

Unsymmetrically Substituted 9,10-Dihydro-9,10-diboraanthracenes as Versatile Building Blocks for Boron-Doped π -Conjugated Systems

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Abstract: The targeted hydrolysis of the 9,10-dihydro-9,10-diboraanthracene adduct $(\text{Me}_2\text{S})\text{HB}(\text{C}_6\text{H}_4)_2\text{BH}(\text{SMe}_2)$ (**1**) with 0.5 equiv of H_2O leads to formation of the borinic acid anhydride $[(\text{Me}_2\text{S})\text{HB}(\text{C}_6\text{H}_4)_2\text{B}]_2\text{O}$ (**2**) and thereby provides access to the field of unsymmetrically substituted 9,10-dihydro-9,10-diboraanthracenes. Compound **2** reacts with $t\text{BuC}\equiv\text{CH}$ to give the corresponding vinyl derivative in an essentially quantitative conversion. Subsequent cleavage of the B-O-B bridge by LiAlH_4 with formation of hydridoborate functionalities is possible but is accompanied by partial B-C(vinyl) bond degradation. This situation changes

when the related mesityl derivative $[\text{MesB}(\text{C}_6\text{H}_4)_2\text{B}]_2\text{O}$ (**7**) is employed, which can be synthesized from $\text{BrB}(\text{C}_6\text{H}_4)_2\text{BBr}$ (**6**) by treatment with 1 equiv of MesMgBr and subsequent hydrolysis. The reaction of **7** with LiAlH_4 in tetrahydrofuran (THF) furnishes $\text{Li}[\text{MesB}(\text{C}_6\text{H}_4)_2\text{BH}_2]$ (**8**); hydride elimination with Me_3SiCl leads to formation of the THF adduct $\text{MesB}(\text{C}_6\text{H}_4)_2\text{BH}(\text{THF})$ (**9**·THF). Alternatively, **7** can be transformed into the

bromoborane $\text{MesB}(\text{C}_6\text{H}_4)_2\text{BBr}$ (**10**) by treatment with BBr_3 . A Br/H-exchange reaction between **10** and Et_3SiH yields the donor-free borane $\text{MesB}(\text{C}_6\text{H}_4)_2\text{BH}$ (**9**), which forms B-H-B bridged dimers (**9**)₂ in the solid state. The vinyl borane $\text{MesB}(\text{C}_6\text{H}_4)_2\text{BC}(\text{H})=\text{C}(\text{H})\text{Mes}$ (**14**) is accessible from $\text{MesC}\equiv\text{CH}$ and either **9**·THF or **9**. Compared with the related compound $\text{Mes}_2\text{BC}(\text{H})=\text{C}(\text{H})\text{Mes}$, the electronic absorption and emission spectra of **14** reveal bathochromic shifts of $\Delta\lambda(\text{abs})=17\text{ nm}$ and $\Delta\lambda(\text{em})=74\text{ nm}$, which can be attributed to the rigid, fully delocalized π framework of the $[\text{MesB}(\text{C}_6\text{H}_4)_2\text{B}]$ chromophore.

Introduction

The incorporation of three-coordinate boron atoms into conjugated π -electron frameworks leads to changes in the electronic structure that often bring about enhanced luminescence and charge-transport properties.^[1-4] Moreover, the ability of boron atoms to form Lewis acid-base pairs and thereby to disrupt the π -conjugation pathway can be exploit-

ed for the development of molecular switches and sensors.^[4-7]

However, the propensity of organoboranes to react with Lewis bases is also a disadvantage, because it renders the compounds intrinsically sensitive to air and moisture. The vast majority of organoboranes employed in materials science and sensor technology therefore contain at least one, in many cases two, bulky substituents for kinetic stabilization (cf. the popular di(mesityl)boryl group).^[8] Even though the concept of steric protection has already furnished a variety of remarkable organoboranes that can be handled in air and purified by chromatography on silica gel, it nevertheless suffers from certain disadvantages: 1) The size of any analyte that can be detected by the corresponding organoborane sensors is very limited (for example, F^- , CN^-). 2) A di(mesityl)boryl group with its single free valence can only act as a peripheral substituent, and not become an integral part of the π -electron system. 3) Steric congestion in triarylboranes leads to twisting of the aryl substituents about the B-C bonds and thereby to decreased π conjugation across the boron center. Thus, attachment of a di(mesityl)boryl group merely adds one vacant boron-centered p-orbital to the π -electron cloud, whereas the two mesityl rings remain more or less spectator groups.

For the design of building blocks other than di(mesityl)borane, we considered that 1) the building block itself should already possess an extended π -conjugated elec-

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tected by a comparatively inert group, whereas the second boron atom bears a reactive substituent (for example, $R^1 = \text{OR}$, Mes; $R^2 = \text{H}$, Br; Mes = mesityl).

Results and Discussion

A potentially viable six-step route to compounds of type **E** has recently been published by Kawashima et al.^[18] However, the only 9,10-dihydro-9,10-diboraanthracene isolated was the symmetrically substituted molecule MesB(C₆H₄)₂BMes. Described below are therefore the first examples of derivatives **E** with $R^1 \neq R^2$, together with reactivity studies and a comparison of the electronic spectra of MesB(C₆H₄)₂BC(H)=C(H)Mes and Mes₂BC(H)=C(H)Mes.

Symmetry breaking by targeted hydrolysis: During investigations into the hydrolytic stability of the ditopic borane adduct **1** (Scheme 2),^[14] we observed the ready formation of borinic acid anhydride **2** (Scheme 2), which could be separated from residual **1** by fractional crystallization from SMe₂. Optimized yields of close to 50% were obtained when 0.5 equiv of H₂O were employed.

An X-ray crystal structure analysis of **2** revealed that the compound contains two unsymmetrically substituted 9,10-dihydro-9,10-diboraanthracene moieties (Figure 1; Table 1).

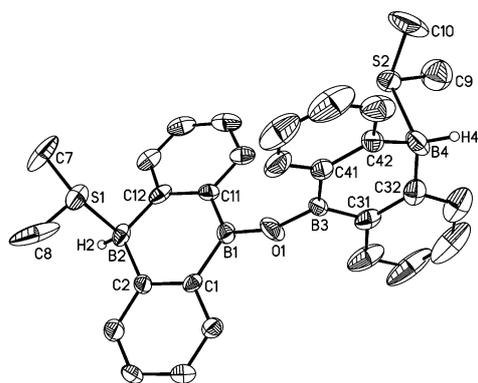


Figure 1. Molecular structure of **2** in the solid state (for S(2)Me₂ only the major occupied site is shown); displacement ellipsoids at the 30% probability level, H atoms (except on boron) omitted for clarity. Selected bond lengths [Å], bond angles [°], and dihedral angle [°]: B1–O1 1.345(7), B3–O1 1.337(7), B2–S1 2.029(6), B4–S2 2.073(8); B1–O1–B3 156.5(5), S1–B2–C2 104.1(4), S1–B2–C12 101.6(3), S2–B4–C32 104.9(5), S2–B4–C42 96.8(5); C1–B1–C11//C31–B3–C41 89.6(5).

The B–O–B bridge possesses an average bond length (B–O)_{av} of 1.341(7) Å, the B–O–B bond angle amounts to 156.5(5)°. These metrical parameters are in good agreement with the corresponding values for one of the two known polymorphs of diphenylborinic acid anhydride ((B–O)_{av} = 1.346(4) Å; B–O–B = 152.7(2)°).^[19] The second polymorph, however, exhibits significantly longer B–O bonds ((B–O)_{av} = 1.370(3) Å), together with a narrower B–O–B angle (147.3(2)°).^[20] Given that the packing motifs of the two polymorphs of diphenylborinic acid anhydride are quite differ-

Table 1. Crystallographic data for **2**, **7**, and **10**.

	2	7	10
formula	C ₂₈ H ₃₀ B ₄ O ₂	C ₄₂ H ₃₈ B ₄ O	C ₂₁ H ₁₉ B ₂ Br
<i>M_r</i>	489.88	601.96	372.89
color, shape	colorless, block	colorless, plate	yellow, plate
<i>T</i> [K]	173(2)	173(2)	173(2)
radiation, λ [Å]	MoK _α , 0.71073	MoK _α , 0.71073	MoK _α , 0.71073
crystal system	orthorhombic	triclinic	monoclinic
space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 1̄	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> [Å]	9.6827(10)	8.8596(18)	15.0527(15)
<i>b</i> [Å]	15.4538(10)	11.720(2)	8.1450(6)
<i>c</i> [Å]	18.1279(11)	17.288(4)	14.8148(18)
<i>α</i> [°]	90	93.33(3)	90
<i>β</i> [°]	90	98.44(3)	93.863(9)
<i>γ</i> [°]	90	100.29(3)	90
<i>V</i> [Å ³]	2712.6(4)	1740.5(7)	1812.2(3)
<i>Z</i>	4	2	4
ρ _{calcd} [g cm ⁻³]	1.200	1.149	1.367
F(000)	1032	636	760
μ [mm ⁻¹]	0.216	0.065	2.266
crystal size [mm]	0.35 × 0.34 × 0.27	0.27 × 0.24 × 0.11	0.27 × 0.25 × 0.13
reflections collected	28017	13 930	7395
independent reflections (<i>R</i> _{int})	5238 (0.1155)	6462 (0.0899)	3187 (0.0741)
data/restraints/parameters	5238/0/325	6462/0/430	3187/0/220
GOF on <i>F</i> ²	0.986	0.807	0.923
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0829, 0.2005	0.0515, 0.0954	0.0521, 0.1101
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.1318, 0.2289	0.1259, 0.1108	0.0832, 0.1187
largest diff peak and hole [e Å ⁻³]	0.565, -0.445	0.176, -0.193	0.907, -0.676

ent, we conclude that B–O–B deformation is associated with a shallow potential well so that the bond lengths and the bond angle are easily influenced by crystal packing forces. As can be expected for a heteroallene derivative, we find a perpendicular arrangement of the two BR₂ planes in **2** (cf. C1–B1–C11//C31–B3–C41 = 89.6(5)°).

All key bond lengths and angles involving the four-coordinate boron atoms of **2** are similar to those in the starting material and are therefore not discussed further.

The ¹¹B NMR spectrum (C₆D₆) of **2** is characterized by two resonances at δ = -3.0 (B(H)SMe₂) and 43.2 ppm (BO). Thus, the three-coordinate boron atoms possess almost the same chemical shift values as those of diphenylborinic acid anhydride (δ(¹¹B) = 46.1 ppm^[19]), whereas the four-coordinate boron centers are much better shielded in the hydrolysis product **2** than in the starting material **1** (δ(¹¹B) = 28.1 ppm^[14]). In both cases, the ¹J(B,H) coupling is not resolved, but broad resonances for the boron-bound hydrogen atoms are detectable in the ¹H NMR spectra. In line with the different substituents at the peripheral and internal boron atoms, the four phenylene rings give rise to two apparent triplets and two doublets in the ¹H NMR spectrum, and to four resonances in the ¹³C NMR spectrum (signals of carbon atoms attached to boron were not detected due to unresolved ¹J(B,C) coupling and quadrupolar broadening^[21]).

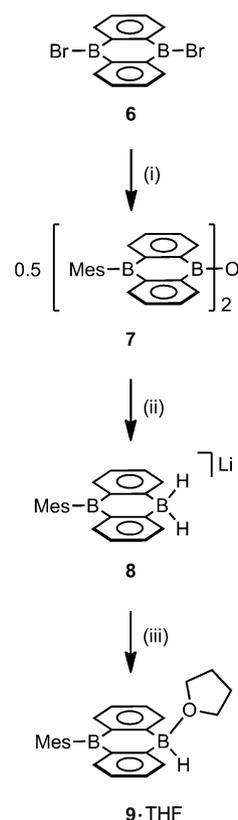
Exploratory investigations into the reactivity of **2** were undertaken on an NMR scale. First, the compound was treated in C₆D₆ with a tenfold excess of *t*BuC≡CH. After

30 min at room temperature, ^1H NMR spectroscopic analysis revealed an essentially quantitative conversion into the divinyl borane **3** (Scheme 2), as evidenced by the presence of two doublets at $\delta=6.66$ and 7.01 ppm ($2\times 2\text{H}$) with a $^3J_{\text{(H,H)}}$ coupling constant of 18.2 Hz, which is typical of *E*-olefins (see the Supporting Information). The related hydroboration product of **1**, $t\text{BuC(H)=C(H)B(C}_6\text{H}_4)_2\text{BC(H)=C(H)tBu}$, shows vinyl resonances at $\delta(^1\text{H})=6.74$ and 6.99 ppm ($^3J_{\text{(H,H)}}=18.1$ Hz).^[13,14] We conclude that **2** represents a versatile building block for the generation of other unsymmetrically substituted 9,10-dihydro-9,10-diboraanthracenes, because its two HB functionalities can readily be used in hydroboration reactions.

Further derivatization of **3** at its B-O-B bridge was attempted by the reaction with excess LiAlH_4 in $[\text{D}_8]\text{THF}$ (see the Supporting Information). In situ ^{11}B NMR spectroscopy revealed a triplet resonance at $\delta=-16.0$ ppm ($^1J_{\text{(B,H)}}=76$ Hz) and a doublet at $\delta=-11.1$ ppm ($^1J_{\text{(B,H)}}=60$ Hz), which points toward a reaction product possessing two chemically different four-coordinate boron centers, H_2BR_2 and HBR_3 , respectively. In the ^1H NMR spectrum, vinyl resonances were present at $\delta=5.63$ (1H) and 5.89 ppm (1H); the latter signal showed fine splitting due to $^3J_{\text{(H,H)}}$ coupling with one BH hydrogen atom. The phenylene resonances appeared as complex overlapping multiplets at $\delta=6.58$ (4H) and 7.24 ppm (4H). We therefore propose that the B-O-B bridge has indeed been cleaved, with formation of the unsymmetrical hydridoborate **4** (Scheme 2). However, it has so far not been possible to develop a fully selective synthetic protocol because the symmetrical hydridoborate $\text{Li}_2[\text{H}_2\text{B(C}_6\text{H}_4)_2\text{BH}_2]$ (**5**) is always generated as a byproduct (at least 15%). Compound **5** was identified by comparison of its NMR data with those of an authentic sample prepared from $\text{HOB(C}_6\text{H}_4)_2\text{BOH}$ and LiAlH_4 (see the Supporting Information for more information and an X-ray crystal structure analysis of the borinic acid).

Symmetry breaking by nucleophilic substitution: Our experiences with the system **3**/ LiAlH_4 indicate that, in principle, such borinic acid anhydrides are useful precursors for the synthesis of unsymmetrically substituted 9,10-dihydro-9,10-diboraanthracenes, but that the B-C(vinyl) bond is too fragile to persist under the reaction conditions applied. We therefore decided to replace the *tert*-butylvinyl substituents in **3** by more robust mesityl groups and to explore the reactivity of the resulting compound **7** (Scheme 3).

Preferential monosubstitution of $\text{BrB(C}_6\text{H}_4)_2\text{BBr}$ (**6**)^[22] is feasible with MesMgBr ^[23] in toluene provided that high dilution is maintained. Nevertheless, $\text{MesB(C}_6\text{H}_4)_2\text{BBr}$ obtained this way was always contaminated with the disubstitution product $\text{MesB(C}_6\text{H}_4)_2\text{BMes}$ and was not readily isolable in pure form. It therefore turned out to be convenient to quench the reaction with H_2O , thereby generating the borinic acid anhydride **7**, which could subsequently be purified by column chromatography (yield: 76%; note: in the presence of H_2O , **7** is in equilibrium with the borinic acid $\text{MesB(C}_6\text{H}_4)_2\text{BOH}$; see the Supporting Information).



Scheme 3. Synthesis of compounds **7–9-THF**. Reagents and conditions: i) 1) MesMgBr (1 equiv), toluene, $-78^\circ\text{C}\rightarrow$ room temperature; 2) H_2O (excess), CHCl_3 , room temperature; ii) LiAlH_4 (1 equiv), $\text{Et}_2\text{O/THF}$, room temperature; iii) Me_3SiCl (excess), $\text{Et}_2\text{O/THF}$, room temperature.

The solid-state structure of **7** reveals the desired compound with peripheral mesityl substituents (Figure 2; Table 1). Compared with **2**, subtle differences are observed for the central B-O-B linker ($(\text{B-O})_{\text{av}}=1.366(4)$ Å (**7**) vs. $1.341(7)$ Å (**2**); B-O-B = $139.4(2)^\circ$ (**7**) vs. $156.5(5)^\circ$ (**2**)). As

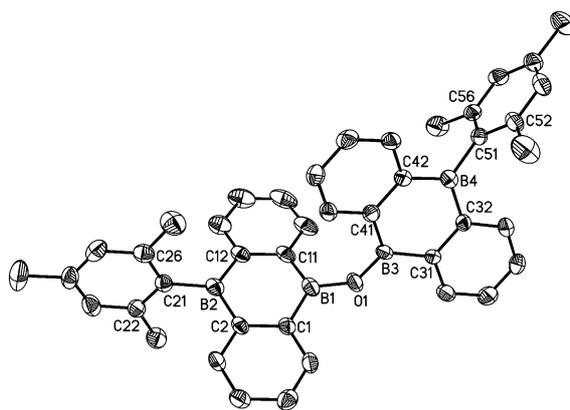


Figure 2. Molecular structure of **7** in the solid state; displacement ellipsoids at the 50% probability level, H atoms omitted for clarity. Selected bond lengths [Å], bond angle [$^\circ$], and dihedral angles [$^\circ$]: B1–O1 $1.371(4)$, B3–O1 $1.361(3)$, B2–C21 $1.568(4)$, B4–C51 $1.571(4)$; B1–O1–B3 $139.4(2)$; C1–B1–C11//C31–B3–C41 $74.5(2)$, C2–B2–C12//C22–C21–C26 $80.3(2)$, C32–B4–C42//C52–C51–C56 $85.8(2)$.

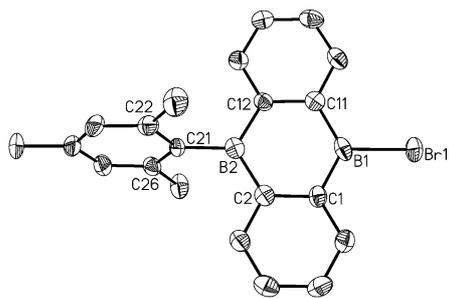


Figure 3. Molecular structure of **10** in the solid state; displacement ellipsoids at the 50% probability level, H atoms omitted for clarity. Selected bond lengths [Å], bond angles [°], and dihedral angle [°]: B1–Br1 1.949(6), B1–C1 1.534(8), B1–C11 1.561(8), B2–C2 1.551(7), B2–C12 1.567(8), B2–C21 1.564(7); C1–B1–C11 123.8(5), C2–B2–C12 119.1(5); C2–B2–C12//C22–C21–C26 81.0(4).

The ^{11}B NMR spectrum of **11** shows signals at $\delta = 69.5$ and 5.5 ppm, testifying to the presence of three- and four-coordinate boron atoms, respectively.^[21] In the ^1H NMR spectrum, the integral ratios of the mesityl, 9,10-dihydro-9,10-diboraanthracene, and 2,2'-bipyridyl resonances indicate a 1:1:1 ratio of the three fragments in the molecule. Most of the ^1H NMR signals of the coordinating 2,2'-bipyridyl ligand appear at lower field than those of the free base. The same is true for most of the ^{13}C NMR signals, a characteristic exception^[25] being the resonance of bipyC-2,2', which experiences an upfield shift of 9.3 ppm in **11**. The X-ray crystal structure analysis of **11** is in full accord with the structure established by NMR spectroscopy (see the Supporting Information).

Compound **9** forms a centrosymmetric B–H–B bridged dimer (**9**)₂ in the solid state (Figure 4; Table 2), which is reminiscent of the coordination polymer (**B**)_n.^[13] The 9,10-dihydro-9,10-diboraanthracene cores of the monomeric moieties in (**9**)₂ deviate significantly from planarity, with a dihedral angle of 146.7(1)° between the two phenylene rings Ar(C1)//Ar(C11). An even stronger folding has been observed in (**B**)_n (133.8°) and is accompanied by an intermono-

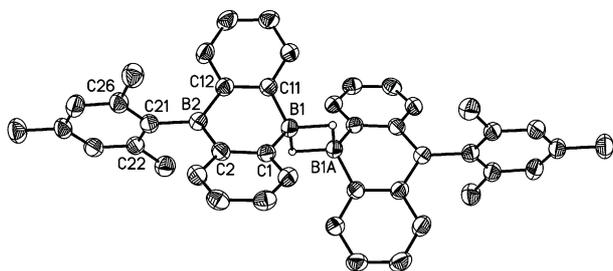


Figure 4. Molecular structure of (**9**)₂ in the solid state; displacement ellipsoids at the 50% probability level, H atoms (except on boron) omitted for clarity. Selected bond lengths [Å], atom...atom distance [Å], bond angles [°], torsion angles [°], and dihedral angles [°]: B1–C1 1.574(3), B1–C11 1.575(3), B2–C2 1.560(3), B2–C12 1.562(3), B2–C21 1.582(3), B1...B1A 1.850(5); C1–B1–C11 117.3(2), C2–B2–C12 118.2(2); B1–C1–C2–B2 –6.6(3), B1–C11–C12–B2 12.2(3); C2–B2–C12//C22–C21–C26 85.7(2), Ar(C1)//Ar(C11) 146.7(1). Symmetry transformation used to generate equivalent atoms: A: –x, –y+1, –z+1.

Table 2. Crystallographic data for (**9**)₂ and **14**.

	(9) ₂	14
formula	C ₄₂ H ₄₀ B ₄	C ₃₂ H ₃₂ B ₂
<i>M_r</i>	587.98	438.20
color, shape	yellow, block	colorless, plate
<i>T</i> [K]	173(2)	173(2)
radiation, λ [Å]	Mo _{Kα} , 0.71073	Mo _{Kα} , 0.71073
crystal system	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> [Å]	7.2197(7)	16.133(4)
<i>b</i> [Å]	13.7689(13)	14.936(3)
<i>c</i> [Å]	16.990(2)	22.143(6)
<i>α</i> [°]	90	90
<i>β</i> [°]	91.156(9)	107.42(2)
<i>γ</i> [°]	90	90
<i>V</i> [Å ³]	1688.6(3)	5091(2)
<i>Z</i>	2	8
ρ_{calcd} [g cm ⁻³]	1.156	1.143
<i>F</i> (000)	624	1872
μ [mm ⁻¹]	0.063	0.063
crystal size [mm]	0.37 × 0.35 × 0.35	0.28 × 0.25 × 0.12
reflections collected	13 587	31 262
independent reflections (<i>R</i> _{int})	2977 (0.1042)	8953 (0.3476)
data/restraints/parameters	2977/0/215	8953/15/624
GOF on <i>F</i> ²	0.926	0.719
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0532, 0.1209	0.0752, 0.1029
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0947, 0.1371	0.3396, 0.1964
largest diff peak and hole [e Å ⁻³]	0.279, –0.187	0.216, –0.176

mer B...B distance of 1.818(12) Å (mean value) as opposed to a longer distance of 1.850(5) Å in (**9**)₂. We note that the B...B distance in (**9**)₂ is also longer than that of ((C₆F₅)₂BH)₂ (1.799(7) Å^[26]), but is comparable to that of the sterically congested molecule (Mes)₂BH)₂ (1.851(3) Å^[27]). The experimentally determined structure of (**9**)₂ is in good agreement with the theoretically predicted structure of the parent dimer HB(C₆H₄)₂B(μ-H)₂B(C₆H₄)₂BH ((**B**)₂).^[13] The following observations can be made: 1) The simultaneous presence of three- and four-coordinate boron centers results in a puckering of the central six-membered ring [absolute values of the torsion angles B–C–C–B = 6.6(3)°, 12.2(3)° ((**9**)₂); 10.4° ((**B**)₂)]. 2) The dihedral angle Ar(C1)//Ar(C11) equals 146.7(1)° in (**9**)₂ vs. 151° in (**B**)₂. 3) The intermonomer B...B distance is 1.850(5) Å in (**9**)₂ and 1.83 Å in (**B**)₂.

DFT calculations indicate that the dimerization of **B** is essentially a thermoneutral process ($\Delta G^{298} = 0.3 \text{ kcal mol}^{-1}$) under gas-phase conditions.^[13] In C₆D₆ solution, the ^{11}B NMR spectrum of **9** is characterized by only one broad resonance at $\delta = 71.0$ ppm, which lies in the typical shift range of three-coordinate boron centers and can be explained in two ways: 1) the BH resonance is broadened beyond detection (for example, as a result of a monomer-dimer equilibrium), or 2) the BH^[27] and BMes signals are overlapping, which would necessarily mean that **9** exists as a monomer under the measurement conditions. The ^1H and ^{13}C NMR spectra in C₆D₆ both reveal one set of signals, all of which are narrow and well-resolved and therefore give no indication of an ongoing slow dynamic process. Remarkably, the ^{13}C nuclei of the 9,10-dihydro-9,10-diboraanthracene core are comparatively deshielded and possess chemical

shift values ($\delta=133.7, 134.2, 139.0,$ and 142.0 ppm) closer to those of **12** (see below; $\delta=132.7, 133.1, 137.1,$ and 139.4 ppm) than to those of **9**·THF ($\delta=126.9, 132.2, 135.5,$ and 138.6 ppm), or **8** ($\delta=121.7, 128.8, 135.0,$ and 138.1 ppm). The IR spectrum of **9** in C_6H_6 shows an absorption at 2481 cm^{-1} , which is typical of terminal B–H stretching bands^[28] (this absorption is absent in the IR spectrum of solid (**9**)₂). In summary, based on our spectroscopic results and on the DFT calculations mentioned above, we suggest that **9** mainly exists as monomeric species in aromatic solvents. This conclusion is also in accord with the evidence we have gathered for an unusually weak B–O bond in **9**·THF (see the Supporting Information). In $[D_8]THF$, the NMR spectra of (**9**)₂ are identical to those of compound **9**·THF.

Upon irradiation with UV light ($\lambda=366\text{ nm}$) at room temperature, compound **9** shows a bright blue-green fluorescence in C_6H_6 or THF solution. When the THF solution is cooled to liquid nitrogen temperature, the emission of the sample becomes more intense; when the UV light was switched off, an intense delayed luminescence remained visible for more than 15 s (the optical properties of **9** and of selected derivatives are the subject of ongoing investigations).

Hydroboration reactions of MesB(C₆H₄)₂BH: Compound **9**·THF as well as donor-free **9** have been employed in our studies on the hydroboration of terminal alkynes. Both reagents undergo quantitative conversion into the corresponding vinyl boranes (NMR spectroscopic monitoring of the reaction).

In a first exploratory NMR experiment, the reaction of **9**·THF with 1.2 equiv of *t*BuC≡CH gave the vinyl borane **12** (Scheme 4) with excellent regioselectivity. Two doublets were observed at $\delta=6.70$ and 7.03 ppm in the ¹H NMR spectrum with a ³*J*(H,H) coupling constant of 18.1 Hz, which is indicative of an *E*-olefin (see the Supporting Information).

The regioselectivity was drastically reduced when *p*-TolC≡CH was used instead of *t*BuC≡CH (*p*-Tol=*para*-tolyl), because the desired addition product **13a** (Scheme 4) was obtained together with its isomer MesB(C₆H₄)₂BC(*p*-Tol)=CH₂ (**13b**) in a 2:1 ratio. Similar to **12**, the olefinic fragment of **13a** gives rise to two doublet proton resonances ($\delta=7.47$ and 7.82 ppm) with a ³*J*(H,H) coupling constant of 18.2 Hz; in contrast, the ¹H NMR spectrum of **13b** is characterized by two doublets ($\delta=5.30$ and 6.27 ppm) with a ²*J*(H,H) coupling constant of only 1.8 Hz (see the Supporting Information).

Given that one goal of the work presented herein was the synthesis of well-defined, fully conjugated, boron-doped π -electron systems, any regioselectivity problem associated with the hydroboration of (aryl)alkynes was a major issue that needed to be resolved. Switching from *p*-TolC≡CH to MesC≡CH,^[29] we tested whether a moderate increase in the steric demand of the aryl group led to the selective formation of species of type **13a**. Indeed, the reactions between **9**·THF or **9** and MesC≡CH furnished isomer **14** exclusively (Scheme 4; BC(*H*)=C(*H*): $\delta(^1H)=7.34, 7.52$ ppm, $2 \times d,$

³*J*(H,H)=18.8 Hz). These syntheses were also conducted on a preparative scale with isolation and full characterization of the product. Crude **14**, prepared from **9**·THF *without* previous isolation of the intermediate **8** (in the form of **8**·(THF)₃, see the Supporting Information), tended to be contaminated with the aluminum complex [AlCl₃(THF)₂]. Compound **14** and [AlCl₃(THF)₂] could be separated from each other by fractional crystallization from hexane at 4 °C ([AlCl₃(THF)₂] and –30 °C (**14**). To obtain analytically pure **14** from **9** and MesC≡CH, it is sufficient to remove all volatiles from the reaction mixture under vacuum and to reprecipitate the product from hexane at –78 °C.

The targeted hydrolysis of **14** with traces of added H₂O gave **7** and H₂C=C(H)Mes in a clean and quantitative reaction, thereby identifying the B–C(vinyl) bond as the weakest link in the molecule.

Compound **14** crystallizes with two crystallographically independent molecules, **14_A** and **14_B**, in the asymmetric unit. The X-ray crystal structure analysis shows the desired *anti*-Markownikow isomer and the expected *E*-configuration of the C=C double bond (Figure 5). Given the poor quality of the data set (Table 2), we refrain from a detailed description of bond lengths and angles.

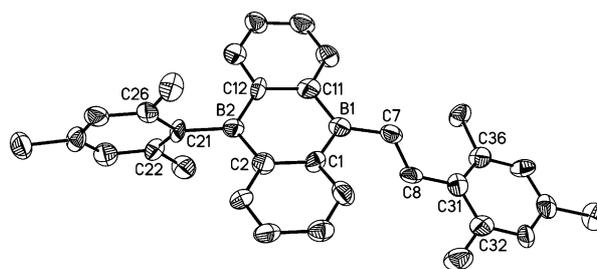


Figure 5. Molecular structure of **14_A** in the solid state; displacement ellipsoids at the 50% probability level, H atoms omitted for clarity. Selected bond lengths [Å], bond angles [°], and dihedral angles [°]: B1–C1 1.568(13), B1–C7 1.548(11), B1–C11 1.580(14), B2–C2 1.581(14), B2–C12 1.562(13), B2–C21 1.551(13), C7–C8 1.329(9); C7–B1–C1 120.5(9), C7–B1–C11 121.6(8), C1–B1–C11 117.5(8), C2–B2–C12 119.2(8), B1–C7–C8 124.8(8), C7–C8–C31 128.8(7); C1–B1–C11//B1–C7–C8 41(1), C2–B2–C12//C22–C21–C26 77.8(7).

Comparison of the electronic spectra of 14 and Mes₂BC(H)=C(H)Mes: To compare the optical properties of the [MesB(C₆H₄)₂B] chromophore with those of the commonly used [Mes₂B] group, we prepared the compound Mes₂BC(H)=C(H)Mes (see the Supporting Information for synthetic details and NMR data), which is an analogue of **14**. The absorption and emission wavelengths of both compounds are compiled in Table 3.

Table 3. Electronic spectral data of **14** and Mes₂BC(H)=C(H)Mes in toluene.

Compound	$\lambda_{\max}(\text{abs})$ [nm]	$\lambda_{\max}(\text{em})$ [nm]
14	350	470 ($\lambda_{\text{ex}}=350$)
Mes ₂ BC(H)=C(H)Mes	333	396 ($\lambda_{\text{ex}}=335$)

In toluene solution, Mes₂BC(H)=C(H)Mes shows its longest wavelength absorption at $\lambda_{\max}(\text{abs})=333$ nm; the emission maximum of the compound lies at $\lambda_{\max}(\text{em})=396$ nm (excitation wavelength: $\lambda_{\text{ex}}=335$ nm). Both λ_{\max} values compare perfectly well with those of the closely related compound Mes₂BC(H)=C(H)Ph ($\lambda_{\max}(\text{abs})=332$ nm/ $\lambda_{\max}(\text{em})=398$ nm in cyclohexane).^[30] Replacement of [Mes₂B] by [MesB(C₆H₄)₂B] had only a moderate effect on the absorption band, which, in the latter case, appears at $\lambda_{\max}(\text{abs})=350$ nm (**14**). The emission band, however, undergoes a bathochromic shift of $\Delta\lambda=74$ nm and is found at $\lambda_{\max}(\text{em})=470$ nm (**14**). These qualitative trends are in line with expectations, because more extended and conformationally constrained dyes are known to absorb and fluoresce more intensely at longer wavelengths relative to smaller and/or unconstrained dyes.^[31]

Conclusion

Two convenient, high-yield protocols for the synthesis of unsymmetrically substituted 9,10-dihydro-9,10-diboraanthracenes have been developed: The first starts from a thioether adduct of the parent borane (i.e., (Me₂S)HB(C₆H₄)₂BH(SMe₂); **1**), the second from BrB(C₆H₄)₂BBr (**6**). In the case of **1**, it is possible to break the symmetry of the molecular framework by targeted hydrolysis, which gives the borinic acid anhydride ((Me₂S)HB(C₆H₄)₂B)₂O (**2**) in almost 50% yield as a crystalline solid. In the case of **6**, the reaction with 1 equiv of MesMgBr under high dilution leads to the preferential formation of MesB(C₆H₄)₂BBr, which is subsequently transformed into the air- and moisture-stable borinic acid anhydride (MesB(C₆H₄)₂B)₂O (**7**; 76% yield) to facilitate purification.

Compound **2** can be used directly for further derivatization through hydroboration. Compound **7** reacts cleanly with BBr₃ to regenerate the monotopic bromoborane MesB(C₆H₄)₂BBr (**10**), which, in turn, reacts with Et₃SiH to furnish the borane MesB(C₆H₄)₂BH (**9**). Having both **9** and **10** available, it is now possible to conveniently attach the [MesB(C₆H₄)₂B] fragment to conjugated π -electron systems either through hydroboration or nucleophilic substitution protocols, respectively.

Compound **9** is also accessible as its THF-adduct **9**·THF by treatment of **7** with LiAlH₄ and then with Me₃SiCl in Et₂O/THF. Compared with the sequence **7** → **10** → **9**, this alternative route has the disadvantage that it usually takes some effort to purify **9**·THF (or its hydroboration products) from residual aluminum complexes.

The electronic absorption and emission spectra of the vinyl borane MesB(C₆H₄)₂BC(H)=C(H)Mes reveal bathochromic shifts of $\Delta\lambda(\text{abs})=17$ nm and $\Delta\lambda(\text{em})=74$ nm, compared with Mes₂BC(H)=C(H)Mes, which bears the more common [Mes₂B] chromophore. This observation strongly suggests that the optoelectronic properties resulting from the more extended 9,10-dihydro-9,10-diboraanthracene π system increase the value of the material. We are therefore

planning to prepare yet larger but still well-defined boron-doped π materials, for example, by replacing the monoalkyne MesC \equiv CH with the aromatic dialkyne HC \equiv C(*p*-C₆Me₄)C \equiv CH.

Experimental Section

Unless otherwise specified, all reactions were carried out under dry nitrogen or argon using Schlenk or glove box techniques. Hexane, toluene, C₆H₆, C₆D₆, Et₂O, THF, and [D₈]THF were dried over Na/benzophenone. Me₂S was stirred over LiAlH₄ for 8 h at room temperature and distilled prior use. Me₃SiCl was stored over CaH₂ and distilled prior to use. *t*BuC \equiv CH and Et₃SiH were distilled from molecular sieves (3 Å). NMR spectra were recorded with Bruker AM 250, DPX 250, Avance 300, or Avance 400 spectrometers at room temperature, if not otherwise specified. Chemical shifts are referenced to (residual) solvent signals (¹H/¹³C[¹H]; C₆D₆: $\delta=7.15/128.0$ ppm; [D₈]THF: $\delta=3.58/67.4$ ppm; CD₃CN: $\delta=1.94/118.2$ ppm) or external BF₃·Et₂O (¹¹B, ¹¹B[¹H]). Abbreviations: s=singlet, d=doublet, t=triplet, app. t=apparent triplet, m=multiplet, br=broad, n.o.=signal not observed. UV/Vis absorption and emission spectra were recorded with a Varian Cary 50 Scan UV/Vis spectrophotometer or a Perkin–Elmer LS 50B fluorescence spectrometer, respectively. Combustion analyses were performed by the Microanalytical Laboratory of the University of Frankfurt and by the Microanalytical Laboratory Pascher. Compounds **1**,^[14] **6**,^[22] HOB(C₆H₄)₂BOH,^[32] 1,2-C₆H₄(SiMe₃)₂,^[12] MesMgBr,^[23] (Mes₂BH)₂,^[33] and MesC \equiv CH^[29] were synthesized according to literature procedures.

Synthesis of 2: A calibrated solution of H₂O in THF (6.1 M, 14.8 μ L, 0.090 mmol) was added at room temperature by using an Eppendorf pipette to a stirred solution of **1** (0.050 g, 0.17 mmol) in anhydrous Me₂S (4 mL). After gas evolution (H₂) had ceased (15 min), the colorless clear solution was stored at -80°C for 2 days. A colorless precipitate formed that was identified as unreacted **1** (0.010 g, 20%). The clear supernatant was decanted in the cold and stored at -80°C for another 4 days to obtain a colorless precipitate. The mother liquor was removed in the cold by using a syringe and discarded. The remaining solid was dried under dynamic vacuum. Yield: 0.015 g (37%; 46% considering the re-isolated starting material). X-ray quality crystals of **2** were obtained through gas-phase diffusion of pentane into a Me₂S solution of **2** at room temperature. ¹H NMR (300.0 MHz, C₆D₆): $\delta=1.29$ (s, 12H; SCH₃), 4.23 (*h*_{1/2}=100 Hz, 2H; BH), 7.19 (app. td, ³J(H,H)=7.4 Hz, ⁴J(H,H)=1.2 Hz, 4H; H-2,7 or H-3,6), 7.43 (app. td, ³J(H,H)=7.4 Hz, ⁴J(H,H)=1.3 Hz, 4H; H-2,7 or H-3,6), 7.87 (d, ³J(H,H)=7.4 Hz, 4H; H-1,8 or H-4,5), 8.17 ppm (d, ³J(H,H)=7.4 Hz, 4H; H-1,8 or H-4,5); ¹¹B NMR (96.3 MHz, C₆D₆): $\delta=-3.0$ (*h*_{1/2}=500 Hz; BH), 43.2 ppm (*h*_{1/2}=1200 Hz; BO); ¹³C[¹H] NMR (62.9 MHz, C₆D₆): $\delta=18.2$ (SCH₃), 126.9 (C-2,7 or C-3,6), 130.6 (C-2,7 or C-3,6), 133.6 (C-1,8 or C-4,5), 136.3 ppm (C-1,8 or C-4,5), n.o. (BC).

Synthesis of 7: A calibrated solution (0.77 M) of the Grignard reagent MesMgBr was prepared in THF. An aliquot (3.4 mL, 2.6 mmol) was transferred into a Schlenk vessel, all volatiles were removed under reduced pressure, the resulting brownish oil was dissolved in toluene (15 mL), and the solution was added dropwise with stirring at -78°C to a turbid solution of **6** (875 mg, 2.62 mmol) in toluene (100 mL). The reaction mixture was allowed to warm to room temperature overnight, whereupon a colorless precipitate formed. After filtration, all volatiles were removed from the filtrate in vacuo to yield a yellow solid. Deionized H₂O (20 mL) and CHCl₃ (50 mL) were added, the resulting two liquid phases were separated, and the aqueous layer was extracted with CHCl₃ (3 \times 15 mL). The combined organic layers were dried over MgSO₄, filtered, and evaporated in vacuo. The crude product was purified by column chromatography (silica gel; mobile phase: CHCl₃) and dried for 4 h at room temperature under dynamic vacuum. Yield: 602 mg (76%). Single crystals of **7** that were suitable for X-ray diffraction were obtained by gas-phase diffusion of hexane into a toluene solution of **7**. *R*_f=0.37 (CHCl₃); ¹H NMR (300.0 MHz, C₆D₆): $\delta=2.16$ (s, 12H; *o*-CH₃), 2.35 (s, 6H; *p*-CH₃), 6.93 (s, 4H; MesH-3,5), 7.10 (app. td, ³J(H,H)=7.4 Hz, ⁴J-

(H,H)=1.4 Hz, 4H; H-2,7 or H-3,6), 7.15 (app. td, $^3J(\text{H,H})=7.4$ Hz, $^4J(\text{H,H})=1.4$ Hz, 4H; H-2,7 or H-3,6), 7.86 (dd, $^3J(\text{H,H})=7.0$ Hz, $^4J(\text{H,H})=1.4$ Hz, 4H; H-1,8 or H-4,5), 7.98 ppm (dd, $^3J(\text{H,H})=7.0$ Hz, $^4J(\text{H,H})=1.4$ Hz, 4H; H-1,8 or H-4,5); $^{11}\text{B}\{^1\text{H}\}$ NMR (96.3 MHz, C_6D_6): $\delta=43.9$ ($h_{1/2}=1500$ Hz; BO), 70.2 ppm (br; BMes); $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, C_6D_6): $\delta=21.4$ (*p*-CH₃), 22.9 (*o*-CH₃), 127.6 (MesC-3,5), 132.8 (C-2,7 or C-3,6), 133.6 (C-2,7 or C-3,6), 133.8 (C-1,8 or C-4,5), 137.0 (MesC-4), 138.1 (MesC-2,6), 139.6 ppm (C-1,8 or C-4,5), n.o. (BC); elemental analysis calcd (%) for $\text{C}_{42}\text{H}_{38}\text{B}_4\text{O}$ (601.99): C 83.80, H 6.36; found: C 83.53, H 6.54.

Synthesis of 10: Neat BBr_3 (32 μL , 83.2 mg, 0.33 mmol) was added at room temperature to **7** (50 mg, 0.08 mmol) in C_6H_6 (2 mL). After the solution had been kept at room temperature for 31 h, all volatiles were removed under reduced pressure over a period of 12 h. The yellow solid residue was treated with C_6H_6 (2 mL) and the resulting solution was separated from small amounts of a colorless solid by using a syringe. After evaporation to dryness under reduced pressure, **10** was obtained as a yellow solid. Yield: 46.7 mg (75%). Single crystals of **10** were grown by slow evaporation of the reaction mixture. ^1H NMR (250.1 MHz, C_6D_6): $\delta=1.96$ (s, 6H; *o*-CH₃), 2.30 (s, 3H; *p*-CH₃), 6.86 (m, 2H; MesH-3,5), 7.09 (app. td, $^3J(\text{H,H})=7.3$ Hz, $^4J(\text{H,H})=1.4$ Hz, 2H; H-2,7 or H-3,6), 7.19 (app. td, $^3J(\text{H,H})=7.3$ Hz, $^4J(\text{H,H})=1.4$ Hz, 2H; 2,7 or H-3,6), 7.61 (dd, $^3J(\text{H,H})=7.3$ Hz, $^4J(\text{H,H})=1.4$ Hz, 2H; H-1,8 or H-4,5), 8.52 ppm (dd, $^3J(\text{H,H})=7.3$ Hz, $^4J(\text{H,H})=1.4$ Hz, 2H; H-1,8 or H-4,5); $^{11}\text{B}\{^1\text{H}\}$ NMR (96.3 MHz, C_6D_6): $\delta=65.0$, 69.4 ppm (BBr, BMes); $^{13}\text{C}\{^1\text{H}\}$ NMR (62.9 MHz, C_6D_6): $\delta=21.4$ (*p*-CH₃), 22.6 (*o*-CH₃), 127.6 (MesC-3,5), 133.9 (C-2,7 or C-3,6), 134.5 (C-2,7 or C-3,6), 137.2 (MesC-4), 138.0 (MesC-2,6), 139.0 (C-1,8 or C-4,5), 139.3 ppm (C-1,8 or C-4,5), n.o. (BC).

Synthesis of 11: Compound **10** (18.6 mg, 0.05 mmol) in C_6H_6 (0.5 mL) was added at room temperature to a solution of 2,2'-bipyridyl (10.4 mg, 0.07 mmol) in toluene (0.1 mL), whereupon a yellow solid precipitated immediately. The solution was removed by using a syringe and discarded; the precipitate was washed with toluene (2×1.5 mL) and dried under dynamic vacuum. $[\text{MesB}(\text{C}_6\text{H}_4)_2\text{B}(\text{bipy})]\text{Br}$ was dissolved in MeOH (2 mL) and treated with an aqueous solution of NH_4PF_6 (0.20 M, 1.0 mL, 0.20 mmol), whereupon a yellow precipitate formed. The solid product was isolated by decanting the supernatant after centrifugation, washed with deionized H_2O (2 mL), and dried under vacuum. Single crystals that were suitable for X-ray diffraction were obtained by gas-phase diffusion of Et_2O into a CH_3CN solution of **11**. Yield: 15.2 mg (51%; crystalline material). ^1H NMR (300.0 MHz, CD_3CN): $\delta=2.12$ (s, 6H; *o*-CH₃), 2.40 (s, 3H; *p*-CH₃), 6.66 (dm, $^3J(\text{H,H})=7.0$ Hz, 2H; H-1,8 or H-4,5), 7.00 (m, 2H; MesH-3,5), 7.32 (app. td, $^3J(\text{H,H})=7.3$ Hz, $^4J(\text{H,H})=1.6$ Hz, 2H; H-2,7 or H-3,6), 7.36 (app. td, $^3J(\text{H,H})=7.3$ Hz, $^4J(\text{H,H})=1.6$ Hz, 2H; H-2,7 or H-3,6), 7.63 (dm, $^3J(\text{H,H})=7.0$ Hz, 2H; H-1,8 or H-4,5), 7.95 (ddd, $^3J(\text{H,H})=7.7$ Hz, $^3J(\text{H,H})=5.7$ Hz, $^4J(\text{H,H})=1.2$ Hz, 2H; bipyH-5,5'), 8.29 (ddd, $^3J(\text{H,H})=5.7$ Hz, $^4J(\text{H,H})=1.3$ Hz, $^5J(\text{H,H})=0.9$ Hz, 2H; bipyH-6,6'), 8.67 (ddd, $^3J(\text{H,H})=8.1$ Hz, $^3J(\text{H,H})=7.7$ Hz, $^4J(\text{H,H})=1.3$ Hz, 2H; bipyH-4,4'), 8.89 ppm (d app. t, $^3J(\text{H,H})=8.1$ Hz, $^4J(\text{H,H})=^5J(\text{H,H})=1.1$ Hz, 2H; bipyH-3,3'); $^{11}\text{B}\{^1\text{H}\}$ NMR (96.3 MHz, CD_3CN): $\delta=5.5$ ($h_{1/2}=250$ Hz; B-bipy), 69.5 ppm ($h_{1/2}=1000$ Hz; BMes); $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CD_3CN): $\delta=21.3$ (*p*-CH₃), 23.0 (*o*-CH₃), 124.5 (bipyC-3,3'), 127.8 (MesC-3,5), 129.9 (C-2,7 or C-3,6), 130.5 (bipyC-5,5'), 131.9 (C-1,8 or C-4,5), 134.5 (C-2,7 or C-3,6), 137.8 (MesC-4), 138.7 (MesC-2,6), 139.7 (C-1,8 or C-4,5), 144.3 (bipyC-6,6'), 146.0 (bipyC-4,4'), 147.6 ppm (bipyC-2,2'), n.o. (BC); MS (ESI⁺): *m/z* (%): 450 (100) [$M-(\text{PF}_6)_3$]⁺; elemental analysis calcd (%) for $\text{C}_{31}\text{H}_{27}\text{B}_2\text{F}_6\text{N}_2\text{P}$ (594.14): C 62.67, H 4.58, N 4.71; found: C 62.02, H 4.55, N 4.45.

Synthesis of (9)₂: Excess neat Et_3SiH (1 mL, 728 mg, 6.26 mmol) was added at room temperature to neat **10** (64.9 mg, 0.17 mmol). The resulting mixture was stored without stirring at room temperature for 1 day, whereupon pale-yellow crystals formed. The mother liquor was removed by using a syringe and the crystalline product (**9**)₂ was dried under vacuum. Yield: 35.6 mg (70%). IR (C_6H_6): $\tilde{\nu}=2481$ cm^{-1} (B-H). ^1H NMR (400.1 MHz, C_6D_6): $\delta=2.03$ (s, 6H; *o*-CH₃), 2.32 (s, 3H; *p*-CH₃), 6.89 (s, 2H; MesH-3,5), 7.12 (app. td, $^3J(\text{H,H})=7.4$ Hz, $^4J(\text{H,H})=1.4$ Hz, 2H; H-2,7 or H-3,6), 7.22 (app. td, $^3J(\text{H,H})=7.4$ Hz, $^4J(\text{H,H})=$

1.4 Hz, 2H; H-2,7 or H-3,6), 7.67 (d, $^3J(\text{H,H})=7.4$ Hz, 2H; H-1,8 or H-4,5), 7.93 ppm (d, $^3J(\text{H,H})=7.4$ Hz, 2H; H-1,8 or H-4,5); ^{11}B NMR (128.4 MHz, C_6D_6): $\delta=71.0$ ppm ($h_{1/2}=1500$ Hz; BMes, BH); $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, C_6D_6): $\delta=21.4$ (*p*-CH₃), 22.7 (*o*-CH₃), 127.5 (MesC-3,5), 133.7 (C-2,7 or C-3,6), 134.2 (C-2,7 or C-3,6), 137.0 (MesC-4), 138.0 (MesC-2,6), 139.0 (C-1,8 or C-4,5), 142.0 ppm (C-1,8 or C-4,5), n.o. (BC); elemental analysis calcd (%) for $\text{C}_{42}\text{H}_{40}\text{B}_4$ (587.98): C 85.80, H 6.86; found: C 85.13, H 6.77.

Synthesis of 14: Neat MesC≡CH (51.3 μL , 47.7 mg, 0.331 mmol) was added at room temperature to **9**-THF (121 mg, 0.331 mmol) in C_6H_6 (7 mL) by using a Hamilton syringe, and the reaction mixture was stirred for 1 h. All volatiles were removed under reduced pressure, the yellow solid residue was treated with hexane (5 mL), and the insoluble material was collected on a frit and extracted into hexane (2×1 mL). The combined hexane solutions were evaporated to dryness in vacuo to obtain a yellow microcrystalline solid of **14** and $[\text{AlCl}_3(\text{THF})_2]$. The two components were separated from each other by fractional crystallization from hexane at 4 °C ($[\text{AlCl}_3(\text{THF})_2]$) and -30 °C (**14**). Single crystals of **14** that were suitable for X-ray diffraction were grown by slow evaporation of a pentane/ C_6H_6 solution (50:1) at room temperature. The yields of **14** reproducibly ranged between 20–30%; yields of **14** close to 90% were obtained under similar conditions with **9** as the hydroboration reagent. ^1H NMR (400.1 MHz, C_6D_6): $\delta=2.08$ (s, 6H; *o*-CH₃), 2.17 (s, 3H; *p*-CH₃), 2.32 (s, 6H; *o*-CH₃), 2.33 (s, 3H; *p*-CH₃), 6.83 (s, 2H; MesH-3,5'), 6.91 (s, 2H; MesH-3,5), 7.21 (app. td, $^3J(\text{H,H})=7.3$ Hz, $^4J(\text{H,H})=1.3$ Hz, 2H; H-2,7), 7.32 (app. td, $^3J(\text{H,H})=7.3$ Hz, $^4J(\text{H,H})=1.3$ Hz, 2H; H-3,6), 7.34 (d, $^3J(\text{H,H})=18.8$ Hz, 1H; BC(H)=C(H)), 7.52 (d, $^3J(\text{H,H})=18.8$ Hz, 1H; BC(H)=C(H)), 7.82 (d, $^3J(\text{H,H})=7.3$ Hz, 2H; H-1,8), 8.24 ppm (d, $^3J(\text{H,H})=7.3$ Hz, 2H; H-4,5); $^{11}\text{B}\{^1\text{H}\}$ NMR (128.4 MHz, C_6D_6): $\delta=71.6$ ppm (shoulder at $\delta=62.8$ ppm; BMes, BC(H)=C(H)); $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, C_6D_6): $\delta=21.1$ (*p*-CH₃), 21.3 (*o*-CH₃'), 21.4 (*p*-CH₃'), 22.8 (*o*-CH₃'), 127.5 (MesC-3,5), 129.4 (MesC-3,5'), 133.0 (C-2,7), 133.2 (C-3,6), 136.1 (MesC-2,6'), 136.5 (MesC-1'), 136.8 (MesC-4), 137.0 (MesC-4'), 137.5 (C-4,5), 138.1 (MesC-2,6), 138.6 (br; BC(H)=C(H)), 139.6 (C-1,8), 141.5 (br; MesC-1), 145.7 (br; $\text{C}_6\text{H}_4\text{-BC}$), 147.5 (br; $\text{C}_6\text{H}_4\text{-BC}$), 149.6 ppm (BC(H)=C(H)); elemental analysis calcd (%) for $\text{C}_{32}\text{H}_{32}\text{B}_2$ (438.20): C 87.71, H 7.36; found: C 87.39, H 7.35. Note: Resonances belonging to the 2-mesitylphenyl substituent are marked with a prime (').

Crystal structure analyses: All crystals except those of $\text{HOB}(\text{C}_6\text{H}_4)_2\text{BOH}$ were measured on a STOE IPDS-II diffractometer with graphite-monochromated MoK_α radiation. An empirical absorption correction with program PLATON^[34] was performed for **2**, **6**, and **10**. The structures were solved by direct methods^[35] and refined with full-matrix least-squares on F^2 using the program SHELXL97.^[36] The hydrogen atoms bonded to boron in **8**, **9**-THF, and (**9**)₂ were isotropically refined. All other hydrogen atoms were placed in ideal positions and refined with fixed isotropic displacement parameters using a riding model.

One sulfur atom and one methyl group of **2** are disordered over two positions with a site occupation factor of 0.656(8) for the major occupied site. The crystal of **6** was a non-merohedral twin with a fraction of 0.576(6) for the major domain. The hydrogen atoms of three methyl groups of **7** are disordered over two positions with equally occupied sites. In **11**, the *para*-methyl group of the mesityl ring is disordered over two equally occupied positions. In one of the two crystallographically independent molecules of **14** (i.e., **14_a**), the atoms of the C=C double bond are disordered over two positions with a site occupation factor of 0.58(2) for the major occupied site. Bond lengths and angles involving the disordered atoms were restrained to be equal to those in the non-disordered molecule.

$\text{HOB}(\text{C}_6\text{H}_4)_2\text{BOH}$ was measured with a Siemens SMART diffractometer. No absorption correction was made. The structure was determined by direct methods^[35] and refined with full-matrix least-squares on F^2 using the program SHELXL97.^[36] The hydrogen atoms were geometrically positioned and were constrained. The crystal was twinned, the twin relations are: $h'=-h$, $k'=-k$, and $l'=0.895h+1$, the twin fraction refined to 0.302(7).

CCDC-824867 ($\text{ClB}(\text{C}_6\text{H}_4)_2\text{BCl}$), CCDC-824869 ($\text{HOB}(\text{C}_6\text{H}_4)_2\text{BOH}$), CCDC-824870 (**2**), CCDC-824868 (**6**), CCDC-824871 (**7**), CCDC-824872

(8), CCDC-824873 (9-THF), CCDC-826346 ((9)₂), CCDC-826345 (10), CCDC-824875 (11), and CCDC-824874 (14) contain the supplementary crystallographic data for this paper.

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