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 $(Me_2S)HB(C_6H_4)_2BH(SMe_2)$ (1) with 0.5 equiv of H₂O leads to formation of the borinic acid anhydride $[(Me_2S)HB(C_6H_4)_2B]_2O$ (2) and thereby provides access to the field of unsymmetrically substituted 9,10-dihydro-9,10-diboraanthracenes. Compound 2 reacts with tBuC=CH to give the corresponding vinyl derivative in an essentially quantitative conversion. Subsequent cleavage of the B-O-B bridge by LiAlH₄ 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 $[MesB(C_6H_4)_2B]_2O$ (7) is employed, which can be synthesized from BrB- $(C_6H_4)_2BBr$ (6) by treatment with 1 equiv of MesMgBr and subsequent hydrolysis. The reaction of 7 with LiAlH₄ in tetrahydrofuran (THF) furnishes Li[MesB(C₆H₄)₂BH₂] (8); hydride elimination with Me₃SiCl leads to formation of the THF adduct MesB- $(C_6H_4)_2BH$ (THF) (9·THF). Alternatively, 7 can be transformed into the

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bromoborane $MesB(C_6H_4)_2BBr$ (10) by treatment with BBr₃. A Br/H-exchange reaction between 10 and Et₃SiH yields the donor-free borane $MesB(C_6H_4)_2BH$ (9), which forms B-H-B bridged dimers $(9)_2$ in the solid state. The vinyl borane $MesB(C_6H_4)_2BC(H)=C(H)Mes$ (14) is accessible from MesC=CH and either 9. THF or 9. Compared with the related compound $Mes_2BC(H)=C(H)Mes$, the electronic absorption and emission spectra of 14 reveal bathochromic shifts of $\Delta\lambda(abs) = 17$ nm and $\Delta\lambda(em) =$ 74 nm, which can be attributed to the rigid, fully delocalized π framework of the $[MesB(C_6H_4)_2B]$ 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. $^{\left[4-7\right] }$

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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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201101701. It contains protocols for the derivatization of **2**; synthesis/analytical data of HOB- $(C_6H_4)_2BOH$, **5**, **6**, MesB $(C_6H_4)_2BOH$, **12**, **13a/13b**, and Mes₂BC(H) = C(H)Mes; discussion of the synthesis, NMR spectra and X-ray crystal structure analyses of **8** and **9**-THF; ¹H NMR spectroscopic monitoring of the reaction **7** \rightarrow **10**; details of the X-ray crystal structure analyses of ClB $(C_6H_4)_2BCI$, **6**, HOB $(C_6H_4)_2BOH$, and **11**; X-ray crystallographic files (CIF) of ClB $(C_6H_4)_2BCI$, HOB- $(C_6H_4)_2BOH$, **2**, **6**, **7**, **8**, **9**-THF, (9)₂, **10**, **11**, and **14**.

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tron system; 2) a rigid planar framework would guarantee maximum π overlap between the boron atoms and the aromatic substituents; 3) a cyclic structure should be most stable. All these requirements are met by the 9,10-dihydro-9,10-diboraanthracene framework, which can be integrated into π -electron systems either by nucleophilic substitution (cf. starting material **A**; Scheme 1) or by hydroboration re-



Scheme 1. Symmetrically substituted 9,10-dihydro-9,10-diboraanthracenes **A** and **B**; polymers **C** obtained by hydroboration polymerization of aromatic dialkynes with **B** (\mathbf{R} =H, OHex); 9*H*-9-borafluorene **D**, which is a monotopic relative of **B**; unsymmetrically substituted 9,10-dihydro-9,10-diboraanthracenes **E**.

actions (cf. starting material B; Scheme 1). 9,10-Dihalo-9,10dihydro-9,10-diboraanthracenes A have been extensively reported in the literature (X=Cl,^[9,10] Br;^[9,11,12] for optimized synthesis protocols, a comprehensive compilation of NMR data, and X-ray crystal structure analyses see the Supporting Information of this paper). In contrast, the parent compound **B** has only recently been described.^[13] Compound **B**, which forms a B-H-B bridged polymer $(\mathbf{B})_n$ in the solid state, can be used for hydroboration polymerization reactions (cf. product C; Scheme 1)^[13] either directly or after conversion into the more soluble dimethyl sulfide adduct (1; Scheme 2).^[14] Polymer C exhibits green photoluminescence, and various low molecular-weight analogues RC(H)= $C(H)B(C_6H_4)_2BC(H)=C(H)R$ are also strongly emissive.^[15] Moreover, appropriately designed 9,10-dihydro-9,10-diboraanthracenes (including B) act as reversible two-electron acceptors, the dianionic form being isoelectronic with anthracene.^[16] Due to these remarkable optoelectronic properties, the entire class of compounds is very promising for applications in organic solar cells (OSCs) or light-emitting devices (OLEDs).

To gain a deeper understanding of the optoelectronic properties of polymers of type C, it is desirable to have facile access to well-defined smaller model systems. We have already tested 9*H*-9-borafluorene (**D**; Scheme 1) as a truncated monotopic analogue of the ditopic 9,10-dihydro-



Scheme 2. Synthesis of compounds 2–5. Reagents and conditions: i) H_2O (0.5 equiv), THF/Me₂S, room temperature; ii) $tBuC\equiv CH$ (excess), C_6D_6 , room temperature; iii) LiAlH₄ (excess), $[D_8]THF$, room temperature.

9,10-diboraanthracene **B**. Compound **D**, which adopts a unique phenyl-bridged dimeric structure $(\mathbf{D})_2$, is not stable in solution over the long-term, but readily undergoes a ring-opening oligomerization reaction.^[17] Nevertheless, provided that freshly prepared samples of the compound are immediately used for further conversions, **D** is a valuable hydroboration reagent.

DFT calculations indicate that the ring-opening polymerization (ROP) of **D** is largely driven by the loss of antiaromaticity in the central borole ring.^[17] Monomeric 9,10-dihydro-9,10-diboraanthracene also possesses a formally antiaromatic central six-membered ring, but shows no tendency toward the ROP reaction. This observation, among others, led us to the conclusion that the electronic structure of 9*H*-9-borafluorene is still too dissimilar to that of 9,10-dihydro-9,10-diboraanthracene to regard the former as a well-designed end cap of low molecular-weight analogues of polymers **C**.

Herein, we describe protocols for the scalable generation of unsymmetrically substituted 9,10-dihydro-9,10-dibora-anthracenes **E** (Scheme 1) in which one boron atom is pro-

tected by a comparatively inert group, whereas the second boron atom bears a reactive substituent (for example, R^1 = OR, Mes; R^2 =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 $MesB(C_6H_4)_2BMes$. 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- $(C_6H_4)_2BC(H)=C(H)Mes$ and $Mes_2BC(H)=C(H)Mes$.

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 $S(2)Me_2$ 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	$C_{28}H_{30}B_4OS_2$	$C_{42}H_{38}B_4O$	$C_{21}H_{19}B_2Br$
M _r	489.88	601.96	372.89
color, shape	colorless, block	colorless, plate	yellow, plate
T [K]	173(2)	173(2)	173(2)
radiation, λ [Å]	Mo _{Kα} , 0.71073	Mo _{Kα} , 0.71073	Mo _{Kα} , 0.71073
crystal system	orthorhombic	triclinic	monoclinic
space group	$P2_{1}2_{1}2_{1}$	$P\bar{1}$	$P2_{1}/c$
a [Å]	9.6827(10)	8.8596(18)	15.0527(15)
b [Å]	15.4538(10)	11.720(2)	8.1450(6)
c [Å]	18.1279(11)	17.288(4)	14.8148(18)
α [°]	90	93.33(3)	90
β[°]	90	98.44(3)	93.863(9)
γ [°]	90	100.29(3)	90
V [Å ³]	2712.6(4)	1740.5(7)	1812.2(3)
Ζ	4	2	4
$ ho_{ m calcd} [m g cm^{-3}]$	1.200	1.149	1.367
F(000)	1032	636	760
$\mu \text{ [mm}^{-1}\text{]}$	0.216	0.065	2.266
crystal size [mm]	$0.35 \times 0.34 \times 0.27$	$0.27 \times 0.24 \times 0.11$	$0.27 \times 0.25 \times 0.13$
reflections collected	28017	13 930	7395
independent reflec-	5238 (0.1155)	6462 (0.0899)	3187 (0.0741)
tions (R_{int})			
data/restraints/pa-	5238/0/325	6462/0/430	3187/0/220
rameters			
GOF on F^2	0.986	0.807	0.923
$R_1, wR_2 [I > 2\sigma(I)]$	0.0829, 0.2005	0.0515, 0.0954	0.0521, 0.1101
R_1, wR_2 (all data)	0.1318, 0.2289	0.1259, 0.1108	0.0832, 0.1187
largest diff peak	0.565, -0.445	0.176, -0.193	0.907, -0.676
and hole [e Å ⁻³]			

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 (C_6D_6) of **2** is characterized by two resonances at $\delta = -3.0$ (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 ${}^{1}J(B,H)$ 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 C_6D_6 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 (2×2H) with a ³*J*-(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*BuC(H)=C(H)B(C₆H₄)₂BC(H)= C(H)*t*Bu, shows vinyl resonances at δ (¹H)=6.74 and 6.99 ppm (³*J*(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 $[D_8]THF$ (see the Supporting Information). In situ ¹¹B NMR spectroscopy revealed a triplet resonance at $\delta = -16.0$ ppm (¹J-(B,H) = 76 Hz) and a doublet at $\delta = -11.1 \text{ ppm} (^{1}J(B,H) =$ 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 ${}^{3}J(H,H)$ 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 $Li_2[H_2B(C_6H_4)_2BH_2]$ (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 HOB(C₆H₄)₂BOH and LiAlH₄ (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 $3/\text{LiAlH}_4$ indicate that, in principle, such borinic acid anhydrides are useful precursors for the synthesis of unsymmetrically substituted 9,10-dihydro-9,10diboraanthracenes, 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 $BrB(C_6H_4)_2BBr$ (6)^[22] is feasible with MesMgBr^[23] in toluene provided that high dilution is maintained. Nevertheless, MesB(C₆H₄)₂BBr obtained this way was always contaminated with the disubstitution product MesB(C₆H₄)₂BMes and was not readily isolable in pure form. It therefore turned out to be convenient to quench the reaction with H₂O, thereby generating the borinic acid anhydride **7**, which could subsequently be purified by column chromatography (yield: 76%; note: in the presence of H₂O, **7** is in equilibrium with the borinic acid MesB-(C₆H₄)₂BOH; see the Supporting Information).

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Scheme 3. Synthesis of compounds **7–9** THF. Reagents and conditions: i) 1) MesMgBr (1 equiv), toluene, -78 °C \rightarrow room temperature; 2) H₂O (excess), CHCl₃, room temperature; ii) LiAlH₄ (1 equiv), Et₂O/THF, room temperature; iii) Me₃SiCl (excess), Et₂O/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 ((B–O)_{av}=1.366(4) Å (**7**) vs. 1.341(7) Å (**2**); B-O-B=139.4(2)° (**7**) vs. 156.5(5)° (**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 [°], and dihedral angles [°]: 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).

alluded to above, these variations are most likely due to crystal packing forces. Similar to **2**, the two 9,10-dihydro-9,10-diboraanthracene fragments of **7** are nearly orthogonal to each other (C1-B1-C11//C31-B3-C41 = 74.5(2)°). The dihedral angles between each 9,10-dihydro-9,10-diboraanthracene moiety and its attached mesityl substituent amount to $80.3(2)^{\circ}$ and $85.8(2)^{\circ}$. As a result, the vacant p-orbitals of B2 and B4 are efficiently shielded by methyl groups, which explains the stability of the triorganylborane units during the quenching process and chromatographic workup.

The ¹¹B NMR spectrum of **7** contains two broad resonances at $\delta = 43.9$ (*BO*) and 70.2 ppm (*B*Mes) in the typical region^[21] of three-coordinate boron atoms. In the ¹H NMR spectrum, signals that can be assigned to the mesityl substituents appear at $\delta = 2.16$ (*o*-CH₃), 2.35 (*p*-CH₃), and 6.93 ppm (MesH-3,5). The general pattern of the phenylene resonances is largely the same as in **2**.

Synthesis of $MesB(C_6H_4)_2BX$ (X=H, Br): For the further derivatization of 7, we first tested the approach involving LiAlH₄ that was employed in the case of **3**. Lithium dihydridoborate 8 (Scheme 3) readily formed upon addition of two equivalents of LiAlH₄ in THF to a solution of 7 in Et₂O. In contrast to the analogous reaction of 3, in this case, we found no indication of any accompanying cleavage of B-C bonds. Addition of excess Me₃SiCl to a solution of 8 in Et₂O/THF led to the abstraction of one of the boron-bound hydride ions accompanied by formation of the THF adduct 9. THF (Scheme 3). Compound 9. THF smoothly hydroborates terminal alkynes $RC \equiv CH$ (stoichiometric ratio=1:1) even at room temperature with formation of the corresponding vinyl boranes (double hydroboration was never observed). However, a drawback of the LiAlH₄ mediated route to 9. THF was that 8, 9. THF, and even the hydroboration products are difficult to purify from contaminating aluminum salts, especially from the highly soluble complex [AlCl₃(THF)₂]. The preparation of analytically pure samples requires fractional crystallization, which is not only time consuming but also reduces the yields considerably. We therefore decided to look for an improved route to compounds of type 9. Thus synthesis details of 8 and 9. THF, a full NMR characterization and their X-ray crystal structure analyses are provided only as Supporting Information.

Because certain alkylaryl ethers are readily cleaved with BBr₃,^[24] we tested whether boronic acid anhydride 7 could also be transformed into a bromoborane upon treatment with BBr₃. Indeed, by stirring a solution of 7 in C₆H₆ with 4 equiv of BBr₃, clean and quantitative O/Br exchange was observed to take place within 31 h at room temperature (Scheme 4; see the Supporting Information for a series of ¹H NMR spectra that show the progress of the reaction). We note in this context that the resulting bromoborane MesB- $(C_6H_4)_2BBr$ (10) had already been observed as the main product of the reaction between BrB(C₆H₄)₂BBr (6) and MesMgBr, but could not be isolated in pure form from the reaction mixture. Generation of the air- and moisture-stable



Scheme 4. Synthesis of compounds (9)₂, **10–14**. Reagents and conditions: i) BBr₃ (2 equiv), C₆H₆, room temperature; ii) 1) 2,2'-bipy (1 equiv), C₆H₆/ toluene, room temperature; 2) NH₄PF₆ (excess), MeOH/H₂O, room temperature; iii) Et₃SiH (excess), room temperature; iv) RC=CH (1 equiv), C₆H₆, room temperature.

borinic acid anhydride **7** now enables convenient access to this important component.

Compound **10** was characterized by NMR spectroscopic and X-ray crystallographic analyses. The ¹¹B NMR spectroscopic data of the compound (δ =65.0 and 69.4 ppm) are very similar to those of **6** on the one hand (δ =63.8 ppm; see the Supporting Information) and MesB(C₆H₄)₂BMes on the other (δ =66.0 ppm^[18]). All ¹H and ¹³C NMR signals of **10** appear in the expected chemical shift regions and therefore are not discussed further. The solid-state structure of **10** (Figure 3, Table 1) shows essentially the same bond lengths and angles about B1 (B1–Br1=1.949(6) Å; C1-B1-C11= 123.8(5)°) and B2 (B2–C21=1.564(7) Å; C2-B2-C12= 119.1(5)°) as those of **6** (see the Supporting Information) and MesB(C₆H₄)₂BMes,^[18] respectively.

Bromoborane **10** cleanly undergoes substitution reactions with reagents as different as 2,2'-bipyridyl and Et₃SiH (Scheme 4). In the first case, we obtained a water-stable 2,2'-bipyridylboronium bromide salt, which was transformed into the hexafluorophosphate salt **11** by metathesis with NH₄PF₆. In the second case, crystals of the hydridoborane (**9**)₂ were grown from a solution of **10** in Et₃SiH.

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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 ¹¹B 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 ¹³C 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.

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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
M _r	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	$P2_1/n$	$P2_1/n$
a [Å]	7.2197(7)	16.133(4)
<i>b</i> [Å]	13.7689(13)	14.936(3)
c [Å]	16.990(2)	22.143(6)
α [°]	90	90
β[°]	91.156(9)	107.42(2)
γ [°]	90	90
V [Å ³]	1688.6(3)	5091(2)
Ζ	2	8
$ ho_{ m calcd} [m gcm^{-3}]$	1.156	1.143
F(000)	624	1872
$\mu [\mathrm{mm}^{-1}]$	0.063	0.063
crystal size [mm]	$0.37 \times 0.35 \times 0.35$	$0.28 \times 0.25 \times 0.12$
reflections collected	13 587	31262
independent reflections (R_{int})	2977 (0.1042)	8953 (0.3476)
data/restraints/parameters	2977/0/215	8953/15/624
GOF on F^2	0.926	0.719
$R_1, wR_2 [I > 2\sigma(I)]$	0.0532, 0.1209	0.0752, 0.1029
R_1, wR_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 $((C_6F_5)_2BH)_2$ (1.799(7) Å^[26]), but is comparable to that of the sterically congested molecule (Mes₂BH)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 ¹¹B 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 monomerdimer 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 ¹³C nuclei of the 9,10-dihydro-9,10-diboraanthracene core are comparatively deshielded and possess chemical

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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 C₆H₆ 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 [D₈]THF, the NMR spectra of (**9**)₂ are identical to those of compound **9**·THF.

Upon irradiation with UV light ($\lambda = 366$ nm) at room temperature, compound **9** shows a bright blue-green fluorescence in C₆H₆ 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 $MesB(C_6H_4)_2BH$: 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 (δ =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 (δ =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*): $\delta(^{1}H)=7.34$, 7.52 ppm, 2 × d,

 ${}^{3}J(\text{H},\text{H}) = 18.8 \text{ Hz}$). 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 H_2O gave **7** and $H_2C=C(H)Mes$ 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 $Mes_2BC(H) = C(H)Mes$: To compare the optical properties of the [MesB- $(C_6H_4)_2B$] chromophore with those of the commonly used [Mes₂B] group, we prepared the compound $Mes_2BC(H) = C(H)Mes$ (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 $Mes_2BC(H) = C(H)Mes$ in toluene.

Compound	$\lambda_{\max}(abs) [nm]$	$\lambda_{\max}(em) [nm]$
14	350	470 ($\lambda_{ex} = 350$)
$Mes_2BC(H) = C(H)Mes$	333	396 ($\lambda_{ex} = 335$)

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In toluene solution, $Mes_2BC(H)=C(H)Mes$ shows its longest wavelength absorption at $\lambda_{max}(abs) = 333$ nm; the emission maximum of the compound lies at $\lambda_{max}(em) = 396$ nm (excitation wavelength: $\lambda_{ex} = 335$ nm). Both λ_{max} values compare perfectly well with those of the closely related compound Mes₂BC(H)=C(H)Ph $(\lambda_{max}(abs) = 332 \text{ nm}/\lambda_{max}(em) =$ 398 nm in cyclohexane).^[30] Replacement of [Mes₂B] by $[MesB(C_6H_4)_2B]$ had only a moderate effect on the absorption band, which, in the latter case, appears at $\lambda_{max}(abs) =$ 350 nm (14). The emission band, however, undergoes a bathochromic shift of $\Delta \lambda = 74 \text{ nm}$ and is found at $\lambda_{max}(em) =$ 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., $(Me_2S)HB(C_6H_4)_2BH-(SMe_2)$; 1), the second from $BrB(C_6H_4)_2BBr$ (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 ($(Me_2S)HB(C_6H_4)_2B)_2O$ (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 $MesB(C_6H_4)_2BBr$, which is subsequently transformed into the air- and moisture-stable borinic acid anhydride ($MesB(C_6H_4)_2B)_2O$ (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- $(C_6H_4)_2BBr$ (10), which, in turn, reacts with Et₃SiH to furnish the borane MesB(C_6H_4)₂BH (9). Having both 9 and 10 available, it is now possible to conveniently attach the [MesB(C_6H_4)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 $7 \rightarrow 10 \rightarrow 9$, 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 $\Delta\lambda$ (abs) = 17 nm and $\Delta\lambda$ (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 borondoped π materials, for example, by replacing the monoalkyne MesC=CH with the aromatic dialkyne HC=C(*p*-C₆Me₄)C=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=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 $({}^{1}H/{}^{13}C{}^{1}H; C_{6}D_{6}: \delta = 7.15/128.0 \text{ ppm}; [D_{8}]THF: \delta = 3.58/67.4 \text{ ppm};$ 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 $\mathbf{1}$,^[14] $\mathbf{6}$,^[22] HOB(C₆H₄)₂BOH,^[32] 1,2- $C_6H_4(SiMe_3)_2$,^[12] MesMgBr,^[23] (Mes₂BH)₂,^[33] and MesC=CH^[29] were synthesized according to literature procedures.

Synthesis of 2: A calibrated solution of H2O in THF (6.1 M, 14.8 µL, 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 gasphase 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, ${}^{3}J(H,H) = 7.4$ Hz, ${}^{4}J(H,H) = 1.2$ Hz, 4H; H-2,7 or H-3,6), 7.43 (app. td, ${}^{3}J(H,H) = 7.4$ Hz, ${}^{4}J(H,H) = 1.3$ Hz, 4H; H-2,7 or H-3,6), 7.87 (d, ³*J*(H,H)=7.4 Hz, 4H; H-1,8 or H-4,5), 8.17 ppm (d, ${}^{3}J(H,H) = 7.4$ Hz, 4H; H-1,8 or H-4,5); ${}^{11}B$ NMR (96.3 MHz, C₆D₆): $\delta = -3.0 \ (h_{1/2} = 500 \ \text{Hz}; \text{BH}), 43.2 \ \text{ppm} \ (h_{1/2} = 1200 \ \text{Hz}; \text{BO}); \ ^{13}\text{C}{^{1}\text{H}} \text{NMR}$ (62.9 MHz, C₆D₆): δ=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 (3×15 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. $R_{\rm f}$ =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, ${}^{3}J(H,H) = 7.4$ Hz, ${}^{4}J$ -

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(H,H) = 1.4 Hz, 4H; H-2,7 or H-3,6), 7.15 (app. td, ${}^{3}J$ (H,H) = 7.4 Hz, ${}^{4}J$ -(H,H) = 1.4 Hz, 4H; H-2,7 or H-3,6), 7.86 (dd, ${}^{3}J$ (H,H) = 7.0 Hz, ${}^{4}J$ -(H,H) = 1.4 Hz, 4H; H-1,8 or H-4,5), 7.98 ppm (dd, ${}^{3}J$ (H,H) = 7.0 Hz, ${}^{4}J$ -(H,H) = 1.4 Hz, 4H; H-1,8 or H-4,5); ${}^{11}B{}^{1}H$ NMR (96.3 MHz, C₆D₆): δ =43.9 (h_{β} = 1500 Hz; BO), 70.2 ppm (br; BMes); ${}^{13}C{}^{1}H$ NMR (75.5 MHz, C₆D₆): δ = 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 C₄₂H₃₈B₄O (601.99): C 83.80, H 6.36; found: C 83.53, H 6.54.

Synthesis of 10: Neat BBr3 (32 µL, 83.2 mg, 0.33 mmol) was added at room temperature to 7 (50 mg, 0.08 mmol) in C₆H₆ (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, C₆D₆): $\delta = 1.96$ (s, 6H; o-CH₃), 2.30 (s, 3H; p-CH₃), 6.86 (m, 2H; MesH-3,5), 7.09 (app. td, ${}^{3}J(H,H) = 7.3$ Hz, ${}^{4}J(H,H) = 1.4$ Hz, 2H; H-2,7 or H-3,6), 7.19 (app. td, ${}^{3}J(H,H) = 7.3$ Hz, ${}^{4}J(H,H) = 1.4$ Hz, 2H; 2,7 or H-3,6), 7.61 (dd, ${}^{3}J(H,H) = 7.3$ Hz, ${}^{4}J(H,H) = 1.4$ Hz, 2H; H-1,8 or H-4,5), 8.52 ppm (dd. ${}^{3}J(H,H) = 7.3 \text{ Hz}, {}^{4}J(H,H) = 1.4 \text{ Hz}, 2H; H-1,8 \text{ or } H-4,5);$ ¹¹B{¹H} NMR (96.3 MHz, C₆D₆): $\delta = 65.0$, 69.4 ppm (BBr, BMes); ¹³C{¹H} NMR (62.9 MHz, C₆D₆): $\delta = 21.4$ (*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 C₆H₆ (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. [MesB(C6H4)2B(bipy)]Br was dissolved in MeOH (2 mL) and treated with an aqueous solution of NH₄PF₆ (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 H₂O (2 mL), and dried under vacuum. Single crystals that were suitable for X-ray diffraction were obtained by gas-phase diffusion of Et₂O into a CH₃CN solution of 11. Yield: 15.2 mg (51%; crystalline material). ¹H NMR (300.0 MHz, CD₃CN): $\delta = 2.12$ (s, 6H; *o*-CH₃), 2.40 (s, 3H; p-CH₃), 6.66 (dm, ${}^{3}J(H,H) = 7.0$ Hz, 2H; H-1,8 or H-4,5), 7.00 (m, 2H; MesH-3,5), 7.32 (app. td, ${}^{3}J(H,H) = 7.3$ Hz, ${}^{4}J(H,H) = 1.6$ Hz, 2H; H-2,7 or H-3,6), 7.36 (app. td, ${}^{3}J(H,H) = 7.3$ Hz, ${}^{4}J(H,H) = 1.6$ Hz, 2H; H-2,7 or H-3,6), 7.63 (dm, ³*J*(H,H) = 7.0 Hz, 2H; H-1,8 or H-4,5), 7.95 (ddd, ${}^{3}J(H,H) = 7.7 \text{ Hz}, {}^{3}J(H,H) = 5.7 \text{ Hz}, {}^{4}J(H,H) = 1.2 \text{ Hz}, 2 \text{ H}; \text{ bipyH-5,5'},$ 8.29 (ddd, ${}^{3}J(H,H) = 5.7 \text{ Hz}, {}^{4}J(H,H) = 1.3 \text{ Hz}, {}^{5}J(H,H) = 0.9 \text{ Hz}, 2 \text{ H};$ bipyH-6,6'), 8.67 (ddd, ${}^{3}J(H,H) = 8.1 \text{ Hz}$, ${}^{3}J(H,H) = 7.7 \text{ Hz}$, ${}^{4}J(H,H) =$ 1.3 Hz, 2H; bipyH-4,4'), 8.89 ppm (d app. t, ${}^{3}J(H,H) = 8.1$ Hz, ${}^{4}J(H,H) =$ ${}^{5}J(H,H) = 1.1 \text{ Hz}, 2 \text{ H}; \text{ bipyH-3,3'}; {}^{11}B{}^{1}H{} \text{NMR} (96.3 \text{ MHz}, \text{ CD}_{3}\text{CN}):$ $\delta = 5.5$ ($h_{\frac{1}{2}} = 250$ Hz; B-bipy), 69.5 ppm ($h_{\frac{1}{2}} = 1000$ Hz; BMes); ¹³C{¹H} NMR (100.6 MHz, CD₃CN): $\delta = 21.3$ (*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-- (PF_6)]⁺; elemental analysis calcd (%) for $C_{31}H_{27}B_2F_6N_2P$ (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 Et₃SiH (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 (C₆H₆): $\tilde{\nu}$ =2481 cm⁻¹ (B–H). ¹H NMR (400.1 MHz, C₆D₆): δ =2.03 (s, 6H; *o*-CH₃), 2.32 (s, 3H; *p*-CH₃), 6.89 (s, 2H; MesH-3,5), 7.12 (app. td, ³J(H,H)=7.4 Hz, ⁴J(H,H)=1.4 Hz, 2H; H-2,7 or H-3,6), 7.22 (app. td, ³J(H,H)=7.4 Hz, ⁴J(H,H)=

1.4 Hz, 2H; H-2,7 or H-3,6), 7.67 (d, ${}^{3}J(H,H) = 7.4$ Hz, 2H; H-1,8 or H-4,5), 7.93 ppm (d, ${}^{3}J(H,H) = 7.4$ Hz, 2H; H-1,8 or H-4,5); ${}^{11}B$ NMR (128.4 MHz, C₆D₆): $\delta = 71.0$ ppm ($h_{\frac{1}{2}} = 1500$ Hz; BMes, BH); ${}^{13}C{}^{1}H$ NMR (75.5 MHz, C₆D₆): $\delta = 21.4$ (*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 C₄₂H₄₀B₄ (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 C6H6 (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 [AlCl₃(THF)₂]. The two components were separated from each other by fractional crystallization from hexane at $4\,^{o}C~([AlCl_{3}(THF)_{2}])$ and $-30\,^{o}C~(14).$ Single crystals of 14 that were suitable for X-ray diffraction were grown by slow evaporation of a pentane/C₆H₆ 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, C₆D₆): $\delta = 2.08$ (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, ${}^{3}J(H,H) = 7.3$ Hz, ${}^{4}J(H,H) = 1.3$ Hz, 2H; H-2,7), 7.32 (app. td, ${}^{3}J(H,H) = 7.3$ Hz, ${}^{4}J(H,H) = 1.3$ Hz, 2H; H-3,6), 7.34 (d, ${}^{3}J(H,H) = 18.8$ Hz, 1H; BC(H) = C(H)), 7.52 (d, ${}^{3}J(H,H) =$ 18.8 Hz, 1 H; BC(H) = C(H)), 7.82 (d, ${}^{3}J(H,H) = 7.3$ Hz, 2H; H-1,8), 8.24 ppm (d, ${}^{3}J(H,H) = 7.3$ Hz, 2H; H-4,5); ${}^{11}B{}^{1}H{}$ NMR (128.4 MHz, C₆D₆): $\delta = 71.6$ ppm (shoulder at $\delta = 62.8$ ppm; BMes, BC(H) = C(H)); ¹³C{¹H} NMR (100.6 MHz, C₆D₆): $\delta = 21.1$ (*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; C₆H₄-BC), 147.5 (br; C_6H_4 -BC), 149.6 ppm (BC(H) = C(H)); elemental analysis calcd (%) for C32H32B2 (438.20): C 87.71, H 7.36; found: C 87.39, H 7.35. Note: Resonances belonging to the 2-mesitylethenyl substituent are marked with a prime (')

Crystal structure analyses: All crystals except those of HOB(C_6H_4)₂BOH were measured on a STOE IPDS-II diffractometer with graphite-monochromated Mo_{Ka} 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**_B), 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.

HOB(C₆H₄)₂BOH 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' = 0.895 h+1, the twin fraction refined to 0.302(7).

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(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. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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