

# One-Electron Reductions of Organodiborane(4) Compounds: Singly Reduced Anions and Rearrangement Reactions

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**Abstract:** One-electron reductions of the tetraaryldiborane(4) compound Mes<sub>2</sub>-BBMes(Ph) (**1**) (Mes = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) with KC<sub>8</sub> to afford the singly reduced radical anions [K(DME)<sub>3</sub>][Mes<sub>2</sub>BBMes(Ph)] (**2**) and [K([18]crown-6)(THF)<sub>2</sub>][Mes<sub>2</sub>-BBMes(Ph)] (**3**) are described. Both **2** and **3** were characterized by IR and EPR spectroscopy, and X-ray diffraction studies of **3** showed it to be a solvent-separated ion pair. Similarly, reduction of Mes(MeO)-BB(OMe)Mes with lithium in diethyl ether under controlled conditions furnished the radical anion [Li(OEt<sub>2</sub>)<sub>2</sub>][Mes(MeO)BB(OMe)Mes] (**4**), which has a contact-ion-pair structure in which lithium is solvated by oxygen atoms from

ether molecules and methoxy groups. The X-ray crystallographic studies of [K([18]crown-6)(THF)<sub>2</sub>][Mes<sub>2</sub>BBMes(Ph)] (**3**) and [Li(OEt<sub>2</sub>)<sub>2</sub>][Mes(MeO)BB(OMe)-Mes] (**4**) revealed shortened B–B bond lengths in both compounds, consistent with the presence of partial (bond order 0.5) B–B π bonds. Interestingly, the B–B distances in the singly reduced species are very similar to those in the doubly reduced dianions [R<sub>2</sub>BBR<sub>2</sub>]<sup>2-</sup>, which have formal π-bond orders of unity. The syn-

thesis and characterization of 2,6-Mes<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>(MeO)BB(OMe)<sub>2</sub> (**5**) and 2,6-Mes<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>(MeO)BB(OMe)Mes (**6**) are also reported. Reduction of **6** or **5** with lithium in diethyl ether solution did not lead to multiply bonded B–B species, but to the isolation of the rearranged products [(Et<sub>2</sub>O)Li][1-mesityl-5,7-dimethyl-9-hydro-10-{mesityl(methoxy)boryl}-10-boraphenanthrenyl] (**7**) and [(Et<sub>2</sub>O)<sub>2</sub>Li][1-mesityl-5,7-dimethyl-9-methoxy-9'-{methyl(methoxy)boryl}-9-borafluorenyl] (**8**), respectively. Products **7** and **8** are derived from the intramolecular insertion of the boron center into C–H or C–C σ bonds. The crystal structure determinations of **5**, **7**, and **8** are also described.

## Keywords

boron compounds · C–C activation · C–H activation · reductions

## Introduction

Stable organosubstituted derivatives of diborane(4) can undergo one- or two-electron reductions to give the singly reduced radical anions [R<sub>2</sub>BBR<sub>2</sub>]<sup>•-</sup><sup>[1]</sup> or the doubly reduced dianions [R<sub>2</sub>BBR<sub>2</sub>]<sup>2-</sup>.<sup>[2]</sup> The former species possess a partial B–B multiple bond with a formal π-bond order of 0.5, whereas the diborane(4) dianions are analogues of ethylene and possess a formal B–B π-bond order of unity. The structures of two diborane(4) dianions have been published<sup>[2a, b]</sup> and the data show that although the B–B bond is significantly shortened, the shortening is less than expected for a formal B–B double bond. This is probably a consequence of Coulombic repulsion between adjacent negative charges on the boron atoms.<sup>[2, 3]</sup> Nonetheless, theoretical calculations for the related hypothetical species Li<sub>2</sub>B<sub>2</sub>H<sub>4</sub> have indicated the presence of a B–B bond with essentially double-bond nature.<sup>[3]</sup> In contrast, neither structural nor theoretical data for singly reduced diborane(4) compounds are available, even though such species are known in solution.<sup>[1]</sup>

Furthermore the relatively large bond shortenings observed upon one-electron reduction of the corresponding dialuminum(4)<sup>[4]</sup> and digallium(4)<sup>[5]</sup> compounds make the structural data for [R<sub>2</sub>BBR<sub>2</sub>]<sup>•-</sup> species of particular interest. In effect, structural data for monoreduced diborane(4) anions would allow, for the first time, a formal comparison of the B–B bond lengths to be made in neutral, singly, and doubly reduced species. This is not possible in the heavier aluminum and gallium congeners, where the doubly reduced species are, at present, unknown.

In addition to focusing on the nature of the B–B multiple bond, we were anxious to determine the types of products obtainable from rearrangements induced by further reduction of a range of diborane(4) species. This problem is of significant interest since it has been shown that two-electron reductions of dialuminum(4) and digallium(4) compounds lead to decomposition and further reactions with solvent.<sup>[4, 5]</sup>

In this paper recent work on the reductions of various substituted diborane(4) derivatives is summarized. It involves the structural and spectroscopic characterization of two singly reduced tetraaryl diborane(4) species, [K([18]crown-6)(THF)<sub>2</sub>][Mes<sub>2</sub>BBMes(Ph)] (**3**) and [Li(OEt<sub>2</sub>)<sub>2</sub>][Mes(MeO)BB(OMe)-Mes] (**4**). The results of one-electron reductions of the compounds 2,6-Mes<sub>2</sub>C<sub>6</sub>H<sub>3</sub>(MeO)BB(OMe)<sub>2</sub> (**5**) and 2,6-Mes<sub>2</sub>-

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$C_6H_3(MeO)BB(OMe)Mes$  (**6**), which lead to 10-boraphenanthrenyl and 9-borafluorenyl derivatives, respectively, are also reported. The latter compounds are derived from C–H or C–C  $\sigma$ -bond activation of an *ortho* substituent group by intramolecular reaction with the boron centers.

## Experimental Section

All reactions were performed by using modified Schlenk techniques under an  $N_2$  atmosphere or a Vacuum Atmospheres HE43-2 drybox. Solvents were freshly distilled under  $N_2$  from Na/K or Na/K/benzophenone ketyl and degassed twice prior to use. NMR spectra were obtained on a General Electric QE-300 NMR spectrometer and referenced to an internal standard.  $^{11}B$  and  $^7Li$  spectra were referenced to the external standards  $BF_3 \cdot OEt_2$  in  $C_7D_8$  and  $LiCl$  in  $D_2O$ . IR spectra were obtained as Nujol mulls between CsI plates on a Perkin-Elmer 1430 spectrometer. EPR and UV/Vis spectra were obtained by using Bruker E200 and Hitachi U-2000 spectrometers, respectively.  $PhLi$ ,<sup>[6]</sup>  $MesLi$ ,<sup>[7]</sup>  $[2,6-Mes_2C_6H_3Li]_2$ ,<sup>[8]</sup>  $B_2(OMe)_4$ ,<sup>[9]</sup>  $Mes(MeO)BB(OMe)Mes$ ,<sup>[10]</sup>  $Mes_2BB(OMe)Mes$ <sup>[10]</sup> and  $KC_8$ <sup>[11]</sup> were synthesized by literature procedures.

**Mes<sub>2</sub>BBMes(Ph) (1)** was prepared by modification of a literature procedure.<sup>[10]</sup>  $Mes_2BB(OMe)Mes$  (4.23 g, 10.3 mmol) dissolved in pentane (30 mL) was added dropwise to a stirred suspension of  $PhLi$  (16 mmol) in pentane (30 mL) cooled to ca.  $-78^\circ C$ . The solution was allowed to warm to room temperature over 1 h and stirred for a further 12 h. The solution was filtered and the precipitate was washed with pentane ( $2 \times 20$  mL). The washings and filtrate were combined and concentrated to ca. 20 mL. Cooling to  $-20^\circ C$  overnight yielded pale yellow crystals of **1** (3.46 g, 7.6 mmol, 74%).  $^1H$  NMR ( $C_6D_6$ ):  $\delta = 7.62$  [m, 2H, *m*-H (Ph)], 7.09 (m, 3H, *o,p*-H), 6.75 [s, 2H, *m*-H (Mes)], 6.73 [s, 4H, *m*-H (Mes)], 2.22 (s, 12H, Me), 2.15 (s, 3H, Me), 2.11 (s, 6H, Me), 2.05 (s, 6H, Me).  $^{13}C$  { $^1H$ } NMR ( $C_6D_6$ ):  $\delta = 147.9$  (s), 146.2 (s), 144.9 (s), 139.8 (s), 139.5 (s), 139.2 (s), 138.1 (s), 134.9 (d), 130.9 (d), 129.6 (d), 129.0 (d), 128.5 (d), 24.9 (q), 24.1 (q), 21.3 (q).  $^{11}B$  NMR ( $C_6D_6$ ):  $\delta = 90.5$  ( $w_{1/2} = 3200$  Hz).

**[K(DME)<sub>2</sub>][Mes<sub>2</sub>BBMes(Ph)] (2)**:  $Mes_2BBMes(Ph)$  (0.75 g, 1.65 mmol) was dissolved in THF (50 mL) and cooled to ca.  $-78^\circ C$ .  $KC_8$  (0.22 g, 1.65 mmol) was added via a solids-addition funnel, and the solution was stirred for 2 h. The dark blue solution was allowed to warm to room temperature and then rapidly filtered through a frit. 1,2-Dimethoxyethane (0.60 mL, 5.8 mmol) and hexane (10 mL) were then added, and the solution was concentrated to ca. 10 mL. The addition of hexane (5 mL) to the THF solution to form a supernatant layer, and slow cooling to  $-20^\circ C$  yielded fine dark purple powder. Yield 0.35 g (0.40 mmol, 23%). M.p.  $245^\circ C$ . UV/Vis (THF):  $\lambda = 630$  nm. EPR (THF):  $g = 1.9734(21)$  at 298 K. IR:  $\tilde{\nu} = 1600$  (w), 1570 (w), 1260 (s), 1150 (w), 1100 (ms, br), 1020 (s), 845 (vs), 800 (ms), 745 (m), 720 (ms), 700 (m)  $cm^{-1}$ .

**[K([18]crown-6)(THF)<sub>2</sub>][Mes<sub>2</sub>BBMes(Ph)]·THF (3·THF)**:  $Mes_2BBMes(Ph)$  (0.75 g, 1.65 mmol) was dissolved in THF (50 mL) and cooled to  $-78^\circ C$ .  $KC_8$  (0.22 g, 1.65 mmol) was added via a solids-addition funnel and the solution was stirred for 1 h. The dark purple solution was allowed to warm to room temperature and then rapidly filtered through a frit. A solution of [18]crown-6 (0.44 g, 1.65 mmol) in THF (10 mL) was added dropwise to the filtrate, and the solution was then concentrated to ca. 15 mL. Hexane (5 mL) was added to the THF solution to form a supernatant layer and slow cooling in a  $-20^\circ C$  freezer yielded dark purple crystals of **3**, suitable for X-ray crystallography (0.75 g, 0.8 mmol, 47%). M.p.  $81-82^\circ C$ . UV/Vis (THF):  $\lambda = 591$  nm. EPR (THF/toluene; 1/1):  $g = 2.0063(10)$  at 5.2 K. IR:  $\tilde{\nu} = 1600$  (vw), 1570 (w), 1345 (m), 1280 (mw), 1260 (m), 1250 (m), 1100 (vs, br), 1055 (s), 1030 (ms), 955 (s), 900 (w), 840 (mw), 800 (w), 740 (w), 720 (w), 690 (w), 610 (w)  $cm^{-1}$ .

**[Li(OEt)<sub>2</sub>][Mes(MeO)BB(OMe)Mes] (4)**:<sup>[12]</sup>  $MeOMesBB(Mes)OMe$  (0.35 g, 1.1 mmol) in diethyl ether (20 mL) was added dropwise to a suspension of lithium powder (0.09 g, 13.5 mmol) in diethyl ether (10 mL) cooled to  $-78^\circ C$ . The solution was stirred for 1 h and was then allowed to warm to room temperature and stirred for a further 3 h. After filtering through a frit,

hexane (10 mL) was added and the volume of the solution was reduced to ca. 15 mL. Slow cooling in a  $-20^\circ C$  freezer overnight yielded dark blue-black crystals of **4** (0.11 g, 0.2 mmol, 21%). M.p.  $69-69.5^\circ C$ . UV/Vis ( $Et_2O$ ):  $\lambda = 307$  (sh, vs), 589 (br m) nm. EPR ( $Et_2O$ , 5.2 K):  $g = 2.0046(10)$ . IR (nujol):  $\tilde{\nu} = 1610$  (ms), 1410 (s), 1320 (s), 1260 (vs), 1150 (s, sh), 1100 (vs, br), 1015 (vs), 975 (ms), 940 (mw), 875 (m), 850 (ms), 800 (vs), 740 (w), 720 (mw), 690 (mw), 550 (w), 480 (mw, br), 395 (mw, br)  $cm^{-1}$ .

Prolonged stirring of the reaction mixture for longer than ca. 4 h caused the dark purple solution to become black, and then pale orange, with precipitation of a white solid. After stirring for an additional 10 h the solution was then filtered through a frit. Hexane (10 mL) was added and the solution was concentrated to ca. 15 mL. After cooling in a  $-20^\circ C$  freezer over several days no product was isolated. The solution was concentrated to dryness under reduced pressure. The  $^{11}B$  NMR spectrum of the resulting yellow oil indicated the presence of at least two major products.

**2,6-Mes<sub>2</sub>C<sub>6</sub>H<sub>3</sub>(MeO)BB(OMe)<sub>2</sub> (5)**:  $[2,6-Mes_2C_6H_3Li]_2$  (2.17 g, 3.4 mmol) was dissolved in hexane (80 mL) and cooled in a dry ice/acetone bath.  $B_2(OMe)_4$  (0.95 mL, 8 mmol) was added by syringe and the solution was stirred for 1 h and then allowed to warm to room temperature. The solution was stirred for a further 12 h and then warmed to ca.  $40^\circ C$  for 2 h. The solution was filtered through Celite and then concentrated to ca. 25 mL. Cooling to  $-20^\circ C$  for several days yielded colorless crystals of **5** (1.40 g). Further concentration of the supernatant solution yielded additional crystals of **5** (0.33 g). Combined yield: 4.0 mmol (59%). M.p.  $111-112^\circ C$ .  $^1H$  NMR ( $C_6D_6$ ):  $\delta = 7.27$  (t,  $J = 7.5$  Hz, 1H, *p*-H), 6.99 [d,  $J = 7.5$  Hz, 2H, *m*-H (Ph)], 6.87 [s, 4H, *m*-H (Mes)], 3.19 (s, 3H, OMe), 3.04 (s, 6H, OMe), 2.24 (s, 12H, Me), 2.20 (s, 6H, Me).  $^{13}C$  NMR ( $C_6D_6$ ):  $\delta = 143.7$  (s), 139.5 (s), 135.5 (s), 134.8 (s), 128.0 (d), 127.6 (d), 126.8 (d), 57.2 (q, OMe), 49.8 (OMe), 20.5 (q, Me), 20.0 (q, Me).  $^{11}B$  NMR ( $C_6D_6$ ):  $\delta = 56.5$  ( $w_{1/2} = 1030$  Hz), 31.8 ( $w_{1/2} = 572$  Hz).

**2,6-Mes<sub>2</sub>C<sub>6</sub>H<sub>3</sub>(MeO)BB(OMe)Mes (6)**:  $2,6-Mes_2C_6H_3(MeO)BB(OMe)_2$  (1.69 g, 4.0 mmol) was dissolved in toluene (30 mL) and  $MesLi$  (0.59 g, 4.5 mmol) was then added through a solids-addition funnel. The solution was heated to ca.  $80^\circ C$  for 12 h, after which all volatile materials were removed under reduced pressure, and the resulting residue was extracted with toluene (80 mL). Filtration and concentration of the solution to ca. 15 mL yielded colorless crystals of **6** on cooling to  $4^\circ C$ . Yield: 1.03 g (2.0 mmol, 50%). M.p.  $154-155^\circ C$ .  $^1H$  NMR ( $C_6D_6$ ):  $\delta = 7.32$  [t,  $J = 7.5$  Hz, 1H, *p*-H (Ph)], 7.05 [d,  $J = 7.5$  Hz, 2H, *m*-H (Ph)], 6.84 [s, 4H, *m*-H (Mes)], 6.58 [s, 2H, *m*-H (Mes)], 3.21 (s, 3H, OMe), 3.12 (s, 3H, OMe), 2.29 (s, 12H, Me), 2.22 (s, 6H, Me), 2.10 (s, 3H, Me), 1.49 (s, 6H, Me).  $^{13}C$  NMR ( $C_6D_6$ ):  $\delta = 142.9$  (s), 140.3 (s), 137.5 (s), 137.0 (s), 136.2 (s), 129.0 (s), 128.9 (s), 127.6 (d), 127.3 (d), 57.0 (q, OMe), 21.4 (q, Me), 21.3 (q, Me), 20.3 (q, Me).  $^{11}B$  NMR ( $C_6D_6$ ):  $\delta = 54.4$  ( $w_{1/2} = 1200$  Hz). IR:  $\tilde{\nu} = 1605$  (mw), 1345 (w), 1300 (vs), 1205 (w), 1180 (w), 1130 (mw), 1030 (w), 1000 (m), 965 (mw), 850 (m, sh), 815 (m), 795 (m), 750 (m), 720 (w), 665 (w), 570 (w, br), 390 (w, br)  $cm^{-1}$ .

**[(Et<sub>2</sub>O)Li][1-mesityl-5,7-dimethyl-9-hydro-10-{mesityl(methoxy)boryl}-10-borophenanthrenyl] (7)**:  $2,6-Mes_2C_6H_3(MeO)BB(OMe)Mes$  (0.52 g, 1.0 mmol) was added through a solids-addition funnel to a suspension of lithium powder (0.12 g, 17 mmol) in diethyl ether (30 mL) cooled to  $-78^\circ C$ . The solution turned dark purple immediately and was allowed to warm to room temperature over 1 h. After ca. 3 h the solution became dark green with precipitation of a fine white powder. Stirring was continued for a further 12 h, after which time the solution had become pale orange. Hexane (10 mL) was added, and the solution filtered through a frit. Concentration of the solution to ca. 15 mL yielded white crystals of **7** (0.38 g, 0.67 mmol, 67%). M.p.  $132^\circ C$  (desolvation)  $164-166^\circ C$  (melt).  $^1H$  NMR ( $C_6D_6$ ):  $\delta = 7.66$  (dd,  $J = 1.5, 7.8$  Hz, 1H, H3), 7.30 (t,  $J = 7.5$  Hz, 1H, H4), 6.85 (dd,  $J = 0.9, 7.5$  Hz, 1H, H5), 6.73 [s, 1H, *m*-H (Mes)], 6.69 [s, 2H, *m*-H (Mes)], 6.67 (s, 1H, *m*-H (Mes)), 6.60 (s, 1H), 6.41 (s, 1H), (H7, H9), 2.97 (s, 3H, OMe), 2.93 (q,  $J = 6.9$  Hz, 4H,  $OCH_2CH_3$ ), 2.65 (s, 3H, Me), 2.50 (dd,  $J = 0.9, 10.8$  Hz, 2H,  $BCH_2$ ), 2.25 (s, 3H, Me), 2.22 (s, 6H, Me), 2.13 (s, 3H, Me), 2.09 (s, 3H, Me), 2.03 (s, 3H, Me), 1.77 (s, 3H, Me), 0.72 (t,  $J = 6.9$  Hz, 6H,  $OCH_2CH_3$ ).  $^{13}C$  NMR ( $C_6D_6$ ):  $\delta = 149.0$  (s), 144.8 (s), 143.5 (s), 141.4 (s), 139.5 (s), 137.8 (s), 136.9 (s), 136.1 (s), 134.4 (s), 134.2 (s), 132.6 (s), 129.5 (d), 129.2 (d), 129.0 (d), 127.5 (d), 127.3 (d), 126.5 (d), 124.6 (d), 123.1 (d), 65.5 (q,  $OCH_2CH_3$ ), 54.2 (q, OMe), 24.0 (q, Me), 22.3 (q, Me), 21.6 (q, Me), 21.4 (q, Me), 21.35 (q, Me), 21.27 (q, Me), 21.24 (q, Me), 21.0 (q, Me), 14.5 ( $OCH_2CH_3$ ).  $^{11}B$  NMR ( $C_6D_6$ ):  $\delta = 77.8$  ( $w_{1/2} = 1200$  Hz), -22.2.  $^7Li$  NMR ( $C_6D_6$ ):

$\delta = -3.6$ . IR:  $\tilde{\nu} = 2720$  (m), 2130 (s, br), 1905 (w), 1800 (w), 1740 (w), 1710 (w), 1600 (s, sh), 1560 (m), 1300 (m), 1220 (ms), 1180 (s), 1100 (vs, br), 960 (ms), 930 (w), 910 (w), 860 (mw), 855 (s), 840 (s, sh), 800 (s), 785 (m), 775 (ms), 745 (s), 680 (m), 655 (mw), 630 (w), 610 (w), 555 (w), 545 (w), 510 (m), 445 (ms)  $\text{cm}^{-1}$ .

**[(Et<sub>2</sub>O)Li]<sub>2</sub>[1-mesityl-5,7-dimethyl-9-methoxy-9'-{methyl(methoxy)boryl}-9-borafluorenyl] (8)**: 2,6-Mes<sub>2</sub>C<sub>6</sub>H<sub>3</sub>(MeO)BB(OMe)<sub>2</sub> (0.53 g, 1.2 mmol) was dissolved in diethyl ether (50 mL) and cooled with a dry ice/acetone bath. Lithium powder (0.08 g, 12 mmol) was added via a solids-addition funnel and the solution was then warmed to room temperature over a period of 1 h. Stirring was continued for 12 h and then hexane (10 mL) was added. The resulting orange solution was then filtered through a Celite-padded frit. Concentration of the solution to ca. 15 mL and cooling to  $-20^{\circ}\text{C}$  overnight yielded large colorless crystals of **8** (0.19 g, 0.35 mmol, 29%). M.p.  $79-83^{\circ}\text{C}$  (melt with gas evolution). <sup>1</sup>H NMR:  $\delta = 8.15$  (d,  $J = 7.8$  Hz, 1H), 7.38 (t,  $J = 7.2$  Hz, 1H, H3), 6.98 [s, 2H, *m*-H, (Mes)], 6.86 (s, 1H), 6.80 (m, br, 3H), 6.68 (s, 1H), 3.14 (q,  $J = 6.9$  Hz, 8H, OCH<sub>2</sub>CH<sub>3</sub>), 2.83 (br s, 6H, OMe), 2.49 (s, 3H, Me), 2.32 (s, 3H, Me), 2.29 (s, 3H, Me), 2.16 (s, 3H, Me), 2.06 (s, 3H, Me), 0.94 (t,  $J = 6.9$  Hz, 12H, OCH<sub>2</sub>CH<sub>3</sub>), 0.14 (br s, 3H, BMe). <sup>11</sup>B NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = 3.1$  ( $w_{1/2} = 660$  Hz),  $-17.6$ . IR  $\tilde{\nu} = 1610$ (w), 1585 (w), 1560 (w), 1300 (m), 1260 (s), 1195 (m), 1140 (ms, br), 1070 (vs, br), 1030 (vs), 930 (m), 875 (mw), 850 (ms), 800 (m), 760 (mw), 740 (ms), 670 (m), 500 (mw, br), 400 (w)  $\text{cm}^{-1}$ .

**X-ray Crystallography**: Crystals of **5**, **7**, and **8** were coated with hydrocarbon oil at room temperature. Crystals of **3** were removed from the flask, placed in a hydrocarbon oil and immediately cooled to ca.  $-78^{\circ}\text{C}$  (on dry ice) before mounting. Suitable crystals for data collection were selected and then mounted in a cold stream (130 K) of a Syntex P2<sub>1</sub> diffractometer employing graphite monochromated CuK $\alpha$  ( $\lambda = 1.54178$  Å) radiation operating at 2 kW. Selected crystallographic data for **3**, **5**, **7**, and **8** are provided in Table 1.

Table 1. Selected crystallographic data for **3**, **5**, **7**, and **8**.

	<b>3</b>	<b>5</b>	<b>7</b>	<b>8</b>
Formula	C <sub>57</sub> H <sub>86</sub> B <sub>2</sub> KO <sub>9</sub>	C <sub>27</sub> H <sub>34</sub> B <sub>2</sub> O <sub>3</sub>	C <sub>38</sub> H <sub>49</sub> B <sub>2</sub> LiO <sub>2</sub>	C <sub>34</sub> H <sub>51</sub> B <sub>2</sub> LiO <sub>4</sub>
<i>M<sub>r</sub></i>	975.98	428.16	566.33	552.31
<i>a</i> /Å	24.392(5)	37.011(11)	11.972(3)	11.445(3)
<i>b</i> /Å	8.546(2)	8.541(2)	11.192(3)	14.856(4)
<i>c</i> /Å	26.632(4)	16.335(6)	25.497(7)	19.975(5)
$\beta$ /deg	94.249(13)	105.35(2)	97.48(2)	
<i>V</i> /Å <sup>3</sup>	5536(2)	4980(3)	3387(2)	3396(2)
<i>Z</i>	4	8	4	4
space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub>
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.171	1.142	1.111	1.080
$\mu/\text{mm}^{-1}$	1.257	0.553	0.489	0.518
no. refls $I > 2\sigma(I)$	4561	2739	3493	2319
no. parameters refined	602	298	403	383
<i>R</i>	0.088	0.0581	0.074	0.055
<i>R<sub>w</sub></i>	0.146	0.150	0.188	0.142
GOF	1.177	1.029	1.017	1.054

The structure of **3** was solved in space group *P*2<sub>1</sub>/*n* by using direct and difference Fourier methods.<sup>[13]</sup> The initial solution gave a partial structure and the remaining nonhydrogen atoms were located on the difference map of a subsequent refinement. The potassium atoms each occupy a center of symmetry and have a site occupancy of one-half. The structure shows disorder in the packing of the Mes<sub>2</sub>BB(Ph)Mes species. It was found that this species can be arranged in two different orientations, which are related by an approximate 90° rotation around an axis that is perpendicular to the B<sub>2</sub>[*ipso*-C]<sub>4</sub> core. The two packing arrangements have similar molecular dimensions at the periphery and give rise to a crossed arrangement of the two B–B bonds in the center. The disordered Mes<sub>2</sub>BB(Ph)Mes fragments were refined freely in two parts (A and B), which converged during refinement to an occupancy of 50.7 and 49.3%, respectively. As a result, each Mes<sub>2</sub>BB(Ph)Mes fragment was then fixed with a site occupancy of 0.5. In addition, the boron atoms and *ipso*-carbon atoms for each disordered part (A and B) were constrained within 0.02 Å by employing SAME<sup>[14]</sup> restraints so as to give an atom connectivity with similar B–B and B–C bond lengths. Both B–B distances were further

Table 2. Selected bond lengths (Å) and angles (°) for **3**, **4**, **5**, **7**, and **8** [a].

Compound <b>3</b>			
B(1A)–C(1A)	1.588(13)	B(1B)–C(16B)	1.589(13)
B(1A)–C(7A)	1.620(13)	B(1B)–C(1B)	1.622(13)
B(1A)–B(2A)	1.654(11)	B(1B)–B(2B)	1.649(11)
B(2A)–C(25A)	1.60(2)	B(2B)–C(25B)	1.61(2)
B(2A)–C(16A)	1.618(14)	B(2B)–C(7B)	1.62(2)
C(1A)–B(1A)–C(7A)	112.0(8)	C(16B)–B(1B)–C(1B)	113.2(8)
C(1A)–B(1A)–B(2A)	123.4(8)	C(16B)–B(1B)–B(2B)	126.4(9)
C(7A)–B(1A)–B(2A)	124.5(8)	C(1B)–B(1B)–B(2B)	120.2(8)
C(25A)–B(2A)–C(16A)	114.3(8)	C(25B)–B(2B)–C(7B)	114.0(8)
C(25A)–B(2A)–B(1A)	124.0(9)	C(25B)–B(2B)–B(1B)	123.4(9)
C(16A)–B(2A)–B(1A)	121.7(9)	C(7B)–B(2B)–B(1B)	122.6(9)
Compound <b>4</b>			
Li(1)–O(1)	1.905(5)	B(1)–B(1) #1	1.636(7)
Li(1)–O(2)	1.968(5)	O(1)–C(10)	1.430(4)
Li(1)–B(1)	2.734(8)	O(2)–C(12)	1.437(5)
B(1)–O(1)	1.454(4)	O(2)–C(13)	1.455(5)
B(1)–C(1)	1.589(5)	C(1)–C(2)	1.413(4)
O(1)–B(1)–C(1)	117.5(3)	C(12)–O(2)–C(13)	111.9(3)
O(1)–B(1)–B(1) #1	114.0(2)	C(2)–C(1)–B(1)	120.7(3)
C(1)–B(1)–B(1) #1	128.4(2)	C(6)–C(1)–B(1)	122.1(3)
C(10)–O(1)–B(1)	122.8(2)		
Compound <b>5</b>			
B(1)–O(1)	1.359(4)	B(2)–O(2)	1.364(4)
B(1)–C(1)	1.599(4)	O(1)–C(25)	1.426(4)
B(1)–B(2)	1.718(5)	O(2)–C(26)	1.426(4)
B(2)–O(3)	1.364(4)	O(3)–C(27)	1.434(4)
O(1)–B(1)–C(1)	112.8(3)	B(1)–O(1)–C(25)	121.6(3)
O(1)–B(1)–B(2)	123.1(3)	B(2)–O(2)–C(26)	122.0(2)
C(1)–B(1)–B(2)	124.0(2)	B(2)–O(3)–C(27)	120.0(2)
O(3)–B(2)–O(2)	116.0(3)	C(6)–C(1)–C(2)	117.6(2)
O(3)–B(2)–B(1)	117.9(3)	C(6)–C(1)–B(1)	121.5(2)
O(2)–B(2)–B(1)	126.1(3)	C(2)–C(1)–B(1)	120.9(2)
Compound <b>7</b>			
Li(1)–O(1)	1.929(6)	B(2)–O(1)	1.406(5)
Li(1)–O(2)	1.931(7)	B(2)–C(25)	1.589(5)
Li(1)–C(16)	2.544(7)	O(1)–C(34)	1.427(4)
Li(1)–C(17)	2.607(7)	C(1)–C(2)	1.419(5)
Li(1)–C(21)	2.785(7)	C(1)–C(6)	1.425(5)
B(1)–C(1)	1.623(5)	C(6)–C(7)	1.508(5)
B(1)–C(13)	1.641(5)	C(7)–C(12)	1.399(5)
B(1)–B(2)	1.727(6)	C(12)–C(13)	1.493(5)
C(1)–B(1)–C(13)	104.4(3)	O(1)–B(2)–B(1)	115.6(3)
C(1)–B(1)–B(2)	113.9(3)	C(25)–B(2)–B(1)	127.3(3)
C(13)–B(1)–B(2)	113.9(3)	B(2)–O(1)–C(34)	122.7(3)
O(1)–B(2)–C(25)	117.0(3)	C(2)–C(1)–C(6)	116.1(3)
C(2)–C(1)–B(1)	124.5(3)	C(8)–C(7)–C(6)	122.2(3)
C(6)–C(1)–B(1)	119.1(3)	C(7)–C(12)–C(13)	119.4(3)
C(1)–C(6)–C(7)	117.5(3)	C(12)–C(13)–B(1)	108.6(3)
C(12)–C(7)–C(6)	117.7(3)	C(17)–C(16)–C(21)	119.3(3)
Compound <b>8</b>			
O(1)–C(24)	1.408(5)	O(4)–C(33)	1.450(6)
O(1)–B(1)	1.517(6)	O(4)–Li(1)	2.005(8)
O(1)–Li(1)	1.883(8)	B(1)–C(12)	1.627(6)
O(2)–B(2)	1.383(6)	B(1)–C(1)	1.634(7)
O(2)–C(25)	1.450(5)	B(1)–B(2)	1.720(7)
O(2)–Li(1)	1.961(8)	B(2)–C(26)	1.588(7)
O(3)–C(29)	1.441(6)	C(1)–C(6)	1.415(6)
O(3)–C(28)	1.445(6)	C(6)–C(7)	1.477(7)
O(3)–Li(1)	1.962(8)	C(7)–C(12)	1.412(6)
O(4)–C(32)	1.430(6)		
C(24)–O(1)–B(1)	115.5(3)	O(2)–B(2)–B(1)	115.9(4)
B(2)–O(2)–C(25)	123.5(4)	C(26)–B(2)–B(1)	125.2(4)
O(1)–B(1)–C(12)	114.6(4)	C(2)–C(1)–C(6)	118.3(4)
O(1)–B(1)–C(1)	119.0(4)	C(2)–C(1)–B(1)	132.6(4)
C(12)–B(1)–C(1)	98.4(3)	C(6)–C(1)–B(1)	109.1(4)
O(1)–B(1)–B(2)	107.8(4)	C(1)–C(6)–C(7)	111.2(4)
C(12)–B(1)–B(2)	103.8(4)	C(8)–C(7)–C(12)	119.8(4)
C(1)–B(1)–B(2)	112.2(4)	C(8)–C(7)–C(6)	130.4(4)
O(2)–B(2)–C(26)	118.6(4)	C(12)–C(7)–C(6)	109.9(4)

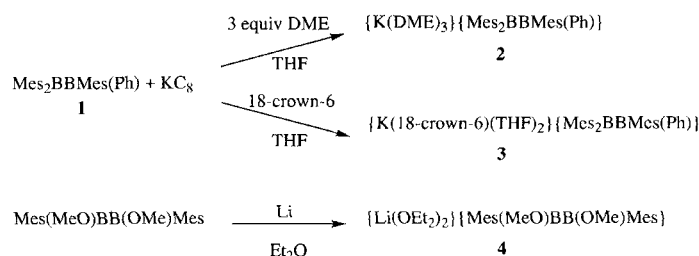
[a] Symmetry transformations used to generate equivalent atoms: #1  $-x + 1/2, y, -z$ .

constrained with a SADI<sup>[14]</sup> restraint. The geometry of the three THF molecules was also constrained with SADI restraints. Hydrogen atoms were added in calculated positions and refined with a riding model. An absorption correction (XABS2) was applied.<sup>[15]</sup> Refinement was performed by full-matrix least-squares methods, based on  $F^2$ , with anisotropic thermal parameters for the nonhydrogen atoms of the cationic K([18]crown-6) species and the THF molecules. The final difference map showed the greatest peak ( $0.40 \text{ e} \text{ \AA}^{-3}$ ) adjacent to the THF solvent molecule. Selected bond lengths and angles for **3**, **5**, **7**, and **8** are given in Table 2.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1220-48. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: Int. code +(1223)336-033; e-mail: teched@chemcrs.cam.ac.uk).

## Results and Discussion

**Diborane(4) Monoanion Derivatives:** The one-electron reduction of the tetraaryldiborane(4) compounds, Mes<sub>2</sub>BBMes(Ph) (**1**) or Mes(MeO)BB(OMe)Mes in ether solution, to give the radical anion salts **2**, **3**, or **4**, is summarized in Scheme 1. The potassi-



Scheme 1. Reduction of **1** and Mes(MeO)BB(OMe)Mes to the radical anions **2**, **3**, and **4**.

um-graphite intercalate KC<sub>8</sub> ( $M_r = 136.06$ ) was employed to facilitate the accurate weighing of a stoichiometric quantity of reductant for the one-electron reductions to give **2** or **3**. The singly reduced species [Mes<sub>2</sub>BBMes(Ph)]<sup>•−</sup> was crystallized as [K([18]crown-6)(THF)<sub>2</sub>][Mes<sub>2</sub>BBMes(Ph)]·THF (**3**·THF), or isolated as the solid [K(DME)<sub>3</sub>][Mes<sub>2</sub>BBMes(Ph)] (**2**), in moderate yield.

The EPR spectra of **2** or **3** in THF solution are identical, and confirm the presence of the radical anion (Figure 1). Hyperfine coupling gives rise to a seven-line spectrum [ $a(^{11}\text{B}) = 13 \text{ G}$ ], which is attributable to equivalent coupling to two <sup>11</sup>B ( $I = 3/2$ )

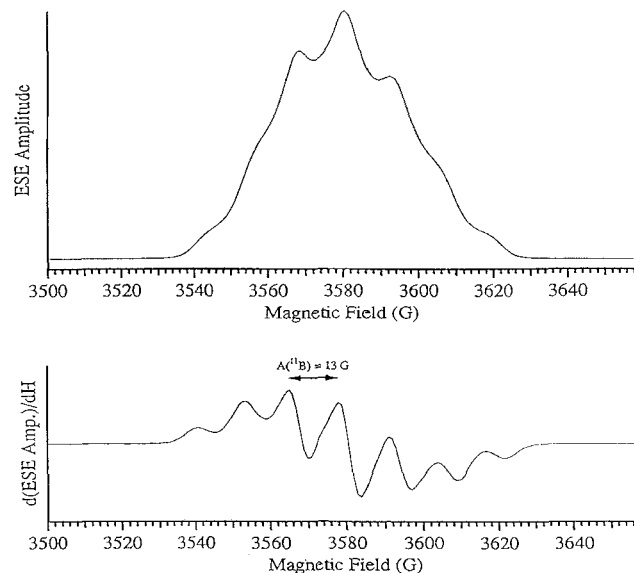


Figure 1. Plot of the absorption (top) and first-derivative (bottom) EPR spectrum of **3** in THF solution at 25 °C.

nuclei. Coupling to the two other possible isotopomers was not discernible. The magnitude of the hyperfine coupling constant, 13 G, is consistent with the presence of the unpaired electron in a  $\pi$ -orbital and is similar to those previously reported for diborane(4) radicals in solution.<sup>[11]</sup> The EPR spectrum of a solution of **4** did not display hyperfine coupling in the broad, first-derivative signal with a  $g$  value near 2.00.

The crystal structure determination of **3** enables the first comparison of the structural features of neutral, singly, and doubly reduced organodiborane(4) species that have the same substituents on boron, in compounds **1**,<sup>[10]</sup> **3**, and [Li(OEt<sub>2</sub>)<sub>2</sub>][Mes<sub>2</sub>BBMes(Ph)]<sup>[2a]</sup> (**9**). For comparison, key bond lengths and angles for these species, as well as for Mes(MeO)BB(OMe)Mes,<sup>[10]</sup> [Li(OEt<sub>2</sub>)<sub>2</sub>][Mes(MeO)BB(OMe)Mes] (**4**),<sup>[12]</sup> and the doubly reduced species [Li(OEt<sub>2</sub>)<sub>2</sub>][Ph(Me<sub>2</sub>N)BB(NMe<sub>2</sub>)Ph]<sup>[2b]</sup> (**10**) are given in Table 3. The structure of **3** was marred by a disorder in the packing of the [Mes<sub>2</sub>BBMes(Ph)]<sup>•−</sup> anion. Nevertheless, a satisfactory solution was achieved, and the structure refined to a residual value of 0.088. The geometry of **3** is shown in Figure 2. The potassium cation is solvated by [18]crown-6 and two THF molecules. The K–O distances observed in **3** are similar [2.793(5) Å avg.]

Table 3. Selected bond lengths (Å) and angles (°) for neutral, anionic, and dianionic diborane derivatives.

	<b>1</b>	<b>3</b>	Ph(Me <sub>2</sub> N)BB(NMe <sub>2</sub> )Ph	Mes(MeO)BB(OMe)Mes <b>4</b>	<b>9</b>	<b>10</b>
B–B	1.706(12)	1.649(11)	1.714(4)	1.724(9)	1.636(7)	1.636(11)
B–C	1.576(12) avg.	1.61(2) avg.	1.585(3)	1.572(9) avg.	1.589(5)	1.637(11) avg.
B–O				1.363(10) avg.	1.454(4)	
B–N			1.408(3)			1.561(5) avg.
Li–B				2.734(8)	2.35(2)	2.26(8) avg.
C–B–C	117.5(7) avg.	113.6(8) avg.			109.2(6) avg.	
C–B–R			119.9(2)	122.5(5) avg.	117.5(3)	114.6(3)
C–B–B	114.5(6) avg.	121.4(9) avg.	118.8(2)	122.5(5) avg.	128.4(2)	123.4(6) avg.
	128.0(6) avg.	124.9(9) avg.				127.3(6) avg.
R–B–B			121.2(2)	115.1(5) avg.	114.0(2)	119.4(3)
B planes [a]	79.1	6.9	88.7	74.9	2.5	7.3

[a] Angle between B planes.

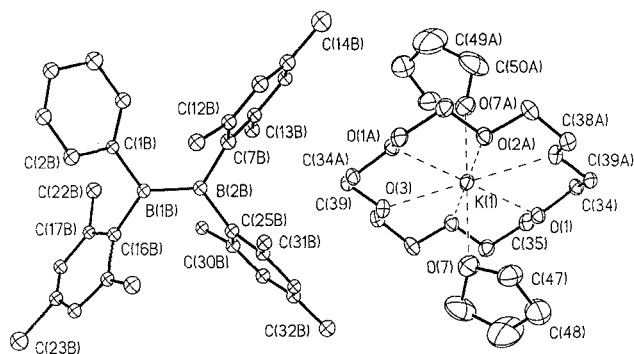


Figure 2. One of the molecules in the asymmetric unit of **3** (thermal ellipsoids at the 30% probability level). The H atoms and the disordering are not shown.

to those reported for other crown ether–potassium compounds.<sup>[16]</sup> As outlined in the experimental section, the  $[\text{Mes}_2\text{BBMes}(\text{Ph})]^-$  anion resides in two orientations. Apparently, the two packing arrangements have similar molecular dimensions at the periphery of the molecule, and give rise to a crossed arrangement of the B–B bonds in the center. The geometry of both these  $\text{Mes}_2\text{BBMes}(\text{Ph})$  species is very similar and, for the purposes of discussion, only one will be considered since the two B–B distances are within one standard deviation of each other. The  $[\text{Mes}_2\text{BBMes}(\text{Ph})]^-$  anion features a B–B bond length [1.649(11) Å] that is shorter than the 1.706(12) Å found for the neutral precursor **1**.<sup>[14]</sup> The torsion angle between the boron coordination planes in **3** is 6.9°, which can be compared with the 79.1° in **1**.<sup>[2a]</sup> There is also a 3–6° narrowing of the C–B–C angles [for B(1B) = 113.2(8)° and for B(2B) = 114.0(8)°] in comparison to those in the neutral precursor. The geometrical features of **3**, including the lengthening of the B–C distances (by ca. 0.02 Å), are thus consistent with the formation of a one-electron B–B  $\pi$  bond.

In a manner similar to **3** the radical anion lithium salt  $[\text{Li}(\text{OEt})_2][\text{Mes}(\text{MeO})\text{BB}(\text{OMe})\text{Mes}]$  (**4**) can be isolated when  $\text{Mes}(\text{MeO})\text{BB}(\text{OMe})\text{Mes}$  is reduced with an excess of lithium powder in diethyl ether under carefully controlled conditions. The structure of **4**, which has already been reported in a preliminary communication,<sup>[12]</sup> is shown in Figure 3. The molecules possess a crystallographically required twofold rotation axis of symmetry defined by a vector between the  $\text{Li}^+$  ion and the mid-point of the B–B bond. Key structural data for **4** and the

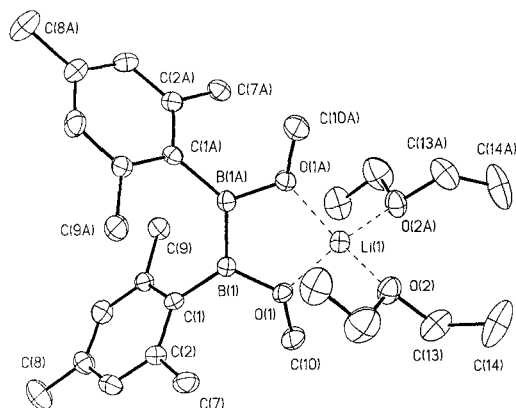


Figure 3. Structure of **4** (thermal ellipsoids at the 30% probability level; H atoms not shown).

neutral precursor  $\text{Mes}(\text{MeO})\text{BB}(\text{OMe})\text{Mes}$  are provided for comparison in Table 3. The one-electron reduction resulted in a closure of the torsion angle between the B planes from 74.9 to 2.5°, and a ca. 0.09 Å shortening of the B–B bond, consistent with  $\pi$ -bond formation. As found for the radical anion **3**, the  $\text{B}_2(\text{C-}i\text{prso})_2\text{O}_2$  core atoms are essentially coplanar [max. deviation from the averaged plane 0.031(1) Å]. The structure of **4** also features a smaller O–B–C angle and a longer B–O distance than those reported for the neutral precursor.<sup>[10]</sup> The lithium ion is four-coordinate and is solvated by two diethyl ether molecules and the oxygen atoms of the methoxy groups. The Li–O distances are similar to those observed in other organolithium solvates.<sup>[16]</sup>

Clearly, the shortened B–B bond lengths observed in the structures of the radical anions **3** and **4** indicate formation of a partial B–B  $\pi$  bond. The B–B bond lengths in both compounds are within two standard deviations of each other, but they are very similar to the B–B bond lengths in the two known doubly reduced species.<sup>[2]</sup> In effect, the B–B bond length scarcely changes upon the addition of a second electron, in spite of the fact that the  $\pi$ -bond order formally increases from 0.5 to 1.0. The absence of any appreciable change in B–B bond length upon the second reduction can be attributed to an approximate balance between the opposing effects of increased electrostatic repulsion between the two negative charges of the dianion, which lengthens the bond, and the increased  $\pi$ -bond order, which shortens it. Negative charges on adjacent boron atoms or an increased coordination number have been found to lengthen B–B single bonds, for example, in  $\text{Li}_2[(\text{Me}_3\text{Si})_2\text{C}(\text{Mes})\text{BB}(\text{Mes})\text{C}(\text{SiMe}_3)_2]$ <sup>[18]</sup> and  $[(\text{pz})_2\text{BB}(\text{pz})_2] \cdot 2\text{Hpz}$  (Hpz = pyrazole).<sup>[19]</sup> The differences in B–B bond length between **3** or **4** and their respective neutral precursors are 0.057 and 0.088 Å (cf. Table 3). These changes are significantly smaller than the 0.177 and 0.172 Å found for the one-electron reductions of the related Al or Ga species  $\text{trip}_2\text{MMtrip}_2$  (trip = 2,4,6-*i*-Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>; M = Al or Ga). In these cases it is believed that the neutralization of the  $\delta^+ - \delta^+$  repulsion across the M–M bond, which is composed of the more electropositive Al or Ga atoms, also contributes to the bond shortening.<sup>[20]</sup>

**Counteraction Effects:** Regarding the bond lengths in Table 3, the following question arises: how do the metal counteractions affect the B–B bond lengths? Except for **3**, the reduced species (**4**, **9**, and **10**) exist in the solid state as contact ion pairs or ion triples. It is notable, however, that in the case of **4**, **9**, and **10** the  $\text{Li}^+$  ion(s) interacts more strongly with the boron substituents than with the boron centers themselves. Thus, in **4** and **10** the  $\text{Li}^+$  ions are most strongly complexed by either methoxy or dimethylamino substituents of the  $[\text{Mes}(\text{MeO})\text{BB}(\text{OMe})\text{Mes}]^-$  or  $[\text{Ph}(\text{Me}_2\text{N})\text{BB}(\text{NMe}_2)\text{Ph}]^{2-}$  anions. In **9** and **4**, the  $\text{Li}^+$  ions also interact closely with the carbon atoms of the aryl ring substituents. Note also that the lithium atoms in the dianions **9** and **10** do not lie in the plane of the molecule, nor do they lie directly above and below the mid-point of the B–B bond, where Li–B interactions might be expected to be maximized. Instead they occupy positions approximately half way between these extremes.

An additional consideration involves a comparison of the structural parameters of **3**, **4**, **9**, and **10** to those calculated for

the hypothetical species  $\text{Li}_2\text{B}_2\text{H}_4$ —the simplest possible lithium derivative of the  $[\text{B}_2\text{H}_4]^{2-}$  dianion.<sup>[3]</sup> The lowest energy configuration of this species involves an arrangement in which its eight atoms are coplanar and the B–B distance is 1.613 Å, as shown in structure **A**, Figure 4. An alternative structure, **B**, in which the lithium atoms lie directly above and below the  $\text{B}_2\text{H}_4$  plane, lies 14.9 kcal mol<sup>-1</sup> above **A** and has a B–B distance of 1.629 Å.

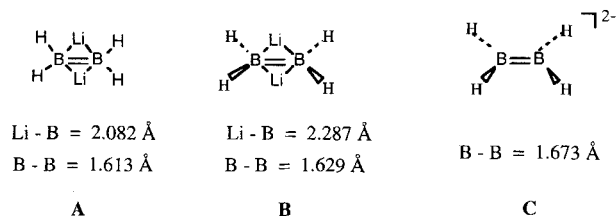


Figure 4. Schematic illustration of some of the possible structures of  $\text{Li}_2\text{B}_2\text{H}_4$ .

These calculated B–B distances are quite close to the 1.627(9) Å seen in **10** and the 1.636(11) Å in **9**. The significant lengthening of the B–B bond to 1.673 Å when the lithium ions are removed (structure **C**) cannot yet be compared with an experimentally determined structure of a free dianion. The calculations do, however, indicate that the presence of lithium ions plays a significant role in reducing Coulombic repulsions between the two adjacent negative charges on the boron atoms. However, the structure of **10**, in which each  $\text{Li}^+$  ion is strongly solvated by  $\text{Et}_2\text{O}$ , an  $-\text{NMe}_2$  group, and an aromatic ring, and the B–B bond length is 1.627(9) Å, suggests that a strong direct interaction between lithium and the boron centers may not be necessary to stabilize these doubly reduced systems.

In the singly reduced species **3** and **4**, the strong Coulombic repulsions between two adjacent negative charges do not exist, and the necessity of a metal counteranion for stabilization is probably of less significance. Thus, the B–B distances in the singly reduced species **3** and **4** differ by only 0.013 Å and, since the largest standard deviation is 0.011 Å, this difference cannot be regarded as significant. In essence, the presence of  $\text{Li}^+$  ion(s) to stabilize the reduced anions appears to have little effect in the case of the singly reduced anions, but for the doubly reduced species, removal of  $\text{Li}^+$  may be expected to destabilize the dianion, although the extent to which this occurs is not yet known experimentally.

**Reduction of Alkoxydiboron Compounds:** Compound **4** could be isolated in moderate yield by reduction of  $\text{Mes}(\text{MeO})\text{BB}(\text{OMe})\text{Mes}$  with an excess of lithium powder in diethyl ether solution. Prolonged stirring for more than ca. 4 h resulted in further reaction, whereby the purple solution became pale yellow and a white solid precipitated. Unfortunately, no pure reaction products have been isolated or definitively characterized from this reaction to date. It was hoped that the replacement of Mes groups with the sterically demanding<sup>[8, 21]</sup> terphenyl substituent 2,6- $\text{Mes}_2\text{C}_6\text{H}_3$ - would enable the isolation of a reduced B–B multiply bonded product from a reduction analogous to that above. The reaction of  $\text{B}_2(\text{OMe})_4$  with 0.5 equiv of  $[\text{2,6-Mes}_2\text{C}_6\text{H}_3\text{Li}]_2$  afforded 2,6- $\text{Mes}_2\text{C}_6\text{H}_3(\text{MeO})\text{BB}(\text{OMe})_2$  (**5**) in good yield. When 1 equiv of  $[\text{2,6-Mes}_2\text{C}_6\text{H}_3\text{Li}]_2$  was treated

with  $\text{B}_2(\text{OMe})_4$ , the only product formed was **5**, which bears only one aryl substituent at boron. Even at elevated temperatures, no 1,2-diaryl-1,2-dimethoxydiborane product could be isolated from this reaction. Seemingly, further substitution of the methoxy groups does not take place for steric reasons.

The structure of **5**, shown in Figure 5, is the only example of a structurally characterized trialkoxyaryldiborane(4). The B–B

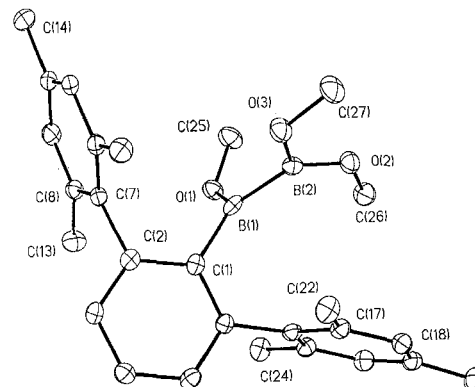


Figure 5. Structure of **5** (thermal ellipsoids at the 30% probability level; H atoms not shown).

bond length [1.718(5) Å] is within the range reported for other organodiborane(4) compounds.<sup>[10, 22]</sup> All three B–O bond lengths, which are virtually identical (ca. 1.36 Å), are similar in length to those previously reported for substituted alkoxy diborane(4) species.<sup>[10, 22a, 22b]</sup> Surprisingly, the angles at the boron centers [C(1)-B(1)-O(1) 112.8(3)° and O(2)-B(2)-O(3) 116.0(3)°] are similar, in spite of the very large aryl substituent. The large angle between the boron coordination planes (64.0°) is unremarkable and within the previously observed range for neutral diborane(4) compounds.<sup>[10, 22]</sup>

The 1,2-diaryl species 2,6- $\text{Mes}_2\text{C}_6\text{H}_3(\text{MeO})\text{BB}(\text{OMe})\text{Mes}$  (**6**), was readily formed in good yield by the reaction of **5** with  $\text{MesLi}$ . Evidently, the difference in size between the Mes and 2,6- $\text{Mes}_2\text{C}_6\text{H}_3$  groups allows further substitution to occur at boron under ambient conditions. The product **6** was then reduced by stirring with an excess of lithium powder in diethyl ether solution. The solution immediately turned deep purple (presumably due to the singly reduced radical anion), and after ca. 3 h became dark green. Prolonged stirring gave a dark orange solution, from which the 10-boraphenanthrenyl compound **7** could be isolated in moderate yield. Attempts to isolate a product from the dark green solution led to rapid decolorization, and only **7** could be isolated. The X-ray crystal structure of **7** is shown Figure 6.

The structure of **7** is unique in that it contains a boron heterocyclic dihydrophenanthrene moiety with a boryl substituent also bonded to the boron atom at the 10-position. A mesityl group occupies the 1-position, methyl groups substitute the 5- and 7-positions, and the boryl substituent is bound to a methoxy group and a mesityl ring. The compound may be regarded as having been formed by the intramolecular insertion of a boranide intermediate into a C–H bond of an *ortho*- $\text{CH}_3$  group of a mesityl ring (vide infra). The central boron-containing, six-membered ring is puckered. The conformation of this ring causes

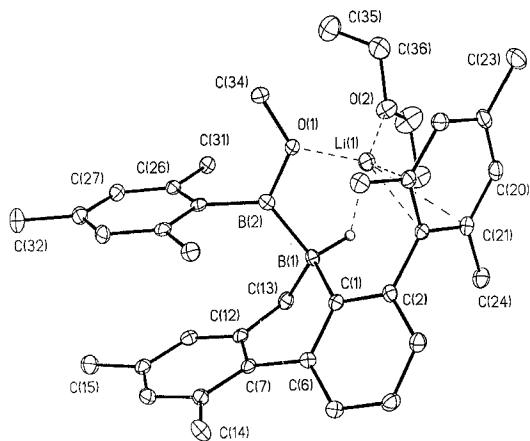
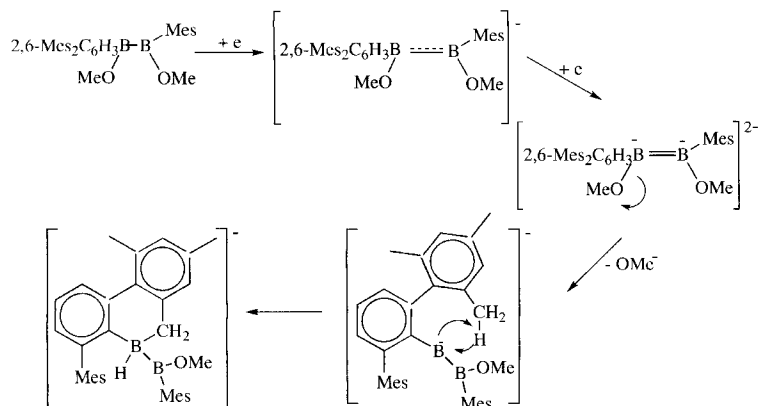


Figure 6. Structure of **7** (thermal ellipsoids at the 30% probability level; H atoms, except B–H, not shown).

es the adjacent phenyl rings to twist such that the dihedral angle between them is  $39.4^\circ$ . The B–B bond through which the boryl group is linked is not particularly long [ $1.727(6) \text{ \AA}$ ], despite the coordination number of four and the formal negative charge at B(1). The B(2)–O(1) distance [ $1.406(5) \text{ \AA}$ ] is slightly lengthened (by ca.  $0.03 \text{ \AA}$ ) in comparison to that found for other alkoxydiborane(4) derivatives.<sup>[10, 22]</sup> This B–O lengthening is probably due to the increased coordination number of the oxygen atom, which solvates the lithium atom. In effect, the ionic contribution to B–O bonding may be diminished due to the competitive attraction of the oxygen electron density by the  $\text{Li}^+$  ion. In addition to solvation of the lithium cation by the methoxy group and diethyl ether, there is an interaction with the mesityl substituent, as well as with a hydrogen atom bound to boron. The Li–O [Li(1)–O(1)  $1.929(6) \text{ \AA}$  and Li(1)–O(2)  $1.931(7) \text{ \AA}$ ] and Li–C ( $2.645(7) \text{ \AA}$  avg.) distances are within known ranges.<sup>[16]</sup> The shortest Li–B interaction is  $2.520(7) \text{ \AA}$  [Li(1)–B(1)], which is significantly longer than the Li–B interactions in **4**, **9**, and **10**.<sup>[23]</sup>

Formation of **7** may be rationalized as outlined in Scheme 2. Initially, one-electron reduction of **6** gives a singly reduced intermediate. Further reduction gives the dianionic species, which then may undergo loss of methoxide. Subsequent insertion of the boron center into a C–H bond<sup>[24]</sup> of an *ortho*-methyl group leads to the observed product **7**.



Scheme 2. Possible mechanism for the formation of **7** from **6**.

The reaction of the trialkoxydiborane(4) derivative **5** with an excess of lithium in diethyl ether afforded the 9-borafluorenyl compound **8**. Its structure is shown in Figure 7, and it consists of a methylmethoxyboryl group linked through a B–B bond to a 9-borafluorenyl moiety. There are methyl groups in the 5- and

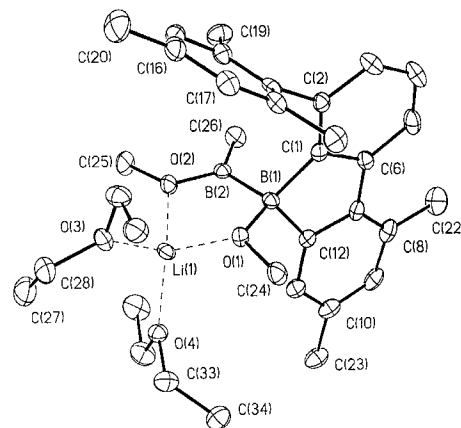
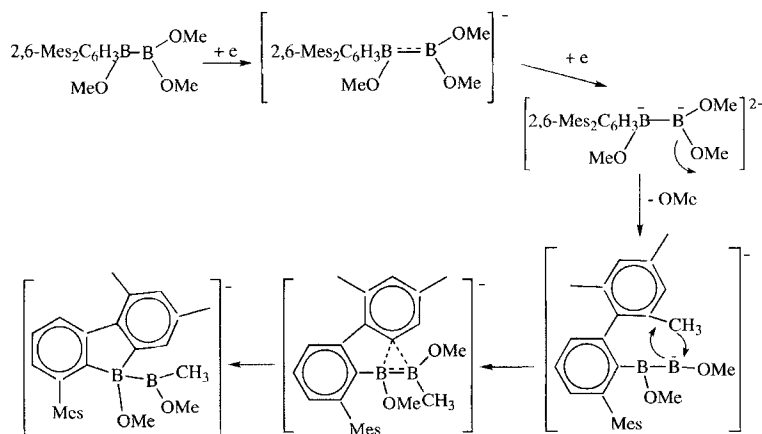


Figure 7. Structure of **8** (thermal ellipsoids at the 30% probability level; H atoms not shown).

7- positions and a mesityl group in the 1-position of the 9-borafluorenyl ring. The lithium cation is solvated by two diethyl ether molecules and by both oxygen atoms of the methoxy groups. The B–C distances within the five-membered ring are similar to those of other related 9-borafluorenyl rings.<sup>[25]</sup> The B(2)–O(2) distance [ $1.383(6) \text{ \AA}$ ] is only slightly lengthened by its coordination to Li(1). The B(1)–O(1) distance [ $1.517(6) \text{ \AA}$ ], however, is significantly lengthened owing to Coulombic repulsion between the oxygen atom and the formally negatively charged boron center. The Li–O distances between the methoxy oxygen atoms and diethyl ether molecules are within reported ranges.<sup>[16]</sup> The closest Li–B interaction [ $2.724(9) \text{ \AA}$ ] involves B(2).

The most remarkable feature of the structure of **8** is the replacement of one of the methoxy groups at B(2) by a methyl group. A possible mechanism by which this occurs is shown in Scheme 3. The initial two steps are similar to those given in Scheme 2 for the formation of **7**. However, in the third step, loss of methoxide leads to an intermediate in which the two-coordinate boron center can be stabilized by  $\pi$ -orbital overlap with the oxygen atom of the OMe group. The insertion of the boron center into the *o*-CH<sub>3</sub>–ring  $\sigma$  bond then gives a nonclassical species with a three-center bond,<sup>[26]</sup> from which **8** is ultimately formed. Formation of an intermediate through C–C  $\sigma$ -bond insertion appears to be reasonable, since the intramolecular distances of both boron centers to the methyl groups and *ortho*-carbon atom of the mesityl rings in **5** are very similar (ca.  $3.6 \text{ \AA}$ ). Related insertions<sup>[27]</sup> of a boron center into C–C bonds have been previously observed in the reduction of  $\text{R}_2\text{NBF}_2$  (R = *i*Pr)<sup>[27c]</sup> and  $2,6\text{-Mes}_2\text{C}_6\text{H}_3\text{BX}_2$  (X = Cl or Br).<sup>[25]</sup> In the latter case, reduction gives a boranediyl species which inserts into an *ortho*-CH<sub>3</sub>–ring C–C  $\sigma$  bond to give a 9-borafluorenyl compound.<sup>[25]</sup>

Scheme 3. Possible mechanism for the formation of **8** from **5**.

## Conclusions

The structural studies of the singly reduced diborane(4) compounds **3** and **4** show that the B–B bond undergoes a shortening which is consistent with the formation of a partial B–B  $\pi$  bond. By a remarkable coincidence, the B–B distances determined in these radical anions are very similar to those observed in the doubly reduced dianions, which have a formal  $\pi$ -bond order of unity. Apparently, the Coulombic repulsions in the dianions are in about equal balance with the shortening produced by the increased B–B  $\pi$ -bond order. The attempted further reduction of the methoxy-substituted **4** did not give well-defined products. However, reductions of the diborane(4) methoxy derivatives **5** and **6** give rearranged products that result from the elimination of methoxide and insertion of a reactive boranide intermediate into C–H or C–C bonds. The results for the reductions of **5** and **6** with lithium in diethyl ether solution suggest that formation of a stable methoxy substituted dianionic species such as  $[\text{Mes}(\text{MeO})\text{BB}(\text{OMe})\text{Mes}]^{2-}$  may be unlikely, at least under these conditions. Instead, further one-electron reduction of the radical anion **4** in solution gives a species which readily loses methoxide and then undergoes an intramolecular rearrangement.

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- [1] a) H. Klusik, A. Berndt, *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 870; b) A. Berndt, H. Klusik, K. Schlüter, *J. Organomet. Chem.* **1981**, *222*, C25; c) Diborane(4) radicals of the type  $[\text{Ar}_2\text{BBAr}_2]^\cdot$  have been implicated in the reduction of  $\text{Ar}_2\text{B}$  species, see: J. E. Leffler, G. B. Watts, T. Tanigaki, E. Dolan, D. S. Miller, *J. Am. Chem. Soc.* **1970**, *92*, 6825.

- [2] a) A. Moezzi, M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **1992**, *114*, 2715; b) A. Moezzi, R. A. Bartlett, P. P. Power, *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1082; c) P. P. Power, *Inorg. Chim. Acta* **1992**, *198*–200, 443.
- [3] E. Kaufmann, P. von R. Schleyer, *Inorg. Chem.* **1988**, *27*, 3987.
- [4] a) C. Pluta, K. R. Pörschke, C. Krüger, K. Hildenbrand, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 388; b) R. J. Wehmschulte, K. Ruhlandt-Senge, M. M. Olmstead, H. Hope, B. E. Sturgeon, P. P. Power, *Inorg. Chem.* **1993**, *32*, 2983.
- [5] a) X. He, R. A. Bartlett, M. M. Olmstead, K. Ruhlandt-Senge, B. E. Sturgeon, P. P. Power, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 717; b) W. Uhl, U. Schütz, W. Kaim, E. Waldhör, *J. Organomet. Chem.* **1995**, *501*, 79; c) W. Uhl, R. Gerding, A. Vester, *J. Organomet. Chem.* **1996**, *513*, 113.
- [6] M. Schlosser, V. J. Ladenberger, *J. Organomet. Chem.* **1967**, *8*, 193.
- [7] H. Goldwhite, G. Milhauser; unpublished results. G. Frankel, S. Dayagi, S. Kobayashi, *J. Phys. Chem.* **1968**, *72*, 953.
- [8] K. Ruhlandt-Senge, J. J. Ellison, R. J. Wehmschulte, F. Pauer, P. P. Power, *J. Am. Chem. Soc.* **1993**, *115*, 11353.
- [9] R. J. Brotherton, A. L. McCloskey, J. L. Boone, H. M. Manasevit, *J. Am. Chem. Soc.* **1960**, *82*, 6245.
- [10] A. Moezzi, M. M. Olmstead, R. A. Bartlett, P. P. Power, *Organometallics* **1992**, *11*, 2383.
- [11] I. S. Weitz, M. Rabinovitz, *J. Chem. Soc. Perkin Trans. 1*, **1993**, 117.
- [12] W. J. Grigsby, P. P. Power, *Chem. Commun.* **1996**, 2235.
- [13] SHELXTL-PLUS, A program for Crystal Structure Determination, Version 5.03, 1994, Siemens Analytical X-ray Instruments, Madison, Wisconsin.
- [14] SAME and SADI are subroutines within the SHELXL-93 program that create geometrical restraints to make chemically but not crystallographically equivalent distances equal.
- [15] S. R. Parkin, B. Moezzi, H. Hope, XABS2: an empirical absorption correction program, *J. Appl. Cryst.* **1995**, *28*, 53.
- [16] C. Schade, P. von R. Schleyer, *Adv. Organomet. Chem.* **1987**, *27*, 169.
- [17] a) W. N. Setzer, P. von R. Schleyer, *Adv. Organomet. Chem.* **1985**, *24*, 353; b) M. A. Beswick, D. S. Wright in *Comprehensive Organometallic Chemistry II* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon, **1995**, Chapt. 1, Vol. 1.
- [18] M. Pilz, J. Allwohn, P. Willershausen, W. Massa, A. Berndt, *Angew. Chem. Int. Ed. Engl.* **1990**, *9*, 146.
- [19] C. P. Brock, M. K. Das, R. P. Minton, K. J. Niedenzu, *J. Am. Chem. Soc.* **1988**, *110*, 817.
- [20] P. J. Brothers, P. P. Power, *Adv. Organomet. Chem.* **1996**, *39*, 1.
- [21] a) J. J. Ellison, K. Ruhlandt-Senge, P. P. Power, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1178; b) X.-W. Li, W. T. Pennington, G. H. Robinson, *Organometallics* **1995**, *14*, 2109.
- [22] a) H. Nöth, *Z. Naturforsch.* **1984**, *39B*, 1463; b) P. T. Brain, A. J. Downs, P. Maccallum, D. W. H. Rankin, H. E. Robinson, G. A. Forsyth, *J. Chem. Soc. Dalton Trans.* **1991**, 1195; c) A. Moezzi, M. M. Olmstead, P. P. Power, *ibid.* **1992**, 2429.
- [23] P. Pauer, P. P. Power, in *Lithium Chemistry: A Theoretical and Experimental Overview* (Eds.: A.-M. Sapse, P. von R. Schleyer), Wiley, New York, **1995**, Chapt. 9.
- [24] T. Mennekes, P. Paetzold, R. Boese, *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 899.
- [25] W. J. Grigsby, P. P. Power, *J. Am. Chem. Soc.* **1996**, *118*, 7981.
- [26] A. Berndt, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 985.
- [27] For examples of diborane(4) insertion into unsaturated systems see a) A. Meller, W. Maringgele, G. Elter, D. Bromm, M. Noltemeyer, G. M. Sheldrick, *Chem. Ber.* **1987**, *120*, 1437; b) A. Meller, D. Bromm, W. Maringgele, D. Bohler, G. Elter, *J. Organomet. Chem.* **1988**, *347*, 11; c) A. Meller, U. Seebold, W. Maringgele, M. Noltemeyer, G. M. Sheldrick, *J. Am. Chem. Soc.* **1989**, *111*, 8299; d) A. Meller, D. Bromm, W. Maringgele, A. Heine, D. Stalke, G. M. Sheldrick, *J. Chem. Soc. Chem. Commun.* **1990**, 741; e) A. Meller, *Pure and Appl. Chem.* **1991**, *63*, 395.