Notes

Synthesis of 1,8-Diborylnaphthalenes by the Ring-Opening Reaction of a New Anionic Boron-Bridged Naphthalene Derivative

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Summary: The reaction of 1,8-dilithionaphthalene with dimesitylboron fluoride affords a rare boron-bridged naphthalene derivative which undergoes ring-opening reactions to afford unsymmetrically substituted 1,8-diborylnaphthalene species.

Introduction

Rigid polydentate boranes are used in molecular recognition,[1−3] anion recognition,[4−8] and catalysis.[7−10] The contribution of Katz is especially noteworthy and demonstrates the ability of these compounds to chelate small anions such as hydride, fluoride, and chloride.[4−6] Extending the chemistry of these derivatives to the area of boron-centered radicals, we reported that the reduction of 1,8-bis(diphenylboryl)naphthalene yields a radical anion that features a one-electron σ-bond between the boron atoms.[11] In the context of these studies, we are currently exploring ways to introduce alternative substituents at the boron centers of 1,8-diborylnaphthalene derivatives.[12] 1,8-Diborylnaphthalene derivatives are typically prepared by the metathesis reaction of 1,8-dilithionaphthalene with boron halides[11] or alkoxides,[5] which affords symmetrically substituted products. Earlier investigations by Pritzkow and Siebert have shown that 1,8-bridged naphthalene[13−16] derivatives such as naphtho[1,8-*bc*]boretes[17] undergo ring-opening reactions. It occurred to us that such reactions could be used to generate unsymmetrically substituted 1,8-diborylnaphthalene compounds. In this contribution, we report on the synthesis of an anionic 1,8-boron-bridged naphthalene compound, namely dimesityl(1,8-naphthalenediyl)borate[18] (**1**), which is converted into unsymmetrically substituted 1,8-diborylnaphthalene derivatives by ring-opening reactions.

Results and Discussion

The reaction of 1,8-dilithionaphthalene with 1 equiv of dimesitylboron fluoride leads to the formation of a precipitate that can be recrystallized from THF to form high yields of crystalline dimesityl(1,8-naphthalenediyl)borate (**1**) as a Li(THF)$_4$ salt (Scheme 1). If pyridine is used instead, borate **1** is isolated as a Li(py)$_4$ salt. Both salts have been characterized by ^{1}H and ^{13}C NMR spectroscopy, which reveals the existence of a symmetrically substituted naphthalene ring and a unique mesityl environment. The ^{11}B NMR resonance observed at 2.7 ppm in d_5-pyridine and 2.3 ppm in d_8-THF is consistent with that typically observed for tetraarylborates such as Ph$_4$B$^-$ (δ −6 ppm in d_8-THF). The same reaction carried out in the presence of 2 equiv of dimesitylboron fluoride does not result in the formation of the expected 1,8-bis(borylated) derivative, which reflects the high steric demand of the dimesitylboryl moiety. **1**−Li(THF)$_4$ forms single crystals that undergo rapid THF loss at ambient temperature and shatter when cooled to low temperatures. In contrast, crystals

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(18) 1,1-Dimesityl-1-borata-cyclobuta[*de*]naphthalene.

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Scheme 1

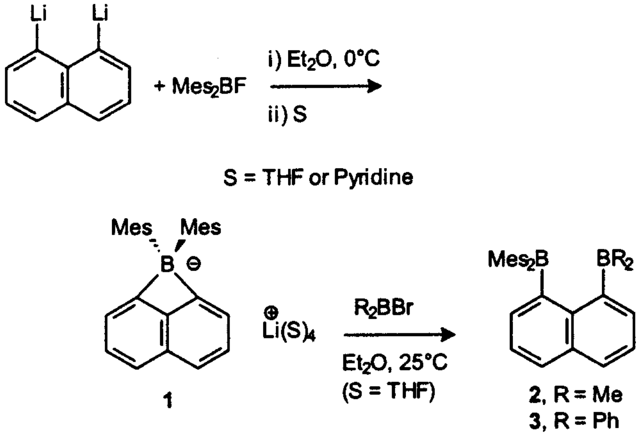

Table 1. Crystallographic Data for 1−3

	1	**2**	**3**
formula	$C_{48}H_{48}BLiN_4$	$C_{30}H_{34}B_2$	$C_{40}H_{38}B_2$
M_r	698.65	416.19	540.32
cryst syst	orthorhombic	monoclinic	monoclinic
space group	$P2_12_12_1$	$P2_1/n$	$P2_1/n$
a (Å)	12.7234(6)	8.2988(13)	9.846(2)
b (Å)	13.4560(6)	19.918(3)	21.250(5)
c (Å)	23.7193(10)	14.876(2)	15.463(3)
β (deg)		98.096(3)	104.576
V (Å^3)	4060.9(3)	2434.5(7)	3131.1(11)
ρ_{calcd} (g cm^{-3})	1.143	1.136	1.146
Z	4	4	4
F(000) (e)	1488	896	1152
μ(Mo Kα) (mm^{-1})	0.066	0.062	0.063
T (K)	110	110	110
2θ range (deg)	3.44−50	3.44−50	3.32−50
scan mode	ω	ω	ω
no. of rflns measd	27 697	12 623	15 925
no. of unique rflns (R_{int})	7145 (0.0473)	4273 (0.0818)	5506 (0.0878)
no. of refined params	487	289	379
R1, wR2 ($I > 2\sigma(I)$)	0.0519, 0.1193	0.0780, 0.2034	0.0589, 0.1152

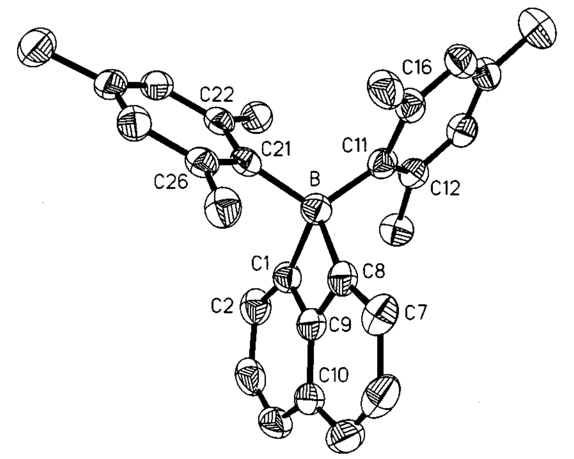

Figure 1. ORTEP view of **1** in the crystal (50% ellipsoids). Selected bond lengths (Å) and angles (deg): B−C(1) = 1.715(4), B−C(8) = 1.696(4), B−C(11) = 1.646(4), B−C(21) = 1.643(4); C(8)−B−C(1) = 80.49(17), C(21)−B−C(11) = 114.4(2), C(9)−C(1)−B = 87.63(19), C(9)−C(8)−B = 88.60(19).

of **1**−Li(py)$_4$ are stable when cooled and were therefore subjected to an X-ray structural analysis (Table 1). The structure of the anionic component of the salt confirms the existence of a strained four-membered boracycle[19] containing a severely distorted tetracoordinated boron center (Figure 1). The acute C(1)−B−C(8) angle (80.5°) and obtuse C(11)−B−C(1) (120.2°) and C(21)−B−C(8) (119.6°) angles are especially noteworthy. Distortions are also apparent in the naphthalenediyl fragment with the C(1)−C(9)−C(8) (103.3°) and C(4)−C(10)−C(5) angles (132.6°) on either side of the ideal value of 120°. While the B−C(ipso-mesityl) bonds (av. 1.645 Å) are comparable to those found in the tetraphenylborate anion,[20] the B−C(peri-naphthalenediyl) bonds (average 1.706 Å) appear slightly lengthened. These B−C bonds are also longer than that observed in the neutral amino-substituted analogue of **1** that contains an sp$_2$-hybridized boron center.[17] Finally, the plane defined by the boron atom and the two peri-naphthalenediyl carbon atoms forms a dihedral angle of 80.7° with the plane containing the boron atom and the two ipso-mesityl carbon atoms.

Compound **1** undergoes ring-opening reactions (Scheme 1). Treatment of **1** with 1 equiv of dimethylboron bromide or diphenylboron bromide in ether leads to the formation of 1-(dimesitylboryl)-8-(dimethylboryl)naphthalene (**2**) and 1-(dimesitylboryl)-8-(diphenylboryl)naphthalene (**3**), respectively. The ^{11}B NMR spectra of **2** and **3** show a single unresolved resonance at 71 ppm ($w_{1/2}$ = 1843 Hz) and 65 ppm ($w_{1/2}$ = 2404 Hz), respectively. The ^{1}H NMR spectrum of **2** and **3** indicates the existence of a rigid structure, since four aryl protons and six distinct methyl groups are observed for the mesityl substituent. The methyl groups attached to the boron center of **2** give rise to two broad resonances which coalesce at 50 °C. Using the Eyring equation, an enthalpy of activation (62(±6) kJ/mol) can be calculated for this fluxional process, which most probably corresponds to the hindered rotation of the dimethylboryl about the B−C(peri-naphthalenediyl) bond. Interestingly, no coalescence or broadening of the mesityl resonances is detected upon heating. This observation indicates that the molecular motion of the dimethylboryl moiety occurs independently. In the case of **3**, elevation of the temperature does not induce any changes in the appearance of the spectrum.

The crystal structures of **2** and **3** have been determined (Table 1). The structure of both compounds presents a number of features characteristic of sterically hindered peri-substituted naphthalene derivatives (Figures 2 and 3).[21] A slight pyramidalization is observed at B(2) (Σ_{angles} = 357.2° in **2** and 357.3° in **3**). The B(1)−C(1)−C(9) (127.5° in **2**, 128.3° in **3**) and B(2)−C(8)−C(9) (129.5° in **2**, 128.5° in **3**) angles substantially deviate from the ideal value of 120°. The core of the naphthalene backbone is slightly twisted, as reflected by the dihedral angle of 3.1° in **2** and 4.7° in **3** formed between the planes defined by C(1)−C(8)−C(9) and C(4)−C(5)−C(10). The resulting intramolecular boron−boron distances are equal to 3.206 Å in **2** and 3.352 Å in **3**, thus slightly exceeding that observed previously in 1,8-bis(diphenylboryl)naphthalene (3.002 Å).[11]

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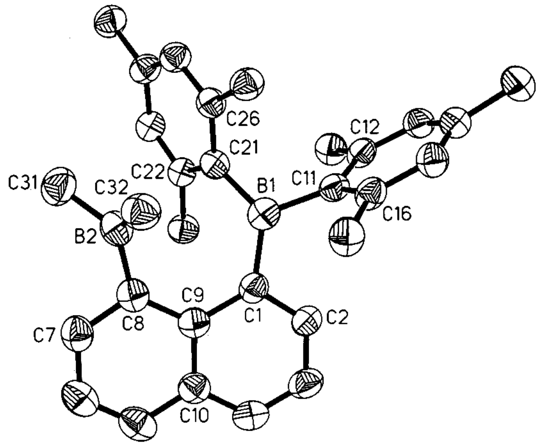

Figure 2. ORTEP view of **2** in the crystal (50% ellipsoids). Selected bond lengths (Å) and angles (deg): B(1)−C(1) = 1.577(6), B(1)−C(11) = 1.595(7), B(1)−C(21) = 1.562(7), B(2)−C(8) = 1.558(7), B(2)−C(31) = 1.591(7), B(2)−C(32) = 1.562(7); C(21)−B(1)−C(1) = 126.0(4), C(21)−B(1)−C(11) = 116.0(4), C(1)−B(1)−C(11) = 117.5(4), C(8)−B(2)−C(32) = 119.5(4), C(8)−B(2)−C(31) = 119.5(4), C(32)−B(2)−C(31) = 118.2(4), C(9)−C(1)−B(1) = 127.5(4), C(9)−C(8)−B(2) = 129.5(4).

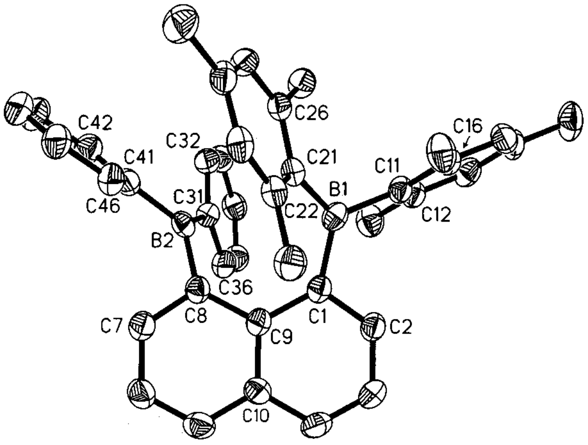

Figure 3. ORTEP view of **3** in the crystal (50% ellipsoids). Selected bond lengths (Å) and angles (deg): B(1)−C(21) = 1.573(4), B(1)−C(1) = 1.577(4), B(1)−C(11) = 1.603(4), B(2)−C(31) = 1.563(4), B(2)−C(41) = 1.575(4), B(2)−C(8) = 1.577(5); C(21)−B(1)−C(1) = 122.0(3), C(21)−B(1)−C(11) = 119.1(3), C(1)−B(1)−C(11) = 118.1(3), C(31)−B(2)−C(41) = 121.3(3), C(31)−B(2)−C(8) = 118.1(3), C(41)−B(2)−C(8) = 117.9(3), C(9)−C(1)−B(1) = 128.3(3), C(9)−C(8)−B(2) = 128.5(3).

Conclusion

In summary, we report the synthesis of an anionic boron-bridged naphthalene derivative that undergoes facile ring-opening reactions to afford unsymmetrically substituted 1,8-diborylnaphthalene derivatives. We note that the ring-opening reactions of **1** should provide access to a variety of heteronuclear bifunctional Lewis acids.

Experimental Section

General Considerations. 1,8-Diiodonaphthalene[22] and diphenylboron bromide[23] were synthesized by following literature procedures. Dimesitylboron fluoride, dimethylboron bromide, and *n*-butyllithium (1.6 M in hexanes) were purchased from Aldrich and used without purification. Solvents were dried by reflux under N_2 over a drying agent and freshly distilled prior to use. THF was dried over Na/K. Ether, chloroform, and acetonitrile were dried over CaH_2. Air-sensitive compounds were handled under an N_2 atmosphere using standard Schlenk and glovebox techniques. Elemental analyses were performed at Atlantic Microlab (Norcross, GA). All melting points were measured on samples in sealed capillaries and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Varian VXR-300 spectrometer at 300 and 75.4 MHz, respectively. ^{11}B NMR spectra were recorded on a Varian Inova 400 broad-band spectrometer at 128.3 MHz. Chemical shifts for ^1H and ^{13}C NMR spectra are reported with respect to Me_4Si standard (δ 0 ppm). Chemical shifts for ^{11}B NMR spectra are reported with respect to $BF_3{\cdot}OEt_2$ standard (δ 0 ppm).

Crystallography. The crystallographic measurements were performed using a Siemens SMART-CCD area detector diffractometer, with graphite-monochromated Mo Kα radiation (λ = 0.710 69 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.

Lithium dimesityl(1,8-naphthalenediyl)borate tetrakis(tetrahydrofuran) (1−Li(THF)$_4$). A 1.6 M hexane solution of *n*-butyllithium (20.0 mL, 32.0 mmol) was added to a solution of 1,8-diiodonaphthalene (5.0 g, 13.1 mmol) in diethyl ether (50 mL) at 0 °C. After 1 h at the same temperature, a solution of dimesitylboron fluoride (3.51 g, 15.7 mmol) in diethyl ether (10 mL) was added through a cannula. The resulting reaction mixture was warmed to room temperature and was stirred overnight. The reaction afforded a tan powdery precipitate that was isolated by filtration and washed with diethyl ether. The resulting solid was further purified by multiple recrystallizations from THF until clear, colorless needles of **1**−Li(THF)$_4$ were obtained. Crystals of **1**−Li(THF)$_4$ become opaque and slowly turn orange when stored at room temperature. Storage at −25 °C is advised. Yield: 3.4 g (39%). Mp: 25 °C dec caused by THF loss. ^1H NMR (pyridine-d_5): δ 2.21 (s, 6H, Mes *p*-CH_3), 2.81 (s, 12H, Mes *o*-CH_3), 6.8 (s, 4H, Mes C*H*), 7.46−7.58 (m, 4H, naph C*H*), 7.82 (d, 2H, naph C*H*). ^{13}C NMR (pyridine-d_5): δ 21.5 (Mes *p*-CH_3), 26.1 (Mes *o*-CH_3), 118.3 (naph *C*3/6), 123.0 (naph *C*4/5), 126.2 (naph *C*9/10), 128.7 (naphth *C*2/7), 129.1 (Mes *C*H), 129.4 (*C*9/10), 130.8 (Mes *p*-*C*), 142.4 (Mes *o*-*C*). Crystals of **1**−Li(THF)$_4$ are very unstable and become brittle through loss of part of the THF component. The results of the elemental analysis suggest partial THF depletion. Anal. Calcd for $C_{44}H_{60}O_4BLi$: C, 78.80; H, 9.02. Found: C, 82.01; H, 7.43.

1-(Dimesitylboryl)-8-(dimethylboryl)naphthalene (2). To a suspension of freshly isolated **1**−Li(THF)$_4$ (500 mg, 0.75 mmol) in diethyl ether (10 mL) at 25 °C was added neat dimethylboron bromide (73 μL, 0.75 mmol). The reaction mixture was stirred at 25 °C for 1 h. The solution was then filtered and the ether removed by evaporation. The crude crystalline solid that remained was recrystallized from pentane, producing large pale yellow crystals. Yield: 250 mg (79%). Mp: 138−143 °C. ^1H NMR (chloroform-*d*): 0.02 (broad s, 3H, B−CH_3), 0.83 (broad s, 3H, B−CH_3), 1.07 (s, 3H, Mes CH_3), 1.60 (s, 3H, Mes CH_3), 1.98 (s, 3H, Mes CH_3), 2.24 (s, 3H, Mes CH_3), 2.31 (s, 3H, Mes CH_3), 2.41 (s, 3H, Mes CH_3), 6.54 (s, 1H, Mes C*H*), 6.71 (s, 1H, Mes C*H*), 6.76 (s, 1H, Mes C*H*), 6.89 (s, 1H, Mes C*H*), 7.33 (d, 1H, naph C*H*), 7.38−7.46 (m, 2H, naph C*H*), 7.82 (m, 2H, naph C*H*), 7.99 (d, 1H, naph C*H*). ^{13}C NMR (chloroform-*d*): 21.36, 22.74, 23.05, 24.52, 24.67,

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26.42 (Mes *C*H$_3$); 125.19, 125.75, 128.43, 128.73, 129.15, 129.53, 129.97, 130.71, 135.20, 139.82 (*C*H); 133.85 (*C*-9 or -10); 138.31, 141.13, 141.31, 141.59, 144.21, 145.51 (*C*−CH$_3$); B−*C*H$_3$, C-*ipso*, and *C*9 or 10 not detected. Anal. Calcd for $C_{30}H_{34}B_2$: C, 86.58; H, 8.23. Found: C, 86.49; H, 8.29.

1-(Dimesitylboryl)-8-(diphenylboryl)naphthalene (3). To a suspension of freshly isolated **1**−Li(THF)$_4$ (4.01 g, 5.97 mmol) in diethyl ether (15 mL) at 25 °C was added neat diphenylboron bromide (1.46 g, 5.97 mmol). The solution was stirred for 12 h at 25 °C, and the solvent was evaporated. The resulting solid was extracted with hot chloroform (10 mL). This solution was filtered, and the chloroform was removed under vacuum to afford **5** as a white powder. Yield: 2.2 g (71%). Mp: 241−244 °C. ^{1}H NMR (chloroform-*d*): 1.10 (s, 3H, Mes C*H*$_3$), 1.22 (s, 3H, Mes C*H*$_3$), 1.58 (s, 3H, Mes C*H*$_3$), 1.75 (s, 3H, Mes C*H*$_3$), 2.08 (s, 3H, Mes C*H*$_3$), 2.26 (s, 3H, Mes C*H*$_3$), 6.31 (s, 1H, Mes C*H*), 6.62 (s, 1H, Mes C*H*), 6.66 (s, 1H, Mes C*H*), 6.69 (s, 1H, Mes C*H*), 7.16−7.31 (m, 9H, naph/phenyl C*H*), 7.34−7.53 (m, 4H, naph/phenyl C*H*), 7.79 (d, 1H, naph C*H*), 8.04 (d, 1H, naph C*H*), 8.13 (d, 1H, naph C*H*). ^{13}C NMR (chloroform-*d*): 21.23, 21.28, 22.38, 22.50, 22.95, 25.62 (Mes *C*H$_3$); 124.3, 126.0, 128.1, 128.3, 129.4, 130.2, 130.5, 131.1, 131.9 135.0 136.5 139.3 (12C, naph/phenyl CH), 126.5, 127.5, 140.0, 140.4 (8C, phenyl *o*-/*m*-*C*H); 134.0, 138.0, 141.6, 141.7, 142.1, 143.9 (*C*-CH$_3$); 141.5, 144.2, 148.3, 149.5 (br, *ipso*-/*peri*-*C*); C9/10 and two *ipso*-C not detected. Anal. Calcd for $C_{40}H_{38}B_2$: C, 88.91; H, 7.09. Found: C, 88.89; H, 7.12.

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Supporting Information Available: Tables of structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for for **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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