

Synthesis, Coupling, and Condensation Reactions of 1,2-Diborylated Benzenes: An Experimental and Quantum-Chemical Study

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Abstract: 1,2-Bis(pinacolboryl)benzene (1,2-C₆H₄(Bpin)₂, **2**) was synthesized in preparatively useful yields from 1,2-C₆H₄Br₂, *i*PrO–Bpin, and Mg turnings in the presence of 1,2-C₂H₄Br₂ as an entrainer. Compound **2** is a versatile starting material for the synthesis of (un)symmetrically substituted benzenes (i.e., 1,2-C₆H₄(Ar¹)(Ar²)) through sequential Suzuki–Miyaura coupling reactions. Alternatively, it can be transformed into bis-borate Li₂[1,2-C₆H₄-(BH₃)₂] (**3**) through reduction with Li[AlH₄]. In the crystal lattice, the diethyl ether solvate **3**·OEt₂ establishes a columnar structure that is reinforced by an intricate network of B–(μ-H)–Li interactions. Hydride-abstraction from compound **3** with Me₃SiCl leads to the transient ditopic borane 1,2-C₆H₄-(BH₂)₂, which can either be used in situ

for subsequent hydroboration reactions or trapped as its stable NMe₂Et diadduct (**6**). In SME₂ solution, the putative diadduct 1,2-C₆H₄(BH₂·SME₂)₂ is not long-term stable but rather undergoes a condensation reaction to give 9,10-dihydro-9,10-diboraanthracene, HB(μ-C₆H₄)₂BH, and BH₃. 9,10-Dihydro-9,10-diboraanthracene was isolated from the reaction mixture as its SME₂ monoadduct (**7**), which dimerizes in the solid state through two B–H–B bridges ((**7**)₂, elucidated by X-ray crystallography). In contrast, hydride-abstraction from compound **3** in THF or CH₂Cl₂ provides the unique *exo*-adduct

H₂B(μ-H)₂B(μ-C₆H₄)₂B(μ-H)₂BH₂ (**8**, elucidated by X-ray crystallography). Quantum-chemical calculations on various conceivable isomers of [1,2-C₆H₄-(BH₂)₂]₂ revealed that compound **8** was the most stable of these species. Moreover, the calculations confirmed the experimental findings that the NMe₂Et diadduct of 1,2-C₆H₄(BH₂)₂ is significantly more stable than the corresponding SME₂ complex and that the latter complex is not able to compete successfully with borane-dimerization and -condensation. The reaction cascade in SME₂, which proceeds from 1,2-C₆H₄(BH₂)₂ to the observed adducts of HB(μ-C₆H₄)₂BH, has been elucidated in detail and the important role of B–C–B-bridged intermediates has been firmly established.

Keywords: boranes • borates • condensation • Grignard reaction • quantum chemistry

Introduction

Borylated arenes are key starting materials for Suzuki–Miyaura coupling reactions^[1] and, therefore, have applications that range from the synthesis of natural products^[2] to the preparation of polycyclic aromatic hydrocarbons (PAHs),^[3,4] which are relevant for organic electronics.^[5–11] Moreover, arylboranes are also interesting in their own right because they can serve as metallocene-catalyst activators,^[12] catalysts,^[13–17] chemosensors,^[18,19] or as luminescent dyes.^[20–25]

The scope of arylboranes can be further expanded when two (or more) boryl substituents are introduced into the same arene system: With respect to synthesis, such compounds offer the possibility of performing double cross-coupling reactions with aromatic (di)halides as a synthetic route to functionalized PAHs (e.g., oligophenyls, phenanthrenes, and dibenzo[*g,p*]chrysenes).^[26–29] In the case of boron-based (co)-catalysts, cooperative binding can lead to improved catalytic performance^[30–36] and, in the case of chemosensors, signal-amplification has been reported.^[37–41]

Therefore, efficient synthetic routes to oligoborylated arenes are in great demand, especially to afford arenes that contain boryl groups at adjacent positions on the ring. 1,2-Diborylbenzenes are prototypical examples of vicinal diborylated arenes and various different strategies for their preparation have been developed; however, many of these syntheses suffer from distinct disadvantages, such as: 1) The reaction of 1,2-C₆H₄(EMe₃)₂ (E = Si, Sn) with BCl₃ provides a route to 1,2-bis(dichloroboryl)benzene (1,2-C₆H₄-(BCl₂)₂),^[42] however, BCl₃ is a hazardous, highly corrosive chemical and 9,10-dichloro-9,10-dihydro-9,10-diboraanthracene (ClB(μ-C₆H₄)₂BCl), as well as partially methylated boranes, are often formed as major byproducts of the Si/B-ex-

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Supporting information for this article, including single-crystal X-ray analysis of compound **2** and RB(μ-C₆H₄)(μ-pzSiMe₃)₂BR (R: C(H)=C(H)*t*Bu), quantum-chemical data, and X-ray crystallographic data of compounds **2**, **3**·OEt₂, (**7**)₂, **8**, and RB(μ-C₆H₄)(μ-pzSiMe₃)₂BR (R: C(H)=C(H)*t*Bu), is available on the WWW under <http://dx.doi.org/10.1002/chem.201201547>.

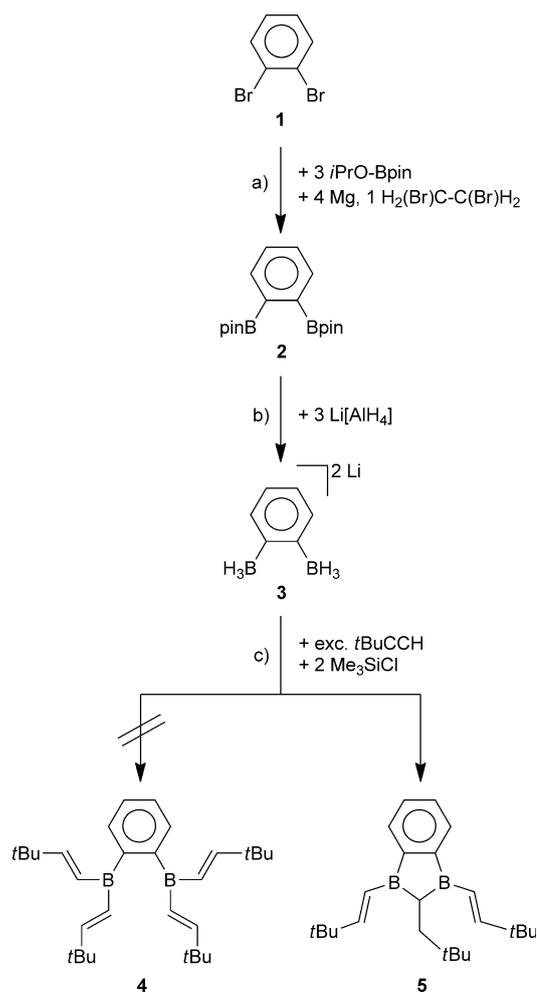
change reaction.^[43] 2) The electrochemical reduction of 1,2-dihalobenzenes (1,2-C₆H₄X₂; X = Cl, Br, I) at a consumable Mg anode in the presence of pinacolborane (HBpin) provides a mixture of 1,2-C₆H₄(Bpin)₂ (<20%), 1,2-C₆H₄(Bpin)(X), and C₆H₅(Bpin).^[44] 3) The cobalt-catalyzed cyclo-trimerization of alkynylboranes gives mixtures of the 1,2,4- and the 1,3,5-isomers;^[45,46] one remarkable exception is the reaction of catB–C≡C–Bcat with [CpCo(CO)₂], which leads to hexaborylbenzene C₆(Bcat)₆ (H₂cat = catechol).^[47] 4) The Pd-catalyzed diborylation of benzyne, which starts from 1,2-C₆H₄(OTf)(SiMe₃) and pinB-Bpin, is costly and requires the purification of the crude product by recycling gel-permeation chromatography; therefore, it has only been applied on a milligram scale.^[48,49] Suginome and co-workers have reported another Pd-catalyzed 1,2-borylation reaction, which leads to 1,2-C₆H₄(Bdans)(Bpin) in 75% yield on a gram scale, but also uses expensive starting materials (i.e., 1,2-C₆H₄(Bdans)(Br) and pinB-Bpin; H₂dans = 1,8-diaminonaphthalene).^[26] A more-economically viable approach has been developed by Percec and co-workers, which relies on a Zn-activated Ni⁰ catalytic system that transforms 1,2-C₆H₄(X)₂ with neopentylglycolborane (HBnpg) into 1,2-C₆H₄(Bnpg)₂ in yields of 76% (X = Cl) and 83% (X = Br).^[50]

Herein, we report a time- and cost-efficient uncatalyzed Grignard route to 1,2-bis(pinacolboryl)benzene (1,2-C₆H₄(Bpin)₂, **2**; Scheme 1). This route uses the “entrainment method”^[51–53] and provides a convenient access to multigram quantities of the product. With the aim of developing new building blocks for boron-containing optoelectronic materials,^[24,25] we have subsequently used compound **2** to synthesize the ditopic trihydroborate Li₂[1,2-C₆H₄(BH₃)₂] (**3**; Scheme 1) and we have investigated the chemical properties of the corresponding ditopic borane 1,2-C₆H₄(BH₂)₂ by experimental and quantum-chemical means.

Results and Discussion

Synthesis and characterization of 1,2-C₆H₄(Bpin)₂ (2**):** In analogy to our recently reported synthesis of 1,2-bis(trimethylsilyl)benzene,^[53] compound **2** was prepared from 1,2-dibromobenzene (**1**), isopropoxy-pinacolborane, and Mg turnings in the presence of 1,2-dibromoethane as an entrainer (Scheme 1). This entrainment method^[51] ensured a continuous activation of the Mg surface by a dropwise addition of the entrainer compound into the reaction mixture. In this case, a stoichiometric ratio of 1,2-dibromoethane/1,2-dibromobenzene was required for optimum conversion into the target compound (**2**). After aqueous workup, analytically pure compound **2** was obtained by recrystallization of the crude product from *n*-pentane in 40% yield. All of the NMR spectroscopic data of compound **2** were in full agreement with published data;^[48] X-ray structural analysis of compound **2** is provided in the Supporting Information.

Yoshida et al. have previously demonstrated that compound **2** is a valuable starting material for the synthesis of symmetrically (i.e., 1,2-C₆H₄(Ar)₂; Ar = aryl) as well as un-



Scheme 1. Synthesis of compounds **2–5**: a) THF, 20–40°C, until the addition of the entrainer was complete, then reflux, 4 h; b) Et₂O/*n*-pentane, 0°C (2 h) to room temperature (16 h); c) Me₂S, room temperature, 36 h.

symmetrically substituted benzenes (i.e., 1,2-C₆H₄(Ar¹)(Ar²)) through (sequential) Suzuki–Miyaura coupling reactions.^[48,49,54] To confirm that compound **2** obtained by using our Grignard procedure could be used for similar purposes, we tested it in the Pd-catalyzed double-arylation reaction with 2,2'-dibromobiphenyl and obtained triphenylene in 75% yield (THF, 60°C, [Pd(PPh₃)₄], 48 h).

Synthesis and characterization of Li₂[1,2-C₆H₄(BH₃)₂] (3**):** Bis-borate **3** is accessible by the treatment of compound **2** with Li[AlH₄] in Et₂O/*n*-pentane (Scheme 1). Crystals of compound **3**·OEt₂ that were suitable for X-ray crystallography were grown by the gas-phase diffusion of *n*-hexane into a solution of the bis-borate in Et₂O/*n*-pentane.

The ¹¹B NMR spectrum of compound **3** is characterized by a quartet at δ = –26.6 ppm with a ¹J(¹¹B,H) coupling constant of 79 Hz (cf. Li[PhBH₃]: δ(¹¹B) = –26.4 ppm, ¹J(¹¹B,H) = 76 Hz^[55]). The corresponding boron-bound hydride substituents give rise to a 1:1:1:1 quartet at δ = 1.03 ppm in the ¹H NMR spectrum. This value is in perfect

agreement with those of the related *p*- and *m*-phenylene-bridged derivatives, that is, $\text{Li}_2[1,4\text{-C}_6\text{H}_2(n\text{-hexyl})_2(\text{BH}_3)_2]$ ($\delta(^1\text{H})=1.02\text{ ppm}^{[56]}$) and $\text{Li}_3[1,3,5\text{-C}_6\text{H}_3(\text{BH}_3)_3]$ ($\delta(^1\text{H})=1.07\text{ ppm}^{[57]}$). Therefore, we note a surprisingly low influence of the distance between the two negatively charged trihydroborate groups on their NMR properties.

The crystal lattice of compound **3**·OEt₂ (Figure 1; Table 1) contains parallel columns $\{\text{Li}[1,2\text{-C}_6\text{H}_4(\text{BH}_3)_2]\}_\infty$, which consist of alternating Li⁺ ions and $[1,2\text{-C}_6\text{H}_4(\text{BH}_3)_2]^{2-}$ ligands: each Li1 atom is coordinated by four trihydroborate moieties in a double-chelating manner^[58,59] and each $[1,2\text{-C}_6\text{H}_4(\text{BH}_3)_2]^{2-}$ ligand bridges two Li1 atoms. All $\{\text{Li}[1,2\text{-C}_6\text{H}_4(\text{BH}_3)_2]\}_\infty$ stacks contain a 2-fold screw axis. As a result, two adjacent phenylene rings within the same column point in opposite directions, with dihedral angles of 5.7(1)°. Each Li2 atom binds to three different trihydroborate substituents and to one Et₂O ligand. The Li2···B1 and Li2···B2C interactions reinforce the $\{\text{Li}[1,2\text{-C}_6\text{H}_4(\text{BH}_3)_2]\}_\infty$ stacks, whilst the Li2···B2B contacts connect two columns. The four Li1···B distances are in the range 2.480(4)–2.666(4) Å and the three Li2···B distances are between 2.479(4)–2.671(4) Å. According to Edelstein's^[60] correlation of the metal–boron distances as a measure of the denticity of a trihydroborate group, B···Li distances of about 2.50 Å are typical of an $\eta^2\text{-RBH}_3\text{-Li}$ coordination mode.^[56,57] However, an inspection of the geometric constraints within the crystal structure of compound **3**·OEt₂ reveals that some of these bonds are better characterized as $\eta^1\text{-RBH}_3\text{-Li}$ (Figure 2). Additional Li1– π interactions are indicated by short Li1···C1 and Li1···C2 distances of 2.408(3) Å and 2.547(4) Å, respectively.

Reactivity of 1,2-C₆H₄(BH₂)₂ in the presence and absence of olefins or Lewis bases: To test the reactivity of 1,2-C₆H₄(BH₂)₂ toward hydroboration, we generated the free ditopic borane in situ by treating a suspension of compound **3**·OEt₂ in Me₂S with Me₃SiCl in the presence of 15 equivalents of *t*BuC≡CH (Scheme 1). An NMR spectroscopic investigation revealed the formation of cyclic hydroboration product **5** as the dominant species. The initially expected 1,2-bis(divinylboryl)benzene (**4**) could not be isolated; it was not even unequivocally identifiable in the reaction mixture. For a targeted synthesis of compound **5**, the experiment was repeated with 3.5 equivalents of *t*BuC≡CH. The compound shows a single ¹¹B{¹H} NMR resonance at $\delta=71.6\text{ ppm}$, which is in the typical region for triorganylboranes.^[61] The ¹H NMR spectrum of compound **5** features two doublets at $\delta=6.73\text{ (2H)}$ and 7.12 ppm (2H; ³*J*(H,H)=17.8 Hz), which are characteristic of two *E*-alkenyl substituents. A doublet at $\delta=2.03\text{ ppm}$ (2H) and a triplet at $\delta=2.14\text{ ppm}$ (1H, ³*J*(H,H)=5.3 Hz) arise from the central diborylalkane moiety. After the addition of potassium 4-(trimethylsilyl)pyrazolide (K[*pz*SiMe₃]) to a solution of compound **5** in THF, MS (ESI[−]) analysis showed a single peak at *m/z*=487.6, which

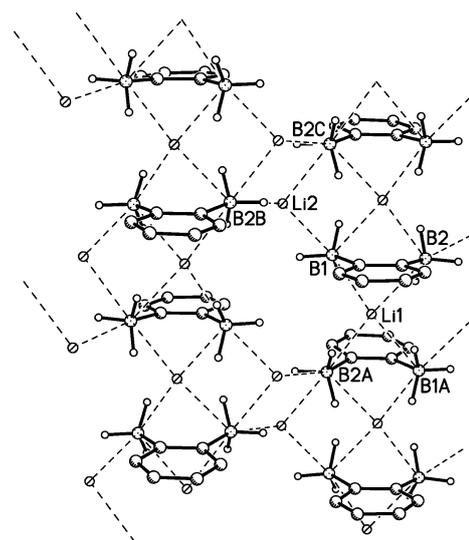


Figure 1. Crystal packing of compound **3**·OEt₂; H atoms (except on boron) and Et₂O ligands are omitted for clarity. Selected distances [Å]: Li1···B1 2.480(4), Li1···B2 2.666(4), Li1···B1A 2.594(4), Li1···B2A 2.573(4), Li2···B1 2.479(4), Li2···B2B 2.496(4), Li2···B2C 2.671(4), Li1···C1 2.408(3), Li1···C2 2.547(4), Li1···Li2A 3.381(5), Li2···Li1C 3.381(5), Li2···Li2D 3.313(6). Symmetry transformations that were used to generate equivalent atoms: A: $-x+1, y-1/2, -z+1/2$; B: $x, -y+3/2, z+1/2$; C: $-x+1, y+1/2, -z+1/2$; D: $-x+1, -y+2, -z+1$.

Table 1. Crystallographic data for compounds **3**·OEt₂, (**7**)₂, and **8**.

	3 ·OEt ₂	(7) ₂	8
formula	C ₁₀ H ₂₀ B ₂ Li ₂ O	C ₂₈ H ₃₂ B ₄ S ₂	C ₁₂ H ₁₆ B ₄
<i>M_w</i>	191.76	475.90	203.49
color, shape	colorless, plate	colorless, block	colorless, needle
<i>T</i> [K]	173(2)	173(2)	173(2)
radiation, λ [Å]	Mo _{Kα} , 0.71073	Mo _{Kα} , 0.71073	Mo _{Kα} , 0.71073
crystal system	monoclinic	triclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 1	<i>C</i> 2/ <i>m</i>
<i>a</i> [Å]	12.058(2)	6.9647(4)	11.3511(16)
<i>b</i> [Å]	8.0725(11)	9.5417(6)	15.0339(16)
<i>c</i> [Å]	13.621(3)	12.0420(7)	7.0878(11)
α [°]	90	107.517(5)	90
β [°]	112.194(14)	97.549(4)	105.470(11)
γ [°]	90	111.210(5)	90
<i>V</i> [Å ³]	1227.6(4)	684.97(7)	1165.7(3)
<i>Z</i>	4	1	4
<i>D</i> _{calcd} [g cm ^{−3}]	1.038	1.154	1.159
<i>F</i> (000)	416	252	432
μ [mm ^{−1}]	0.058	0.209	0.060
crystal size [mm]	0.18 × 0.16 × 0.09	0.33 × 0.32 × 0.27	0.46 × 0.08 × 0.08
total refls	9122	22256	6315
unique refls (<i>R</i> _{int})	2156 (0.1010)	3516 (0.0457)	1073 (0.0783)
data/restraints/parameters	2156/0/160	3516/0/164	1073/0/95
GOF on <i>F</i> ²	0.927	1.107	0.999
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0492, 0.1048	0.0317, 0.0835	0.0473, 0.1102
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0863, 0.1189	0.0335, 0.0847	0.0631, 0.1164
largest diff peak and hole [e Å ^{−3}]	0.170, −0.137	0.312, −0.264	0.233, −0.260

can be assigned to the pyrazolide adduct of compound **5** (for more information on the use of pyrazolides in MS investigations of ditopic boron Lewis acids, see reference [62]). Attempts to crystallize compound **5** or

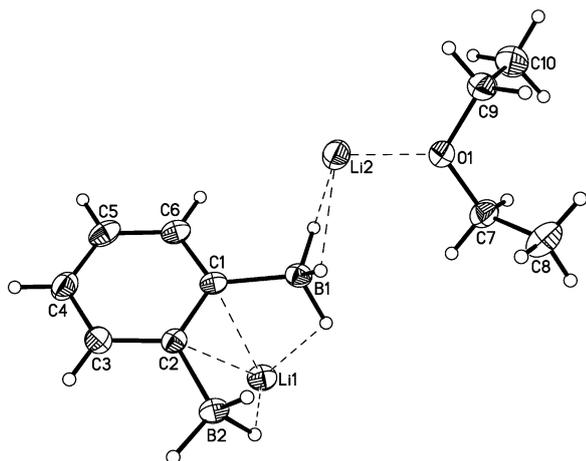
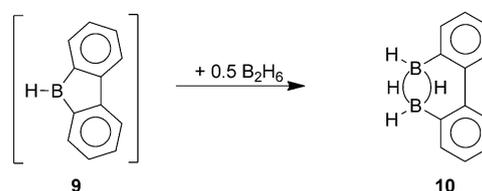
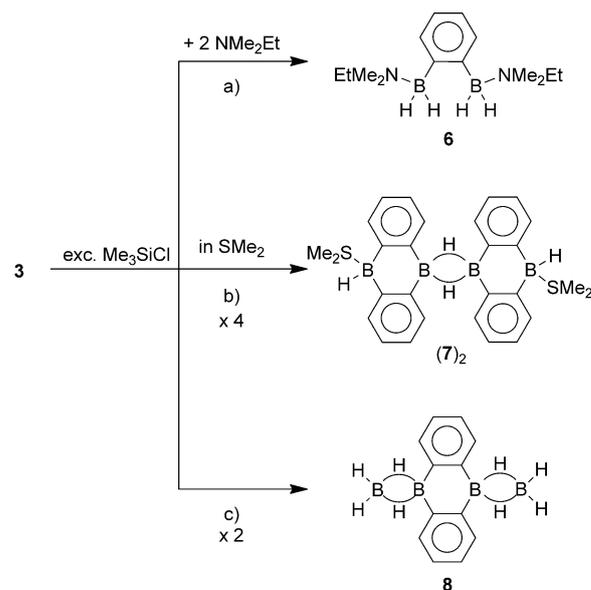


Figure 2. Plot of the asymmetric unit of compound **3**-OEt₂ in the solid state; ellipsoids are set at 50% probability. Selected bond lengths [Å] and angles [°]: B1–C1 1.626(3), B2–C2 1.618(3), Li2–O1 1.940(4); B1–C1–C2 123.1(2), B2–C2–C1 122.1(2).

K[**5**-pzSiMe₃] failed. However, leaving a solution of K[**5**-pzSiMe₃] in C₆D₆ to slowly evaporate at room temperature in an open NMR tube afforded crystals of the 1,2-phenylene-bridged pyrazabole RB(μ-C₆H₄)(μ-pzSiMe₃)₂BR (R: C(H)=C(H)*t*Bu). Thus, under these (hydrolytic) conditions, the methanediide bridge in compound **5** was replaced by a pyrazolide linker, thereby generating an uncharged B–N analogue of triptycene (for X-ray structure analysis, see the Supporting Information).^[63]

Next, we tried to trap the transient borane, 1,2-C₆H₄-(BH₂)₂, by adding selected Lewis bases. The amine adduct (**6**) is readily accessible through hydride-abstraction from compound **3**-OEt₂ with Me₃SiCl in the presence of two equivalents of NMe₂Et (Scheme 2). Under an inert atmosphere, a solution of compound **6** in CD₂Cl₂ is stable for days at room temperature (monitored by NMR spectroscopy). The ¹¹B NMR spectrum of compound **6** shows one poorly resolved triplet at δ = –1.3 ppm (¹J(¹¹B,H) ≈ 90 Hz). The BH₂ protons give a broad signal at δ(¹H) = 2.66 ppm and the ratio of the integrals of the aromatic/aliphatic resonances in the ¹H NMR spectrum is in agreement with the proposed di-adduct structure.

In contrast to NMe₂Et, SMe₂ is not able to stabilize 1,2-C₆H₄(BH₂)₂ in solution for extended periods of time. Monitoring a solution of in situ generated 1,2-C₆H₄(BH₂)₂ in SMe₂ by ¹¹B NMR spectroscopy reveals a broadened doublet at δ = 2.1 ppm and a quartet at δ = –19.1 ppm (¹J(¹¹B,H) = 105 Hz), thus indicating the formation of the known SMe₂ diadduct (Me₂S)(H)B(μ-C₆H₄)₂B(H)(SMe₂)^[62] of 9,10-dihydro-9,10-diboraanthracene (DBA), together with BH₃·SMe₂.^[61] Moreover, we observe two poorly resolved triplets at δ = –6.9 and –8.4 ppm. At the start of the investigation, the two triplets are the dominant signals; however, their relative intensities decrease over several hours, thus suggesting that these resonances belong to short-lived aryl-BH₂·SMe₂ species. To shed more light on the reaction be-



Scheme 2. Synthesis of compounds **6–8** and insertion of BH₃ into 9H-9-borafluorene (**9**) to give compound **10**: a) toluene, room temperature, 12 h; b) Me₂S, room temperature, 14 h; c) CH₂Cl₂, room temperature, 19 h.

tween compound **3**-OEt₂ and Me₃SiCl in SMe₂, we repeated it on a preparative scale. After removal of the formed LiCl, the colorless filtrate was stored at 4 °C until single crystals had grown. X-ray analysis revealed a C_i-symmetric dimer of the SMe₂ monoadduct of DBA (i.e., compound (**7**)₂; Scheme 2, Figure 3, top). The dimer is held together by two central B–H–B two-electron-three-center bonds. The resulting interdimer B2...B2# distance is 1.817(2) Å, which compares well with the respective intermonomer B...B distances in polymeric DBA ((DBA)_n; Figure 3, bottom; average value: 1.818(12) Å^[64]). Furthermore, similar to (DBA)_n, the monomeric units of compound (**7**)₂ deviate significantly from planarity with a dihedral angle of 135.8° between the two phenylene rings (cf. (DBA)_n: 133.8°). It has been suggested that monomer-folding in (DBA)_n is the result of otherwise-unfavorable steric interactions between adjacent DBA moieties and the same reasoning is probably true for compound (**7**)₂.^[64,65] Compound (**7**)₂ features B1–S1 bond lengths of 1.997(1) Å, which are somewhat shorter than in the corresponding *syn*-diadduct of DBA, that is, (Me₂S)(H)B(μ-C₆H₄)₂B(H)(SMe₂) (average value: 2.031(2) Å^[62]).

In an attempt to record NMR spectra of compound (**7**)₂, one large crystal was treated with [D₈]THF in an NMR tube. The volume of the crystal gradually decreased, whilst

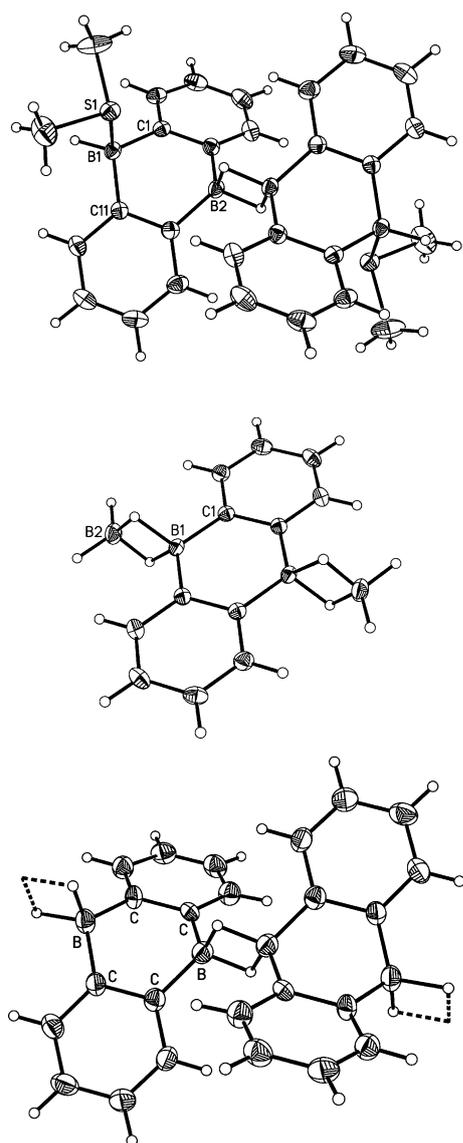


Figure 3. Molecular structures of compounds $(7)_2$ (top), 8_A (middle), and $(DBA)_n$ (bottom) in the solid state; ellipsoids in structures $(7)_2$ and 8_A are set at 50% probability. Selected distances [\AA] and angles [$^\circ$] for compound $(7)_2$: B1–S1 1.997(1), B1–C1 1.602(2), B1–C11 1.604(1), B2···B2# 1.817(2); C1–B1–C11 112.5(1), Ar(C1)//Ar(C11) 135.8. Symmetry transformation that was used to generate equivalent atoms: #: $-x+1, -y+1, -z+1$. 8_A : B1–C1 1.577(2), B1···B2 1.793(3); C1–B1–C1# 120.6(2). Symmetry transformation that was used to generate equivalent atoms: #: $x, -y, z$.

part of it went into the liquid phase and another part was transformed into a colorless powder. The supernatant gave characteristic NMR spectra of $(\text{Me}_2\text{S})(\text{H})\text{B}(\mu\text{-C}_6\text{H}_4)_2\text{B}(\text{H})(\text{SMe}_2)^{[62]}$ and the precipitate was identified as $(\text{DBA})_n$.^[64] This result leads to the conclusion that, upon dissolution, compound $(7)_2$ undergoes a redistribution of its SMe_2 ligands so that two of them are attached to the same DBA molecule, whilst the other molecule stabilizes itself by polymerization through B–H–B two-electron-three-center bonds.

We isolated crystals of the adduct between DBA and two equivalents of BH_3 from mixtures of compound 3-OEt_2 and

Me_3SiCl in either THF or CH_2Cl_2 (**8**; Scheme 2, Table 1). The same compound is obtained when the solution in SMe_2 (see above) is evaporated almost to dryness and the residue is recrystallized from C_6H_6 . Compound **8** is insoluble at room temperature in all common non-donating solvents, which precludes its NMR spectroscopic investigation. A solution of compound **8** in pyridine exclusively revealed resonances of the known pyridine diadduct of DBA^[64] and of $\text{BH}_3\cdot\text{pyridine}$.^[61] The crystal lattice of compound **8** contains two crystallographically independent molecules in the asymmetric unit (8_A and 8_B). Both molecules possess an inversion center, a mirror plane, and a 2-fold rotation axis, which lead to a crystallographically imposed planar 9,10-diboraanthracene core. Because all key metric parameters of molecules 8_A and 8_B are very similar, only structure 8_A will be discussed herein (Figure 3, middle). Structure 8_A can be regarded as a low-molecular-weight analogue of $(\text{DBA})_n$.^[64–66] We observe a B1···B2 distance of 1.793(3) \AA and a C1–B1–C1# bond angle of 120.6(2) $^\circ$, as compared to an average B···B distance of 1.818(12) \AA and an average C–B–C bond angle of 114.8(4) $^\circ$ in $(\text{DBA})_n$.

Compound **8** represents the first crystallographically characterized organyldiborane(6) with the unsymmetrical $\text{R}_2\text{B}(\mu\text{-H})_2\text{BH}_2$ structure. The fact that, in compound **8**, a BH_3 molecule coordinates in an exocyclic manner to the DBA framework is in striking contrast to the behavior of B_2H_6 toward the in situ generated 9H-9-borafluorene (**9**): In this latter case, the insertion of BH_3 into one B–C bond is the preferred reaction pathway and gives endocyclic adduct **10**.^[67,68] (Scheme 2).^[59,68,69]

The generation of compound **8** from two equivalents of 1,2- $\text{C}_6\text{H}_4(\text{BH}_2)_2$ formally represents a substituent-redistribution reaction with complete conservation of the number of atoms. As mentioned above, monitoring a solution of 1,2- $\text{C}_6\text{H}_4(\text{BH}_2)_2$ in SMe_2 by ^{11}B NMR spectroscopy indicated that an excess of the Lewis base can stabilize the separated DBA and BH_3 species as their respective thioether adducts. However, B–H–B two-electron-three-center bonding, assisted by the poor solubility of compound **8**, is obviously able to successfully compete with σ -adduct formation. The assembly of a DBA scaffold from 1,2- $\text{C}_6\text{H}_4(\text{BH}_2)_2$ proceeds within minutes at room temperature. In contrast, the conventional synthesis of 9,10-dibromo-9,10-dihydro-9,10-diboraanthracene requires heating of 1,2-bis(trimethylsilyl)benzene with excess BBr_3 in a sealed glass ampoule (120 $^\circ\text{C}$, 6 d, 54% yield).^[65]

Furthermore, the related condensation reaction of 1,1'- $\text{fc}(\text{BH}_2)_2$ in SMe_2 provides the BH-bridged poly(ferrocenylene) $[-\text{fc}-\text{B}(\text{H})-]_n$ with the liberation of $\text{BH}_3\cdot\text{SMe}_2$ ($\text{fc} = (\text{C}_5\text{H}_4)_2\text{Fe}$).^[58,70,71] Despite numerous efforts, we have so far not been able to provide evidence for the formation of 8-type cyclic dimer **11**, even though [1.1]diborataferrocenophanes (**12**) are known (Figure 4).^[72,73] Thus, the preorganized rigid structure of 1,2- $\text{C}_6\text{H}_4(\text{BH}_2)_2$ appears to be an important factor in promoting the formation of cyclic dimers rather than polymerization.

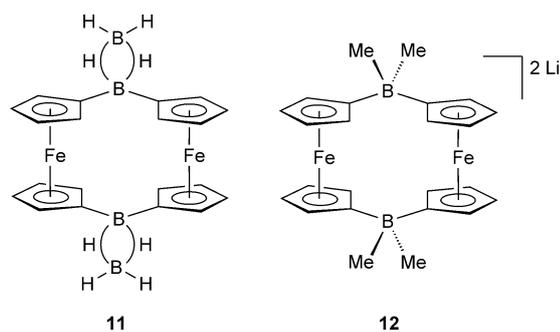


Figure 4. Hypothetical cyclic dimer (**11**) of the diborylated ferrocene 1,1'-fc(BH₂)₂ and the crystallographically characterized [1.1]diborataferrocene (**12**).

DFT calculations: To establish the underlying thermochemistry in the reactivity of 1,2-C₆H₄(BH₂)₂ (Figure 5, **A**), we

first investigated the relative stabilities of several dimers of structure **A** and of its mono- and diadducts with the Lewis bases NMe₂Et and SMe₂ by using quantum-chemical methods. The structures of the resulting minima are shown in Figure 5.

In the absence of coordinating donor bases, compound **A** compensates for its inherent electron deficiency by undergoing dimerization; thus, we explored the relative free energies of various conceivable species. Initial B–H/B–H interactions^[68] between two monomers (**A**) lead to the formation of two isomeric dimers (**B** and **C**), both of which feature two classical B–H–B bridges. Compared to the dimerization of BH₃ to B₂H₆, for which $\Delta G_R = -27.9$ kcal mol⁻¹, the exergonicity of these steps is only moderate (**B**: $\Delta G_R = -16.0$ kcal mol⁻¹, **C**: $\Delta G_R = -17.0$ kcal mol⁻¹). Clearly, this result is a consequence of significant intramolecular aryl–BH₂ π -conjugation in the planar structure **A** moderating the

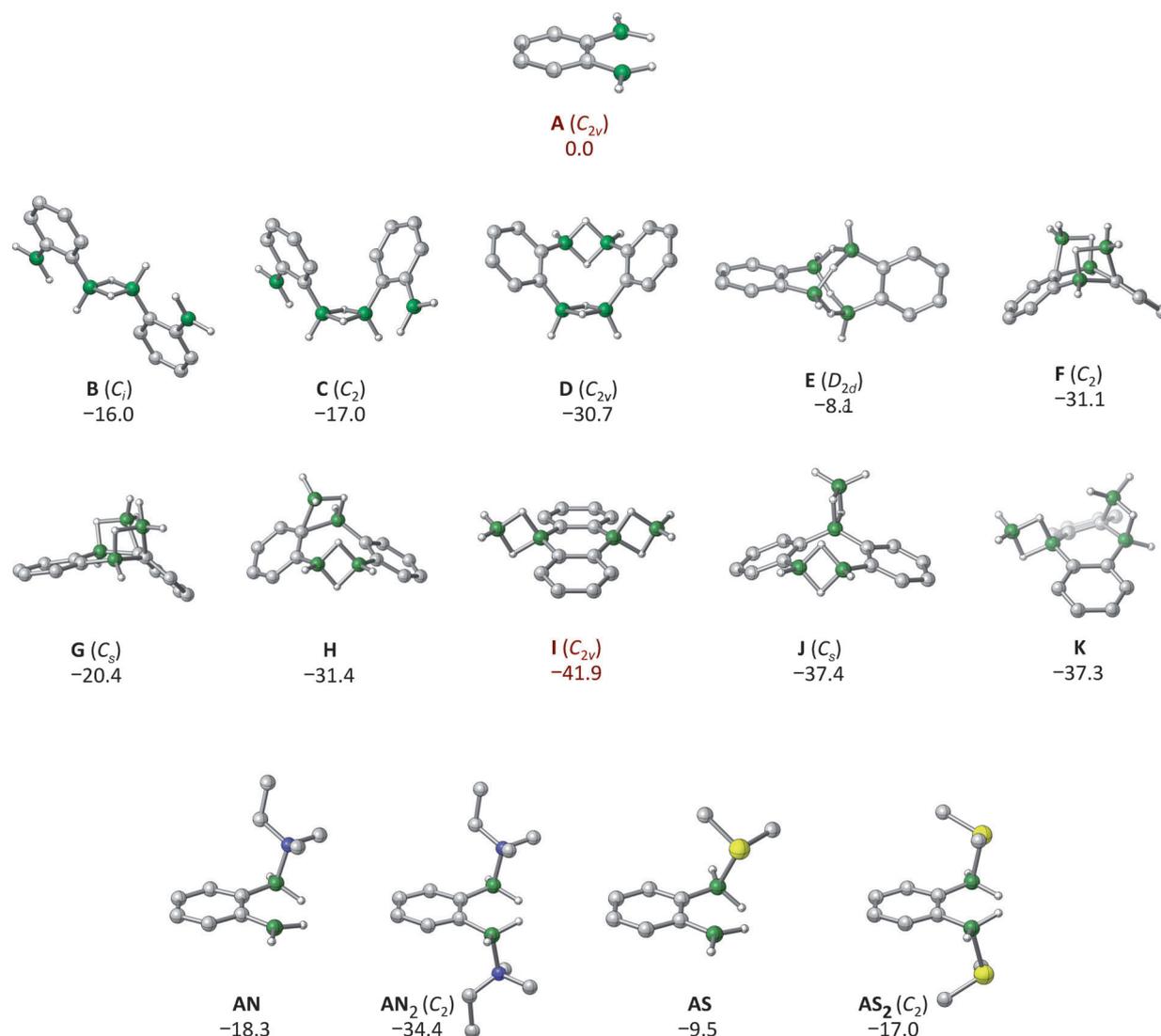


Figure 5. Optimized molecular structures of dimeric isomers (**B–K**) of structure **A** and the mono- and diadducts of NMe₂Et (**AN**, **AN₂**) and SMe₂ (**AS**, **AS₂**); non-trivial symmetry point groups are given in parentheses. Gibbs free energies (in kcal mol⁻¹) of dimers **B–K** refer to two molecules of **A**; relative Gibbs free energies for the base adducts refer to **A** and the uncoordinated bases.

Lewis acidity of the boron atoms. Whereas further stabilization of the two dangling BH_2 groups in the *trans* isomer (**B**) is only possible through oligomerization (which we did not investigate further herein), the slightly more stable *cis* isomer (**C**) can readily undergo subsequent intramolecular B–H/B–H addition to form a second *cis*- B_2H_4 bridge. Although this intramolecular step does not suffer the loss in entropy that accompanies the intermolecular formation of isomer **C**, closure of the second B_2H_4 bridge only stabilizes the resulting dimer (**D**) by an additional $-13.7 \text{ kcal mol}^{-1}$. Clearly, the substantial amount of strain energy that is inherent in the rather stiff, bowl-shaped molecular structure of dimer **D** partially outweighs the stabilization that is brought about by the second B_2H_4 linker. Our attempts to localize other, potentially less strained conformers of dimer **D**, or isomers that contain *trans*- B_2H_4 bridges, failed. Instead, we localized a D_{2d} -symmetric isomer (**E**), which is bound through a distributed B–H–B bridging network. However, isomer **E** is significantly higher in energy than all of the other isomers identified so far and, hence, is not considered further.

Alternative isomers are accessible through B–H/B–C addition between two monomers (**A**). In a previous work on the mechanisms for the oligomerization of 9*H*-9-borafluorene, we showed that this elementary step results in the formation of dimers that are joined together by the remarkable combination of classical B–H–B bridges and B–C–B linkages through B–B-bridging aryl rings.^[68] For the systems studied herein, we investigated the possibility of realizing doubly phenyl-bridged dimers, which are conceivable owing to the particular *ortho*-substitution pattern that is present in structure **A**. Indeed, we identified two corresponding isomers that are thermochemically relevant despite their seemingly strained structures: Dimer **F** shows two singly bridging phenylene rings and its strongly exergonic formation ($\Delta G_{\text{R}} = -31.1 \text{ kcal mol}^{-1}$) is comparable to that of dimer **D** ($\Delta G_{\text{R}} = -30.7 \text{ kcal mol}^{-1}$). In contrast, dimer **G** features a hitherto-unknown doubly bridging phenylene ring that contributes two adjacent carbon atoms to two B–C–B linkages. Notwithstanding its lower thermodynamic stability ($\Delta G_{\text{R}} = -20.4 \text{ kcal mol}^{-1}$) than dimer **F**, structure **G** still represents a sufficiently exergonic species to render the molecular design of kinetically stabilized derivatives a rewarding synthetic goal. We note in passing that a combination of both binding motifs in the two energetically most favorable isomers (**D** and **F**) results in an equally stable isomer (**H**; $\Delta G_{\text{R}} = -31.4 \text{ kcal mol}^{-1}$). The rearrangement of isomer **F** into *exo*-B–H/B–H adduct **I** liberates another 11 kcal mol^{-1} and yields the thermodynamically most favored species that was identified in our computational study. The plausible alternative scenario, that is, the dimerization of BH_3 ($\Delta G_{\text{R}} = -27.9 \text{ kcal mol}^{-1}$) and the polymerization of DBA, which is essentially thermoneutral,^[64] is thermodynamically disfavored compared to the formation of isomer **I** ($\Delta G_{\text{R}} = -41.9 \text{ kcal mol}^{-1}$). In line with these results, compound **I** was isolated from aged solutions of in situ generated structure **A** in CH_2Cl_2 (cf. crystallographically characterized compound

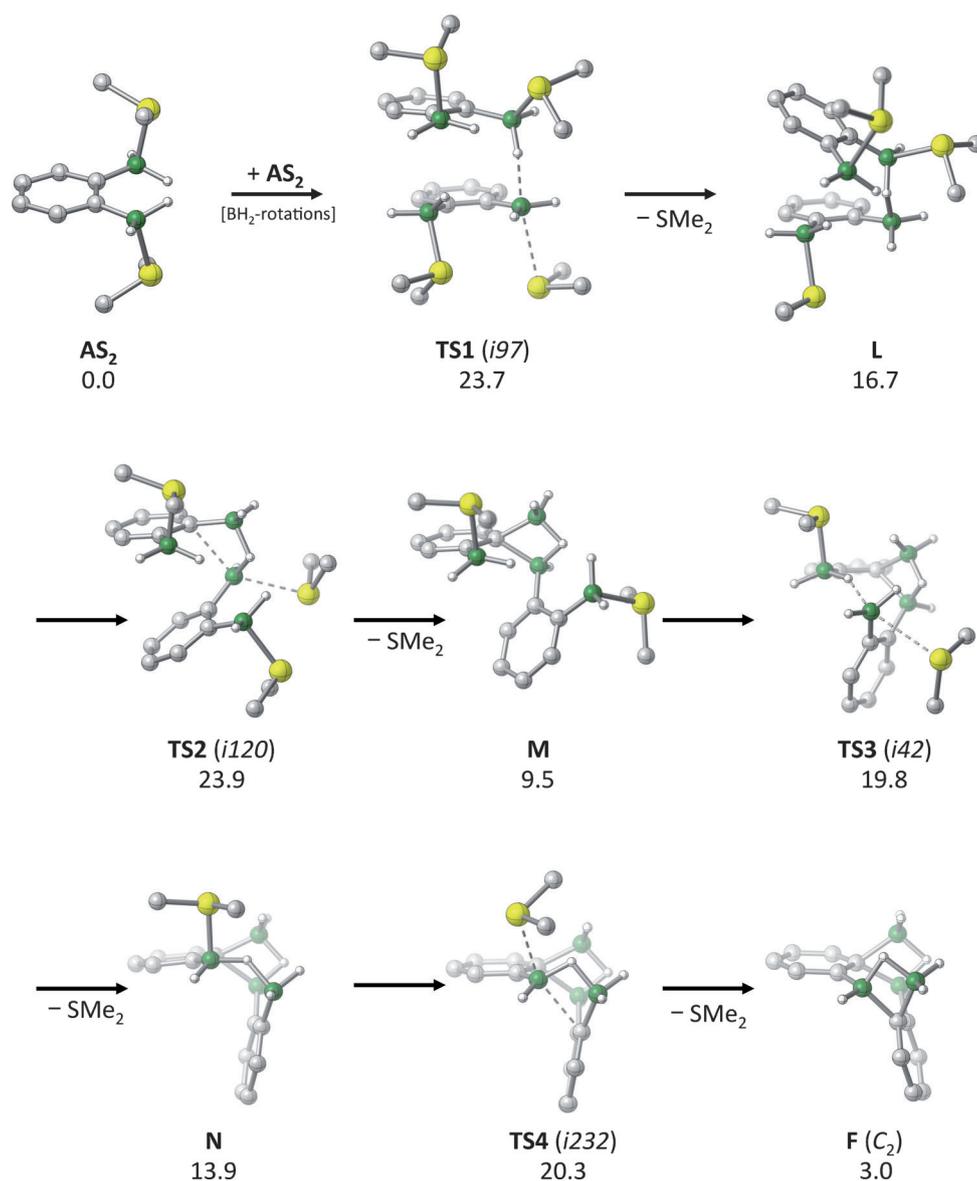
8); we will discuss potential reaction pathways that lead to isomer **I** further below. Finally, mixed *exo/endo*-isomer **J** and the *exo*-analogue of isomer **H** (i.e., isomer **K**) also represent rather stable species.

In the presence of the N-donor base NMe_2Et , adduct formation (**AN**, Figure 5) is energetically favored over the dimerization of structure **A**. However, the entropic penalty that is associated with the reaction $\text{AN} + \text{NMe}_2\text{Et} \rightarrow \text{AN}_2$ lowers the stability of AN_2 to a similar extent that the ring strain destabilizes the intramolecular second B_2H_4 bridge in isomer **D**. We note in passing that the optimized structure of adduct AN_2 validates the proposed structure for compound **6** (Scheme 2).

The sequential binding of two SMe_2 molecules to structure **A** is substantially less exergonic than NMe_2Et -coordination (**AS**: $\Delta G_{\text{R}} = -9.5 \text{ kcal mol}^{-1}$, **AS**₂: $\Delta G_{\text{R}} = -17.0 \text{ kcal mol}^{-1}$, with reference to fully separated molecules) and is fully in line with the experimental observations described above; also, the formation of an SMe_2 adduct cannot compete thermodynamically with the dimerization of compound **A**. Whilst it is reasonable to assume that the in situ generation of structure **A** in SMe_2 leads to an **AS**₂ intermediate, this species is unstable under the experimental conditions and, accordingly, only transient NMR signatures that are assignable to aryl- $\text{BH}_2\cdot\text{SMe}_2$ species, such as **AS**₂, have been detected. Furthermore, NMR evidence for the formation of $\text{DBA}\cdot(\text{SMe}_2)_2$ and $\text{BH}_3\cdot\text{SMe}_2$ in solution, together with the isolation of compounds (**7**)₂ and **8**, indicate the lability of SMe_2 -donor adducts and the existence of intriguing rearrangement processes.

To shed further light on the origins of these findings, we investigated potential mechanisms for the formation of DBA in the presence of SMe_2 solvent molecules. As an initial step in the reaction sequence that commences from **AS**₂, we identified an $\text{S}_{\text{N}}2$ -like transition state (**TS1**): The boron-bound hydride atom of one monomer (**AS**₂) attacks the $\text{BH}_2\cdot\text{SMe}_2$ group of a second monomer with the synchronous liberation of the SMe_2 donor, thereby yielding a B–H–B-bridged dimeric intermediate (**L**, Scheme 3). This step has an appreciable activation barrier ($\Delta G^\ddagger = 23.7 \text{ kcal mol}^{-1}$) and is endoergic by $16.7 \text{ kcal mol}^{-1}$. Subsequent B–C bond formation occurs with the concomitant loss of a second SMe_2 molecule via transition state **TS2** and leads to a B–B phenyl-bridged intermediate (**M**) with a negligible activation barrier of $\Delta G^\ddagger = 7.2 \text{ kcal mol}^{-1}$. The second half of the reaction sequence that leads to donor-free structure **F** (Scheme 3) is comprised of identical elementary steps with lower barrier heights.

As alluded to in our general evaluation of conceivable isomers (Figure 5), the primary product (**F**) is less stable than isomer **I** (which corresponds to the experimentally characterized product **8**; Scheme 2, Figure 3). Indeed, we found that SMe_2 mediates the exergonic rearrangement of isomer **F** into isomer **I** with low barriers (Scheme 4). Attack of SMe_2 on isomer **F** yields isomer **O** and $\text{BH}_3\cdot\text{SMe}_2$. This step is essentially driven by the exergonicity of the latter B–S adduct ($\Delta G_{\text{R}} = -14.8 \text{ kcal mol}^{-1}$). The three-coordinate



Scheme 3. Reaction sequence from **AS₂** to **F**; relative Gibbs free energies are given in kcal mol⁻¹ and the imaginary modes of the transition states are given in parentheses.

boron atom in isomer **O** can either bind one SMe_2 molecule from the solvent (i.e., $\text{P}_{cis}/\text{P}_{trans}$; Scheme 4a) or reaccept BH_3 in an exocyclic fashion from $\text{BH}_3\cdot\text{SMe}_2$ that was liberated in the preceding step (**K**; Scheme 4b). Along path a, both P_{cis} and P_{trans} are efficiently funneled into isomer **Q** with low activation barriers. Under the experimental conditions, isomer **Q** is generated in neat SMe_2 and, therefore, is likely to add a second SMe_2 molecule. The resulting diadduct (**R**) is slightly more stable than isomer **Q** and represents a major component of the reaction mixture, as indicated by in situ ^{11}B NMR spectroscopic analysis (see above). Within the assumed limits of the accuracy of our calculations, the dimerization of isomer **Q** to afford dimer (**Q**)₂ is equally favorable. Thus, in SMe_2 , structures **R** and (**Q**)₂ will readily interconvert through **Q**, which is in agreement with

the observation of crystalline (**Q**)₂ (= (**7**)₂; Scheme 2, Figure 3) precipitating from cooled reaction mixtures. With lower amounts of SMe_2 , by evaporation of the reaction mixture and redissolution of the residue in C_6H_6 , path b becomes increasingly relevant. Here, a BH_3 -exchange cascade between $\text{BH}_3\cdot\text{SMe}_2/\text{SMe}_2$ and DBA rearranges isomer **O** into isomer **I** (= **8**; Scheme 2, Figure 3) under a kinetic regime that is comparable to that of path a.

Conclusion

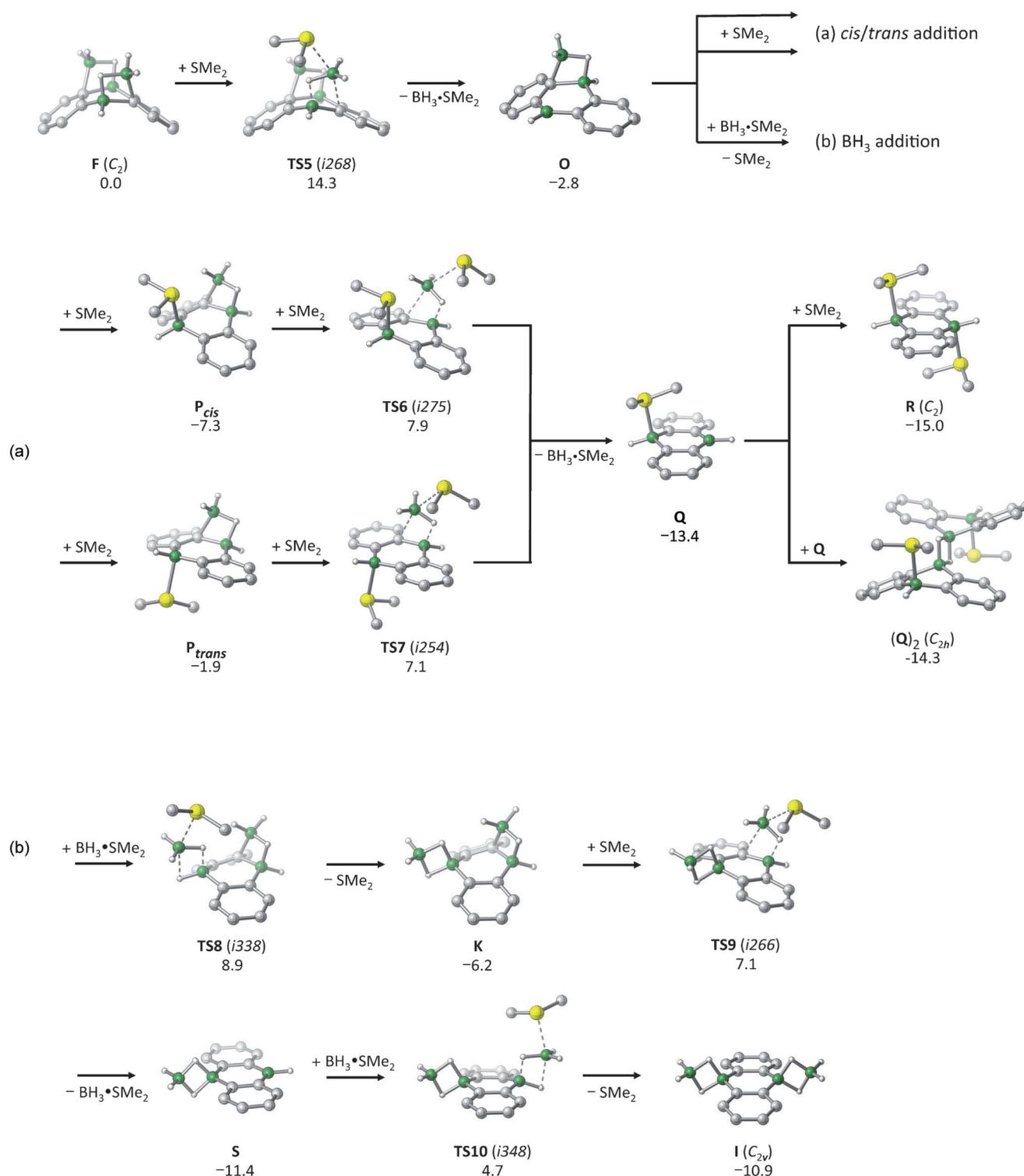
The Grignard reaction between 1,2- $\text{C}_6\text{H}_4\text{Br}_2$ and *i*PrO-Bpin with 1,2- $\text{C}_2\text{H}_4\text{Br}_2$ as an entrainer is an exceptionally convenient method for the preparation of the versatile synthetic building block 1,2- $\text{C}_6\text{H}_4(\text{Bpin})_2$ (**2**; HBpin = pinacolborane).

Compound **2** can be employed in double cross-coupling reactions for the synthesis of functionalized polycyclic aromatic hydrocarbons. However, we focused on its transformation into the vicinal bis-borate $\text{Li}_2[1,2\text{-C}_6\text{H}_4(\text{BH}_3)_2]$ (**3**), which was crystallographically characterized as its diethyl ether solvate, **3**·OEt₂. The intricate coordination polymer network that is established by solvate **3**·OEt₂ in the solid state holds promise

for various applications because the well-developed chemistry of the $[\text{BH}_4]^-$ ion as a terminal or bridging ligand in a wide range of (transition)-metal complexes^[74–79] can now be expanded by using bis-borates like $[1,2\text{-C}_6\text{H}_4(\text{BH}_3)_2]^{2-}$ as a chelating variant.

Hydride-abstraction from compound **3** yields the free ditopic borane 1,2- $\text{C}_6\text{H}_4(\text{BH}_2)_2$. Its properties as a hydroboration reagent are governed by the proximity of the two boryl groups, which undergo a cyclic double-hydroboration reaction with the formation of a benzannulated 1,3-diborolene (**5**).

In the presence of the strong Lewis base NMe_2Et , 1,2- $\text{C}_6\text{H}_4(\text{BH}_2)_2$ exists as stable B–N diadduct. Weaker bases, such as SMe_2 or THF, are not able to stabilize the 1,2- $\text{C}_6\text{H}_4\text{-(BH}_2)_2$ scaffold. Instead, the compound undergoes scram-



Scheme 4. Reaction sequence from **F** to: a) base adducts **R** and **(Q)₂** and b) **BH₃** adduct **I**; relative Gibbs free energies are given in kcalmol⁻¹ and the imaginary modes of the transition states are given in parentheses.

bling of the substituents with the formation of 9,10-dihydro-9,10-diboraanthracene within a short period of time at room temperature. For comparison, the conventional synthesis of 9,10-dibromo-9,10-dihydro-9,10-diboraanthracene requires prolonged heating of 1,2-bis(trimethylsilyl)benzene with

excess **BBr₃** in a sealed glass ampoule (120°C, 6 d). Therefore, we conclude that the process of substituent-redistribution in aryl(hydro)boranes, which has mainly been regarded as a nuisance in the past, can be turned into a versatile method for the construction of sophisticated boron-contain-

ing π systems. Modern density functional theory has provided a detailed insight into the underlying reaction mechanisms. We compared theoretical and experimental findings wherever possible and, pleasingly, found a good agreement between the two. Therefore, we are confident that our theoretical approach represents a powerful tool for predicting key facets of the dynamic covalent chemistry of aryl-(hydro)boranes in the synthesis of boron-doped organic materials.

In summary, we have shown that strong Lewis bases, such as trialkylamines, stabilize the vicinal borane groups in 1,2- $C_6H_4(BH_2)_2$ by the formation of isolable adducts. Bases with moderate donor properties, such as thioethers, also form adducts but do not entirely block the reactive borane sites, which undergo base-assisted rearrangement processes that ultimately lead to DBA with remarkable selectivity.

Experimental Section

Unless otherwise specified, all reactions were carried out in rigorously dried solvents under dry nitrogen/argon atmospheres by using Schlenk or glove-box techniques. *n*-Pentane, *n*-hexane, C_6H_6 , C_6D_6 , toluene, Et_2O , THF, and $[D_8]THF$ were dried over Na/benzophenone; $CDCl_3$, CH_2Cl_2 , CD_2Cl_2 , Me_2S , Me_3SiCl , and NMe_2Et were dried over CaH_2 . NMR spectra were recorded on Bruker AM 250, DPX 250, Avance 300, and Avance 400 spectrometers at RT if not otherwise specified. Chemical shifts were referenced to (residual) solvent peaks ($^1H/^{13}C\{^1H\}$: C_6D_6 7.16/128.06, $CDCl_3$ 7.26/77.16, CD_2Cl_2 5.32/53.84, $[D_8]THF$ 3.58/67.21) or to external $BF_3 \cdot Et_2O$ ($^{11}B, ^{11}B\{^1H\}$). Abbreviations: s=singlet, t=triplet, q=quartet, m=multiplet, br=broad, n.o.=not observed. Combustion analysis was performed by the Microanalytical Laboratory of the University of Frankfurt and by the Microanalytical Laboratory Pascher, Remagen (Germany).

Synthesis of compound 2: Mg turnings (2.45 g, 101 mmol) were heated with a heat gun in a Schlenk flask that was equipped with a reflux condenser and a dropping funnel under vacuum for 15 min. After the flask had cooled back to RT, THF (100 mL), neat isopropoxy-pinacolborane (16.0 mL, 14.6 g, 78.4 mmol), and neat 1,2-dibromoethane (3.0 mL, 5.9 g, 25 mmol) were added. After an induction period of approximately 5 min, the color of the mixture changed from colorless to yellow and the exothermic reaction started. Therefore, the flask was cooled in a water bath to maintain the temperatures between 20–40°C throughout the entire reaction period. After 15 min, a solution of 1,2-dibromoethane (2.1 mL, 4.6 g, 24 mmol) in THF (15 mL) was added dropwise to the vigorously stirred slurry over 1 h. After the addition was complete, the yellow reaction mixture was heated at reflux for 4 h before being allowed to cool back to RT. All of the volatile compounds were removed under reduced pressure. The remaining solid residue was treated at 0°C with *n*-hexane (50 mL) and with a saturated aqueous solution of $NaHCO_3$ (50 mL). After stirring for 15 min, the two liquid phases were separated and the aqueous phase was extracted with *n*-hexane (2 × 20 mL). The combined organic phases were extracted with H_2O (2 × 20 mL), dried over anhydrous $MgSO_4$, and filtered. All of the volatile compounds were removed from the filtrate under reduced pressure and the remaining yellow oil was dissolved in *n*-pentane (20 mL). Slow evaporation of the solvent at RT over 2 d gave colorless crystals that were immersed in a pale-yellow oil. On storing the sample at 4°C, large crystals formed, which were collected on a frit (G2) and dried between two sheets of pulp to remove any residual oil. Yield: 3.3 g (40%); 1H NMR (300.0 MHz, $CDCl_3$): δ = 7.68–7.62 (m, 2H; ArH), 7.40–7.34 (m, 2H; ArH), 1.37 ppm (s, 24H; CH_3); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ = 133.6 (ArC), 129.3 (ArC), 84.0 (CCH_3), 25.0 ppm (CH_3), n.o. (CB); $^{11}B\{^1H\}$ NMR (96.3 MHz, $CDCl_3$): δ = 31.6 ppm ($h_{1/2}$ = 280 Hz); MS (ESI⁺): *m/z* (%):

331.2 (100) $[M+H]^+$; elemental analysis calcd (%) for $C_{18}H_{28}B_2O_4$: C 65.51, H 8.55; found: C 65.88, H 8.49.

Synthesis of compound 3: Compound 2 (1.01 g, 3.06 mmol) was dissolved in a mixture of Et_2O (16 mL) and *n*-pentane (4 mL) and the solution was cooled to 0°C in an ice bath. A solution of $Li[AlH_4]$ (1 M in Et_2O , 9.2 mL, 9.2 mmol) was added by using a syringe. The resulting suspension was stirred for 2 h at 0°C and for a further 16 h at RT. The colorless precipitate was filtered off and the filtrate was concentrated to a volume of approximately 10 mL. Gas-diffusion of *n*-hexane into the filtrate gave colorless crystals of compound 3-OEt₂. Yield: 0.48 g (81%); 1H NMR (300.0 MHz, $[D_8]THF$): δ = 7.30 (br, 2H; H_{3,6}), 6.68–6.62 (m, 2H; H_{4,5}), 3.40 (q, $^3J(H,H)$ = 7 Hz, 4H; CH_2), 1.12 (t, $^3J(H,H)$ = 7 Hz, 6H; CH_3), 1.03 ppm (q, $^1J(^{11}B,H)$ = 79 Hz, 6H; BH_3); $^{13}C\{^1H\}$ NMR (75.5 MHz, $[D_8]THF$): δ = 155.9 (q, $^1J(^{11}B,C)$ ≈ 50 Hz; CB), 137.9 (C_{3,6}), 123.2 (C_{4,5}), 66.1 (CH_2), 15.5 ppm (CH_3); $^{11}B\{^1H\}$ NMR (96.3 MHz, $[D_8]THF$): δ = –26.6 ppm ($h_{1/2}$ = 15 Hz); ^{11}B NMR (96.3 MHz, $[D_8]THF$): δ = –26.6 (q, $^1J(^{11}B,H)$ = 79 Hz); elemental analysis calcd (%) for $C_{10}H_{20}B_2Li_2O$: C 62.63, H 10.51; found: C 62.70, H 10.49.

Synthesis of compound 5: Compound 3-OEt₂ (0.27 g, 1.4 mmol) was suspended in dry Me_2S (20 mL) at RT. Neat $tBuC\equiv CH$ (0.6 mL, 0.4 g, 5 mmol) and neat Me_3SiCl (0.4 mL, 0.3 g, 3 mmol) were added to the suspension by using a syringe. The mixture was stirred at RT for 36 h, filtered, and the filtrate was evaporated to dryness under vacuum to give a colorless oil. The crude product was treated with C_6H_6 (15 mL) and the resulting suspension was filtered again. The filtrate was evaporated to dryness under vacuum to give a highly viscous, colorless oil. Yield: 0.41 g (84%); 1H NMR (300.0 MHz, C_6D_6): δ = 8.18–8.11 (m, 2H; H_{3,6}), 7.45–7.39 (m, 2H; H_{4,5}), 7.12 (d, $^3J(H,H)$ = 17.8 Hz, 2H; $CH=CHtBu$), 6.73 (d, $^3J(H,H)$ = 17.8 Hz, 2H; $CH=CHtBu$), 2.14 (t, $^3J(H,H)$ = 5.3 Hz, 1H; B(CH)₂), 2.03 (d, $^3J(H,H)$ = 5.3 Hz, 2H; CH_2tBu), 1.04 (s, 9H; C(CH_3)₃), 1.03 ppm (s, 18H; C(CH_3)₃); $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6): δ = 168.6 ($CH=CHtBu$), 157.3 (C_{1,2})*, 132.5 (C_{3,6}), 131.0 (C_{4,5}), 125.2 ($CH=CHtBu$)*, 43.6 (CH_2tBu), 35.6 (C(CH_3)₃), 32.6 ($CH_2C(CH_3)_3$), 30.0 ($CH_2C(CH_3)_3$), 29.0 ppm (C(CH_3)₃), n.o. (B(CH)₂); $^{11}B\{^1H\}$ NMR (96.3 MHz, C_6D_6): δ = 71.6 ppm ($h_{1/2}$ = 1500 Hz); MS (ESI[–]): *m/z* (%): 487.6 (100) $[M+pzSiMe_3]^-$. *: This signal was not observed in the 1D $^{13}C\{^1H\}$ NMR spectrum but was located by HMBC experiments.

Synthesis of compound 6: Compound 3-OEt₂ (0.58 g, 3.0 mmol) was suspended in toluene (20 mL) at RT. Neat, dry NMe_2Et (0.7 mL, 0.5 g, 6 mmol) and neat Me_3SiCl (1.0 mL, 0.86 g, 7.9 mmol) were added to the suspension by using a syringe. The mixture was stirred at RT for 12 h, filtered, and the filtrate was evaporated to dryness under vacuum to give a colorless solid. The crude product was treated with C_6H_6 (15 mL) and the resulting suspension was filtered again. The filtrate was evaporated to dryness under vacuum to give a colorless solid. Yield: 0.41 g (55%); 1H NMR (300.0 MHz, CD_2Cl_2): δ = 7.47–7.41 (m, 2H; H_{3,6}), 7.04–6.98 (m, 2H; H_{4,5}), 2.84 (q, $^3J(H,H)$ = 7.4 Hz, 4H; CH_2CH_3), 2.66 (br, 4H; BH_2), 2.37 (s, 12H; CH_3), 1.14 ppm (t, $^3J(H,H)$ = 7.4 Hz, 6H; CH_2CH_3); $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2): δ = 154.6 (C_{1,2})*, 139.6 (C_{3,6}), 124.6 (C_{4,5}), 56.9 (CH_2CH_3), 47.9 (CH_3), 8.5 ppm (CH_2CH_3); $^{11}B\{^1H\}$ NMR (96.3 MHz, CD_2Cl_2): δ = –1.3 ppm ($h_{1/2}$ = 120 Hz); ^{11}B NMR (96.3 MHz, CD_2Cl_2): δ = –1.3 ppm (t, $^1J(^{11}B,H)$ ≈ 90 Hz); elemental analysis calcd (%) for $C_{14}H_{30}B_2N_2$: C 67.80, H 12.19, N 11.29; found: C 68.01, H 12.10, N 10.70. *: This signal was not observed in the 1D $^{13}C\{^1H\}$ NMR spectrum but was located by HMBC experiments.

Synthesis of compound (7)₂: Compound 3-OEt₂ (0.05 g, 0.3 mmol) was suspended in dry Me_2S (5 mL). Neat Me_3SiCl (0.1 mL, 0.09 g, 0.8 mmol) was added at RT by using a syringe. After the mixture was stirred for 14 h, a colorless precipitate had formed, which was removed by filtration, and the filtrate was stored at 4°C to grow colorless single crystals of compound (7)₂. Yield: 9 mg (25%); 1H NMR (250.1 MHz, $[D_8]THF$): δ = 7.62–7.55 (m, 4H; H_{1,4,5,8}), 7.19–7.13 (m, 4H; H_{2,3,6,7}), 4.42 (br, 2H; BH), 1.95 ppm (s, 12H; S(CH_3)₂); ^{13}C NMR (62.9 MHz, $[D_8]THF$): δ = 152.5 (CB)*, 136.3 (C_{1,4,5,8}), 127.2 (C_{2,3,6,7}), 18.6 ppm (S(CH_3)₂); $^{11}B\{^1H\}$ NMR (80.3 MHz, $[D_8]THF$): δ = 19.9 ppm ($h_{1/2}$ = 360 Hz). *: This signal was not observed in the 1D $^{13}C\{^1H\}$ NMR spectrum but was located by HMBC experiments. In addition to the solution, a colorless solid was present in the NMR tube.

Synthesis of compound 8: *Method A.* Compound **3**·OEt₂ (0.08 g, 0.4 mmol) was suspended in dry Me₂S (5 mL). Neat Me₃SiCl (0.5 mL, 0.4 g, 4 mmol) was added at RT by using a syringe. After the mixture was stirred for 12 h, a colorless precipitate had formed, which was removed by filtration, and the filtrate was evaporated to dryness under vacuum to give a colorless oil. The oil was redissolved in C₆H₆ (5 mL) and the solution was stored at 4 °C for 5 d to afford needle-shaped crystals of compound **8**. *Method B.* Compound **3**·OEt₂ (0.08 g, 0.4 mmol) was placed in a narrow Schlenk tube, dissolved in THF (5 mL), and the solution was carefully layered with neat Me₃SiCl (0.3 mL, 0.3 g, 2 mmol) at RT. After the tube had been stored at RT for 2 h, a colorless solid had formed, together with colorless, needle-shaped crystals of compound **8**, which were isolated by manual crystal picking. *Method C.* Compound **3**·OEt₂ (0.66 g, 3.4 mmol) was suspended in dry CH₂Cl₂ (20 mL). Neat Me₃SiCl (1.0 mL, 0.86 g, 7.9 mmol) was added at RT by using a syringe. After the mixture was stirred for 19 h, a colorless precipitate had formed, which was removed by filtration, and the filtrate was stored at 4 °C for 1 d to obtain colorless needle-shaped crystals of compound **8**. All three methods reproducibly gave yields of about 10%.

The solubility of the crystals in all common non-donor solvents was too low to obtain NMR data; elemental analysis calcd (%) for C₁₂H₁₆B₄: C 70.82, H 7.92; found: C 71.05, H 7.81.

Crystal-structure analysis: Diffraction patterns were measured on a STOE IPDS-II diffractometer with graphite-monochromated Mo K α radiation. An empirical absorption correction was performed with PLATON^[80] for compounds (**7**)₂ and *t*BuC(H)=C(H)B(μ -C₆H₄)(μ -pzSiMe₃)₂BC(H)=C(H)*t*Bu. The structures were solved by direct methods^[81] and refined with full-matrix least-squares on *F*² by using SHELXL97.^[82] The H atoms that were bonded to boron in compounds **3**·OEt₂, (**7**)₂, and **8** were refined isotropically. All other hydrogen atoms were placed at ideal positions and were refined with fixed isotropic displacement parameters by using a riding model. The Bpin substituents on compound **2** were disordered over two positions with site-occupancy factors of 0.56(2) and 0.51(1) for the major occupied site. The disordered atoms were refined isotropically. The C–C distances in the C₆D₆ ring of *t*BuC(H)=C(H)B(μ -C₆H₄)(μ -pzSiMe₃)₂BC(H)=C(H)*t*Bu were restrained to 1.39(1) Å.

CCDC-878339 (**2**), CCDC-878340 (**3**·OEt₂), CCDC-878341 ((**7**)₂), CCDC-878342 (**8**), CCDC-878343 (*t*BuC(H)=C(H)B(μ -C₆H₄)(μ -pzSiMe₃)₂BC(H)=C(H)*t*Bu) 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.

Computational details: Geometry optimizations and harmonic frequency calculations were performed with the Gaussian09 program^[83] by using the dispersion-corrected B97D^[84] GGA-functional in combination with the 6–311++G(d,p)^[85,86] basis set. All structures were optimized within the highest possible molecular symmetry. The connectivity between minima and transition structures implied in the figures was validated by intrinsic reaction-coordinate-following calculations.^[87,88] Unscaled zero-point vibrational energies, as well as thermal and entropy corrections, were obtained from Hessians computed at this level of DFT by using the standard procedures in Gaussian09. Based on the optimized structures, subsequent single-point energy calculations were performed with the program ORCA^[89,90] by using the “general purpose” B2GP-PLYP double-hybrid functional that was developed by Martin and co-workers.^[91] Energies that were computed with the def2-SVP and def2-TZVP basis sets^[92,93] were extrapolated to the basis-set limit by making use of the automatic, parameterized procedure that was implemented in ORCA. The RI-JK algorithm^[94,95] was used in the SCF part and RI-MP2^[96] was used for the perturbative correlation part of these calculations and the corresponding auxiliary basis sets^[94,97] were automatically chosen by ORCA. Empirical dispersion corrections^[84,98] (scaling factor *s*₆=0.4^[91]) and free-energy corrections that were obtained at the B97D level were added to the extrapolated energies. Relative energies discussed in the text refer to Gibbs free energies at 298.15 K, which were obtained at the RI-B2GP-PLYP+D/CBS(2/3)//B97D/6–311++G(d,p) level of theory.

Acknowledgements

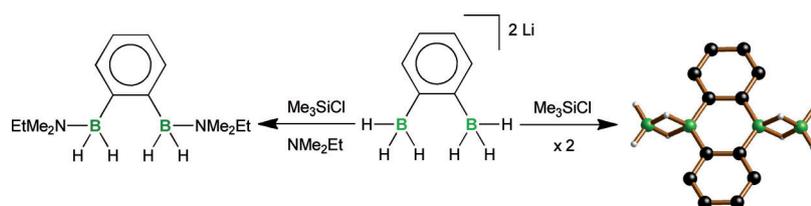
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- [1] N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457–2483.
- [2] K. C. Nicolaou, P. G. Bulger, D. Sarlah, *Angew. Chem.* **2005**, *117*, 4516–4563; *Angew. Chem. Int. Ed.* **2005**, *44*, 4442–4489.
- [3] A. J. Berresheim, M. Müller, K. Müllen, *Chem. Rev.* **1999**, *99*, 1747–1785.
- [4] F. Babudri, G. M. Farinola, F. Naso, *Synlett* **2009**, 2740–2748.
- [5] M. D. Watson, A. Fechtenkötter, K. Müllen, *Chem. Rev.* **2001**, *101*, 1267–1300.
- [6] M. Bendikov, F. Wudl, D. F. Perepichka, *Chem. Rev.* **2004**, *104*, 4891–4945.
- [7] J.-L. Brédas, D. Beljonne, V. Coropceanu, J. Cornil, *Chem. Rev.* **2004**, *104*, 4971–5003.
- [8] J. E. Anthony, *Chem. Rev.* **2006**, *106*, 5028–5048.
- [9] J. Wu, W. Pisula, K. Müllen, *Chem. Rev.* **2007**, *107*, 718–747.
- [10] A. R. Murphy, J. M. J. Fréchet, *Chem. Rev.* **2007**, *107*, 1066–1096.
- [11] C. Li, M. Liu, N. G. Pschirer, M. Baumgarten, K. Müllen, *Chem. Rev.* **2010**, *110*, 6817–6855.
- [12] W. E. Piers, T. Chivers, *Chem. Soc. Rev.* **1997**, *26*, 345–354.
- [13] K. Ishihara, H. Yamamoto, *Eur. J. Org. Chem.* **1999**, 527–538.
- [14] E. J. Corey, *Angew. Chem.* **2002**, *114*, 1724–1741; *Angew. Chem. Int. Ed.* **2002**, *41*, 1650–1667.
- [15] W. E. Piers, *Adv. Organomet. Chem.* **2004**, *52*, 1–76.
- [16] D. W. Stephan, *Dalton Trans.* **2009**, 3129–3136.
- [17] D. W. Stephan, G. Erker, *Angew. Chem.* **2010**, *122*, 50–81; *Angew. Chem. Int. Ed.* **2010**, *49*, 46–76.
- [18] T. D. James, S. Shinkai, *Top. Curr. Chem.* **2002**, *218*, 159–200.
- [19] C. R. Wade, A. E. J. Broomsgrove, S. Aldridge, F. P. Gabbaï, *Chem. Rev.* **2010**, *110*, 3958–3984.
- [20] C. D. Entwistle, T. B. Marder, *Angew. Chem.* **2002**, *114*, 3051–3056; *Angew. Chem. Int. Ed.* **2002**, *41*, 2927–2931.
- [21] C. D. Entwistle, T. B. Marder, *Chem. Mater.* **2004**, *16*, 4574–4585.
- [22] S. Yamaguchi, A. Wakamiya, *Pure Appl. Chem.* **2006**, *78*, 1413–1424.
- [23] F. Jäkle, *Coord. Chem. Rev.* **2006**, *250*, 1107–1121.
- [24] F. Jäkle, *Chem. Rev.* **2010**, *110*, 3985–4022.
- [25] A. Lorbach, A. Hübner, M. Wagner, *Dalton Trans.* **2012**, *41*, 6048–6063.
- [26] H. Noguchi, T. Shioda, C.-M. Chou, M. Sugimoto, *Org. Lett.* **2008**, *10*, 377–380.
- [27] M. Shimizu, I. Nagao, Y. Tomioka, T. Hiyama, *Angew. Chem.* **2008**, *120*, 8216–8219; *Angew. Chem. Int. Ed.* **2008**, *47*, 8096–8099.
- [28] M. Shimizu, Y. Tomioka, I. Nagao, T. Hiyama, *Synlett* **2009**, 3147–3150.
- [29] M. Shimizu, Y. Tomioka, I. Nagao, T. Kadowaki, T. Hiyama, *Chem. Asian J.* **2012**, *7*, 1644–1651.
- [30] K. Nozaki, M. Yoshida, H. Takaya, *Angew. Chem.* **1994**, *106*, 2574–2576; *Angew. Chem. Int. Ed. Engl.* **1995**, *33*, 2452–2454.
- [31] V. C. Williams, W. E. Piers, W. Clegg, M. R. J. Elsegood, S. Collins, T. B. Marder, *J. Am. Chem. Soc.* **1999**, *121*, 3244–3245.
- [32] P. A. Chase, L. D. Henderson, W. E. Piers, M. Parvez, W. Clegg, M. R. J. Elsegood, *Organometallics* **2006**, *25*, 349–357.
- [33] A. Sundararaman, K. Venkatasubbaiah, M. Victor, L. N. Zakharov, A. L. Rheingold, F. Jäkle, *J. Am. Chem. Soc.* **2006**, *128*, 16554–16565.
- [34] S. N. Kessler, H. A. Wegner, *Org. Lett.* **2010**, *12*, 4062–4065.
- [35] S. N. Kessler, M. Neuburger, H. A. Wegner, *Eur. J. Org. Chem.* **2011**, 3238–3245.
- [36] H. A. Wegner, S. N. Kessler, *Synlett* **2012**, 699–705.
- [37] D. T. McQuade, A. E. Pullen, T. M. Swager, *Chem. Rev.* **2000**, *100*, 2537–2574.

- [38] M. Miyata, Y. Chujo, *Polym. J.* **2002**, *34*, 967–969.
- [39] A. Sundararaman, M. Victor, R. Varughese, F. Jäkle, *J. Am. Chem. Soc.* **2005**, *127*, 13748–13749.
- [40] K. Parab, K. Venkatasubbaiah, F. Jäkle, *J. Am. Chem. Soc.* **2006**, *128*, 12879–12885.
- [41] H. Li, R. A. Lalancette, F. Jäkle, *Chem. Commun.* **2011**, *47*, 9378–9380.
- [42] D. Kaufmann, *Chem. Ber.* **1987**, *120*, 901–905.
- [43] J. J. Eisch, B. W. Kotowicz, *Eur. J. Inorg. Chem.* **1998**, 761–769.
- [44] C. Laza, C. Pintaric, S. Olivero, E. Dunach, *Electrochim. Acta* **2005**, *50*, 4897–4901.
- [45] A. Geny, D. Lebœuf, G. Rouquié, K. P. C. Vollhardt, M. Malacria, V. Gandon, C. Aubert, *Chem. Eur. J.* **2007**, *13*, 5408–5425.
- [46] L. Iannazzo, K. P. C. Vollhardt, M. Malacria, C. Aubert, V. Gandon, *Eur. J. Org. Chem.* **2011**, 3283–3292.
- [47] A. Maderna, H. Pritzkow, W. Siebert, *Angew. Chem.* **1996**, *108*, 1664–1666; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1501–1503.
- [48] H. Yoshida, K. Okada, S. Kawashima, K. Tanino, J. Ohshita, *Chem. Commun.* **2010**, *46*, 1763–1765.
- [49] H. Yoshida, S. Kawashima, Y. Takemoto, K. Okada, J. Ohshita, K. Takaki, *Angew. Chem.* **2012**, *124*, 239–242; *Angew. Chem. Int. Ed.* **2012**, *51*, 235–238.
- [50] P. Leowanawat, A.-M. Resmerita, C. Moldoveanu, C. Liu, N. Zhang, D. A. Wilson, L. M. Hoang, B. M. Rosen, V. Percec, *J. Org. Chem.* **2010**, *75*, 7822–7828.
- [51] D. E. Pearson, D. Cowan, J. D. Beckler, *J. Org. Chem.* **1959**, *24*, 504–509.
- [52] J. F. Garst, M. P. Soriaga, *Coord. Chem. Rev.* **2004**, *248*, 623–652.
- [53] A. Lorbach, C. Reus, M. Bolte, H.-W. Lerner, M. Wagner, *Adv. Synth. Catal.* **2010**, *352*, 3443–3449.
- [54] M. Shimizu, I. Nagao, Y. Tomioka, T. Kadowaki, T. Hiyama, *Tetrahedron* **2011**, *67*, 8014–8026.
- [55] B. Singaram, T. E. Cole, H. C. Brown, *Organometallics* **1984**, *3*, 774–777.
- [56] D. Franz, M. Bolte, H.-W. Lerner, M. Wagner, *Dalton Trans.* **2011**, *40*, 2433–2440.
- [57] D. Franz, A. Haghiri Ilkhechi, M. Bolte, H.-W. Lerner, M. Wagner, *Eur. J. Inorg. Chem.* **2011**, 5414–5421.
- [58] M. Scheibitz, H. Li, J. Schnorr, A. Sánchez Perucha, M. Bolte, H.-W. Lerner, F. Jäkle, M. Wagner, *J. Am. Chem. Soc.* **2009**, *131*, 16319–16329.
- [59] A. Das, A. Hübner, M. Weber, M. Bolte, H.-W. Lerner, M. Wagner, *Chem. Commun.* **2011**, *47*, 11339–11341.
- [60] N. Edelstein, *Inorg. Chem.* **1981**, *20*, 297–299.
- [61] H. Nöth, B. Wrackmeyer, *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds, in NMR Basic Principles and Progress* (Eds.: P. Diehl, E. Fluck, R. Kosfeld), Springer, Berlin, **1978**.
- [62] A. Lorbach, M. Bolte, H.-W. Lerner, M. Wagner, *Chem. Commun.* **2010**, *46*, 3592–3594.
- [63] Pyrazole- and pyridazine-bridged DBAs have been reported, which can also be regarded as B–N analogues of triptycene (see ref. [62]). Compounds of type **5** that contain a 1,1'-ferrocenediyl linker instead of the 1,2-phenylene moiety have also been reported: a) F. Jäkle, T. Priermeier, M. Wagner, *J. Chem. Soc., Chem. Commun.* **1995**, 1765–1766; b) F. Jäkle, T. Priermeier, M. Wagner, *Organometallics* **1996**, *15*, 2033–2040; c) E. Herdtweck, F. Jäkle, G. Opromolla, M. Spiegler, M. Wagner, P. Zanello, *Organometallics* **1996**, *15*, 5524–5535.
- [64] A. Lorbach, M. Bolte, H. Li, H.-W. Lerner, M. C. Holthausen, F. Jäkle, M. Wagner, *Angew. Chem.* **2009**, *121*, 4654–4658; *Angew. Chem. Int. Ed.* **2009**, *48*, 4584–4588.
- [65] E. Januszewski, A. Lorbach, R. Grewal, M. Bolte, J. W. Bats, H.-W. Lerner, M. Wagner, *Chem. Eur. J.* **2011**, *17*, 12696–12705.
- [66] A. Lorbach, M. Bolte, H.-W. Lerner, M. Wagner, *Organometallics* **2010**, *29*, 5762–5765.
- [67] R. Köster, H.-G. Willemsen, *Liebigs Ann. Chem.* **1974**, 1843–1850.
- [68] A. Hübner, Z.-W. Qu, U. Englert, M. Bolte, H.-W. Lerner, M. C. Holthausen, M. Wagner, *J. Am. Chem. Soc.* **2011**, *133*, 4596–4609.
- [69] H. Hong, T. C. Chung, *J. Organomet. Chem.* **2004**, *689*, 58–64.
- [70] M. Scheibitz, J. W. Bats, M. Bolte, H.-W. Lerner, M. Wagner, *Organometallics* **2004**, *23*, 940–942.
- [71] J. B. Heilmann, M. Scheibitz, Y. Qin, A. Sundararaman, F. Jäkle, T. Kretz, M. Bolte, H.-W. Lerner, M. C. Holthausen, M. Wagner, *Angew. Chem.* **2006**, *118*, 934–939; *Angew. Chem. Int. Ed.* **2006**, *45*, 920–925.
- [72] M. Scheibitz, R. F. Winter, M. Bolte, H.-W. Lerner, M. Wagner, *Angew. Chem.* **2003**, *115*, 954–957; *Angew. Chem. Int. Ed.* **2003**, *42*, 924–927.
- [73] 1,2-Diborylated ferrocene dimers that are reminiscent of DBAs have been reported by Jäkle and co-workers: a) K. Venkatasubbaiah, L. N. Zakharov, W. S. Kassel, A. L. Rheingold, F. Jäkle, *Angew. Chem.* **2005**, *117*, 5564–5569; *Angew. Chem. Int. Ed.* **2005**, *44*, 5428–5433; b) K. Venkatasubbaiah, I. Nowik, R. H. Herber, F. Jäkle, *Chem. Commun.* **2007**, 2154–2156; c) T. Pakkirisamy, K. Venkatasubbaiah, W. S. Kassel, A. L. Rheingold, F. Jäkle, *Organometallics* **2008**, *27*, 3056–3064; d) K. Venkatasubbaiah, A. Doshi, I. Nowik, R. H. Herber, A. L. Rheingold, F. Jäkle, *Chem. Eur. J.* **2008**, *14*, 444–458; e) K. Venkatasubbaiah, T. Pakkirisamy, R. A. Lalancette, F. Jäkle, *Dalton Trans.* **2008**, 4507–4513.
- [74] T. J. Marks, J. R. Kolb, *Chem. Rev.* **1977**, *77*, 263–293.
- [75] M. Ephritikhine, *Chem. Rev.* **1997**, *97*, 2193–2242.
- [76] D. S. Marynick, W. N. Lipscomb, *Inorg. Chem.* **1972**, *11*, 820–823.
- [77] J. A. Jensen, J. E. Gozum, D. M. Pollina, G. S. Girolami, *J. Am. Chem. Soc.* **1988**, *110*, 1643–1644.
- [78] J. P. White III, H. Deng, S. G. Shore, *Inorg. Chem.* **1991**, *30*, 2337–2342.
- [79] N. Kumar, Y. Yang, W. Noh, G. S. Girolami, J. R. Abelson, *Chem. Mater.* **2007**, *19*, 3802–3807.
- [80] A. L. Spek, *J. Appl. Crystallogr.* **2003**, *36*, 7–13.
- [81] G. M. Sheldrick, *Acta Crystallogr. A* **1990**, *46*, 467–473.
- [82] G. M. Sheldrick, *SHELXL-97, A Program for the Refinement of Crystal Structures*, Universität Göttingen, Göttingen (Germany), **1997**.
- [83] Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima et al., Gaussian, Inc., Wallingford CT, **2009**.
- [84] S. Grimme, *J. Comput. Chem.* **2006**, *27*, 1787–1799.
- [85] A. D. McLean, G. S. Chandler, *J. Chem. Phys.* **1980**, *72*, 5639–5648.
- [86] R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.* **1980**, *72*, 650–654.
- [87] K. Fukui, *Acc. Chem. Res.* **1981**, *14*, 363–368.
- [88] H. P. Hratchian, H. B. Schlegel, *J. Chem. Theory Comput.* **2005**, *1*, 61–69.
- [89] F. Neese, U. Becker, D. Bykov, D. Ganyushin, A. Hansen, R. Izsak, D. G. Liakos, C. Kollmar, S. Kossmann, D. A. Pantazis, T. Petrenko, C. Reimann, C. Riplinger, M. Roemelt, B. Sandhöfer, I. Schapiro, K. Sivalingam, B. Weizsl, *ORCA V.2.9.0, An ab initio, DFT and Semi-empirical Electronic Structure Package*, Max Planck Institute for Bioinorganic Chemistry, Mülheim/Ruhr (Germany).
- [90] F. Neese, *WIREs Comput. Mol. Sci.* **2012**, *2*, 73–78.
- [91] A. Karton, A. Tarnopolsky, J.-F. Lamère, G. C. Schatz, J. M. L. Martin, *J. Phys. Chem. A* **2008**, *112*, 12868–12886.
- [92] A. Schäfer, H. Horn, R. Ahlrichs, *J. Chem. Phys.* **1992**, *97*, 2571–2577.
- [93] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.
- [94] F. Weigend, *Phys. Chem. Chem. Phys.* **2002**, *4*, 4285–4291.
- [95] S. Kossmann, F. Neese, *Chem. Phys. Lett.* **2009**, *481*, 240–243.
- [96] F. Weigend, M. Häser, *Theor. Chem. Acc.* **1997**, *97*, 331–340.
- [97] F. Weigend, M. Häser, H. Patzelt, R. Ahlrichs, *Chem. Phys. Lett.* **1998**, *294*, 143–152.
- [98] S. Grimme, *J. Comput. Chem.* **2004**, *25*, 1463–1473.

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Dynamic covalent chemistry: Bis-borate $\text{Li}_2[1,2\text{-C}_6\text{H}_4(\text{BH}_3)_2]$ is a useful source of bis-borane $1,2\text{-C}_6\text{H}_4(\text{BH}_2)_2$, which can be trapped or used in hydro-

boration reactions; in the absence of a trapping reagent, redistribution affords 9,10-dihydro-9,10-diboraanthracene.

Boranes

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Synthesis, Coupling, and Condensation Reactions of 1,2-Diborylated Benzenes: An Experimental and Quantum-Chemical Study 