

Isolation and Reduction of Sterically Encumbered Arylboron Dihalides: Novel Boranediyl Insertion into C–C σ -Bonds

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Abstract: The synthesis and subsequent reduction of the arylboron dihalides 2,6-Mes₂C₆H₃BX₂ (X = Cl (**1**); Br (**2**)) and 2,6-Trip₂C₆H₃BBR₂ (**3**) (Mes = 2,4,6-Me₃C₆H₂- and Trip = 2,4,6-*i*-Pr₃C₆H₂-) are described. Treatment of **2** with lithium metal in diethyl ether gave the novel lithium 9-borafluorenyl compounds **4** and **5** (see Scheme 1) in which the boranediyl intermediate has inserted into an *o*-Me-ring C–C σ -bond to form a borafluorenyl structure incorporating boron in a delocalized five-membered ring. Boranediyl insertion into C–C σ -bonds, as distinct from boranediyl induced rearrangements involving C=C cleavage in delocalized aromatic substrates, is unknown. The main difference between the structures of these products is that **5** is dimerized as a consequence of the reduction in the number of solvating ethers. Reduction of **2** with KC₈ led to the isolation of the 9-borafluorenyl “ate” compounds **6** and **7**. These products also result from C–C bond insertion by boron as seen in **4** and **5**. However, the delocalization is not observed owing to the addition of hydrogen (presumably from solvent) to the borons affording borate salts. Reduction of **3** with 3 equiv of KC₈ furnishes the new “diborate” species **8**. This compound features a unique B–B bonded dianionic structure with a long (1.83(2) Å) B–B bond which arises from the association of two borate radical anion fragments that have a 9-borafluorenyl structure similar to those described above. Compounds **2–8** were characterized by ¹H, ¹³C, ⁷Li, and ¹¹B NMR spectroscopy and by X-ray crystallography. Crystal data at 130 K with Cu K α (λ = 1.54178 Å) radiation: **1**, C₁₂H_{12.5}B_{0.5}Br, a = 15.562(5) Å, b = 9.156(2) Å, c = 16.368(5) Å, β = 111.23(2)°, Z = 4, space group *C2/c*, R = 0.060 for 1338 ($I > 2\sigma(I)$) data. **3**, C₁₈H_{14.5}B_{0.5}Br, a = 11.001(2) Å, b = 12.194(2) Å, c = 25.473(5) Å, Z = 8, space group *Pbcm*, R = 0.065 for 1876 ($I > 2\sigma(I)$) data. **4**, C₃₂H₄₅-BLi₂O₂, a = 23.611(6) Å, b = 12.812(5) Å, c = 10.194(3) Å, Z = 4, space group *Pbn2₁*, R = 0.085 for 1212 ($I > 2\sigma(I)$) data. **5**, C₄₈H₇₀B₂Li₄O₂, a = 14.398(3) Å, b = 17.739(4) Å, c = 19.885(4) Å, β = 97.64(3)°, Z = 4, space group *P2₁/c*, R = 0.120 for 3125 ($I > 2\sigma(I)$) data. **6**, C₃₂H₄₄BKO₂, a = 9.235(4) Å, b = 22.292(7) Å, c = 14.301(8) Å, β = 100.51(4)°, Z = 4, space group *P2₁/n*, R = 0.074 for 2968 ($I > 2\sigma(I)$) data. **7**•C₆H₆, C₃₃H₃₅BK, a = 10.867(4) Å, b = 12.197(5) Å, c = 12.358(5) Å, α = 108.28(3)°, β = 111.76(3)°, γ = 101.96(3)°, Z = 2, space group *P1*, R = 0.044 for 3291 ($I > 2\sigma(I)$) data. **8**•1.5Et₂O•hexane, C₁₅₂H₂₂₄B₄K₄O_{3.5}, a = 17.686(13) Å, b = 17.659(5) Å, c = 23.568(10) Å, β = 104.41(4)°, Z = 2, space group *Pc*, R = 0.097 for 4672 ($I > 2\sigma(I)$) data.

Introduction

The reduction of organoboron halide compounds of the formula R₂BX or RBX₂ (R = alkyl or aryl substituent, X = halide) to give B–B bonded products of the type R₂BBR₂ or (RBBR)_{*n*} (*n* > 1) has been investigated for many years.^{1,2} With few exceptions, however, high yields of B–B bonded products are rarely found. Usually, it is necessary that the boron halide precursor species have at least one π -electron donor substituent group such as -NR₂, -PR₂, or -OR to stabilize the boron fragment.^{1b} Important exceptions to this generalization concern the reported reduction of PhBCl₂ with alkali metals to form species of the type (BPh)_{*n*} (*n* = 6–9),³ the reduction of *t*-BuBF₂ to give [B(*t*-Bu)]₄⁴ (tetrahedral B₄ skeleton), and the reduction of (Me₃Ge)(Dur)CC{B(Dur)Cl}₂ (Dur = 2,3,5,6-Me₄C₆H-) to give a non-classically bridged methyleneborane.⁵ The presence

of B–B bonds in the reduction products has been verified by X-ray crystallography in the case of the latter two compounds. For the (BPh)_{*n*} (*n* = 6–9) products, however, the formulation is based on spectroscopic and chemical properties as well as analytical data.³ A more common result of the reduction of organo and amido boron halide compounds appears to be the isolation of various rearranged products. Recent examples of such reactions involved the reduction of (Me₃Si)₃CBCl₂ with Na/K alloy to give the C–H bond inserted μ -hydrido-bridged product {(Me₃Si)₂C(Me₂Si)BCH₂(μ -H)}₂⁶ or the reduction of *i*-Pr₂NBCl₂ or *i*-Pr₂NBF₂ in the presence of aromatic molecules such as benzene, naphthalene, or toluene to give a variety of interesting species that result from the addition of an intermediate boranediyl (*i*-Pr)₂NB: fragment to an unsaturated ring system.⁷ It is notable that even in the presence of the *i*-Pr₂N π -donor stabilizing group, B–B bonded species have not been reported, although a product of this general type, i.e. the interesting and unique compound (BNMe₂)₆ (featuring a B₆ ring), was isolated in minor yield from the reduction of ClB-(NMe₂)₂ with Na/K alloy.⁸ In this laboratory attempts to make compounds featuring B–B multiple bonds have concentrated on organoboron compounds with sterically encumbered aryl

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substituents⁹ since it was observed that in certain cases these have greater stability than their alkyl counterparts.¹⁰ Thus one possibility in the reduction of sterically hindered arylboron dihalides (i.e., ArBX₂; Ar = aryl group) was the isolation of products of formula [M]₂⁺[ArBBAr]₂²⁻ (M = alkali metal) whose anions are isoelectronic to the corresponding acetylenes. In this paper it is shown that the reduction of orthosubstituted arylboron dihalides gives products that can be rationalized on the basis of the existence of intermediate boranediyl ArB: species.² These intermediates do not result in the intended [ArBBAr]₂²⁻ products under the conditions described here. Instead, a variety of different products were obtained which resulted from the novel insertion of boranediyl fragments into simple C–C σ -bonds.

Experimental Details

General Procedures. All reactions were performed by using modified Schlenk techniques under an inert atmosphere of N₂ or in a Vacuum Atmospheres HE43-2 drybox. Solvents were freshly distilled under N₂ from Na/K or Na/K/benzophenone ketyl and degassed twice before use. NMR spectra were obtained on a General Electric QE-300 NMR spectrometer and referenced to an internal standard. ¹¹B and ⁷Li NMR spectra were referenced to the external standards BF₃·OEt₂ and LiCl, respectively. IR spectra were obtained by using a Perkin-Elmer 1430 spectrometer. Lithium powder, BCl₃ (1M in heptane), and *n*-BuLi (1.6 M in hexanes) were purchased commercially and used as received. BBr₃ was freshly distilled prior to use. KC₈,¹¹ 2,6-Mes₂C₆H₃Li¹² and 2,6-Trip₂C₆H₃Li·OEt₂¹³ were synthesized by literature procedures.

2,6-Mes₂C₆H₃BCl₂ (1). 2,6-Mes₂C₆H₃Li (2.55 g, 8.0 mmol) was dissolved in hexane (60 mL). BCl₃ (8.0 mmol, 8 mL, 1.0 M solution in heptane) was added and the solution was stirred for 2 h. All the volatile materials were then removed under reduced pressure and the resulting white residue was extracted with toluene (50 mL). The solution was then concentrated to incipient crystallization (ca. 15 mL). Cooling in a –20 °C freezer yielded large colorless crystals of 2,6-Mes₂C₆H₃BCl₂ (**1**) (1.59 g, 4.02 mmol, 62%). Mp 235–236 °C. ¹H NMR (C₆D₆, 60 °C) δ 7.16 (t, *J* = 7.5 Hz, 1H, *p*-H, Ph), 6.90 (d, *J* = 7.5 Hz, 2H, *m*-H, Ph), 6.81 (s, 4H, *m*-H, Mes), 2.14 (s, 12H, CH₃), 2.13 (s, 6H, CH₃). ¹³C NMR (C₆D₆, 60 °C) δ 143.9 (s, ipso-C, Mes), 138.3 (s, *o*-C, Ph), 137.9 (s, *p*-C, Mes), 136.7 (s, *o*-C, Mes), 130.8 (d, *p*-C, Ph), 128.8 (d, *m*-C, Mes), 128.1 (d, *m*-C, Ph), 21.3 (q, *p*-CH₃), 21.0 (q, *p*-CH₃). ¹¹B NMR (C₆D₆, 60 °C) δ 58.5 (s, *w*_{1/2} = 440 Hz).

2,6-Mes₂C₆H₃BBr₂ (2). 2,6-Mes₂C₆H₃Li (1.82 g, 5.7 mmol) was dissolved in hexane (80 mL). BBr₃ (0.75 mL, 8.0 mmol) was added dropwise and the solution was stirred for 2 h. All volatile materials were removed under reduced pressure and the resulting white residue was extracted with toluene (40 mL). The solution was then concentrated to incipient crystallization. Cooling in a –20 °C freezer yielded larger colorless crystals of 2,6-Mes₂C₆H₃BBr₂ (**2**) (2.21 g, 4.56 mmol, 79%). Mp 235 °C. ¹H NMR (C₆D₆) δ 7.17 (t, *J* = 7.5 Hz, 1H, *p*-H),

6.88 (dd, *J* = 1.0, 7.5 Hz, 2H, *m*-H, Ph), 6.80 (s, 4H, *m*-H, Mes), 2.16 (s, 12H, CH₃), 2.12 (s, 6H, CH₃). ¹³C NMR (C₆D₆) δ 142.9 (s, *o*-C, Ph), 142.8 (s, ipso-C, Mes), 138.0 (s, *p*-C, Mes), 136.7 (s, *o*-C, Mes), 130.8 (d, *p*-C, Ph), 128.8 (d, *m*-C, Mes), 128.4 (d, *m*-C, Ph), 21.5 (q, *o*-CH₃), 21.4 (q, *p*-CH₃). ¹¹B NMR (C₆D₆) δ 61.7 (s, *w*_{1/2} = 1060 Hz).

2,6-Trip₂C₆H₃BBr₂ (3). 2,6-Trip₂C₆H₃LiOEt₂ (1.28 g, 2.27 mmol) was dissolved in hexane (50 mL) and BBr₃ (0.50 mL, 5.3 mmol) was added. The solution was stirred for 3 h at ambient temperature and then all the volatile materials were removed under reduced pressure. The remaining white residue was extracted with toluene (50 mL) and the solution was concentrated to incipient crystallization (ca. 10 mL). Slow cooling to ca. –20 °C afforded large colorless crystals of 2,6-Trip₂C₆H₃BBr₂ (**3**) (0.99 g, 1.52 mmol, 67%). Mp 240–241 °C. ¹H NMR (C₆D₆) δ 7.13 (s, 4H, *m*-H, Trip), 7.12 (m, 3H, *o*-, *m*-H, Ph), 2.91 (sept, *J* = 6.9 Hz, 4H, *o*-CHCH₃), 2.78 (sept, *J* = 6.9 Hz, 2H, *p*-CHCH₃), 1.34 (d, *J* = 6.9 Hz, 12H, CHCH₃), 1.18 (d, *J* = 6.6 Hz, 12H, CHCH₃), 1.05 (d, *J* = 6.9 Hz, 12H, CHCH₃). ¹³C NMR (C₆D₆) δ 149.9 (s, *p*-C, Trip), 147.6 (s, *o*-C, Trip), 142.1 (s, ipso-C, Trip), 136.4 (s, *o*-C, Ph), 130.1 (d, *m*-C, Ph), 128.9 (d, *p*-C, Ph), 121.1 (d, *m*-C, Trip), 35.0 (d, *p*-CHCH₃), 31.4 (d, *o*-CHCH₃), 26.7 (q, CHCH₃), 24.4 (q, CHCH₃), 22.7 (q, CHCH₃). ¹¹B NMR (C₆D₆) δ 56.1 (s, *w*_{1/2} = 1060 Hz).

Bis[(diethyl ether)lithium][(4a,4b,8a,9,9a- η)-(1-mesityl-5,7,9-trimethyl-9-borafluorenyl)] (4). **Method A.** 2,6-Mes₂C₆H₃BBr₂ (1.18 g, 2.44 mmol) was added via a solid addition funnel to a suspension of lithium powder (0.13 g, 18.5 mmol) in diethyl ether (40 mL) at –78 °C. The solution immediately became dark green, and then assumed a purple color. After ca. 5 min the solution became a dark red color which persisted. The solution was stirred for a further 3 h at –78 °C then allowed to warm to ambient temperature. The dark red solution was filtered through a fine frit and hexane (10 mL) was added. The solution was then concentrated to incipient crystallization and warmed slightly. Cooling in a –20 °C freezer over several days yielded the product as a single large red crystal (dimensions ca. 12 × 8 × 6 mm) of **4** (0.63 g, 1.29 mmol, 53%). Concentration of the supernatant liquid and cooling yielded additional crystals of **4** (0.25 g). Mp 290 °C dec. ¹H NMR (C₆D₆) δ 8.41 (d, *J* = 8.7 Hz, 1H, H₂), 7.21 (s, 2H, *m*-H, Mes), 7.00 (m, 1H, H₃), 6.79 (d, *J* = 6.0 Hz, 1H, H₄), 6.21 (br, s, 2H, H₆, H₈), 3.04 (s, 3H, Me), 2.65 (m, 11H, Me, OCH₂CH₃), 2.43 (s, 6H, *o*-Me, Mes), 2.38 (s, 3H, *p*-Me, Mes), 0.84 (s, 3H, *B*-Me), 0.64 (t, *J* = 6.9 Hz, 12H, OCH₂CH₃). ¹³C NMR (C₆D₆) δ 144.1 (s, ipso-C, Mes), 143.9 (s), 135.9 (s), 134.9 (s), 125.5 (s, br), 123.4 (d, *m*-C, Mes), 116.3, 115.9 (d), 115.0 (d), 66.1 (t, OCH₂CH₃), 24.6 (q, Me), 22.1 (q, *p*-Me, Mes), 120.9 (s, br), 21.6 (q, *o*-Me, Mes), 21.1 (q, Me), 14.5 (q, OCH₂CH₃). ¹¹B NMR (C₆D₆) δ 14.3 (s, *w*_{1/2} = 380 Hz), ⁷Li NMR (C₆D₆) δ –10.5 (s, *w*_{1/2} = 82 Hz).

Method B. 2,6-Mes₂C₆H₃BCl₂ (0.94 g, 2.38 mmol) was dissolved in diethyl ether (40 mL) and cooled with a dry ice/acetone bath. Lithium metal (0.11 g, 16 mmol) was added via a solid addition funnel and the solution stirred for 1 h. Then the solution was allowed to warm to ambient temperature and stirred for a further 12 h. All volatile materials were removed under reduced pressure and the dark red residue was dissolved in warm hexane/ether (5:1, 50 mL). The solution was quickly filtered through a frit and then concentrated to ca. 15 mL. Slow cooling to –20 °C gave dark red crystals of **4** (0.25 g, 0.51 mmol, 22%).

[Bis{(diethyl ether)lithium(μ -lithium)}][bis{(4a,4b,5,6,7,8,8a,9,9a- η)-(1-mesityl-5,7,9-trimethyl-9-borafluorenyl)] (5). 2,6-Mes₂C₆H₃BBr₂ (1.06 g, 2.19 mmol) was added via solids-addition funnel to a suspension of lithium powder (0.13 g, 18.5 mmol) in benzene (50 mL). After stirring for 4 days at ambient temperature the dark purple solution was filtered through a fine frit and all volatile materials were removed from the filtrate under reduced pressure. The dark purple residue was dissolved in hexane/ether (5:1, 50 mL) and the solution concentrated to ca. 10 mL. Slow cooling to ca. 4 °C yielded dark red plates of **5** (0.16 g, 0.2 mmol, 18%). Mp 120 °C (loses solvent), 295 °C dec. ¹H NMR (C₆D₆) δ 8.34 (d, *J* = 6.6 Hz, 1H, H₂), 7.24 (s, 2H, *m*-H, Mes), 7.01 (m, 1H, H₃), 6.81 (d, *J* = 6.6 Hz, 1H, H₄), 6.04 (s, 2H, H₆, H₈), 2.97 (s, 3H, Me), 2.43 (s, 6H, *o*-Me, Mes), 2.35 (m, 7H, Me, OCH₂-

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Table 1. Selected Crystallographic Data for Compounds 2–8

	2	3	4	5	6	7	8
formula	C ₁₂ H _{12.5} B _{0.5} Br	C ₁₈ H _{14.5} B _{0.5} Br	C ₃₂ H ₄₅ BLi ₂ O ₂	C ₄₈ H ₇₀ B ₂ Li ₄ O ₂	C ₃₂ H ₄₄ BKO ₂	C ₃₃ H ₃₅ BK	C ₁₅₂ H ₂₂₄ B ₄ K ₄ O _{3.5}
<i>M</i>	484.07	652.38	486.38	824.50	510.58	481.52	2306.95
<i>a</i> , Å	15.562(5)	11.001(2)	23.611(6)	14.398(3)	9.235(4)	10.867(4)	17.686(13)
<i>b</i> , Å	9.156(2)	12.194(2)	12.812(5)	17.739(4)	22.292(7)	12.197(5)	17.659(5)
<i>c</i> , Å	16.368(5)	25.473(5)	10.194(3)	19.885(4)	14.301(8)	12.358(5)	23.568(10)
α , deg						108.28(3)	
β , deg	111.23(2)			97.64(3)	100.51(4)	111.76(3)	104.41(4)
γ , deg						101.96(3)	
<i>V</i> , Å ³	2173.9(11)	3417.2(12)	3084(4)	5034(2)	2895(2)	1343.7(9)	7129(6)
<i>Z</i>	4	8	4	4	4	2	2
space group	<i>C2/c</i>	<i>Pbcm</i>	<i>Pbn2₁</i>	<i>P2₁/c</i>	<i>P2₁/n</i>	<i>P$\bar{1}$</i>	<i>Pc</i>
<i>d</i> (calc), g·cm ⁻¹	1.479	1.268	1.048	1.088	1.172	1.190	1.075
μ , mm ⁻¹	4.75	3.15	0.463	0.460	1.790	1.850	1.477
no. of reflns with <i>I</i> > 2 σ (<i>I</i>)	1338	1876	1212	3125	2968	3291	4672
no. of paramtrs refnd	124	185	344	593	333	326	721
<i>R</i>	0.060	0.065	0.085	0.120	0.074	0.044	0.097
<i>R_w</i>	0.160	0.158	0.121	0.254	0.189	0.103	0.215
GoF	1.087	0.972	1.035	1.061	1.046	0.722	1.035

CH₃), 2.24 (s, 3H, *p*-Me, Mes), 0.77 (s, 3H, B-Me), 0.41 (t, *J* = 6.6 Hz, H₆, OCH₂CH₃). ¹³C NMR (C₆D₆) δ 144.1 (s, ipso-C, Mes), 143.5 (s), 135.9 (s), 135.0 (s, *o*-C, Mes), 129.3 (s), 126.2 (s), 123.3 (d, *m*-C, Mes), 122.6 (s), 116.3 (d), 115.6 (d), 112.3 (s), 106.2 (s), 66.1 (t, OCH₂-CH₃), 24.4 (q, Me), 21.9 (q, *p*-Me, Mes), 21.5 (q, *o*-Me, Mes), 21.3 (q, Me), 14.1 (q, OCH₂CH₃). ¹¹B NMR (C₆D₆) δ 14.1 (s, *w*_{1/2} = 510 Hz). ⁷Li NMR (C₆D₆) δ -10.7 (s, *w*_{1/2} = 56 Hz).

[Bis{(tetrahydrofuran)potassium}][bis(1-mesityl-5,7,9-trimethyl-9-hydro-9-borafluorenyl)] (6). 2,6-Mes₂C₆H₃BBr₂ (1.35 g, 2.79 mmol) was dissolved in diethyl ether (40 mL) and cooled in a dry ice acetone bath. KC₈ (1.50 g, 11.1 mmol) was added via solids-addition funnel. After 1 h the solution was allowed to warm to ambient temperature and stirred for an additional 12 h. The dark red solution was rapidly filtered through a fine frit and concentrated until incipient concentration. Addition of THF/hexane (1:1, 10 mL) and slow cooling to ca. -20 °C furnished colorless crystals of **6** (0.47 g, 0.92 mmol, 33%). Mp 314–316 °C. ¹H NMR (*d*₈-THF) δ 7.68 (d, *J* = 7.5 Hz, 1H, H₂), 7.05 (s, 1H, H₆), 6.99 (t, *J* = 7.5 Hz, 1H, H₃), 6.76 (s, 2H, *m*-H, Mes), 6.57 (s, 1H, H₈), 6.53 (d, *J* = 7.5 Hz, 1H, H₄), 3.58 (br, s, 8H, OCH₂CH₂, THF), 2.63 (s, 3H, Me), 2.26 (s, 3H, *o*-Me, Mes), 2.24 (s, 3H, *o*-Me, Mes), 2.01 (s, 3H, *p*-Me, Mes), 1.90 (s, 3H, Me), 1.74 (br, s, 8H, OCH₂CH₂, THF), -0.58 (s, 3H, B-Me). ¹³C NMR (*d*₈-THF) δ 150.8 (s), 145.0 (s), 144.7 (s), 144.1 (s), 137.3 (s), 136.3 (s), 134.3 (s), 132.9 (s), 131.1 (s), 129.3 (d), 128.2 (d), 127.9 (d), 127.7 (d), 124.6 (d), 123.9 (d), 121.7 (d), 68.3 (t, OCH₂CH₂, THF), 26.5 (t, OCH₂CH₂, THF), 23.5 (q, Me), 21.9 (q, Me), 21.8 (q, Me), 21.5 (q, Me), 21.3 (q, Me). ¹¹B NMR (*d*₈-THF) δ -15.4 (d, ²*J*_{B-H} = 73 Hz).

[Bis{(η^6 -benzene)potassium}][bis(1-mesityl-5,7,9-trimethyl-9-hydro-9-borafluorenyl)] (7). 2,6-Mes₂C₆H₃BBr₂ (1.21 g, 2.50 mmol) was dissolved in benzene (50 mL). KC₈ (1.45 g, 10.7 mmol) was added via solids-addition funnel and stirred at ambient temperature for 4 days. The deep red purple solution was filtered and concentrated to ca. 5 mL. Slow cooling to ca. 4 °C gave colorless prisms of **7**·C₆H₆ (0.47 g, 1.0 mmol, 40%). Mp 320–322 °C. ¹H NMR (C₆D₆) δ 8.10 (d, *J* = 7.6 Hz, 1H, H₂), 7.44 (t, *J* = 7.6 Hz, 1H, H₃), 7.15 (m, 8H, ArH), 6.96 (s, 1H, *m*-H, Mes), 6.94 (s, 1H, *m*-H, Mes), 6.68 (s, 1H, H₆), 2.81 (s, 3H, Me), 2.50 (s, 3H, Me), 2.16 (s, 3H, Me), 2.10 (s, 3H, Me), 2.07 (s, 3H, Me), -0.46 (s, 3H, B-Me). ¹¹B NMR (C₆D₆, 60 °C) δ -16.1 (d, ²*J*_{B-H} = 67 Hz).

[μ -{(Diethyl ether)potassium}(μ -potassium)][bis{1-(2,4,6-triisopropylphenyl-5,7-diisopropyl-9-hydro-9-borafluorenyl)}](B-B) (8). 2,6-Trip₂C₆H₃BBr₂ (0.94 g, 1.44 mmol) was dissolved in diethyl ether (50 mL) and cooled in a dry ice/acetone bath. KC₈ (0.65 g, 4.8 mmol) was added via a solid addition funnel and the solution was stirred for 1 h. The solution was then allowed to warm to ambient temperature and stirred for a further 12 h. All volatile materials were removed under reduced pressure and the resulting orange residue was dissolved in diethyl ether/hexane (1:1, 50 mL). After filtering through a fine frit the solution was concentrated to incipient crystallization. Slow cooling to -20 °C yielded fine orange crystals of **8** (0.11 g, 0.10 mmol, 13% based on boron). Mp darkens at 190 °C before melting at 204

°C. ¹H NMR (C₆D₆) δ 8.10 (d, *J* = 7.2 Hz, 1H, H₂), 7.50 (m, 1H, H₃), 7.18 (m, 2H, *m*-H, Trip), 6.91 (s, 1H), 6.40 (s, 1H), 6.36 (s, 1H), 4.03 (m, 1H, CHCH₃), 3.89 (m, 1H, CHCH₃), 3.25 (m, 3H, CHCH₃), 2.65 (m, 2H, OCH₂CH₃), 1.81–0.95 (m, br, 30H, CHCH₃), 0.85 (s, 3H, OCH₂CH₃). ¹¹B NMR (C₆D₆) δ -7.0 (d, ²*J*_{BH} = 80 Hz).

[Bis(diethyl ether)sodium][(4a,4b,8a,9,9a- η)-(1-mesityl-5,7,9-trimethyl-9-borafluorenyl)] (9). 2,6-Mes₂C₆H₃BCl₂ (0.89 g, 2.32 mmol) was dissolved in diethyl ether (20 mL) and sodium metal (0.16 g, 6.95 mmol) was added via a solid addition funnel. The solution was stirred for 5 days during which the solution turned dark green before becoming a persistent dark purple color. All volatile materials were removed under reduced pressure and the resulting black residue was dissolved in diethyl ether/hexane (3:1, 50 mL). After filtering through a fine frit the dark purple solution was concentrated to incipient crystallization. Slow cooling to -20 °C yielded fine purple crystals of **9** (0.40 g, 0.95 mmol, 41%). Mp 209 °C. ¹H NMR (C₆D₆) δ 6.90 (m, br, 7H, ArH), 2.27–1.95 (m, br, 23H, Me, OCH₂CH₃), 0.84 (s, 12H, OCH₂CH₃), 0.66 (s, 3H, B-Me). ¹¹B NMR (C₆D₆) δ -19.6 (d, *w*_{1/2} = 796 Hz). EPR (THF) X band at *g* = 2.0.

X-ray Crystallography. Suitable crystals for data collection were mounted in the cold stream (130 K) of a Syntex P2₁ (2–7) or Siemens P4/RA (8) diffractometer employing Cu K α radiation (λ = 1.54178 Å) operating at 2 kW (Syntex P2₁) or 15 kW (Siemens P4/RA).

The structures of 2–5, 7, and 8 were solved¹⁴ by employing direct and difference Fourier methods. The structure of 6 was solved¹⁴ by using Patterson and difference Fourier methods. Hydrogen atoms were added in calculated positions and refined by using a riding model. Absorption corrections (XABS2¹⁵) were applied to all data. Refinement was by full-matrix least-squares methods based on *F*², with anisotropic thermal parameters for all non-hydrogen atoms except those modeled for disorder.

In the structure of 6 one of the solvating THF groups exhibited disorder. This was adequately modeled by using split occupancies of 55.1(3)% for O(1), C(25)–C(28) and 44.9(3)% for O(1A), C(25A)–C(28A). H1 and the hydrogen atoms bound to C(24) were located in the difference map. H1 was refined freely without constraints while the hydrogens bound to C(24) were refined as riding without constraints.

For the structure of 8 the non-hydrogen atoms of the diethyl ether solvent molecules were refined with fixed positional parameters and fixed occupancy factors of 0.75 respectively after each refined to site occupancy of 0.76. The B–B bond distances and the B–C and C–C bond distances of the five-membered borole rings were constrained employing SADI¹⁶ restraints. The hydrogen atoms on boron (H(1)–

(14) SHELXTL-PLUS, A program for Crystal Structure Determination, Version 5.03, 1994, Siemens Analytical X-ray Instruments: Madison, Wisconsin.

(15) Parkin, S. R.; Moezzi, B.; Hope, H. XABS2: an empirical absorption correction program. *J. Appl. Crystallogr.* **1995**, *28*, 53.

(16) A geometrical restraint which makes chemically, but not crystallographically, equivalent distances equal. SADI is a subroutine of SHELXL-PLUS.

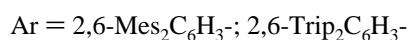
Table 2. Selected Bond lengths (Å) and Angles (deg) for Compounds 2–8

Compound 2							
Br(1)–B(1)	1.902(5)	C(1)–B(1)–Br(1)	121.8(2)	Br(1)–B(1)–Br(1A)	116.3(4)	C(2)–C(1)–B(1)	120.2(3)
B(1)–C(1)	1.565(11)	C(1)–B(1)–Br(1A)	121.8(2)	C(2)–C(1)–C(2A)	119.5(7)	C(1)–C(2)–C(5)	119.4(5)
Compound 3							
Br(1)–B(1)	1.902(7)	C(1)–B(1)–Br(2)	123.1(5)	Br(2)–B(1)–Br(1)	116.3(5)	C(2)–C(1)–B(1)	119.7(3)
Br(2)–B(1)	1.892(7)	C(1)–B(1)–Br(1)	120.5(5)	C(2)–C(1)–C(2A)	120.6(6)	C(1)–C(2)–C(5)	121.1(5)
B(1)–C(1)	1.589(11)						
Compound 4							
Li(1)–O(1)	1.88(2)	B(1)–C(1)	1.538(14)	C(12)–B(1)–C(1)	103.5(9)	C(7)–C(6)–C(5)	131.4(10)
Li(2)–O(2)	1.93(2)	B(1)–C(12)	1.524(14)	C(12)–B(1)–C(21)	126.4(9)	C(7)–C(6)–C(1)	110.9(9)
Li(1)–C(av)	2.21(2)	B(1)–C(21)	1.603(13)	C(1)–B(1)–C(21)	130.1(10)	C(5)–C(6)–C(1)	117.7(9)
Li(2)–C(av)	2.15(2)	C(1)–C(6)	1.478(13)	C(2)–C(1)–C(6)	118.2(9)	C(8)–C(7)–C(6)	131.7(10)
Li(1)–B(1)	2.30(2)	C(6)–C(7)	1.435(13)	C(2)–C(1)–B(1)	134.1(10)	C(6)–C(7)–C(12)	107.5(9)
Li(2)–B(1)	2.18(2)	C(7)–C(12)	1.472(13)	C(6)–C(1)–B(1)	107.7(9)	C(11)–C(12)–B(1)	132.9(10)
Compound 5							
Li(1)–O(1)	1.90(2)	B(1)–C(1)	1.530(12)	C(12)–B(1)–C(1)	102.3(7)	C(7)–C(12)–B(1)	111.3(7)
Li(2)–O(2)	1.87(2)	B(1)–C(12)	1.515(12)	C(12)–B(1)–C(13)	126.4(7)	C(27)–C(26)–C(31)	117.8(7)
Li(1)–C(av)	2.17(2)	B(1)–C(13)	1.608(12)	C(37)–B(2)–C(26)	101.7(7)	C(17)–C(26)–B(2)	132.4(8)
Li(2)–C(av)	2.21(2)	B(2)–C(26)	1.534(12)	C(37)–B(2)–C(49)	126.2(8)	C(31)–C(26)–B(2)	109.8(6)
Li(1)–B(1)	2.30(2)	B(2)–C(37)	1.525(12)	C(2)–C(1)–C(6)	117.1(7)	C(32)–C(31)–C(30)	130.9(8)
Li(2)–B(2)	2.32(2)	B(2)–C(49)	1.579(12)	C(2)–C(1)–B(1)	132.8(8)	C(32)–C(31)–C(26)	109.7(7)
Li(3)–B(1)	2.42(2)	C(1)–C(6)	1.468(11)	C(6)–C(1)–B(1)	110.1(7)	C(31)–C(32)–C(33)	132.4(8)
Li(3)–C(av)	2.24(2)	C(6)–C(7)	1.459(11)	C(5)–C(6)–C(7)	132.0(8)	C(31)–C(32)–C(37)	107.6(7)
Li(3)–C(av)	2.41(2)	C(7)–C(12)	1.474(11)	C(7)–C(6)–C(1)	109.0(7)	C(36)–C(37)–C(32)	116.1(7)
Li(4)–B(1)	2.70(2)	C(26)–C(31)	1.479(11)	C(8)–C(7)–C(6)	132.8(8)	C(36)–C(37)–B(2)	132.7(7)
Li(4)–B(2)	2.27(2)	C(31)–C(32)	1.423(10)	C(6)–C(7)–C(12)	107.2(7)	C(32)–C(37)–B(2)	111.1(7)
Li(4)–C(av)	2.24(2)	C(32)–C(37)	1.484(11)	C(11)–C(12)–B(1)	131.8(8)		
Li(4)–C(av)	2.29(2)						
Compound 6							
K(1)–O(1)	2.714(8)	B(1)–C(21)	1.626(6)	C(24)–B(1)–C(1)	116.6(3)	C(5)–C(6)–C(16)	129.6(4)
K(1)–O(2)	2.711(3)	B(1)–C(24)	1.622(6)	C(24)–B(1)–C(21)	113.2(3)	C(1)–C(6)–C(16)	110.0(3)
K(1)–B(1)	3.419(5)	C(1)–C(6)	1.432(6)	C(1)–B(1)–C(21)	98.3(3)	C(17)–C(16)–C(6)	130.0(4)
K(1)–C(av)	3.28(1)	C(6)–C(16)	1.486(6)	C(2)–C(1)–B(1)	131.2(4)	C(21)–C(16)–C(6)	109.9(3)
B(1)–C(1)	1.624(6)	C(16)–C(21)	1.420(6)	C(6)–C(1)–B(1)	110.5(3)	C(20)–C(21)–B(1)	129.7(4)
						C(16)–C(21)–B(1)	111.1(3)
Compound 7							
K(1)–B(1)	3.365(4)	B(1)–C(15)	1.640(4)	C(1)–B(1)–C(15)	116.7(2)	C(8)–C(7)–C(6)	128.6(2)
K(1)–C(av)	3.256(4)	C(1)–C(6)	1.416(3)	C(2)–C(1)–B(1)	131.1(2)	C(12)–C(7)–C(6)	109.6(2)
K(1)–C(benzene av)	3.303(4)	C(6)–C(7)	1.490(3)	C(6)–C(1)–B(1)	110.7(2)	C(11)–C(12)–B(1)	130.6(2)
B(1)–C(1)	1.622(4)	C(7)–C(12)	1.412(4)	C(5)–C(6)–C(7)	128.8(2)	C(7)–C(12)–B(1)	111.2(2)
B(1)–C(12)	1.623(4)	C(1)–B(1)–C(12)	98.2(2)	C(1)–C(6)–C(7)	110.2(2)		
Compound 8							
K(2)–O(1)	2.70(2)	C(1)–C(6)	1.428(14)	C(34)–B(2)–C(45)	96(2)	C(7)–C(12)–B(1)	111(2)
K(1)–B(1)	3.11(2)	C(6)–C(7)	1.488(14)	C(34)–B(2)–B(1)	119(2)	C(39)–C(34)–B(2)	112(2)
K(1)–B(2)	3.17(2)	C(7)–C(12)	1.439(14)	C(45)–B(2)–B(1)	111(2)	C(35)–C(34)–B(2)	133(2)
K(1)–C(av)	3.10(2)	C(34)–C(35)	1.48(3)	C(2)–C(1)–B(1)	133(2)	C(34)–C(39)–C(40)	111(2)
K(2)–C(av)	3.11(2)	C(34)–C(39)	1.417(14)	C(6)–C(1)–B(1)	110(2)	C(38)–C(39)–C(40)	126(2)
B(1)–B(2)	1.83(2)	C(39)–C(40)	1.489(14)	C(5)–C(6)–C(7)	128(2)	C(41)–C(40)–C(39)	131(2)
B(1)–C(1)	1.62(2)	C(40)–C(45)	1.442(14)	C(1)–C(6)–C(7)	111(2)	C(45)–C(40)–C(39)	106(2)
B(1)–C(12)	1.599(14)	C(12)–B(1)–C(1)	99(2)	C(8)–C(7)–C(6)	130(2)	C(40)–C(45)–B(2)	114(2)
B(2)–C(34)	1.61(2)	C(12)–B(1)–B(2)	108(2)	C(12)–C(7)–C(6)	109(2)	C(44)–C(45)–B(2)	128(2)
B(2)–C(45)	1.618(14)	C(1)–B(1)–B(2)	117(2)	C(11)–C(12)–B(1)	134(2)		

H(4) were located in the difference map and refined as riding, assuming a B–H distance of 1.05 Å.

Results and Discussion

Synthesis of Monoarylborene Dihalide Precursors. The preparation of 2,6-Mes₂C₆H₃BBR₂ (**2**) and 2,6-Trip₂C₆H₃BBR₂ (**3**) (Mes = 2,4,6-Me₃C₆H₂- and Trip = 2,4,6-*i*-Pr₃C₆H₂-) via the reaction of BBr₃ and 1 equiv of the appropriate aryl lithium compound was as shown in eq 1. The reactions proceeded smoothly and the arylboron dibromides were obtained in good yield. The dichloride 2,6-Mes₂C₆H₃BCl₂ (**1**) was obtained similarly by the reaction of 2,6-Mes₂C₆H₃Li with BCl₃.



The X-ray structural determinations of the dibromides **2** and **3** were undertaken and these are illustrated in Figures 1 and 2,

respectively. Molecules of **2** were characterized by a crystallographically required mirror plane that is perpendicular to the boron coordination plane. Both the B–Br (1.902(5) Å) and B–C (1.565(11) Å) distances are similar to those reported¹⁷ in other boron bromide compounds, for example 2,2,5,5-tetramethyl-3,4-bis((dimethylamino)bromoboryl)-3-hexene.^{17a} The angles at B(1), Br–B–C (121.8(2)°) and Br–B–Br (116.3(4)°), deviate from regularity owing to the disparity in the size of the substituents. The structure of **3** also involves a crystallographically required mirror plane. In this case, however, it is coincident with the boron coordination plane. The B–Br and B–C distances and the angles surrounding boron in **3** are similar to those of **2**.

Reduction of Arylborene Dihalides. The products arising from the reduction of **2** and **3** are summarized in Scheme 1.

(17) (a) Siebert, W.; Hildenbrand, M.; Hornbach, P.; Karger, G.; Pritzkow, H. *Z. Naturforsch., Teil B* **1989**, *44*, 1179. (b) Schmid, G.; Alraun, F.; Boese, R. *Chem. Ber.* **1991**, *124*, 2255.

Scheme 1. The Products of the Reduction of 2,6-Mes₂C₆H₃BX₂ (X = Cl or Br) and 2,6-Trip₂C₆H₃BBr₂

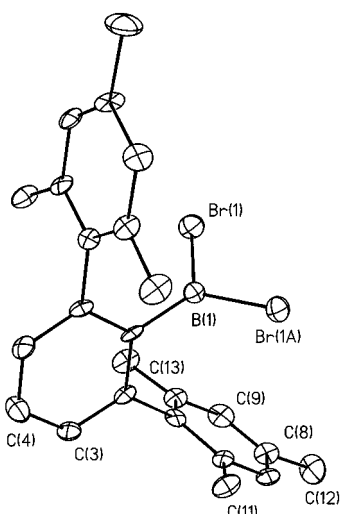
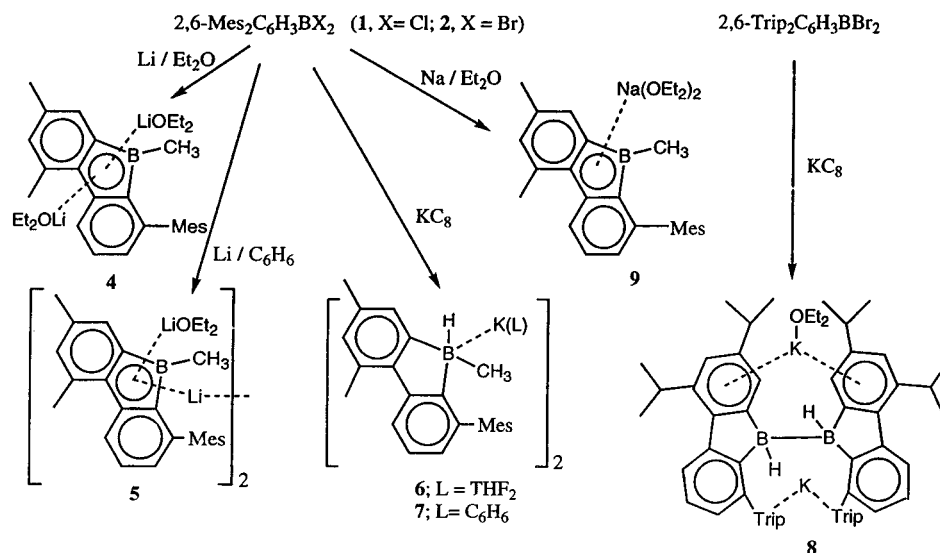


Figure 1. Computer-generated thermal ellipsoid plot (30% probability) of **2**. H atoms are omitted for clarity.

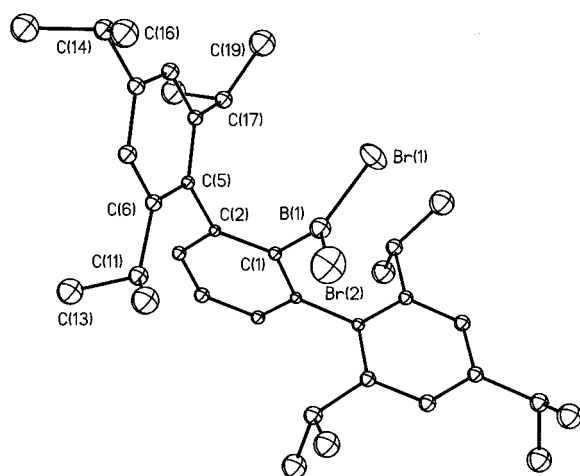


Figure 2. Computer-generated thermal ellipsoid plot (30% probability) of **3**. H atoms are omitted for clarity.

Reduction of the arylboron dibromide **2** with an excess of lithium metal in diethyl ether gave a deep red solution from which the bislithium-9-borafluorenyl complex **4** was isolated in good yield. Compound **4** may also be obtained, although in lower isolated yield, when the dichloride, **1**, is similarly reduced. In spite of the fact that structures of both reduced borole and

benzoborole complexes have been reported,¹⁸ **4** represents the first structurally characterized 9-borafluorenyl dianion. In addition, the reduced 5-membered borole ring of **4** may be viewed as being closely related to the cyclopentadienide anion. The central Li₂C₃B₂ skeleton may also be regarded as a *closo*-carborane structure and is isoelectronic to the recently reported Li₂NC₂B₂ array.^{18f} The geometry of compound **4** is shown in Figure 3. The 9-borafluorenyl ring is planar (maximum deviation from the averaged plane = 0.03(1) Å) and has methyl substituents in the 5-, 7-, and 9-positions and the 1-position is substituted by mesityl. Both lithium ions are solvated by diethyl ether and are also η⁵-coordinated to the five-membered borole ring (B(1), C(1), C(6), C(7), C(12)). The B–C distances (B(1)–C(1) = 1.54(1) Å, B(1)–C(12) = 1.52(1) Å) within this borole ring are similar to those previously reported¹⁸ for reduced borole and benzoborole systems and are indicative of charge delocalization. Both Li–O distances (Li(1)–O(1) 1.88(2) Å and Li(2)–O(2) 1.93(2) Å) are within the range observed for organolithium compounds which involve Li⁺–π-interactions.^{19,20} The short average Li–C bond distances (2.15(2) and 2.21(2) Å) observed for **4** are similar to those reported for other lithium salts of borole dianions.^{18a,b,e} The Li(2)–B(1) distance (2.18(2) Å), however, is considerably shorter than that determined for Li(1)–B(1) (2.30(2) Å) which is similar to that observed in other structures.^{18a,b,e}

Reduction of **2** in benzene with lithium metal over 5 days gave a dark red-purple solution. Extraction with an ether/hexane (1:3) mixture led to the isolation of **5**. Although crystal quality prevented the usual accuracy in the finer details, the structure nevertheless has been unambiguously established as shown in Figure 4. The structure of dimer **5** is analogous to that of **4**; there are, however, two types of lithium ion coordination spheres in the structure. Two of the four lithiums are each solvated by diethyl ether and are η⁵-coordinated to a five-membered borole

(18) (a) Herberich, G. E.; Hostalek, M.; Laven, R.; Boese, R. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 317. (b) Herberich, G. E.; Eigendorf, U.; Englert, U. *Chem. Ber.* **1993**, *126*, 1397. (c) Michel, H.; Steiner, D.; Wocadlo, S.; Allwohn, J.; Stamatis, N.; Massa, W.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 607. (d) Heberich, G. E.; Ohst, H. *Z. Naturforsch., Teil B* **1983**, *38*, 1388. (e) Herberich, G. E.; Wagner, T.; Marx, H.-W. *J. Organomet. Chem.* **1995**, *502*, 67. (f) Paetzold, P.; Redenz-Stormanns, B.; Boese, R. *Chem. Ber.* **1991**, *124*, 2435. For examples of transition metal complexes see: (g) Herberich, G. E. In *Comprehensive Organometallic Chemistry II*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds. Pergamon: Oxford, 1995; Vol. 1, Chapter 5, p 197; (h) Herberich, G. E.; Carstensen, T.; Koffer, D. P. J.; Klaff, N.; Boese, R.; Hyla-Krystin, I.; Gleiter, R.; Stephan, M.; Meth, H.; Zenneck, U. *Organometallics* **1994**, *13*, 619 and references cited therein.

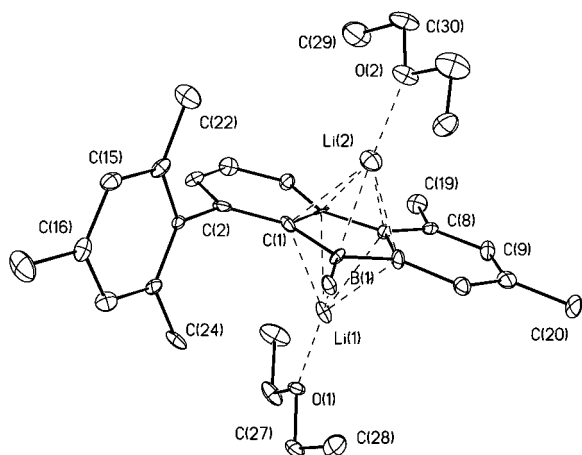


Figure 3. Computer-generated thermal ellipsoid plot (30% probability) of **4**. H atoms are omitted for clarity.

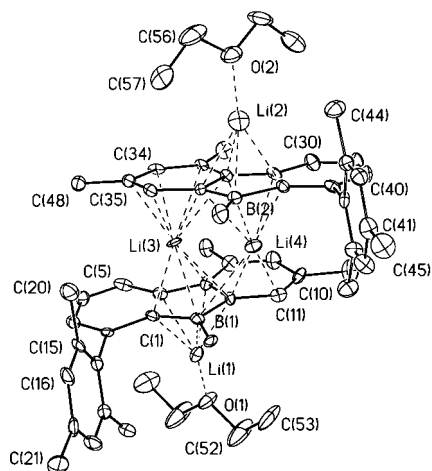


Figure 4. Computer-generated thermal ellipsoid plot (30% probability) of **5**. H atoms are omitted for clarity.

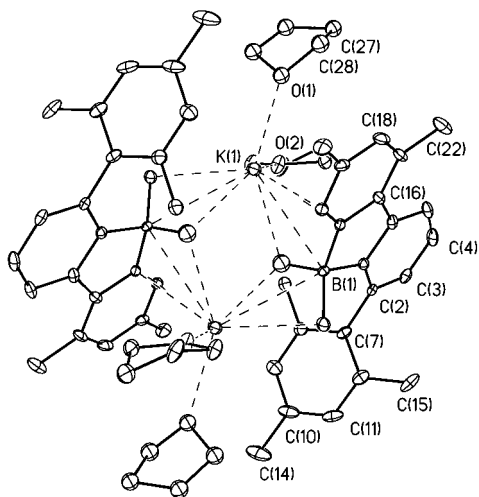


Figure 5. Computer-generated thermal ellipsoid plot (30% probability) of **6**. H atoms (except H(1) and H(1A)) are omitted for clarity.

ring, and the remaining two lithiums are each solvated, with differing η -coordination, by both 9-borafluorenyl rings (Li(3) η^6 , η^5 and Li(4) η^5 , η^3). As in **4**, the 9-borafluorenyl rings of **5** are planar (maximum deviation = 0.09(1) Å) and have similar B–C bond distances within the borole ring. The Li–O distance (1.89(2) Å av) is similar to that observed in **4**. The diethyl ether solvated lithium ions Li(1) and Li(2), as in **4**, have relatively^{19a,b,e} short Li–C distances of 2.17(2) and 2.21(2) Å, respectively. Li(3) and Li(4) have Li–C distances which are

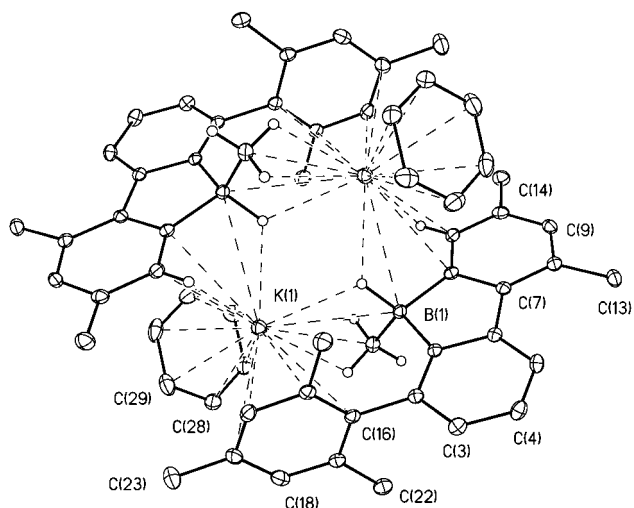


Figure 6. Computer-generated thermal ellipsoid plot (30% probability) of **7**. H atoms (except H(1) and H(15A)–H(15C)) are omitted for clarity.

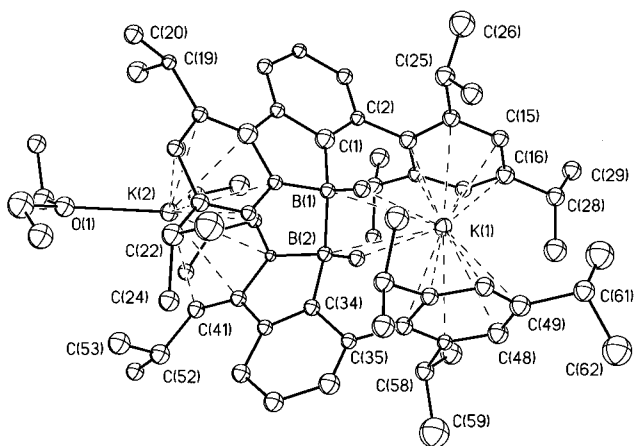


Figure 7. Computer-generated thermal ellipsoid plot (30% probability) of **8**. H atoms (except H(1) and H(2)) are omitted for clarity.

in the range observed for other organolithium compounds.¹⁹ Additionally, the differing hapticity for Li(3) is also reflected in the Li–C distances (Li–C (η^5) = 2.24(2) Å; (η^6) = 2.41(2) Å); however, for Li(4) the difference in Li–C distances is less pronounced (Li–C (η^5) = 2.24(2) Å; (η^3) = 2.29(2) Å).

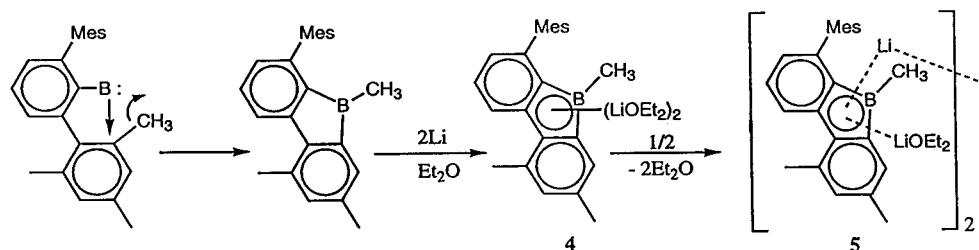
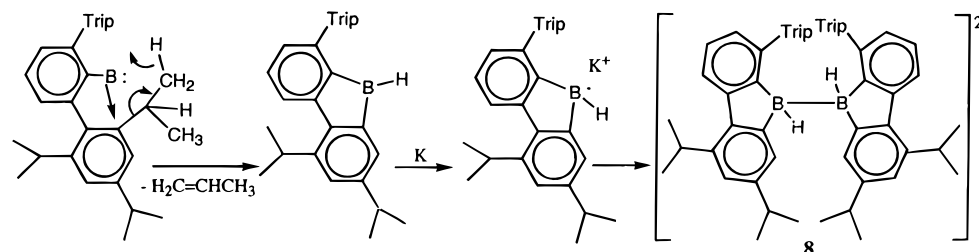
Reduction of the arylboron dibromide **2** with 4 equiv of KC_8^{11} in diethyl ether gave a deep-red solution from which the colorless potassium 9-borafluorenyl salt **6** was isolated in moderate yield. The structure of **6** is shown in Figure 5. It is located on a crystallographic inversion center. Two THF molecules solvate each potassium ion and also interact with the 9-H and 9-Me groups of the 9-borafluorenyl rings. The 9-borafluorenyl ring is planar (maximum deviation from the averaged plane = 0.05(1) Å) and within the borole ring the B–C bond lengths are comparatively longer (1.62(1) Å) than those found for the delocalized complexes **4** and **5** (ca. 1.53 Å). Both the K–O (2.712 Å av) and K–C (3.28(1) Å av) distances observed in **6** are well within the range observed for organopotassium compounds.²¹

When **2** was reduced with excess KC_8^{11} in benzene solution only colorless crystals of the potassium 9-borafluorenyl salt **7** could be isolated from the purple solution. The structure of **7**

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Scheme 2. Stepwise Reduction Sequence To Give **4** and **5****Scheme 3.** Stepwise Route to the Diborate Salt **8**

is shown in Figure 6. As found for the structure of **6**, a half molecule of **7** is in the asymmetric unit which is located on a crystallographic imposed center of inversion. Each potassium ion is η^6 -coordinated by benzene in addition to the solvation by 9-H and 9-Me groups from the 9-borafluorenyl rings. The structure of **7** is similar to that found for **6** and, not unexpectedly, the 9-borafluorene ring of **7** exhibits very similar geometrical features to that observed for **6**. The average K–C distance (3.303(4) Å) is close to those previously reported for a potassium ion solvated by benzene (3.37 Å).²¹

Reduction of the arylboron dibromide 2,6-Trip₂C₆H₃BBr₂, **3**, with 3 equiv of KC₈¹¹ in diethyl ether solution led to the isolation of the novel diborate compound **8** in low yield. Compound **8** crystallized in space group *Pc* and contains two, almost identical, crystallographically independent molecules of **8** per asymmetric unit. The geometry of one of the independent molecules of **8** is shown in Figure 7. It consists of two 9-borafluorenyl motifs which are linked through a B–B bond. Each 9-borafluorenyl ring has a Trip group in the 1-position and isopropyl substituents in the 5- and 7-positions. One of the potassium ions is η^6 -coordinated by both Trip groups while the remaining potassium ion is solvated by both diethyl ether and a 6-membered ring of each 9-borafluorenyl ring. The most notable feature of the structure of **8** is the long B–B distance (1.83(2) Å av). A similarly lengthened B–B distance (1.859(8) Å) has been observed in a dianionic 2,3-diboratabutadiene complex.²² In neutral borane compounds featuring three coordinate borons the B–B bond length is usually near 1.70 Å,^{9,23} and this distance is lengthened (e.g. to 1.767(3) Å) when the coordination number of the borons is increased to four.²⁴ The lengthened B–B distance in **8** is thus the consequence of the Coulombic repulsion of the two adjacent anionic moieties and the increased coordination number of the boron. Also, the 9-borafluorenyl rings deviate from planarity (maximum deviation from the averaged plane = 0.23(1) Å), which contrasts with other structures reported here. This distortion in both 9-borafluorene rings is essentially due to the η^6 -coordination to K(2) of the rings. Although K(2) is solvated by diethyl ether this does not lead to a significant change in the K–C distances. The K–C distance

for both potassium ions is identical (ca. 3.10 Å), which is in the range observed for other organopotassium compounds.^{21,25}

Mechanism. The range of products isolated from the reduction of compounds **1** and **2** may be rationalized by assuming that they have been formed by further reaction of a common boranediyl intermediate ArB: (Ar = 2,6-Mes₂C₆H₃ or 2,6-Trip₂C₆H₃). The intramolecular insertion of this boranediyl fragment into an *o*-Me-ring carbon–carbon bond of the Ar substituent leads to a 9-borafluorene species (Scheme 2). Further reduction of the five-membered borole ring with lithium leads to the isolation of products **4** and **5**. It can be envisaged that the 9-borafluorenyl compounds are similarly formed with potassium. The appearance of the extra hydrogen (presumably from solvent) leads to the isolation of these products as the 9-borafluorene salts **6** and **7**. Boranediyl species may be trapped by employing acetylenes to give borirene compounds.^{2,26} However, the reduction of either **1** or **2** with lithium in the presence of bis(trimethylsilyl)acetylene did not afford any product incorporating a trimethylsilyl moiety.

Formation of compounds **4**–**7** provides unique examples of boron insertion into a carbon–carbon σ -bond. Previous instances of boranediyl ArB: insertions have involved either C–H bonds as in the reduction of (Me₃Si)₃CBCl₂⁶ or interactions with delocalized systems as in the reduction of *i*-Pr₂NBF₂.⁷ In this work described here, the insertion of an ArB: species into a carbon–carbon σ -bond leads to the observed 9-borafluorenyl products rather than rearrangements of π -systems. It is not clear at present why the electrophilic boranediyl fragment does not intramolecularly add to an *o*-methyl C–H bond^{6,28} to give dihydro-9-boraphenanthrene species upon reduction of **1** or **2**.

The mechanism of formation of **8** from **3** is presumed to be analogous to that found for compounds **4** and **5**. However, the reduction to the boranyl fragment, ArB:, and its subsequent reaction leads to **8** and not the expected C–C inserted product. Formation of **8** may be rationalized by either the insertion of

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the borandiyl moiety into the aryl–methine (isopropyl) bond with subsequent loss of propene or by an attack of the *ortho* carbon of a Trip group and subsequent elimination of propene. Dimerization of the resulting radical, formed by one-electron reduction, leads to **8** (Scheme 3).

In contrast to the arylboron dihalide reductions described here, treatment of the analogous ArGaCl₂ (Ar = 2,6-Mes₂C₆H₃-) with sodium has been reported to give the reduced cyclometallopropene analogue [(ArGa)₃]²⁻ which has delocalized character.²⁸ No insertion products were reported for this reaction. It may be tentatively concluded that the high reactivity of the arylboranediyl fragment results in further immediate insertion reactions rather than B–B formation as observed for the gallium species.

Conclusion

The arylboron dihalides **1–3** can be prepared in good yield. Reduction of these compounds with alkali metals leads not to (RB)_n species but a range of 9-borafluorenyl derivatives. The

9-borafluorenyl products arise from an intermediate boranediyl ArB: species which inserts into an *ortho*-methine-ring carbon–carbon σ -bond to give the observed products. Formation of the 9-borafluorenyl compounds can be facilitated in both coordinating and nonpolar solvents and further investigations in this area are in hand.

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Supporting Information Available: Full tables of the data collection parameters, atom coordinates, bond distances and angles, hydrogen coordinates, and anisotropic thermal parameters together with notes on structure solution and refinement (93 pages). See any current masthead page for ordering and Internet access instructions.

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