texas 77843-3255, USA. E-mail: francois@tamu.edu; Fax: 979-845-4719

Received 18th December 2003, Accepted 24th February 2004 First published as an Advance Article on the web 12th March 2004 Dalton www.rsc.org/dalton

The anionic boron *peri*-bridged naphthalene derivative, namely dimesityl-1,8-naphthalenediylborate (1), undergoes a hydrolysis reaction to afford dimesityl-1-naphthylborane (2) whose structure has been determined. Upon standing at room temperature in toluene for an extended period of time, 1 undergoes a ring expansion reaction to afford 8,10,11a-trimethyl-7-mesityl-11a*H*-7-boratabenzo[de]anthracene (3). As shown by its crystal structure, compound 3 constitutes a rare example of a borataalkene and features a carbon-boron double bond of 1.475(6) Å incorporated in a conjugated hexa-1-boratatriene system. The reaction of 1 with 9-chloro-9-borafluorene and 5-bromo-10,11dihydrodibenzo[b,f]borepin results in the formation of diboranes 4 and 5 which bear two different boryl moieties at the *peri*-positions of naphthalene. These diboranes have been characterized by multinuclear NMR spectroscopy and X-ray single crystal analysis. The boron center of the borafluorenyl moiety is π -coordinated to the *ipso*-carbon of a mesityl group with which it forms a contact of 2.730(3) Å. The cyclic voltammogram of 2 in THF shows a quasireversible reduction wave at $E_{1/2} - 2.41$ V (*vs.* Fc/Fc⁺) corresponding to the formation of the radical anion. In the case of diboranes 4, 5 and 1-(dimesitylboryl)-8-(diphenylboryl)naphthalene (6), two distinct waves are observed at $E_{1/2} - 2.14$ and -2.56 V for 4, $E_{1/2} - 2.26$ and -2.78 V for 5, and $E_{1/2} - 2.41$ and -2.84 V for 6. The first reduction wave most likely indicates the formation of a radical anion in which the unpaired electron is σ -delocalized over the two boron centers.

Introduction

Bidentate boranes constitute one of the simplest class of polyfunctional Lewis acids. Such species exhibit a rich chemistry and are used as selective receptors for neutral^{1,2} and anionic substrates³⁻⁵ as well as Lewis acid activators for various organic^{6,7} and organometallic reactions.^{4,5} 1,8-DiboryInaphthalene derivatives constitute one of the best studied classes of such compounds.^{8,9} As demonstrated by previous investigations, these bidentate Lewis acids can complex small anions such fluoride and hydroxide.³ In addition, our group showed that the one-electron reduction of 1,8-bis(diphenylboryl)naphthalene can lead to the generation of σ -delocalized radicals.¹⁰ As part of our general interest in this chemistry, we have recently described a rare example of a boron peri-bridged naphthalene derivative,11 namely dimesityl-1,8-naphthalenediviborate (1).¹² This strained cyclic borate undergoes ring opening reactions in the presence of various electrophiles 13 and its reaction with diorganylboronhalides afford unsymmetrically substituted 1,8-diborylnaphthalenes.¹² In this contribution, we report a series of results that further document the unique reactivity of this anionic boron peri-bridged naphthalene derivative.

Results and discussion

The salt 1-Li(THF)₄ is soluble in polar solvents such as THF or pyridine and partially soluble in aromatic solvents. In the presence of moisture, 1 undergoes a hydrolysis reaction to afford dimesityl-1-naphthylborane (2), which has been previously described (Scheme 1).^{13,14} In the course of our investigations, we were able to obtain single crystals of 2 and have determined its crystal structure (Fig. 1, Table 1). As expected, the carbonboron bond lengths of 2 are unremarkable and the boron adopts a strictly trigonal planar geometry ($\Sigma_{angles} = 359.9^{\circ}$). Nevertheless, we note that, as a result of the steric crowding, the dihedral angles formed between the plane containing the three carbon atoms bound to the boron center and the plane contain



Scheme 1 Reagents and conditions: (i) THF–H₂O, 25 °C; (ii) toluene, 25 °C, 7 days/tmeda, -30 °C; (iii) 9-chloro-9-borafluorene, Et₂O, -40 °C; (iv) 5-bromo-10,11-dihydrodibenzo[b,f]borepin, Et₂O, 25 °C.

ing the aromatic core of each mesityl ligand (51.1 and 64.3°) are significantly larger than that involving the plane containing the naphthyl group (36.5°). Interestingly, while compound 1 is indefinitely stable as a solid in a dry inert atmosphere, we observed that suspensions of its lithium salt in toluene turn to a red-orange solution after seven days. The same experiment carried out in toluene-d₈ indicated the clean conversion of 1 into a new product (3) which featured two ¹H NMR singlets at 5.1 and 5.7 ppm characteristic of ethylenic CH groups. Integration of the NMR spectrum obtained after 7 days indicated that 3 had formed in a 70-80% yield (non-isolated). The formation of 3 is accompanied by formation of a small amount of the hydrolysis product which is also readily detected. Addition of tmeda to such a solution, followed by storing at -30 °C overnight results in the crystallization of the new compound (3-Li(tmeda)₂·PhMe) in the form of deep purple needle like

 Table 1
 Crystal data, data collection, and structure refinement for 2, 3-Li(tmeda)₂, 4 and 5.

	2	3-Li(tmeda) ₂ ·PhMe	4	5
Crystal data				
Formula	$C_{28}H_{29}B$	C47H68BLiN4	$C_{40}H_{36}B_{2}$	$C_{42}H_{40}B_2$
Mr	376.32	706.80	538.31	566.36
Crystal size/mm	$0.21 \times 0.18 \times 0.13$	$0.19 \times 0.09 \times 0.07$	$0.18 \times 0.17 \times 0.13$	$0.49 \times 0.35 \times 0.30$
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	$Pna2_1$	Cc	$P2_1/n$	$P2_1/c$
a/Å	21.9952(19)	18.007(2)	15.8947(14)	16.0226(14)
b/Å	8.0123(7)	14.3779(19)	10.8667(10)	11.1521(9)
c/Å	12.4897(11)	16.731(2)	17.9558(16)	18.2407(16)
βl°		97.703(3)	101.358(2)	97.448(2)
$V/Å^3$	2201.1(3)	4292.7(10)	3040.6(5)	3231.9(5)
Ζ	4	4	4	4
$D_{\rm c}/{\rm g}~{\rm cm}^{-3}$	1.136	1.094	1.176	1.164
μ (Mo-K α)/mm ⁻¹	0.063	0.062	0.065	0.065
F(000)/e	808	1544	1144	1208
Data collection				
T/K	293(2)	110(2)	110(2)	293(2)
Scan mode	ω	ω	ω	ω
hkl Range	-26/24, -7/9, -14/14	-21/13, -17/15, -16/19	-18/18, -12/8, -20/20	-19/20, -12/15, -24/13
Measured refl.	10972	11105	14345	19987
Unique refl. (R_{int})	3867 (0.0423)	5499 (0.0540)	4766 (0.0656)	7472 (0.0455)
Refl. used for refinement	3867	5499	4766	7472
Refinement				
Refined parameters	263	478	380	397
$R1^{a} w R2^{b} [I > 2\sigma(I)]$	0.0584, 0.1353	0.0541, 0.1245	0.0642, 0.1843	0.0791, 0.1841
$\rho_{\rm fm}$ (max./min.)/e Å ⁻³	0.214/-0.180	0.213/-0.201	0.282/-0.180	0.304/-0.212

 ${}^{a}R1 = \Sigma(F_{o} - F_{c})/\Sigma F_{o}.{}^{b}wR2 = \{[\Sigma w(F_{o}^{2} - F_{c}^{2})^{2}]/[\Sigma w(F_{o}^{2})^{2}]\}^{1/2}; w = 1/[\sigma^{2}(F_{o}^{2}) + (ap)^{2} + bp]; p = (F_{o}^{2} + 2F_{c}^{2})/3; a = 0.07$ (2), 0.067 (3), 0.1434 (4), 0.0800 (5); b = 0 (2), 0 (3), 0.1177 (4), 0 (5).



Fig. 1 ORTEP view of **2** in the crystal (30% ellipsoids). Selected bond lengths (Å) and angles (°): B–C(1) 1.567(5), B–C(21) 1.587(5), B–C(11) 1.593(5); C(1)–B–C(21) 124.1(3), C(1)–B–C(11) 115.2(3), C(21)–B–C(11) 120.6(3).

crystals (Scheme 1). While the high air-sensitivity of these crystals has complicated their analysis, a single crystal X-ray diffraction study (Table 1, Fig. 2) indicated the formation of 8,10,11a-trimethyl-7-mesityl-11aH-7-boratabenzo[de]anthracene (3), a structural isomer of 1. The isomerization of 1 into 3 can be rationalized on the basis of a mechanism involving the heterolytic cleavage of one of the boron peri-carbon bonds followed by nucleophilic attack at the ortho-carbon of one of the mesityl groups (Scheme 2). Examination of the structure of 3 indicates that the boron atom adopts a trigonal planar geometry ($\Sigma_{angles} = 360.0^{\circ}$) (Fig. 2). The resulting coordination plane forms a dihedral angle of 9.9° with the naphthalene plane. More importantly, inspection of the bond distances indicates the existence of a conjugated hexa-1-boratatriene fragment with localized double bonds at B-C(21) (1.475(6) Å), C(22)–C(23) (1.370(6) Å) and C(24)–C(25) (1.310(6) Å). It is important to point out that the borataalkenes



Fig. 2 ORTEP view of **3** in the crystal (30% ellipsoids). Selected bond lengths (Å) and angles (°): B–C(21) 1.475(6), B–C(1) 1.570(6), B–C(11) 1.608(6), C(21)–C(22) 1.422(6), C(21)–C(26) 1.552(5), C(22)–C(23) 1.370(6), C(23)–C(24) 1.440(5), C(24)–C(25) 1.310(6), C(25)–C(26) 1.534(5); C(21)–B–C(1) 117.7(4), C(21)–B–C(11) 127.0(4), C(1)–B–C(11) 115.3(4), C(22)–C(21)–B 126.4(4), C(22)–C(21)–C(26) 113.8(3), B–C(21)–C(26) 119.8(4).



are relatively rare.¹⁵⁻¹⁸ The length of the B–C(21) double bond falls within the range previously established for such a linkage (1.44 Å in [Mes₂BCH₂]⁻ and 1.52 Å in [CH₂C₆H₂(3,5-Me₂)-(4-B{2,4,6-Me₃C₆H₂}₂)]⁻).^{16,17} It is also shorter than the B=C distances of 1.51–1.52 Å observed for coordinated [(C₆F₅)₂-BCH₂]⁻ ligands.¹⁹ The ¹H NMR spectrum of **3**-Li(tmeda)₂ in THF-d₈ shows two distinct resonances for the aromatic CH

View Article Online

groups of the intact mesityl group indicating that the latter is not freely rotating. The two singlets corresponding to ethylenic CH groups of the conjugated hexa-1-boratatriene fragment appear at 4.7 and 5.7 ppm.

While we have previously studied the reaction of 1 with dialkyl and diaryl boron halide fragments,12 it occurred to us that the introduction of flat cyclic boryl moieties at the periposition of naphthalene could lead to reduced steric hindrance and closer approach of the boron centers. With this in mind, diboranes 4 and 5 were prepared by reaction of compound 1 with 9-chloro-9-borafluorene,20 and 5-bromo-10,11-dihydrodibenzo[b,f]borepin (Scheme 1). The latter reagent was synthesized by reaction of 1,2-bis(2-trimethylsilylphenyl)ethane²¹ with BBr₃. Diboranes 4 and 5 are soluble in chloroform as well as in more polar solvents such as pyridine and acetonitrile. The ¹H NMR spectra of 4 and 5 confirms the attachment of the 9-borafluorenyl or 10,11-dihydrodibenzo-[b,f]borepin moieties and exhibit six distinct resonances that correspond to the aromatic CH groups of the unsymmetrically substituted naphthalene backbone. In addition, the spectra indicate the existence of rigid structures since four aryl protons and six distinct methyl groups are observed for the mesityl substituent. The ¹¹B NMR spectrum of 4 shows two resonances at 57 and 71 ppm confirming the presence of two different boron centers. In the case of 5, the ¹¹B resonances of the two boron centers merge into a broad signal that is observed at 72 ppm. Single crystals of both derivatives were readily obtained. The structures of 4 and 5 are similar to those of previous diboranes such as 1-(dimesitylboryl)-8-(diphenylboryl)naphthalene¹² (6) (Figs. 3 and 4, Table 1). As in other sterically hindered perisubstituted naphthalene derivatives, the B(1)-C(1)-C(9) (127.8° in 4, 129.4° in 5) and B(2)-C(8)-C(9) (130.6° in 4, 132.1° in 5) angles substantially deviate from the ideal value of 120°. An interesting feature in the structure of 4 concerns the presence of an interaction that occurs between one of the boron mesityl groups and the boron of the borafluorenyl unit. As shown by the presence of a short B(2)–C(21) distance of 2.730(3) Å, this interaction involves the η^1 -coordination of the *ipso*-carbon (C21) of the mesityl group. As a result of this interaction, the boron center, B(2) is slightly pyramidalized ($\Sigma_{angle} = 355.7^{\circ}$). Interestingly, compound 5 assumes a similar molecular structure with an apparent intramolecular contact occurring between the boron center B(2) and the ipso-carbon (C21) of one of the mesityl groups. In this case, the resulting B(2)-C(21)distance is much longer (3.153 Å) indicating a weaker interaction, which nevertheless, results in a detectable pyramidalization of the B(2) boron center ($\Sigma_{angle} = 357.6^{\circ}$). The differences



Fig. 3 ORTEP view of 4 in the crystal (30% ellipsoids). Selected bond lengths (Å) and angles (°): B(1)-C(1) 1.569(3), B(1)-C(21) 1.579(3), B(1)-C(11) 1.595(3), B(2)-C(8) 1.552(3), B(2)-C(31) 1.570(3), B(2)-C(41) 1.574(4), B(2)-C(21) 2.730(3); C(1)-B(1)-C(21) 123.64(18), C(1)-B(1)-C(11) 117.40(18), C(21)-B(1)-C(11) 117.96(17), C(8)-B(2)-C(31) 126.8(2), C(8)-B(2)-C(41) 125.5(2), C(31)-B(2)-C(41) 103.4(2), C(9)-C(1)-B(1) 127.77(19), C(9)-C(8)-B(2) 130.62(19).



Fig. 4 ORTEP view of 5 in the crystal (20% ellipsoids). Selected bond lengths (Å) and angles (°): B(1)-C(1) 1.565(4), B(1)-C(21) 1.571(4), B(1)-C(11) 1.590(4), B(2)-C(41) 1.554(4), B(2)-C(31) 1.585(4), B(2)-C(8) 1.588(4), B(2)-C(21) 3.153(4); C(1)-B(1)-C(21) 122.9(3), C(1)-B(1)-C(11) 117.2(2), C(21)-B(1)-C(11) 118.8(2), C(41)-B(2)-C(31) 126.1(3), C(41)-B(2)-C(8) 115.2(2), C(31)-B(2)-C(8) 116.3(3), C(9)-C(1)-B(1) 129.4(2), C(9)-C(8)-B(2) 132.1(3).

observed in the structures of **4** and **5** substantiate the increased Lewis acidity of the B(2) boron center of **4**. This increased acidity results from the antiaromatic character of the 9borafluorenyl moiety, which favors coordination events that removes the boron p-orbital from conjugation.^{22,23} The relief of strain energy in the borole ring upon boron pyramidalization also contributes to the increased acidity of the B(2) boron center.²³ Finally, we note that the boron–boron separation in **4** and **5** are, respectively, equal to 3.212 and 3.385 Å.

The cyclic voltammogram of **2** in THF is characteristic of a triarylborane and shows a partially reversible reduction wave at $E_{1/2} - 2.41$ V (vs. Fc/Fc⁺). It is followed by an irreversible event at $(E_p)_{red} - 3.36$ V. As for other triarylboranes,²⁴ the first reduction corresponds to the formation of the radical anion. In the case of diboranes **4**–**6** (Fig. 5), a partially reversible wave is observed at $E_{1/2} - 2.14$ V for **4**, $E_{1/2} - 2.26$ V for **5** and $E_{1/2} - 2.41$ V for **6**. By analogy with some of our earlier work on related diboranes,¹⁰ we suggest that this reduction corresponds to the formation of the radical anion. In the formation of the radical anion, which experiences some σ -delocalization over the two boron centers (Scheme 3). Interest-



ingly, this first reduction wave is followed by a second partially reversible wave at $E_{1/2}$ -2.56 V for 4, $E_{1/2}$ -2.78 V for 5 and $E_{1/2}$ -2.84 V for 6 possibly corresponding to the formation of a dianion, which exists either as a boron-boron σ -bonded derivative or as a diradical (Fig. 5).²⁵ In comparison to the other diboranes, the reduction of 4 is relatively facile as it occurs at a more positive potential than that of 5 and 6. Once again, this





property can be correlated to the antiaromatic character of the 9-borafluorenyl moiety which favors its reduction.²⁶⁻²⁸ The chemical reduction of 4 and 5 has also been studied. Combination of the diboranes with 18-C-6 and K (4) or Na/Hg (5) results in the production of dark brown (4) or dark purple (5) paramagnetic solutions, which presumably contain the radical anion 4^{•-} and 5^{•-}, respectively. The EPR spectra of these solutions both consist of a broad signal at g = 2.00. While a seven-line signal resulting from ¹¹B hyperfine coupling was observed for the radical anion obtained by reduction of 1,8-bis(diphenylboryl)naphthalene,¹⁰ the ¹¹B hyperfine coupling for the presumed 4^{•-} and 5[•] radicals could not be resolved, possibly because of the unsymmetrical nature of these diboranes. Attempts to generate the dianions chemically have not been successful.

Experimental

General considerations

Compound 1,12 9-chloro-9-borafluorene20 and 2,2'-dilithiobibenzyl²⁹ were synthesized by following the experimental procedures described in the literature. Trimethylchlorosilane was purchased from Aldrich and boron tribromide from Alfa Aesar. Solvents were refluxed over the appropriate drying agent under N2 and were distilled prior to use. THF and ether were dried over Na/K. Dichloromethane, chloroform and acetonitrile were dried over CaH2. Air-sensitive compounds were handled in an N2 atmosphere using standard Schlenk and glovebox techniques. All melting points were measured on samples in sealed capillaries and are uncorrected. The ¹H and ¹³C NMR spectra were recorded on a Varian VXR-300 spectrometer at 300 and 75.4 MHz, respectively. ¹¹B NMR spectra were recorded on a Varian Inova 400 broadband spectrometer at 128.3 MHz. Chemical shifts for the ¹H and ¹³C NMR spectra are reported with respect to Me₄Si standard ($\delta = 0$ ppm). Chemical shifts for the ¹¹B NMR spectra are reported with respect to BF₃·OEt₂ standard ($\delta = 0$ ppm). EPR spectra were recorded on a Bruker X-band EPR spectrometer (model ESP 300E).

Crystallography

The crystallographic measurements were performed using a Siemens SMART-CCD area detector diffractometer, with graphite-monochromated Mo-K α radiation ($\lambda = 0.71069$ Å). Specimens of suitable size and quality were selected and mounted onto glass fibers with Apiezon grease. The structures were solved by direct methods, which successfully located most of the non-hydrogen atoms. Subsequent refinement on F^2 using the SHELXTL/PC package (version 5.1) allowed location of the remaining non-hydrogen atoms. Further crystallographic details can be found in Table 1.

CCDC reference numbers 227178–227181.

See http://www.rsc.org/suppdata/dt/b3/b316505a/ for crystallographic data in CIF or other electronic format.

Synthesis of the borataalkene salt 3-Li(tmeda)₂

A suspension of solid 1-Li(THF)₄ in toluene (5 mL) was left to stand for 7 days under N₂ which resulted in the production of a red-orange solution. Addition of TMEDA (5 mL) resulted in the immediate formation of a deep purple solution. Storage at -30 °C overnight led to the crystallization of the borataalkene salt 3-Li(tmeda)₂ which was isolated as a toluene solvate. The compound was purified by successive washings with cold pentane (2 mL). The compound decomposes upon heating above room temperature. Because of the high sensitivity of the compound, an elemental analysis could not be obtained. NMR yield: 70–80%. ¹H NMR (THF-d₈): 0.97 (s, 3H, Mes-CH₃), 1.56 (s, 3H, Mes-CH₃), 1.73 (s, 3H, Mes-CH₃), 1.75 (s, 3H, Mes-CH₃), 2.04 (s, 3H, Mes-CH₃), 2.24 (s, 3H, Mes-CH₃), 4.73 (s, 1H, C=C*H*), 5.66 (s, 1H, C=C*H*), 6.64 (s, 1H, Mes-C*H*), 6.66 (s, 1H, Mes-C*H*), 6.72 (dd, 1H, ${}^{3}J(HH) = 7.0 Hz$, ${}^{4}J(HH) = 1.5 Hz$, Naphth-C*H*), 6.93 (dd, 1H, ${}^{3}J(HH) = 7.0 Hz$, ${}^{3}J(HH) = 7.0 Hz$, Naphth-C*H*), 7.25 (t, 1H, ${}^{3}J(HH) = 8.0 Hz$, Naphth-C*H*), 7.28 (dd, 1H, ${}^{3}J(HH) = 8.0 Hz$, ${}^{4}J(HH) = 1.5 Hz$, Naphth-C*H*), 7.33 (dd, 1H, ${}^{3}J(HH) = 8.0 Hz$, ${}^{4}J(HH) = 1.5 Hz$, Naphth-C*H*), 7.55 (dd, 1H, ${}^{3}J(HH) = 8.0 Hz$, ${}^{4}J(HH) = 1.5 Hz$, Naphth-C*H*), 7.55 (dd, 1H, ${}^{3}J(HH) = 8.0 Hz$, ${}^{4}J(HH) = 1.5 Hz$, Naphth-C*H*). ¹¹B NMR (THF-*d*₈): 45.5 (br). ¹³C NMR (toluene-*d*₈): 21.59, 22.25, 23.27, 25.06, 25.24, 25.53 (6C, CH₃), 122.7, 123.9, 125.1, 125.4, 126.6, 126.9, 128.9, 129.2, 132.3, 134.7 (10C, CH), quaternary C not observed.

Synthesis of diborane 4

To a suspension of freshly isolated 1-Li(THF)₄ (0.80 g, 1.19 mmol) in diethyl ether (5 mL) at -40 °C was added a solution of 9-chloro-9-borafluorene (0.30 g, 1.51 mmol) in diethyl ether (5 mL) at -40 °C. An immediate reaction was observed. The solution was stirred for 12 h at 25 °C, and the solvent was removed by evaporation. The residue was extracted with chloroform. Following filtration and evaporation of the solvent, the product was recrystallized from a pentane-hexane mixture, which afforded yellow crystals of 4. Yield: 0.25 g, 39%. ¹H NMR (chloroform-d): 1.33 (s, 3H, Mes-CH₃), 1.33 (s, 3H, Mes-CH₃), 1.55 (s, 3H, Mes-CH₃), 1.90 (s, 3H Mes-CH₃), 2.32 (s, 3H, Mes-CH₃), 2.48 (s, 3H, Mes-CH₃), 6.04 (s, 1H, Mes-CH), 6.48 (s, 1H Mes-CH), 6.69 (s, 1H, Mes-CH), 6.88 (s, 1H, Mes-CH), 6.90–7.01 (m, 3H, CH), 7.15 (d, 1H, ${}^{3}J(HH) = 7.0$ Hz, CH), 7.24 (m, 2H, CH), 7.31 (d, 1H, ${}^{3}J(HH) = 7.0$ Hz, CH), 7.38 (d, 1H, ${}^{3}J(HH) = 7.5$ Hz, CH), 7.53 (dd, 1H, ${}^{3}J(HH)$ = 7.0 Hz, ${}^{3}J(HH) = 7.5$ Hz, CH), 7.59 (dd, 1H, ${}^{3}J(HH) = 7.5$ Hz, ${}^{3}J(HH) = 8.0$ Hz, CH), 7.68 (d, 1H, ${}^{3}J(HH) = 7.5$ Hz, CH), 8.03 $(d, 1H, {}^{3}J(HH) = 7.5 \text{ Hz}, CH), 8.07 (d, 1H, {}^{3}J(HH) = 7.0 \text{ Hz},$ CH), 8.17 (d, 1H, ${}^{3}J(HH) = 8.0$ Hz, CH). ${}^{13}C$ NMR (chloroform-d): 21.01, 21.30, 22.21, 22.86, 23.20, 25.40 (6C, Mes-CH₃), 118.2, 119.3, 125.0, 125.8, 126.6, 126.7, 127.9, 128.3, 129.2, 129.7, 130.7, 131.3, 131.4, 132.3, 132.5, 135.4, 136.0, 141.0 (18C, CH), 128.8, 130.8, 133.8, 135.9, 137.7, 140.5, 141.3, 141.4, 142.2 (br), 142.6 (br), 143.9 (br), 145.4 (br), 147.5, 152.8, 153.5 (16C, C-C and B-C). ¹¹B NMR (chloroform-d): 57 (Bfluorenyl), 71 (B-Mes₂).

Synthesis of 1,2-bis(2-trimethylsilanylphenyl)ethane

Trimethylchlorosilane (6.4 mL, 50.0 mmol) was added to a solution of 2,2'-dilithiobibenzyl (20 mmol) in 100 mL of diethyl ether at -78 °C. This reaction mixture was allowed to warm to room temperature and was stirred for 1 h. The reaction mixture was quenched with HCl_{aq} (1 M, 100 mL) and extracted three times with ether (100 mL). The organic phases were combined and dried over anhydrous magnesium sulfate. After filtration, the solvent was removed to yield 1,2-bis(2-trimethyl-silanylphenyl)ethane as a crude yellow oil. Yield: 98%, 6.45 g. This compound was found to be spectroscopically identical to that previously reported.²¹ It was used without further purification.

Synthesis of 5-bromo-10,11-dihydrodibenzo[b,f]borepin

A solution of boron tribromide (4.34 mL, 45.9 mmol) in dichloromethane (10 mL) was added dropwise under nitrogen to a solution of 1,2-bis(2-trimethylsilanylphenyl)ethane (5.00 g, 15.3 mmol) in dichloromethane (40 mL) at -78 °C. This reaction mixture was allowed to warm to room temperature and was stirred for 1 h. The solvent was evaporated and the resulting solid was extracted with diethyl ether (20 mL). This solution was filtered and concentrated. The product, namely 5-bromo-10,11-dihydrodibenz[b,f]borepin, crystallized upon standing at -50 °C. The solvent was removed by filtration and the crystals were washed with cold diethyl ether (2 × 20 mL) and dried under vacuum. Yield: 1.70 g, 41%; mp. 85°C. ¹H NMR (chloroform-*d*): 3.15 (s, 4H, CH₂), 7.20 (d, 2H, ${}^{3}J(H,H) =$ 7.6 Hz, H₂C–C–CH), 7.34 (td, 2H, ${}^{3}J(H,H) =$ 7.6 Hz, ${}^{4}J(H,H) =$ 1.2 Hz, H₂C–C–CH–CH), 7.47 (td, 2H, ${}^{3}J(H,H) =$ 7.6 Hz, ${}^{4}J(H,H) =$ 1.6 Hz, BC–CH–CH), 8.53 (dd, 2H, ${}^{3}J(H,H) =$ 7.6 Hz, ${}^{4}J(H,H) =$ 1.2 Hz, BC–CH). 13 C NMR (chloroform-*d*): 36.96 (2C, CH₂), 125.9, 128.7, 133.7, 140.9 (8C, CH), 150.3 (2C, CH₂–C), 138.4 (br, 2C, B–C). 11 B NMR (chloroform-*d*): 68.6.

Synthesis of diborane 5

solution of 5-bromo-10,11-dihydrodibenzo[b,f]borepin A (0.15 g, 0.54 mmol) in diethyl ether (10 mL) was added to a suspension of freshly isolated 1-Li(THF)₄ (0.30 g, 0.45 mmol) in diethyl ether (10 mL) at 25 °C. The mixture was stirred for 2 h at room temperature and the solution was filtered. The solvent was removed under vacuum and the resulting solid was extracted with dichloromethane (20 mL). Following filtration and evaporation of the solvent, the beige solid was washed with ethanol (2×20 mL) and dried under vacuum. The product was recrystallized from a dichloromethane-hexane mixture. Yield: 89 mg, 35%; mp 327 °C (decomp.). Large monocrystals could be obtained by slow evaporation of a diethyl ether solution. ¹H NMR (chloroform-d): 1.21 (s, 3H, Mes-CH₃), 1.31 (s, 3H, Mes-CH₃), 1.48 (s, 3H, Mes-CH₃), 1.57 (s, 3H, Mes-CH₃), 1.76 (s, 3H, Mes-CH₃), 2.19 (s, 3H, Mes-CH₃), 2.88 (m, 1H, CH(H)), 2.95 (m, 2H, CH₂), 3.44 (m, 1H, CH(H)), 6.14 (s, 1H, Mes-CH), 6.27 (s, 1H, Mes-CH), 6.46 (d, 1H, ${}^{3}J$ (HH) = 6.8 Hz, CH), 6.59 (s, 2H, Mes-CH), 6.73 (td, 1H, ${}^{3}J(HH) = 7.6$ Hz, ${}^{4}J(\text{HH}) = 1.2 \text{ Hz}, \text{CH}), 6.85 (t, 1\text{H}, {}^{3}J(\text{HH}) = 7.6 \text{ Hz}, \text{CH}),$ 6.94 (d, 1H, ${}^{3}J(HH) = 7.2$ Hz, CH), 7.10–7.24 (m, 5H, CH), 7.40 (m, 2H, CH), 7.75 (dd, 1H, ${}^{3}J(HH) = 7.2$ Hz, ${}^{4}J(HH) =$ 1.6 Hz, CH), 7.94 (dd, 1H, ${}^{3}J(HH) = 8.0$ Hz, ${}^{4}J(HH) = 1.6$ Hz, CH), 8.09 (dd, 1H, ${}^{3}J(HH) = 8.0$ Hz, ${}^{4}J(HH) = 1.6$ Hz, CH). ¹³C NMR (chloroform-d): 20.86, 21.03, 22.32, 23.34, 23.64, 24.61 (6C, Mes-CH₃), 36.87, 37.77 (2C, CH₂), 123.6, 124.0, 125.4, 125.6, 127.3, 127.7, 127.8, 128.2, 128.8, 130.2, 130.7, 130.8, 132.1, 134.5, 135.3, 138.9, 144.7, 144.9 (18C, CH), 133.8, 137.7, 139.8, 140.8, 141.1, 141.1, 141.5, 142.9, 152.3, 154.4 (10C, C–C), 137.7, 139.1, 149.1, 149.5, (4C, B–C). Two B–C not observed. ¹¹B NMR (chloroform-*d*): 72.2 (br, 2B).

Electrochemistry

Electrochemical experiments were performed with an electrochemical analyzer from CH Instruments (Model 610A) with a glassy-carbon working electrode and a platinum auxiliary electrode at a scan rate of 100 mV s⁻¹. The reference electrode was built from a silver wire inserted a small glass tube fitted with a porous Vycor frit at the tip and filled with a CH₃CN solution containing (ⁿBu)₄NPF₆ (0.1 M) and AgNO₃ (0.005 M). All three electrodes were immersed in a THF solution (8 mL) containing (ⁿBu)₄NPF₆ (0.1 M) as a support electrolyte and the borane (0.003 M). The electrolyte was dried under vacuum prior to use. In all cases, ferrocene was used as an internal standard, and all reduction potentials are reported with respect to the $E_{1/2}$ of the Fc⁺/Fc redox couple.

Acknowledgements

Support from the Welch Foundation (Grant A-1423), the National Science Foundation (CAREER CHE-0094264) and the Department of Chemistry at Texas A&M University, is gratefully acknowledged. The purchase of the X-ray diffract-ometer was made possible by a grant from the National Science Foundation (CHE-9807975). Finally, we thank the referees for their constructive comments.

References

- 1 H. E. Katz, J. Org. Chem., 1989, 54, 2179-2183.
- 2 K. Nozaki, T. Tsutsumi and H. Takaya, J. Org. Chem., 1995, 60, 6668–6669.
- 3 H. E. Katz, J. Org. Chem., 1985, 50, 5027-5032.
- 4 L. Jia, X. Yang, C. Stern and T. J. Marks, *Organometallics*, 1994, **13**, 3755–3757; M. V. Metz, D. J. Schwartz, C. L. Stern, P. N. Nickias and T. J. Marks, *Angew. Chem., Int. Ed. Engl.*, 2000, **39**, 1312–1316; E. Y.-X Chen and T. J. Marks, *Chem. Rev.*, 2000, **100**, 1391–1434.
- 5 K. Köhler, W. E. Piers, A. P. Jarvis, S. Xin, Y. Feng, A. M. Bravakis, S. Collins, W. Clegg, G. P. A. Yap and T. B. Marder, *Organometallics*, 1998, **17**, 3557–3566; V. C. Williams, W. E. Piers, W. Clegg, M. R. J. Elsegood, S. Collins and T. B. Marder, *J. Am. Chem. Soc.*, 1999, **121**, 3244–3245; V. C. Williams, C. Dai., Z. Li, S. Collins, W. E. Piers, W. Clegg, M. R. J. Elsegood and T. B. Marder, *Angew. Chem., Int. Ed.*, 1999, **38**, 3695–3698; W. E. Piers, G. J. Irvine and V. C. Williams, *Eur. J. Inorg. Chem.*, 2000, 2131–2142; V. C. Williams, G. J. Irvine, W. E. Piers, Z. Li, S. Collins, W. Clegg, M. R. J. Elsegood and T. B. Marder, *Organometallics*, 2000, **19**, 1619–1621.
- 6 M. Reilly and T. Oh, *Tetrahedron Lett.*, 1995, 35, 7209–7212;
 M. Reilly and T. Oh, *Tetrahedron Lett.*, 1995, 36, 221–224.
- 7 B. Schilling, V. Kaiser and D. Kaufmann, *Chem. Ber.*, 1997, **130**, 923–932.
- 8 J. D. Hoefelmeyer, M. Schulte, M. Tschinkl and F. P. Gabbaï, *Coord. Chem. Rev.*, 2002, 235, 93–103.
- 9 F. P. Gabbaï, Angew. Chem., Int. Ed., 2003, 42, 2218-2221.
- 10 J. D. Hoefelmeyer and F. P. Gabbaï, J. Am. Chem. Soc., 2000, 122, 9054–9055.
- 11 A. Hergel, H. Pritzkow and W. Siebert, Angew. Chem., Int. Ed. Engl., 1994, 33, 1247–1248.
- 12 J. D. Hoefelmeyer and F. P. Gabbaï, Organometallics, 2002, 21, 982–985.
- 13 M. Schulte and F. P. Gabbaï, Chem. Eur. J., 2002, 8, 3802-3807.
- 14 A. F. Cunningham, M. Kunz, K. Hisatoshi, (Ciba Specialty Chemicals Corporation, USA) US 5952152, 1999.
- 15 M. K. Rathke and R. J. Kow, J. Am. Chem. Soc., 1972, 94, 6854– 6856; R. J. Kow and M. W. Rathke, J. Am. Chem. Soc., 1973, 95, 2715–2716; J. W. Wilson, J. Organomet. Chem., 1980, 186, 297–300.
- 16 M. M. Olmstead, P. P. Power and K. Weese, J. Am. Chem. Soc., 1987, 109, 2541–2542.
- H. Klusik and A. Berndt, *Angew. Chem.*, 1983, **95**, 895–896;
 C. Wieczorek, J. Allwohn, G. Schmidt-Lukasch, R. Hunold,
 W. Massa and A. Berndt, *Angew. Chem.*, 1990, **102**, 435–436.
- 18 R. A. Bartlett and P. P. Power, Organometallics, 1986, 5, 1916–1917.
- 19 K. S. Cook, W. E. Piers, T. K. Woo, S. J. Rettig and R. McDonald, Organometallics, 2001, 20, 3927–3937.
- 20 C. K. Narula and H. Nöth, J. Organomet. Chem., 1985, **281**, 131–134.
- 21 R. Corriu, G. Lanneau, C. Priou, F. Soulairol, N. Auner, R. Probst, R. Conlin and C. Tan, J. Organomet. Chem., 1994, 466, 55–68.
- 22 (a) J. J. Eisch, J. E. Galle and S. Kozima, J. Am. Chem. Soc., 1986, 108, 379–385; G. E. Herberich, G. Buller, B. Hessner and W. Oschmann, J. Organomet. Chem., 1980, 195, 253–259.
- 23 P. A. Chase, W. E. Piers and B. O. Patrick, J. Am. Chem. Soc., 2000, 122, 12911–12912.
- 24 E. Krause and H. Polack, Ber. Dtsch. Chem. Ges., 1926, 59, 777–785;
 T. L. Chu and T. J. Weissman, J. Am. Chem. Soc., 1956, 78, 23–26;
 J. E. Leffler, G. B. Watts, T. Tanigaki, E. Dolan and D. S. Miller, J. Am. Chem. Soc., 1970, 92, 6825–6830; M. S. Olmstead and P. P. Power, J. Am. Chem. Soc., 1986, 108, 4235–4236; J. J. Eisch, T. Dluzniewski and M. Behrooz, Heteroat. Chem., 1993, 4, 235–241;
 C. J. Harlan, T. Hascall, E. Fujita and J. R. Norton, J. Am. Chem. Soc., 1999, 121, 7274–7275; H. C. Brown and V. H. Dodson, J. Am. Chem. Soc., 1957, 79, 2302–2306; S. I. Weissman and H. van Willigen, J. Am. Chem. Soc., 1965, 87, 2285–2286; C. Elschenbroich, P. Kuhlkamp, A. Behrendt and H. K. Harms, Chem. Ber., 1996, 129, 859–869; R. J. Kwaan, C. J. Harlan and J. R. Norton, Organometallics, 2001, 20, 3818–3820.
- 25 D. Scheschkewitz, H. Amii, H. Gornitzka, W. W. Schoeller, D. Bourissou and G. Bertrand, *Science*, 2002, **295**, 1880–1881.
- 26 P. E. Romero, W. E. Piers, S. A. Decker, D. Chau, T. K. Woo and M. Parvez, *Organometallics*, 2003, **22**, 1266–1274.
- 27 W. J. Grigsby and P. P. Power, J. Am. Chem. Soc., 1996, 118, 7981–7988.
- 28 (a) R. J. Wehmschulte, M. A. Khan, B. Twamley and B. Schiemenz, Organometallics, 2001, 20, 844–849; (b) R. J. Wehmschulte, A. A. Diaz and M. A. Khan, Organometallics, 2003, 22, 83–92.
- 29 S. Warren and P. Wyatt, J. Chem. Soc., Perkin Trans. 1, 1998, 249–255.