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ARTICLE

Luminescent Symmetrically and Unsymmetrically Substituted Diboranes(4)

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Dedicated to Prof. Manfred Scheer on Occasion of his 65th Birthday

Abstract. A series of 4-(dimethylamino)phenyl and pentafluorophenyl-substituted 1,2-bis(dimethylamino)diboranes(4) of type **A**, benzo-fused cyclic 1,4-diaza-2,3-diborinanes of type **B**, and 1,2-didurylidiboranes(4) of type **C** were synthesized and structurally characterized. Spectroscopic studies revealed that the substitution pattern is a decisive factor for the observation of fluorescence in most of the derivatives **A** to **C**. For diboranes(4) of type **A**, unsymmetrical substitution with electron-donating and -withdrawing groups at the boron centers is crucial to invoke fluorescence, albeit weak. Substitution at the boron atoms of 1,4-diaza-2,3-diborinane species **B** leads to a modified skeletal structure. Finally, the grafting of 4-(dimethylamino) phenyl groups to diboranes(4) of type **C** results in extraordinary Stokes shifts in nonpolar solvents.

Introduction

The luminescence of three-coordinate arylmonoboranes has been thoroughly investigated leading to numerous applications,[1] e.g. as anion sensors,[2] in bioimaging,[3] or as OLED materials.[4] The boron center with its formally vacant p_z orbital mostly acts as π acceptor. In particular, the $BMes_2$ group is frequently applied due to its strong electron-accepting properties combined with steric protection.[5] Through π conjugation with an appropriate donor, e.g. amino substituents,[6] mediated by a suitable linking unit,[5m,5p,7] the HOMO–LUMO gap can be narrowed, in some cases down to energy values corresponding to transitions in the near-IR.[8] Even simple donor substituents such as 4-*N*,*N*-dimethylaniline lead to a redshift of the longest wavelength absorption and emission bands.[5a,5g] In addition, the HOMO–LUMO gap can be affected by increasing the electron-deficiency at the boron center through incorporation of electron-withdrawing substituents.[7e,9] Notably, diboranes(4) have rarely been investigated in this regard.

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Diboranes(4) were discovered as early as 1925[10] making available a versatile and extremely useful class of reagents. In particular, the isolation of the remarkably stable tetrakis(dimethylamino)diborane(4) (already observed by *Urry* et al. in 1954[12]) by *Brotherton* and co-workers in 1960[11] opened up a wide range of synthetic possibilities. For example, the treatment of tetrakis(dimethylamino)diborane(4) with HCl[13] or BX_3[14] yields the mixed 1,2-bis(dimethylamino)-1,2-dihalodiboranes(4), which can subsequently be converted to various 1,2-bis(dimethylamino)diboranes(4) by reaction with aryl and/or alkyllithium compounds (Figure 1).[10a,14b,15] Transformation of the amino into chloro groups[16] provides synthetic access to donor-free tetraaryldiboranes(4).[17]

Cyclic 1,4-diaza-2,3-diborinanes have been scarcely reported because their 1,1-isomers with 1,3,2-diazaborole moieties are thermodynamically favored.[18] *Nöth* et al. were the first to selectively synthesize a cyclic 1,4-diaza-2,3-diborinane.[18] Later, more cyclic 1,4-diaza-2,3-diborinane species were synthesized by *Şahin* et al. and the *Braunschweig* group.[19] *Norman* and *Russel* et al. isolated both possible isomers from the reaction between *o*-phenylenediamine and tetrakis(dimethylamino)diborane(4) via transamination.[20] With R = Me at the nitrogen atoms, Norman and Russel found both isomers to be fluorescent.[21] While diazaboroles are known to be fluorescent,[22] 1,4-diaza-2,3-diborinane derivatives have not been intensely investigated in this regard.

We were therefore curious about the effect on fluorescence of attaching *para*-dimethylaminophenyl (as electron-rich substituent) and pentafluorophenyl groups (as electron-poor substituent) to the boron centers of simple 1,2-bis(dimethylamino) diboranes(4) **A**, modified cyclic 1,4-diaza-2,3-diborinane derivatives **B**, and donor-free diboranes(4) **C** (Figure 1). Herein we report synthesis, characterization, and fluorescence studies (where applicable) of the novel diboranes(4) of type **A** to **C**.

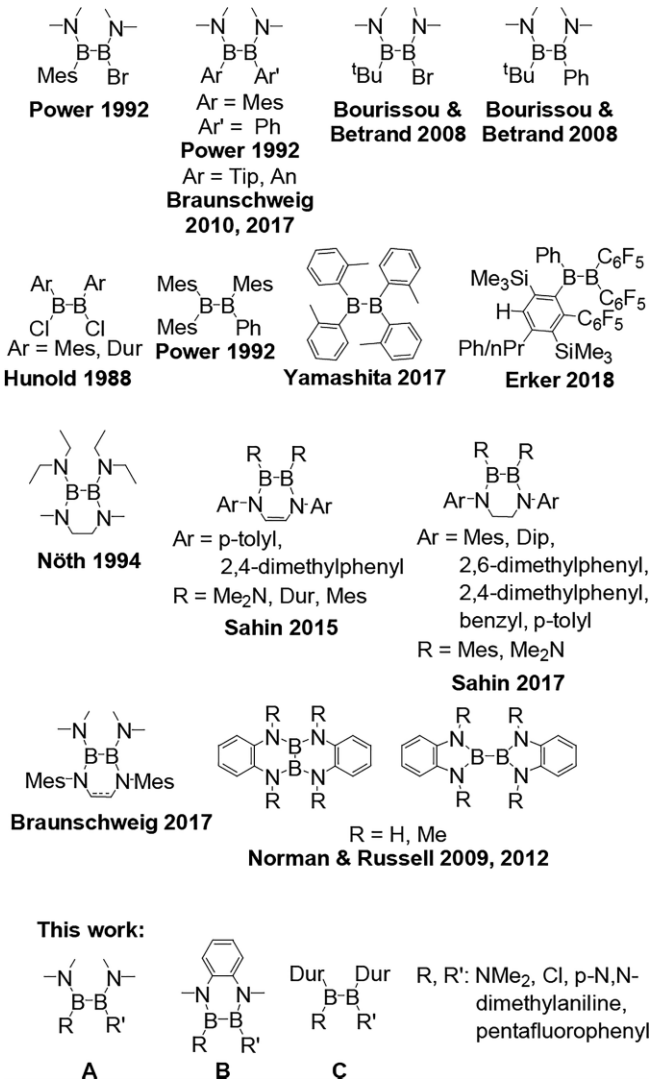
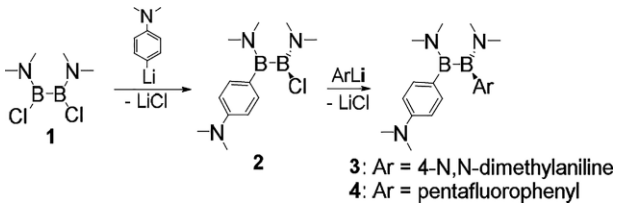


Figure 1. Selected diboranes(4) (Mes = 2,4,6-trimethylphenyl, Ph = phenyl, Tip = 2,4,6-triisopropylphenyl, An = 9-anthracenyl, Dur = 2,3,5,6-tetramethylphenyl, Dip = 2,6-diisopropylphenyl).[10a,14b,15,17–21]

Results and Discussion

Synthesis and Nuclear Magnetic Resonance Data

The reaction of 1,2-dichloro-1,2-bis(dimethylamino)diborane(4) (**1**)[13,14] with 1.2 equivalents of 4-(dimethylamino) phenyllithium was carried out based on procedures for analogous substitution reactions.[14b,15a] 4-(Dimethylamino)phenyllithium was prepared from 4-bromo-*N*,*N*-dimethylaniline and *n*BuLi in ethyl ether at low temperatures according to a modified literature procedure[23] and isolated prior to use. Diborane(4) **2** was isolated as bright yellow crystals in acceptable yield (46 %) (Scheme 1). The ^{11}B NMR spectrum of **2** shows one broad signal at δ = 43.9 ppm within the expected range for 1,2-bis(dimethylamino)diboranes(4).[10a] Considering analogous structural motifs,[14b,15a] two signals would be expected for **2**, but are probably too close in chemical shift to be resolved.

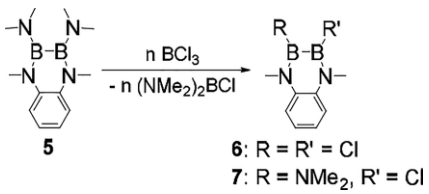


Scheme 1. Synthesis of substituted 1,2-bis(dimethylamino)diboranes(4) **2** to **4**.

The symmetric 1,2-bis(dimethylamino) diborane(4) **3** was synthesized by adding an additional equivalent of 4-(dimethylamino)phenyllithium to **2** in Et_2O at low temperatures. After warming to room temperature, the solvent was exchanged to toluene and subsequent heating of the mixture to 100 °C for one hour completed the reaction. Diborane(4) **3** was isolated as yellow crystals in moderate yields (32 %) (Scheme 1). The ^{11}B NMR spectrum of **3** shows one broad signal at δ = 49.4 ppm within the expected range for 1,2-bis(dimethylamino)diboranes(4).[14b,15] Conversely, all attempts to prepare **3** directly from **1** remained unsuccessful.

The pentafluorophenyl substituent was introduced by reaction of **2** in ethyl ether at low temperatures affording diborane(4) **4** as colorless crystals in acceptable yield (52 %) (Scheme 1). Pentafluorophenyllithium was prepared in situ following a modified literature procedure by adding *n*-butyllithium to a cooled solution of bromopentafluorobenzene in Et_2O.[24] Addition of a precooled solution of **2** in Et_2O at –90 °C is crucial for the stability of the anion. The ^{11}B NMR spectrum of **4** shows one broad signal at δ = 45.8 ppm in the expected range for 1,2-bis(dimethylamino)diboranes(4).[14b,15] The 1,2-bis(dimethylamino)diboranes(4) **2**, **3** and **4** are air and moisture sensitive in solution, although **3** and **4** are mostly stable under air in the solid state overnight.

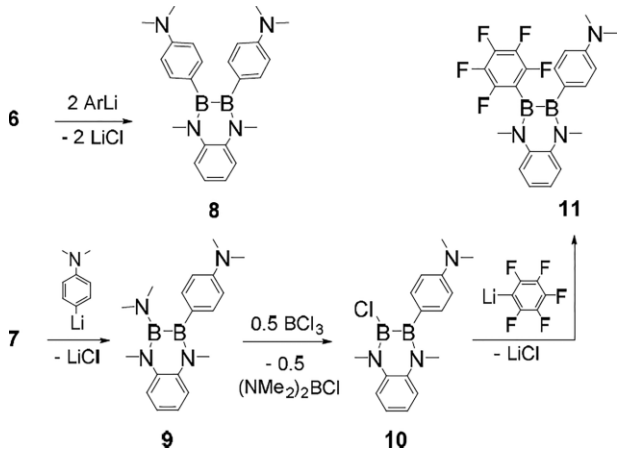
Diborane **5** was prepared in analogy to literature procedures.[18,19] ^{11}B NMR spectrum of **5** shows one signal at δ = 33.7 ppm in the expected range for cyclic 1,4-diaza-2,3-diborinanes.[25] Replacement of the dimethylamino groups in **5** by two or one chlorine atom(s) in hexane at 0 °C using 1 and 0.5 equivalents of BCl_3 gave **6** and **7**, respectively (Scheme 2). The chlorinated diboranes **6** and **7** were used without further purification, since the ^{11}B NMR spectra of the crude products show only signals that could be assigned to compounds **6** (δ = 40.0 ppm) and **7** (δ = 47.2 ppm, 34.0 ppm), respectively.



Scheme 2. Synthesis of substituted cyclic 1,4-diaza-2,3-diborinanes **6** and **7**.

The dichlorinated 1,4-diaza-2,3-diborinane **6** reacts in a salt metathesis with two equivalents of the appropriate anion to the

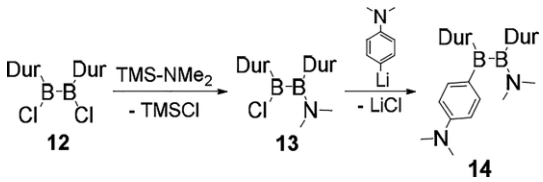
bis(4-dimethylaminophenyl)-substituted **8**, which was isolated as yellow crystals in mediocre yield (21 %), (Scheme 3). ^{11}B NMR spectrum shows one broad signal (δ = 46.4 ppm) in the same range as cyclic 1,4-diaza-2,3-diborinane **6**.



Scheme 3. Synthesis of substituted cyclic 1,4-diaza-2,3-diborinanes **8** to **11**.

The attempted monosubstitution of one chloride of **6** with 4-(dimethylamino)phenyllithium failed due to selectivity issues. Therefore, the mono(dimethylamino)-substituted derivative **7** was prepared from **5** (see above). Subsequent reaction with 4-(dimethylamino)phenyllithium affords **9** as yellow crystals in moderate yields (31 %) (Scheme 3). The ^{11}B NMR spectrum shows signals at δ = 47.2 ppm and δ = 34.0 ppm, similar to those of **7**. The dimethylamino group of **9** can be exchanged by a chloro substituent with 0.5 equivalents of BCl_3 to give **10** as colorless crystals in moderate yield (42 %) (Scheme 3). The ^{11}B NMR spectrum of **10** shows only one broad signal at δ = 43.2 ppm in the expected range.[19] As in the case of **2**, the expected two signals are probably close in chemical shift and too broad to be resolved. In situ generated pentafluorophenyllithium[24] was then reacted with **10** in a mixture of toluene and ethyl ether at –100 °C to selectively yield the unsymmetrically substituted cyclic diazadiborinane **11** in acceptable yields (49 %) as a colorless powder (Scheme 3). Crystallization from hexane afforded single crystals. The ^{11}B NMR spectrum shows one broad signal at δ = 45.3 ppm in the same range as **10**. Again, the expected two signals are presumably too close in chemical shift to be resolved.

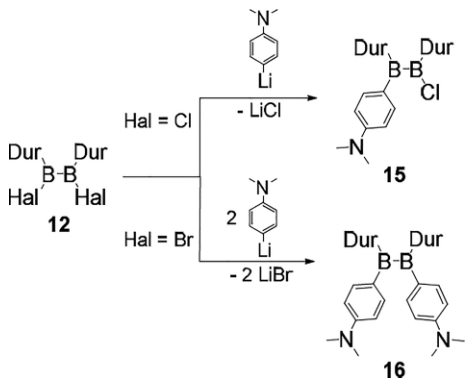
1,2-Dihalo-1,2-diduryldiborane(4) (**12**) was synthesized according to the literature procedure.[16] Protection of one reactive site by reaction of **12** with Me_3SiNMe_2 in hexane at low temperatures afforded **13** in very good yields (83 %) as a colorless solid (Scheme 4). The ^{11}B NMR spectrum shows a very broad peak at δ = 88.0 ppm for the chloro-substituted boron atom, as expected,[16] and one broad signal at δ = 47.2 ppm for the amino-substituted, also in the expected range.[14b,15] The cyclic 1,4-diaza-2,3-diborinanes **5**, **6**, **7**, **8**, **9**, **10**, **11** are air and moisture sensitive in solution, although **8** and **11** are stable under air in the solid state overnight.



Scheme 4. Synthesis of substituted 1,2-diduryl diboranes(4) **13** and **14** (Dur = 2,3,5,6-tetramethylphenyl).

For the incorporation of the donor substituent, **13** and 4-(dimethylamino)phenyllithium were mixed in solid form, Et_2O was added and the reaction mixture stirred overnight. Diborane(4) **14** was isolated in acceptable yield (51 %) (Scheme 4). The ^{11}B NMR spectrum exhibited the anticipated two broad signals, one at δ = 87.1 ppm due to the 4-(dimethylamino) phenyl-substituted boron atom and the second at δ = 53.2 ppm for the amino-substituted one. The chemical shifts are comparable to the signals of **13**.

Diboranes(4) **15** and **16** were synthesized from 1,2-dihalodiduryl diborane(4) **12** by reaction with the appropriate number of equivalents of 4-(dimethylamino)phenyllithium (Scheme 5). In order to increase selectivity, a temperature of –78 °C had to be maintained during the synthesis of **15**, whereas **16** is readily obtained by reaction at room temperature. While **15** was isolated in moderate yield of 45 %, **16** could only be obtained in mediocre crystalline yield of 19 %. The ^{11}B NMR spectrum of **15** shows one broad signal at δ = 81.1 ppm. In case of **16**, no ^{11}B NMR signal could be observed at room temperature. At 343 K, however, sufficient sharpening occurred to give rise to a clearly distinguishable, nevertheless still broad signal at δ = 87.1 ppm. All attempts to prepare a mono(pentafluorophenyl) derivative of **15** failed as the pentafluorophenyl anion decomposed before reaction with **15** could take place. 1,2-Diduryldiboranes(4) **13**, **15** are air and moisture sensitive in solution and the solid state, whereas **14** and **16** are stable under air in solution and the solid state for at least days.



Scheme 5. Synthesis of substituted 1,2-diduryl diboranes(4) **15** and **16** (Dur = 2,3,5,6-tetramethylphenyl).

X-ray Structures

In case of the open-chained diboranes(4) **2** and **3**, single crystals were obtained from hexane at 5 °C, whereas single

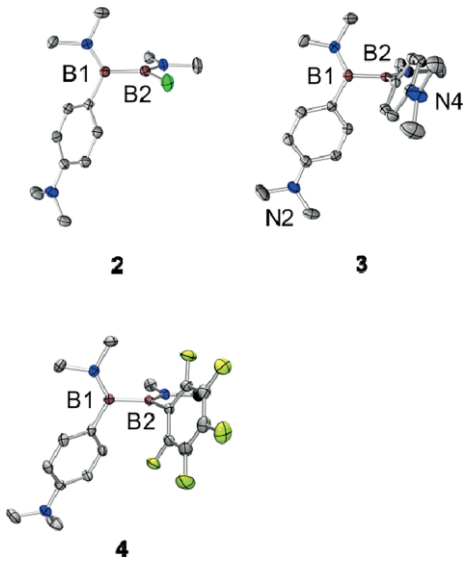


Figure 2. Molecular structures of **2**, **3** and **4** in the solid state (hydrogen atoms omitted for clarity; thermal ellipsoids drawn at 50% probability).

crystals of **4** were grown from *ortho*-difluorobenzene at –26 °C. The solid-state structures are shown in Figure 2 and selected structural parameters are listed in Table 1. The B–B bond lengths in **2** to **4** [**2**: 1.7017(15) Å, **3**: 1.716(3) Å, **4**: 1.7132(14) Å] are similar to those in *Power's* $N(Me_2)MesBBN(Me_2)Br$ (1.682 Å), $N(Me_2)MesBBN(Me_2)Mes$ (1.717 Å), and $N(Me_2)PhBBN(Me_2)Ph$ (1.714 Å).[14b] In all cases of **2** to **4**, the sum of angles around the B atoms (Σ angles ≈ 360°) indicates trigonal planar coordination environments, which are nearly orthogonal to each other (angle between B-coordination planes in **2**: 88.9°, **3**: 83.8° and **4**: 85.6°). The B–N bond lengths between 1.386(1) Å and 1.405(3) Å are in the typical range[14b,15] and the planar coordination environments of the NMe_2 nitrogen atoms demonstrate the significant B-N double bond character, as usual for this class of compounds.[14b,15] On the other hand, the N atoms of the phenyl-bonded NMe_2 groups are slightly pyramidalized in **2** and **4** (Σ angles = 355.9° and 353.6°, respectively). In the bis(4-dimethylaminophenyl) derivative **3**, however, N2 is nearly planar (Σ angles = 359.5°) and N4 is pyramidalized to a certain extent (Σ angles = 350.1°). Irrespective of the degree of pyramidalization at the nitrogen atoms, the N–C(phenyl) distances are of comparable size. This demonstrates that π donation of the phenyl-bonded NMe_2 group is of smaller importance in **2**, **3** and **4** than in, for instance, *p*-$Me_2N(C_6H_4)BMes_2$ as characterized by *Marder* et al.,[5g] in which the NMe_2 group is coordinated in a trigonal planar fashion and the N–C distance is shorter by at least 0.02 Å.

Single crystals of **5**, **9** and **11** were obtained from hexane, whereas single crystals of **8** and **10** were grown from a mixture of hexane and toluene. Solid state structures of substituted cyclic 1,4-diaza-2,3-diborinane derivatives **5** and **8** to **11** are shown in Figure 3 and selected structural parameters are listed in Table 2. B–B bond lengths of **5** and **8** to **11** [in the range from 1.663(2) Å to 1.687(4) Å] are slightly shorter than those in **2** to **4** in accordance with the bond lengths observed in the 1,4-diaza-2,3-diborinines prepared by *Braunschweig* et al. (1.686 Å, 1.673 Å).[19c] Monocycles with a saturated endocyclic C–C unit reported by *Braunschweig* et al. (1.699 Å)[19c] and *Sahin* et al. (1.725 Å, 1.715 Å, 1.723 Å, 1.710 Å)[19b] have slightly longer B–B bonds, whereas the B–B bond in the bicyclic 1,4-diaza-2,3-diborinane reported by *Norman* and *Russell* et al. (1.650 Å)[25] is shorter. The sum of angles around the boron and endocyclic nitrogen atoms in all cyclic 1,4-diaza-2,3-diborinanes **5** and **8** to **11** show trigonal planar coordination geometries (Σ angles ≈ 360°). The largest deviation from planarity of the CNBBNC-ring plane in the cyclic 1,4-diaza-2,3-diborinanes **5** and **8** to **11** differs considerably, ranging from 0.0233 Å to 0.1702 Å. Cyclic 1,4-diaza-2,3-diborinanes **8**, **10**, **11** show a nearly planar arrangement of the six-membered ring (standard deviation in **8**: 0.0322 Å, **10**: 0.0233 Å and **11**: 0.0325 Å) while those of **5** and **9** are strongly distorted (standard deviation in **5**: 0.1702 Å and **9**: 0.0809 Å). *Sahin* et al. explained the deviation from planarity in analogous compounds by steric interactions between the substituents.[19a] In addition, the strong π-donor properties of the exocyclic NMe_2 group might suppress the formation of endocyclic B–N π bonds, an assumption that finds support in the comparison of the B–N bond lengths.

The endocyclic B–N bond lengths are significantly shorter (ca. 1.41 Å) in cyclic 1,4-diaza-2,3-diborinanes without NMe_2 substituents [**8**: 1.428(3) Å, 1.416(3) Å; **10**: 1.4095(17) Å, 1.3998(18) Å;**11**: 1.4219(13) Å, 1.4019(13) Å] than in those with NMe_2 substituents [**5**: 1.4576(16) Å, 1.4531(16) Å; **9**:

Table 1. Selected structural data of the compounds **2**, **3**, and **4**.[a)].

	2	**3**	**4**
B1–B2	1.7017(15)	1.716(3)	1.7132(14)
B1–NMe_2	1.3948(12)	1.399(3)	1.3985(13)
B2–NMe_2	1.3855(14)	1.405(3)	1.3868(13)
B–C_{ipso}(Ph–NMe_2)	1.5774(13)	1.585(3) [b)] , 1.576(3) [c)]	1.5717(14)
N–C(Ph)	1.3841(13)	1.384(3) [d)], 1400(3) [e)]	1.3892(13)
Σ angles B1	360.0	359.9	360.0
Σ angles B2	360.0	360.0	360.0
Σ angles N(B1)	360.0	359.9	360.0
Σ angles N(B2)	360.0	360.0	360.0
Σ angles N(Ph),	355.9	359.5 [f)], 350.1 [g)]	353.6
Angle between B-coord. planes	88.9	83.8	85.6

a) Bond lengths /Å and angles /°. b) B1–C_{ipso}(Ph–NMe_2). c) B2–C_{ipso}(Ph–NMe_2). d) N2–C(Ph). e) N4–C(Ph). f) Σ angles N2. g) Σ angles N4.

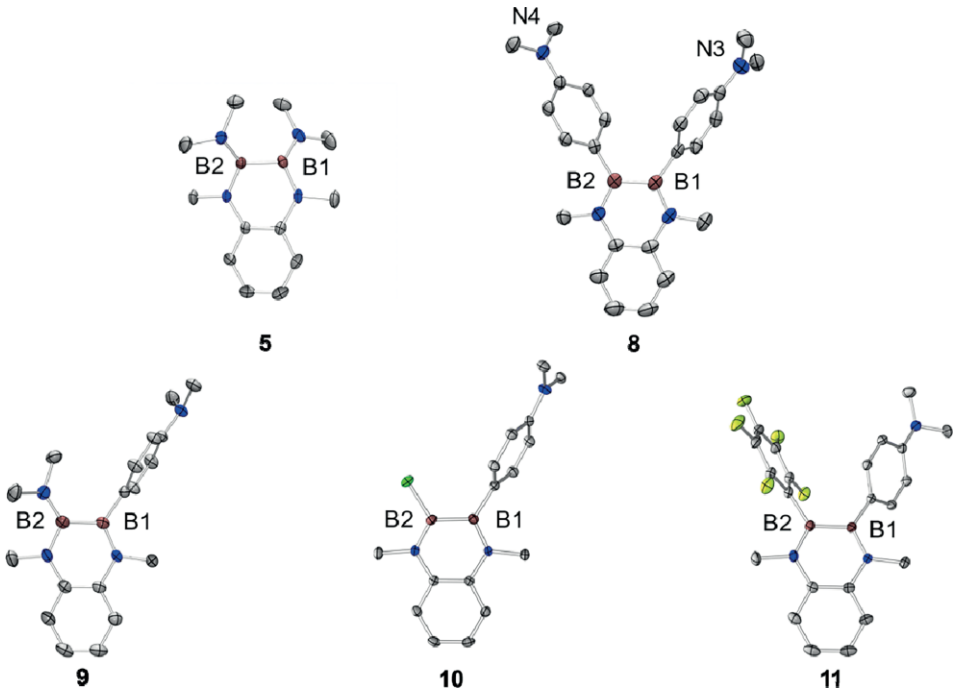


Figure 3. Molecular structures of **5** and **8** to **11** in the solid state (hydrogen atoms omitted for clarity; thermal ellipsoids drawn at 50% probability).

Table 2. Selected structural data of the compounds **5** and **8** to **11**.[a)]

	5	**8**	**9**	**10**	**11**
B1–B2	1.6869(17)	1.687(4)	1.686(3)	1.663(2)	1.6757(15)
B1–N [b)]	1.4576(16)	1.428(3)	1.423(3)	1.4095(17)	1.4219(13)
B2–N [b)]	1.4531(16)	1.416(3)	1.449(3)	1.3998(18)	1.4019(13)
B–NMe_2	1.4106(16) [c)], 1.4136(16) [d)]	–	1.421(3)	–	–
B–C_{ipso}(Ph–NMe_2)	–	1.571(3)[e)], 1.572(4) [f)]	1.584(3)	1.5697(18)	1.5713(14)
N–C(Ph)	–	1.377(3) [g)], 1.383(3)[h)]	1.412(2)	1.3802(16)	1.4043(13)
Σ angles B1	359.8	359.9	360.0	360.0	360.0
Σ angles B2	359.6	360.0	359.9	359.9	360.0
Σ angles N(B1) [i)]	360.0	360.0	360.0	360.0	360.0
Σ angles N(B2) [i)]	360.0	359.93	360.0	360.0	360.0
Σ angles N(Ph)	–	360.0 [j)], 359.8 [k)]	348.2	359.9	348.5
Largest dev. [l)] from planarity (CNBBNC ring)	0.1702	0.0322	0.0809	0.0233	0.0325

a) Bond lengths /Å and angles /°. b) Endocyclic bond. c) B1–NMe_2. d) B2–NMe_2. e) B1–C_{ipso}(Ph–NMe_2). f) B2–C_{ipso}(Ph–NMe_2). g) N3–C(Ph). h) N4–C(Ph). i) Endocyclic N. j) Σ angles N3. k) Σ angles N4. l) In Å.

1.423(3) Å, 1.449(3) Å], indicating a weaker endocyclic B–N π-bond in **5** and **9**. In addition the exocyclic B–NMe_2 bond lengths in **5** and **9** [**5**: 1.4106(16) Å, 1.4136(16) Å; **9**: 1.421(3) Å], though slightly elongated compared to the B–NMe_2 bond lengths in **2** to **4**, are much shorter than in B–N single bonds, i.e. $F_5C_6(F_3C)_2B$–NMe_3 (1.643 Å),[26a] $(F_5C_2)_3B$–NMe_3 (1.674 Å),[26b] $(F_5C_6)_3B$–NMe_2Bn (1.807 Å),[26c] indicating a pronounced B–N double bond character. The coordination environment of the aniline nitrogen atoms in **8** and **10** is trigonal planar (Σ angles ≈ 360°), whereas the aniline nitrogen atoms of **9** and **11** show slightly pyramidalized coordination with Σ angles = 348.2° and 348.5°. This circumstance provides a hint at π donor contribution of the NMe_2-aniline group in **8** and **10**, which is also reflected in shorter N-phenyl bond lengths [**8**: 1.377(3) Å, 1.383(3) Å; **10**: 1.3802(16) Å] compared to those in **9** and **11** [**9**: 1.412(2) Å, **11**: 1.4043(13) Å]. The N–C_{phenyl} bond lengths of **8** and **10**, however, are in the same range as those in **2** to **4** so that donor effects of the NMe_2-aniline group are most likely weak as well.

Single crystals of **13** (from hexane at room temperature) and **15** (from toluene at –26 °C) allowed for the determination of their structures in the solid state (Figure 4, Table 3), which are exemplary for the two types of diduryldiboranes(4) reported in this work. The B–B bond lengths [**13**: 1.704(2) Å, **15**: 1.690(3) Å] of both compounds are slightly longer than those in the cyclic 1,4-diaza-2,3-diborinanes above (Table 2) and hence in the range of bis(dimethylamino)diborane(4) B–B bonds (Table 1). They compare well to $Mes_2BBMesPh$ [1.706(12) Å[17a]] and the equally unsymmetric diborane(4) reported by *Erker* et al. [1.714(5) Å[17c]] but are slightly longer than the B–B bonds

in the two conformers of $(o\text{-tol})_2BB(o\text{-tol})_2$ (1.686 Å / 1.695 Å[17b]). The diduryldiboranes(4) **13** and **15** show planar coordination arrangement around the boron centers (sum of angles close to 360° at each B). Moreover, the coordination arrangement around the NMe_2 group in **13** is planar and the B–N bond length is similar to those in the bis(dimethylamino) diboranes(4) **2** to **4**, leading to the conclusion that the same bonding situation between boron and nitrogen can be assumed. The angles between the coordination planes at the boron atoms are smaller (**13**: 62.7°, **15**: 64.1°) than in **2** to **4**. The $B–C_{Dur}$ distances [**13**: 1.5886(18) Å/ 1.5682(19) Å, **15**: 1.573(3) Å/ 1.592(3) Å] are in the usual range for B-aryl bonds.[14b,15b] Unlike in the previous cases (**2**, **3**, **4**, **8**, **9**, **10**, **11**), the π donation of the NMe_2 group in the aniline substituent of **15** is substantial as shown by the almost planar coordination around the aniline nitrogen (Σ angles = 358.7°) and the N–C(Ph) bond length [1.365(2) Å], which is the shortest of all diboranes(4) reported here.

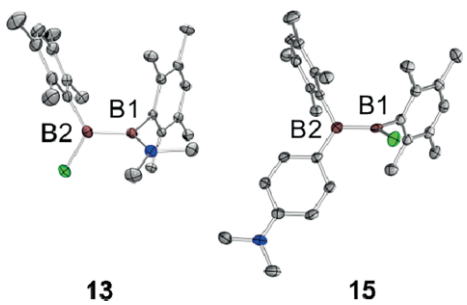


Figure 4. Molecular structures of **13** and **15** in the solid state (hydrogen atoms omitted for clarity; thermal ellipsoids drawn at 50% probability).

Table 3. Selected structural data of compounds **13** and **15**.[a)].

	13	**15**
B1–B2	1.704(2)	1.690(3)
$B1–C_{Dur}$	1.5886(18)	1.573(3)
$B2–C_{Dur}$	1.5682(19)	1.592(3)
$B–NMe_2$	1.3881(17)	–
$B–C_{ipso}(Ph–NMe_2)$	–	1.531(3)
N–C(Ph)	–	1.365(2)
Σ angles B1	360.0	360.0
Σ angles B2	359.4	360.0
Σ angles $N(Me_2)$	360.0	–
Σ angles N(Ph)	–	358.7
Angle between B-coord. planes	62.7	64.1

a) Bond lengths /Å and angles /°.

Photophysical Properties

para-Dimethylaminophenyl-substituted 1,2-bis(dimethylamino)diboranes(4) **2** and **3** both show absorption bands at $\lambda_{abs,max}$ = 282 nm and $\lambda_{abs,max}$ = 281 nm in hexane, respectively, but no emission of light. In contrast, fluorescence was detected in hexane with 5% Et_2O at $\lambda_{em,max}$ = 335 nm for **4** when exciting the molecule at $\lambda_{exc,max}$ = 290 nm ($\lambda_{abs,max}$ = 287 nm, in Et_2O), albeit with a quantum yield below 5%.

UV/Vis spectra of cyclic 1,4-diaza-2,3-diborinanes **5**, **8**, **9**, **10** and **11** show multiple absorption bands with those at longest wavelength in the range of $\lambda_{abs,max}$ = 314 nm to $\lambda_{abs,max}$ = 349 nm (Table 4, Figure 5). Irradiation in the range of $\lambda_{exc,max}$ = 297 nm to $\lambda_{exc,max}$ = 341 nm prompts emission in solution in the range of $\lambda_{em,max}$ = 325 nm to $\lambda_{em,max}$ = 511 nm in the cases **5**, **8** and **9** (Table 4, Figure 5) suggesting the cyclic 1,4-diaza-2,3-diborinane scaffold as origin of a common fluorescence slightly modified by the different substituents. In comparison to *Norman* and *Russell's* cyclic 1,4-diaza-2,3-diborinane isomer[21] emission of cyclic 1,4-diaza-2,3-diborinanes **5** and **9** is hypsochromically shifted, probably due to the absence of one half of the fused cyclic system. Upon formal replacement of one NMe_2 group in **5** by *para*-dimethylaminophenyl as in **9**, a bathochromic shift of 30 nm in emission is observed, which is indicative of the expansion of the conjugated system. Similarly, the presence of an additional aminophenyl substituent (**8**) results in a bathochromic shift compared to Norman and Russell's cyclic 1,4-diaza-2,3-diborinane isomer.[21] The emission band is split into two maxima at $\lambda_{em,max}$ = 473 nm and $\lambda_{em,max}$ = 511 nm due to vibronic coupling (the corresponding excitation band is at $\lambda_{exc,max}$ = 341 nm; Table 4, Figure 5). The chloro derivative **10**, however, shows no emission at all. Pentafluorophenyl-substituted **11** is almost equally excited at three distinct maxima at $\lambda_{exc,max}$ = 266 nm, $\lambda_{exc,max}$ = 300 nm and $\lambda_{exc,max}$ = 350 nm but exhibits only one emission maximum at $\lambda_{em,max}$ = 406 nm in accordance with Kasha's rule[27] (Table 4, Figure 5). An acceptable quantum yield was determined by an integrating sphere for **5** and **9** with 55% and 48%, respectively. The bis(dimethylaminophenyl) species **8** exhibits a somewhat elevated quantum yield of 17% and a poor quantum yield (7%) was detected for **11**.

The monochlorinated dimethylamino-1,2-diduryldiborane(4) **13** shows a weak absorption band at $\lambda_{abs,max}$ = 313 nm in hexane, but almost no emission. In contrast, fluorescence was detected in hexane for the dimethylaminophenyl-substituted 1,2-diduryldiboranes(4) **14**, **15**, and **16**, which all show maximum wavelength absorptions at around $\lambda_{abs,max} \approx 340$ nm (Table 5, Figure 5) indicating that the absorbing system in all three compounds is the aminophenylboron moiety (absorption of the corresponding dimesitylmonoborane is reported in the same range[5a,5g]).

The longest wavelength absorptions also correlate perfectly with the excitation band maximum for each compound. Although fluorescence was measured in a non-polar solvent, the Stokes shifts are exceptionally large for all three compounds. The dimethylamino derivative **14** shows an emission band maximum at $\lambda_{em,max}$ = 430 nm [Stokes shift = 93 nm (6418 cm^{-1}); Table 5, Figure 5], while the corresponding monochlorinated **15** exhibits an emission band maximum at $\lambda_{em,max}$ = 520 nm [Stokes shift = 181 nm (10268 cm^{-1}); Table 5, Figure 5].

The bis(dimethylaminophenyl) derivative **16** features even two emission band maxima originating from the same excitation band [$\lambda_{em,max}$ = 474 nm, $\lambda_{em,max}$ = 558 nm; Stokes shift = 133 nm (8229 cm^{-1}), 217 nm (11404 cm^{-1}); Table 5, Figure 5] suggesting either vibronic coupling or excitation to a

Table 4. Spectral data of compounds **5** and **8** to **11**.[a].

	5 [b]	**8** [c]	**9** [b]	**10** [c]	**11** [b]
$\lambda_{abs,max}$ (ε)	234 (34900) 272 (9840) 308 (12100) 314 (11800)	232 (27300) 261 (34700) 342 (35500)	216 (35000) 243 (24900) 315 (14800) 327 (15800)	232 (18900) 255 (18700) 334 (21200)	263 (21000) 313 (15000) 349 (16900)
$\lambda_{exc,max}$	297 / 303	341	313	–	266 / 300 / 350
$\lambda_{em,max}$	325	473 / 511	355	–	406
$\Delta\lambda$ ($\Delta\nu$)	28 (2901) 22 (2234)	132 (8184) 170 (9756)	42 (3780)	–	140 (12963) 106 (8703) 56(3941)
Φ_{fl}	55 ± 5 %	17 ± 5 %	48 ± 5 %	–	7 ± 5 %

a) Wavelengths [nm], wavenumbers [cm^{-1}], and extinction coefficient [$L{\cdot}mol^{-1}{\cdot}cm^{-1}$]. b) Absorption, fluorescence, and quantum yield(s) measured in hexane. c) Absorption measured in ethyl ether and fluorescence plus quantum yield measured in hexane with 5 % ethyl ether.

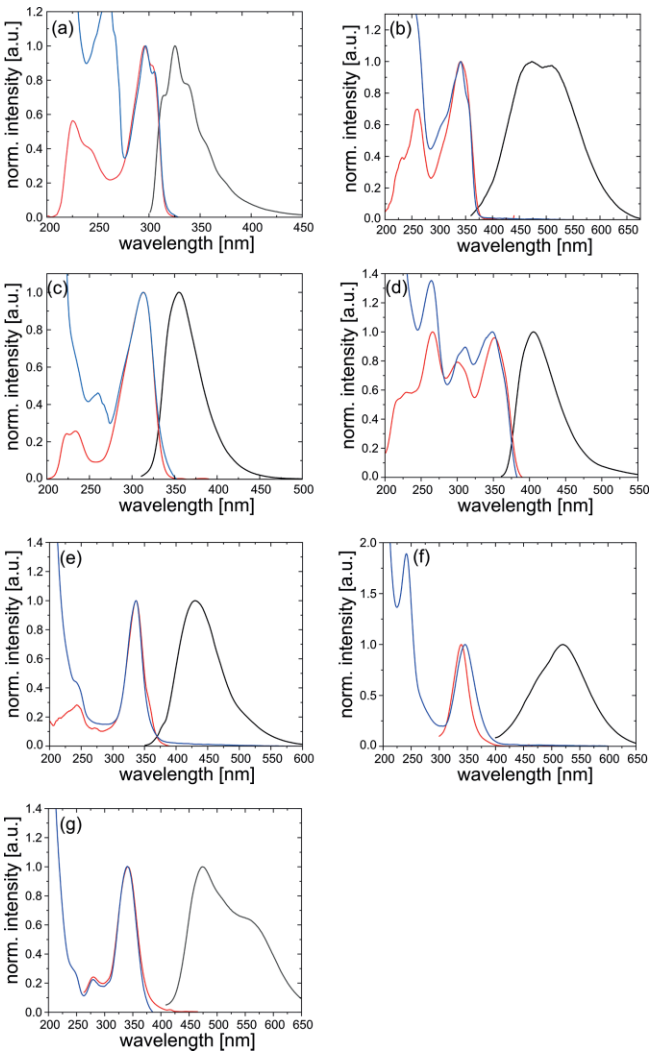


Figure 5. Absorption spectra (blue), excitation spectra (red) and emission spectra (black) of **5** (a), **8** (b), **9** (c), **11** (d), **14** (e), **15** (f), and **16** (g).

higher state with a significant delay of non-radiative decay to the S_1 state (i.e. a violation of Kasha's rule[27]). Due to the high stability of **16** under air, it is at least very unlikely that impurities or decomposition products are responsible for the second emission. The aforementioned dimethylaminophenyl-substituted dimesityl-monoborane is reported to show much less pronounced Stokes shifts [33 nm (2636 cm^{-1}),[5a] 14 nm (1075 cm^{-1})[5g]] in nonpolar solvent (cyclohexane). Large Stokes shifts suggest a pronounced geometric distortion in the excited state and intramolecular charge-transfer (ICT), as known for the related dimethylaminophenyl-substituted dimesitylborane[5a] In the case of **16** the second emission band could even occur from a twisted ICT state, although this is normally stabilized only by polar solvents.[28] The quantum yield for **14** is poor (below 5 %), but **15** and **16** display higher quantum yields of 14 % and 20 %, respectively, approaching that of the aforementioned dimethylaminophenyl-substituted dimesitylmonoborane (42 %) in cyclohexane.[5a] Unfortunately, both **15** and **16** turned out to be photolabile and decompose to unknown species upon irradiation.

Table 5. Spectral data of compounds **14**–**16**.[a].

	14	**15**	**16**
$\lambda_{abs,max}$ (ε)	242 (15800) 337 (44000)	347 (33800)	244 (17100) 279 (13900) 341 (48200)
$\lambda_{exc,max}$	337	339	341
$\lambda_{em,max}$	430	520	474/558
$\Delta\lambda$ ($\Delta\nu$)	93 (6418)	181 (10268)	133 (8229)/ 217 (11404)
Φ_{fl}	< 5 %	14 ± 5 %	20 ± 5 %

a) Wavelengths [nm], wavenumbers [cm^{-1}] and extinction coefficient [$L{\cdot}mol^{-1}{\cdot}cm^{-1}$], all spectra recorded in hexane solution.

Conclusions

We reported the synthesis and structural characterization of 4-dimethylaminophenyl and pentafluorphenyl-substituted 1,2-bis(dimethylamino)diboranes(4), **2** to **4**, benzo fused cyclic 1,4-diaza-2,3-diborinanes **5** and **8** to **11** as well as 1,2-diduryldiboranes(4) **13** and **15**. Spectroscopic studies showed that in principle fluorescence can be invoked in 1,2-bis(dimethylamino)diboranes(4) by unsymmetrical substitution with electron donating and withdrawing groups at the boron centers, i.e. diborane(4) **4**. Substitution on the cyclic 1,4-diaza-2,3-diborinane boron center mostly modified the electronic constitution of the skeletal structure (**5**, **8** to **11**). Finally, substitution on 1,2-diduryldiboranes(4) with 4-dimethylaminophenyl groups

(**14**, **15**, **16**) gave partly extraordinary Stokes shifts in nonpolar solvent.

Experimental Section

All reactions were carried out in a protective argon atmosphere and using the Schlenk technique or gloveboxes. Pentane and benzene were refluxed with sodium/benzophenone and distilled prior to use. Hexane, Et_2O, thf and toluene were taken directly from a solvent purification system (Innovative Technology PureSolv MD7). *o*-Difluorobenzene was refluxed over CaH_2 and distilled prior to use. C_6D_6 was refluxed over potassium and distilled prior to use. 1,2-Bis(dimethylamino)-1,2-dichloro diborane(4),[13,14] 1,2-diduryldihalo diborane(4),[16] 4-(dimethylamino)-phenyllithium[23] and *N*,*N*'-dilithum dimethyl-1,2-diaminobenzene[29,30] were synthesized according to literature procedure and isolated prior to use. NMR spectra were recorded at 300 K on a Bruker Avance III 300 (^{1}H: 300.13 MHz, ^{11}B: 96.29 MHz, ^{13}C: 75.47 MHz, ^{19}F: 282.40 MHz) and a Bruker Avance III HD 400 (^{1}H: 400.13 MHz, ^{11}B: 128.38 MHz, ^{13}C: 100.61 MHz). Chemical shifts are reported relative to $SiMe_4$, BF_3-OEt_2 or $CFCl_3$. UV/Vis spectra were measured using a Shimadzu UV-2600 spectrometer in quartz cells with a path length of 1 mm. Fluorescence spectra were measured using Jasco FP-6500 spectrofluorometer in quartz cells with a path length of 10 mm. The corresponding UV/Vis spectra were measured with a Jasco V-650 spectrometer. Quantum yields were measured using Hamamatsu Quantaurus-QY C11347–11. Bromopentafluorobenzene was purchased from Alfa Aesar, *n*BuLi solution (2.5 M in hexanes) and BCl_3 solution (1 M in hexanes) were purchased from Sigma Aldrich, (*N*,*N*.dimethylamino)-trimethylsilane was purchased from abcr. All were used without further purification. For crystallographic details and plots of spectra see the Supporting Information.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1971389 (**2**), CCDC-1971390 (**3**), CCDC-1971391 (**4**), CCDC-1971392 (**5**), CCDC-1971393 (**8**), CCDC-1971394 (**9**), CCDC-1971395 (**10**), CCDC-1971396 (**11**), CCDC-1971397 (**13**), and CCDC-1971398 (**15**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Synthesis of 2-Chloro-1,2-bis(dimethylamino)-1-*para*-*N*,*N*-dimethylaniline diborane(4) (2): 1,2-Bis(dimethylamino)-dichloro diborane(4) **1** (4.0 mL, 23.9 mmol, 1 equiv.) was dissolved in Et_2O (130 mL) and cooled to –78 °C (2-propanol/ liquid nitrogen). A solution of 4-(dimethylamino)phenyllithium (3.86 g, 27.3 mmol, 1.1 equiv.) in Et_2O (70 mL) was added dropwise via dropping funnel. The reaction mixture was stirred in the cooling bath for 5 min and then allowed to reach room temperature. Stirring was continued for 1 h. Removal of solvent and volatile species in vacuo was followed by filtration from hexane. Reducing the filtrate volume gave a yellow solution from which 2.94 g (46 %) of diborane(4) **2** were obtained as bright yellow crystals at 5 °C. **^{1}H NMR** (300.13 MHz, C_6D_6, 300 K, TMS): δ = 7.56 (d, ^3J = 8.7 Hz, 2 H, Me_2N-Ph*H*), 6.71 (d, ^3J = 8.8 Hz, 2 H, Me_2N-Ph*H*), 2.80 (s, 3 H, B-NCH_3), 2.74 (s, 3 H, B-NCH_3), 2.70 (s, 3 H, B-NCH_3), 2.57 [s, 6 H, (CH_3)$_2$N-Ph], 2.56 (s, 3 H, B-NCH_3) ppm. **^{11}B NMR** (96.29 MHz, C_6D_6, 300 K, BF_3–Et_2O): δ = 43.9 (br. s) ppm **^{13}C NMR** (75.47 MHz, C_6D_6, 300K, TMS): δ = 150.5 (Me_2N-Ph*C*$_{quart.}$), 134.1 (s, Me_2N-Ph*C*H), 131.0 (br. s, Me_2N-Ph*C*$_{quart.}$-B), 112.6 (s, Me_2N-Ph*C*H), 44.8 (s, B-N*C*H_3), 41.9 (s, B-N*C*H_3), 40.1 [s, (*C*H_3)$_2$N-Ph], 40.1 (s, B-N*C*H_3), 37.5 (s, B-N*C*H_3) ppm. **UV/Vis** (hexane): λ_{max} = 282 nm (ε = 13160 L mol^{-1} cm^{-1}). $C_{12}H_{22}B_2ClN_3$ (265.40): C 53.07 (calcd. 54.31); H 7.69 (8.36); N 15.77 (15.83) %. MP: 61–62 °C.

Synthesis of 1,2-Bis(dimethylamino)-1,2-bis(*para*-*N*,*N*-dimethylaniline) diborane(4) (3): Diborane(4) **2** (500 mg, 1.88 mmol, 1 equiv.) was dissolved in Et_2O (25 mL) and cooled to –78 °C (2-propanol/ liquid nitrogen). A solution of 4-(dimethylamino)phenyllithium (250 mg, 1.88 mmol, 1 equiv.) in Et_2O (25 mL) was added slowly via cannula. The reaction mixture was stirred in the cooling bath for 5 min and then allowed to reach room temperature. The solvent was exchanged for toluene and the reaction mixture was heated to 100 °C for 1 h. Removal of solvent and volatile species in vacuo was followed by filtration from hexane. Reducing the filtrate volume gave a yellow solution from which 212 mg (32 %) of diborane(4) **3** were obtained as yellow crystals at 5 °C. **^{1}H NMR** (400.13 MHz, C_6D_6, 300 K, TMS): δ = 7.54 (d, ^3J = 8.6 Hz, 4 H, Me_2N-Ph*CH*), 6.75 (d, ^3J = 8.7 Hz, 4 H, Me_2N-Ph*CH*), 2.98 (s, 6 H, B-NCH_3), 2.87 (s, 6 H, B-NCH_3), 2.58 [s, 12 H, (CH_3)$_2$N-Ph] ppm. **^{11}B NMR** (96.29 MHz, C_6D_6, 300 K, BF_3–Et_2O): δ = 49.4 (br. s) ppm **^{13}C NMR** (100.61 MHz, C_6D_6, 300K, TMS): δ = 150.1 (s, Me_2N-Ph*C*$_{quart.}$), 134.1 (s, Me_2N-Ph*C*H), 133.4 (br. s, Me_2N-Ph*C*$_{quart.}$-B), 112.8 (s, Me_2N-Ph*C*H), 45.0 (s, B-N*C*H_3), 40.3 [s, (*C*H_3)$_2$N-Ph], 40.1 (s, B-N*C*H_3) ppm. **UV/Vis** (hexane): λ_{max} = 281 nm (ε = 34910 L mol^{-1} cm^{-1}). $C_{20}H_{32}B_2N_4$ (350.12): C 68.12 (calcd. 68.61); H 9.04 (9.21); N 15.57 (16.00) %. **MP**: 130–131 °C.

Synthesis of 1,2-Bis(dimethylamino)-1-*para*-*N*,*N*-dimethylaniline-2-pentafluorphenyl diborane(4) (4): Bromopentafluorobenzene (0.15 mL, 1.18 mmol, 1.1 equiv.) was dissolved in Et_2O (10 mL) and cooled to –100 °C (ethanol/ liquid nitrogen). *n*Buthyllithium solution in hexanes (0.49 mL, 2.5 M), 1.24 mmol, 1.15 equiv.) was added dropwise via syringe. Stirring was continued for 15 min at –100 °C. A solution of diborane(4) **2** (285 mg, 1.07 mmol, 1 equiv.) in Et_2O (10 mL) was added via cannula. The mixture was stirred for 30 min in the cooling bath and was then allowed to reach room temperature. Removal of solvent and volatile species in vacuo was followed by filtration from toluene. The solvent was exchanged for *o*-difluorobenzene. Reducing the volume gave a pale-yellow solution from which 253 mg (52 %) of diborane(4) **4** (with 0.5 equiv. *o*-difluorobenzene) were obtained at –26 °C as colorless crystals. **^{1}H NMR** (400.13 MHz, C_6D_6, 300 K, TMS): δ = 7.37 (d, ^3J = 8.6 Hz, 4 H, Me_2N-Ph*H*), 6.71 (d, ^3J = 8.7 Hz, 4 H, Me_2N-Ph*H*), 2.93 (s, 3 H, B-NCH_3), 2.80 (s, 3 H, B-NCH_3), 2.78 (s, 3 H, B-NCH_3), 2.54 [s, 6 H, (CH_3)$_2$N-Ph], 2.43 (s, 3 H, B-NCH_3) ppm. **^{11}B NMR** (96.29 MHz, C_6D_6, 300 K, BF_3–Et_2O): δ = 45.8 (br. s) ppm. **^{13}C NMR** (100.61 MHz, C_6D_6, 300K, TMS): δ = 150.4 (s, Me_2N-Ph*C*$_{quart.}$), 145.3 (dm, $^1J_{C,F}$ = 237 Hz, F_5Ph*C*-F), 140.3 (dm, $^1J_{C,F}$ = 248 Hz, F_5Ph*C*-F), 137.5 (dm, $^1J_{C,F}$ = 249 Hz, F_5Ph*C*-F), 134.0 (s, Me_2N-Ph*C*H), 130.8 (s, Me_2N-Ph*C*$_{quart.}$-B), 112.4 (s, Me_2N-Ph*C*H), 44.7, 43.9, 41.0, 40.4 (each s, each B-N*C*H_3), 40.0 (s, $(CH_3)_2$N-Ph) ppm. **^{19}F NMR** (282.40 MHz, C_6D_6, 300 K, $CFCl_3$): δ = –132.6 (dd, 2F, $^3J_{F-F}$ = 24, $^4J_{F-F}$ = 8 Hz, F_5Ph-*oF*), –156.8 (t, 1F, $^3J_{F-F}$ = 20 Hz, F_5Ph-*pF*), –162.6 (ddd, 2F, $^3J_{F-F}$ = 25, $^3J_{F-F}$ = 21, $^4J_{F-F}$ = 10 Hz, F_5Ph-*mF*) ppm. **UV/Vis** (Et_2O): λ_{max} = 286 nm (ε = 17250 L mol^{-1} cm^{-1}). $C_{18}H_{22}B_2F_5N_3$ (397.01): C 53.96 (calcd. 54.46); H 5.48 (5.59); N 10.55 (10.58) %. MP: 80–85 °C.

Synthesis of 1,4-Dimethyl-2,3-bis(dimethylamino)-1,2,3,4-tetrahydrobenzo[e][1,4,2,3]diazadiborinane (5): *N*,*N*'-Dilithio-*N*,*N*'-dimethyl-1,2-diaminobenzene (3.00 g, 14.9 mmol, 1.05 equiv.) was dissolved in thf (250 mL) and cooled to –78 °C (2-propanol/ liquid nitrogen). A solution of 1,2-bis(dimethylamino)-dichlorodiborane(4) **1** (2.6 mL, 15.5 mmol, 1 equiv.) in Et_2O (45 mL) was added dropwise via dropping funnel over 20 min. Stirring was continued in the cooling bath for 1 hour and then allowed to reach room temperature. Stirring

was maintained for another hour. Removal of solvent and volatile species in vacuo was followed by filtration from hexane. Reducing the filtrate volume gave a yellow solution from which 1.64 g (two fractions, 43 %) of cyclic 1,4-diaza-2,3-diborinane **5** were obtained as colorless crystals at room temperature. **^{1}H NMR** (300.13 MHz, D_6D_6, 300K, TMS): δ = 7.14–7.07 (m, 2 H, ArH), 7.02–6.96 (m, 2 H, ArH), 2.99 (s, 6 H, Ar-NCH_3), 2.65 (s, 12 H, B-N(CH_3)$_2$) ppm. **^{11}B NMR** (96.29 MHz, C_6D_6, 300 K, BF_3–Et_2O): δ = 33.7 (s) ppm. **^{13}C NMR** (75.47 MHz, C_6D_6, 300K, TMS): δ = 137.6 (s, Ar$C_{quart.}$), 118.6 (s, Ar*C*H), 112.9 (s, Ar*C*H), 42.3 [s, B-N(*C*H$_3$)$_2$], 36.7 (s, Ar-N*C*H$_3$) ppm. **UV/Vis** (hexane): λ_{max} = 314 nm (ε = 11830 L mol^{-1} cm^{-1}), 308 nm (ε = 12110 L mol^{-1} cm^{-1}), 272 nm (ε = 9840 L mol^{-1} cm^{-1}), 234 nm (ε = 34860 L mol^{-1} cm^{-1}). $C_{12}H_{22}B_2N_4$ (243.96): C 58.79 (calcd. 59.08); H 8.67 (9.09); N 22.78 (22.97) %. MP: 135–138 °C.

Synthesis of 2,3-Dichloro-1,4-dimethyl-1,2,3,4-tetrahydrobenzo[e][1,4,2,3]diazadiborinane (6): Cyclic 1,4-diaza-2,3-diborinane **5** (822 mg, 3.37 mmol, 1 equiv.) was dissolved in pentane (120 mL) and cooled to 0 °C (ice bath). BCl_3 solution in hexanes (3.5 mL, 1 M, 3.5 mmol, 1.04 equiv.) was added via syringe. The reaction mixture was stirred in the ice bath for 30 min and 1 h at room temperature. Removal of solvent and volatile species in vacuo afforded the colorless cyclic 1,4-diaza-2,3-diborinane **6** in quantitative yield which was used without further purification. **^{1}H NMR** (400.13 MHz, D_6D_6, 300K, TMS): δ = 6.99–6.95 (m, 2 H, Ar*H*), 6.91–6.87 (m, 2 H, Ar*H*), 3.05 (s, 6 H, Ar-NCH_3) ppm. **^{11}B NMR** (128.38 MHz, C_6D_6, 300 K, BF_3–Et_2O): δ = 40.0 (s) ppm.

Synthesis of 3-Chloro-1,4-dimethyl-2-dimethylamino-1,2,3,4-tetrahydrobenzo[e][1,4,2,3]diazadiborinane (7): Cyclic 1,4-diaza-2,3-diborinane **5** (1.64 g, 6.74 mmol, 1 equiv.) was dissolved in hexane (120 mL) and cooled to 0 °C (ice bath). BCl_3 solution in hexanes (3.0 mL, 1.1 M, 3.3 mmol, 0.49 equiv.) was added slowly via syringe. The reaction mixture was stirred in the ice bath for 15 min and 30 min at room temperature. Removal of solvent and volatile species in vacuo afforded the colorless, oily intermediate **7**. The crude product was twice dissolved in hexane which was evacuated again for complete removal of chloro bis(dimethylamino)borane. The crude product was used without further purification. **^{1}H NMR** (300.13 MHz, D_6D_6, 300K, TMS): δ = 7.11 (ddd, ^3J = 8.5, ^3J = 6.6, ^4J = 1.9 Hz, 1 H, Ar*H*), 7.01–6.93 (m, 3 H, Ar*H*), 3.21 (s, 3 H, B-NCH_3), 2.85 (s, 3 H, B-NCH_3), 2.81 (s, 6 H, Ar-NCH_3) ppm. **^{11}B NMR** (96.29 MHz, C_6D_6, 300 K, BF_3–Et_2O): δ = 40.2 (s), 31.8 (s) ppm.

Synthesis of 2,3-Bis(*para*-*N*,*N*-dimethylaniline)-1,4-dimethyl-1,2,3,4-tetrahydrobenzo[e][1,4,2,3]diazadiborinane (8): Dichloro cyclic 1,4-diaza-2,3-diborinane **6** (212 mg, 0.939 mmol, 1 equiv.) and 4-(dimethylamino)phenyllithium (312 mg, 2.35 mmol, 2.5 equiv.) were mixed as solids and benzene (30 mL) was added at room temperature. Stirring was continued for 1 h. Removal of solvent and volatile species in vacuo was followed by filtration from toluene. Crystals were grown from a yellow solution of the crude product in a mixture of toluene (5 mL) and hexane (10 mL), affording 77 mg (21 %) of the desired product **8** at room temperature. **^{1}H NMR** (400.13 MHz, D_6D_6, 300K, TMS): δ = 7.36 (d, ^3J = 8.6 Hz, 4 H, Me$_2$N-Ph*H*), 7.35–7.33 (m, 2 H, Ar*H*), 7.22–7.18 (m, 2 H, Ar*H*), 6.67 (d, ^3J = 8.7 Hz, 4 H, Me$_2$N-Ph*H*), 3.40 (s, 6 H, Ar-NCH_3), 2.55 (s, 12 H, (CH_3)$_2$N-Ph) ppm. **^{11}B NMR** (128.38 MHz, C_6D_6, 300 K, BF_3–Et_2O): δ = 46.4 (br. s) ppm. **^{13}C NMR** (100.61 MHz, C_6D_6, 300K, TMS): δ = 150.0 (s, Me$_2$N-Ph$C_{quart.}$), 138.1 (s, Ar$C_{quart.}$), 134.9 (s, Me$_2$N-Ph*C*H), 132.2 (br. s, Me$_2$N-Ph$C_{quart.}$-B), 122.0 (s, Ar*C*H), 117.0 (s, Ar*C*H), 112.1 (s, Me$_2$N-Ph*C*H), 40.1 [s, (*C*H$_3$)$_2$N-Ph], 38.1 (s, Ar-N*C*H$_3$) ppm. **UV/Vis** (Et_2O): λ_{max} = 342 nm (ε = 35480 L mol^{-1} cm^{-1}), 261 nm (ε = 34650 L mol^{-1} cm^{-1}), 232 nm (ε = 27300 L mol^{-1} cm^{-1}). $C_{24}H_{30}B_2N_4$ (396.15): C 72.69 (calcd. 72.77); H 7.58 (7.63); N 13.96 (14.14) %. MP: 180–182 °C.

Synthesis of 1,4-Dimethyl-2-dimethylamino-3-*para*-*N*,*N*-dimethylaniline-1,2,3,4-tetrahydrobenzo[e][1,4,2,3]diazadiborinane (9): Crude product **7** (6.74 mmol) was dissolved in benzene and filtered. 4-(dimethylamino)phenyllithium (942 mg, 7.08 mmol, 1.05 equiv.) was suspended in benzene (80 mL) and added to the filtrate of **7** at room temperature. Stirring was continued for 3 h. Removal of solvent and volatile species in vacuo was followed by filtration from hexane. Reducing the filtrate volume gave a yellow solution from which 663 mg (two fractions, 31 %) of **9** were obtained as yellow crystals. **^{1}H NMR** (300.13 MHz, D_6D_6, 300K, TMS): δ = 7.28 (d, ^3J = 8.7 Hz, 2 H, Me$_2$N-Ph*H*), 7.20 (d, ^3J = 7.5 Hz, 2 H, Ar*H*), 7.14–7.11 (m, 1 H, Ar*H*), 7.04 (ddd, ^3J = 8.3, ^3J = 6.9, ^4J = 1.7 Hz, 1 H, Ar*H*), 6.80 (d, ^3J = 8.7 Hz, 2 H, Me$_2$N-Ph*H*), 3.19 (s, 3 H, B-NCH_3), 3.05 (s, 3 H, B-NCH_3), 2.65 (s, 6 H, Ar-NCH_3), 2.60 (s, 6 H, (CH_3)$_2$N-Ph) ppm. **^{11}B NMR** (96.29 MHz, C_6D_6, 300 K, BF_3–Et_2O): δ = 47.2 (br. s), 34.0 (br. s) ppm. **^{13}C NMR** (75.47 MHz, C_6D_6, 300K, TMS): δ = 149.6 (s, Me$_2$N-Ph$C_{quart.}$), 140.8 (s, Ar$C_{quart.}$), 136.4 (s, Ar$C_{quart.}$), 135.3 (br. s, Me$_2$N-Ph$C_{quart.}$-B), 131.3 (s, Me$_2$N-Ph*C*H), 122.5 (s, Ar*C*H), 119.0 (s, Ar*C*H), 116.8 (s, Ar*C*H), 115.5 (s, Ar*C*H), 113.1 (s, Me$_2$N-Ph*C*H), 42.1 (s, Ar-N*C*H$_3$), 40.3 (s, (*C*H$_3$)$_2$N-Ph), 38.1 [s, B-N*C*H$_3$], 37.6 (s, B-N*C*H$_3$) ppm. **UV/Vis** (hexane): λ_{max} = 327 nm (ε = 15810 L mol^{-1} cm^{-1}), 315 nm (ε = 14840 L mol^{-1} cm^{-1}), 243 nm (ε = 24880 L mol^{-1} cm^{-1}), 216 nm (ε = 34980 L mol^{-1} cm^{-1}). $C_{18}H_{26}B_2N_4$ (320.05): C 66.98 (calcd. 67.55); H 8.19 (8.19); N 17.77 (17.51) %. MP: 115–120 °C.

Synthesis of 2-Chloro-1,4-dimethyl-3-*para*-*N*,*N*-dimethylaniline-1,2,3,4-tetrahydrobenzo[e][1,4,2,3]diazadiborinane (10): Cyclic 1,4-diaza-2,3-diborinane **9** (518 mg, 1.62 mmol, 1 equiv.) was dissolved in hexane (40 mL) and cooled to 0 °C (ice bath). BCl_3 solution in hexanes (0.74 mL, 1.1 M, 0.814 mmol, 0.5 equiv.) was added slowly via syringe. Stirring was continued in the ice bath for 40 min and 30 min at room temperature. Removal of solvent and volatile species in vacuo was followed by filtration from toluene. Crystals were grown from a colorless solution of the crude product in a mixture of toluene (3 mL) and hexane (1 mL), affording 256 mg (42 %) of the desired **10**. **^{1}H NMR** (300.13 MHz, D_6D_6, 300K, TMS): δ = 7.69 (d, ^3J = 8.8 Hz, 2 H, Me$_2$N-Ph*H*), 7.19–7.16 (m, 1 H, Ar*H*), 7.14–7.07 (m, 3 H, Ar*H*), 6.82 (d, ^3J = 8.7 Hz, 2 H, Me$_2$N-Ph*H*), 3.27 (s, 3 H, Ar-NCH_3), 3.27 (s, 3 H, Ar-NCH_3), 2.60 (s, 6 H, (CH_3)$_2$N-Ph) ppm. **^{11}B NMR** (96.29 MHz, C_6D_6, 300 K, BF_3–Et_2O): δ = 43.2 (br. s) ppm. **^{13}C NMR** (75.47 MHz, C_6D_6, 300K, TMS): δ = 150.7 (s, Me$_2$N-Ph$C_{quart.}$), 137.4 (s, Ar$C_{quart.}$), 136.3 (s, Ar$C_{quart.}$), 135.4 (s, Me$_2$N-Ph*C*H), 129.3 (s, Me$_2$N-Ph$C_{quart.}$-B), 122.6 (s, Ar*C*H), 122.3 (s, Ar*C*H), 117.3 (s, Ar*C*H), 117.0 (s, Ar*C*H), 112.3 (s, Me$_2$N-Ph*C*H), 40.1 [s, (*C*H$_3$)$_2$N-Ph], 38.2 (s, Ar-N*C*H$_3$), 34.6 (s, Ar-N*C*H$_3$) ppm. **UV/Vis** (Et_2O): λ_{max} = 334 nm (ε = 21235 L mol^{-1} cm^{-1}), 255 nm (ε = 18680 L mol^{-1} cm^{-1}), 232 nm (ε = 18895 L mol^{-1} cm^{-1}). $C_{16}H_{20}B_2ClN_3$ (311.43): C 61.34 (calcd. 61.71); H 6.27 (6.47); N 13.36 (13.49) %. MP: 148–153 °C.

Synthesis of 1,4-Dimethyl-3-*para*-*N*,*N*-dimethylaniline-2-pentaflourphenyl-1,2,3,4-tetrahydrobenzo[e][1,4,2,3]diazadiborinane (11): Bromopentafluorobenzene (degassed, 44 µL, 0.353 mmol, 1.1 equiv.) was dissolved in Et_2O (5 mL) and cooled to –100 °C (ethanol/ liquid nitrogen) before n-Buthyllithium solution (2.5 M in hexanes, 0.15 mL, 0.375 mmol, 1.15 equiv.) was added. Stirring was continued for 30 min at –100 °C. **10** (100 mg, 0.321 mmol, 1 equiv.) was dissolved in toluene (8 mL) and cooled to –100 °C (ethanol/ liquid nitrogen). The cyclic 1,4-diaza-2,3-diborinane solution (**10**) was transferred to the anion solution via cannula and the reaction mixture was

allowed to warm slowly to –45 °C. After stirring another hour at room temperature removal of solvent and volatile species in vacuo was followed by filtration from toluene. Removal of solvent affords 70 mg (49 %) as colorless powder of the desired **11**. **^{1}H NMR** (400.13 MHz, D_6D_6, 300K, TMS): δ = 7.26 (d, ^3J = 8.6 Hz, 2 H, Me_2N-Ph*H*), 7.24 – 7.18 (m, 3 H, Ar*H*), 7.15 – 7.11 (m, 1 H, Ar*H*), 6.59 (d, ^3J = 8.6 Hz, 2 H, Me_2N-Ph*H*), 3.25, 3.08 (each s, each 3 H, Ar-NCH_3), 2.47 (s, 6 H, (CH_3)$_2$N-Ph) ppm. **^{11}B NMR** (128.38 MHz, C_6D_6, 300 K, BF_3–Et_2O): δ = 45.3 ppm. **^{13}C NMR** (100.61 MHz, C_6D_6, 300K, TMS): δ = 149.9 (s, Me_2N-Ph$C_{quart.}$), 145.0 (dm, $^1J_{C,F}$ = 237 Hz, F_5Ph*C*-F), 140.4 (dm, $^1J_{C,F}$ = 249 Hz, F_5Ph*C*-F), 137.3 (dm, $^1J_{C,F}$ = 249 Hz, F_5Ph*C*-F), 137.8 (s, Ar$C_{quart.}$), 135.8 (s, Ar$C_{quart.}$), 133.2 (s, Me_2N-Ph*C*H), 130.0 (s, Me_2N-Ph$C_{quart.}$-B), 123.2, 121.8, 117.1, 116.9 (each s, Ar*C*H), 116.8 (br. s, F_5Ph*C*-B), 111.8 (s, Me_2N-Ph*C*H), 39.5 (s, (*C*H_3)$_2$N-Ph), 38.3, 37.5 (each s, Ar-N*C*H_3) ppm. **^{19}F NMR** (282.40 MHz, C_6D_6, 300 K, $CFCl_3$): δ = –132.3 (dd, 2F, $^3J_{F–F}$ = 25, $^4J_{F–F}$ = 10 Hz, F_5Ph-*oF*), –155.8 (t, 1F, $^3J_{F–F}$ = 21 Hz, F_5Ph-*pF*), –162.3 (ddd, 2F, $^3J_{F–F}$ = 25, $^3J_{F–F}$ = 21, $^4J_{F–F}$ = 10 Hz, F_5Ph-*mF*) ppm. **UV/Vis** (hexane): λ_{max} = 349 nm (ε = 16875 L mol^{-1} cm^{-1}), 313 nm (ε = 14960 L mol^{-1} cm^{-1}), 263 nm (ε = 21000 L mol^{-1} cm^{-1}). $C_{22}H_{20}B_2F_5N_3$ (443.04): C 60.58 (calcd. 59.64); H 4.78 (4.55); N 9.92 (9.48) %. MP: 131–135 °C.

Synthesis of 1-Chloro-2-dimethylamino-1,2-(2,3,5,6-tetramethylphenyl) Diborane(4) (13): 1,2-Dichlorodiduryl diborane(4) **12** (500 mg, 1.39 mmol, 1.0 equiv.) was dissolved in hexane (30 mL) and cooled to –78 °C (2-propanol/ liquid nitrogen). *N*,*N*-dimethyltrimethylsilylamine (0.223 mL, 1.39 mmol, 1.0 equiv.) was added dropwise to the diborane(4) solution via syringe. The reaction mixture was slowly allowed to reach room temperature and stirring was continued for 30 min. Removal of solvent and volatile species in vacuo was followed by filtration from hexane. Solvent was removed again which gave 422 mg (83 %) of diborane(4) **13**, a colorless solid. **^{1}H NMR** (300.13 MHz, D_6D_6, 300K, TMS): δ = 6.81 (s, 1 H, Dur*H*), 6.79 (s, 1 H, Dur*H*), 2.98 (s, 3 H, (CH_3)$_2$N), 2.44 (s, 3 H, (CH_3)$_2$N), 2.06, 2.02, 1.99, 1.83 (each s, each 6 H, Dur-CH_3) ppm. **^{11}B NMR** (96.29 MHz, C_6D_6, 300 K, BF_3–Et_2O): δ = 88.0 (br. s), 47.8 (br., s) ppm. **^{13}C NMR** (100.61 MHz, C_6D_6, 300K, TMS): δ = 145.8, 143.2 (each s, Dur$C_{quart.}$-B), 134.3, 133.2, 133.2, 131.8 (each s, Dur$C_{quart.}$Me), 131.7, 131.0, (each s, Dur*C*H), 43.3, 40.6 [each s, (*C*H_3)$_2$N], 19.7, 19.2, 18.6, 18.6 (each s, Dur-*C*H_3) ppm. **UV/Vis** (hexane): λ_{max} = 313 nm (ε = 3380 L mol^{-1} cm^{-1}. $C_{22}H_{32}B_2ClN$ (367.58): C 71.78 (calcd. 71.89); H 8.67 (8.78); N 3.51 (3.81) %. MP: 123–126 °C.

Synthesis of 2-Dimethylamino1-*para*-*N*,*N*-dimethylaniline-1,2-(2,3,5,6-tetramethylphenyl) Diborane(4) (14): 1-Chloro-2-dimethylamino didurylldiborane(4) **13** (235 mg, 0.639 mmol, 1.0 equiv.) and 4-(dimethylamino)phenyllithium (102 mg, 0.767 mmol, 1.2 equiv.) were mixed as solids and Et_2O (30 mL) was added. Stirring was continued overnight. Removal of solvent and volatile species in vacuo was followed by filtration from hexane. Reducing the filtrate volume gave a yellow solution from which 147 mg (51 %) of diborane(4) **14** was obtained as yellow amorphous solid. **^{1}H NMR** (300.13 MHz, D_6D_6, 300K, TMS): δ = 8.07 (d, ^3J = 7.5 Hz, 2 H, Me_2N-Ph*H*), 6.92 (s, 1 H, Dur*H*), 6.85 (s, 1 H, Dur*H*), 6.53 (d, ^3J = 8.8 Hz, 2 H, Me_2N-Ph*H*), 3.17, 2.72 [each s, each 3 H, (CH_3)$_2$N], 2.45 [s, 6 H, (CH_3)$_2$N-Ph], 2.17, 2.12 (each s, each 6 H, Dur-CH_3), 2.36, 1.76 (each br. s, each 6 H, Dur-CH_3) ppm. **^{11}B NMR** (96.29 MHz, C_6D_6, 300 K, BF_3–Et_2O): δ = 87.1 (br. s), 53.2 (br. s) ppm. **^{13}C NMR** (100.61 MHz, C_6D_6, 300K, TMS): δ = 153.8 (s, Me_2N-Ph$C_{quart.}$),150.2, 146.5 (each s, Dur$C_{quart.}$-B), 142.6 (s, Me_2N-Ph*C*H), 134.0, 132.5, 132.2, 132.0 (each s, Dur$C_{quart.}$Me), 130.7, (s, Me_2N-Ph$C_{quart.}$-B) 130.1, 129.5, (each s, Dur*C*H), 111.2 (s, Me_2N-Ph*C*H), 45.2, 41.0 [each s, (*C*H_3)$_2$N], 39.4 [s, (*C*H_3)$_2$N-Ph], 19.9, 19.6, 19.2, 18.5 (each s, Dur-*C*H_3) ppm. **UV/Vis** (hexane): λ_{max} = 337 nm (ε = 44020 L mol^{-1} cm^{-1}), 242 nm (ε = 15780 L mol^{-1} cm^{-1}). $C_{30}H_{42}B_2N_2$ (452.30): C 79.39 (calcd. 79.67); H 9.20 (9.36); N 5.83 (6.19) %. MP: 152–157 °C.

Synthesis of 2-Chloro-1-*para*-*N*,*N*-dimethylaniline-1,2-(2,3,5,6-tetramethylphenyl) Diborane(4) (15): 1,2-Dichlorodiduryl diborane(4) **12** (1.00 g, 2.79 mmol, 1.0 equiv.) was dissolved in toluene (10 mL) and (4-(dimethylamino)phenyl)lithium (330 mg, 2.79 mmol, 1.0 equiv.) was dissolved in Et_2O (10 mL). Both were cooled to –78 °C (2-propanol/ liquid nitrogen). The anion solution was added to the diborane(4) solution via cannula. Stirring was continued for 10 min. Then the reaction mixture was allowed to reach room temperature. Removal of solvent and volatile species in vacuo was followed by filtration from hexane. Reducing the filtrate volume gave a yellow solution from which 553 mg (45 %) of diborane(4) **15** were obtained as yellow amorphous solid. Recrystallization from toluene affords single crystals. **^{1}H NMR** (300.13 MHz, D_6D_6, 300K, TMS): δ = 8.09 (d, ^3J = 8.8 Hz, 2 H, Me_2N-Ph*H*), 6.91 (s, 1 H, Dur*H*), 6.83 (s, 1 H, Dur*H*), 6.43 (d, ^3J = 8.9 Hz, 2 H, Me_2N-Ph*H*), 2.36 [s, 6 H, (CH_3)$_2$N-Ph], 2.10, 2.08, 2.06, 2.00 (each s, each 6 H, Dur-CH_3) ppm. **^{11}B NMR** (96.29 MHz, C_6D_6, 300 K, BF_3–Et_2O): δ = 81.1 (br. s) ppm. **^{13}C NMR** (75.47 MHz, C_6D_6, 300K, TMS): δ = 154.3 (s, Me_2N-Ph$C_{quart.}$),146.6, 145.7 (each s, Dur$C_{quart.}$-B), 142.4 (s, Me_2N-Ph*C*H), 133.5, 133.3, 132.5, 132.0 (each s, Dur$C_{quart.}$Me), 131.9, 130.6, (each s, Dur*C*H), 129.0 (s, Me_2N-Ph$C_{quart.}$-B), 111.4 (s, Me_2N-Ph*C*H), 39.2 [s, (*C*H_3)$_2$N-Ph], 20.0, 19.3, 19.2, 19.0 (each s, Dur-*C*H_3) ppm. **UV/Vis** (hexane): λ_{max} = 347 nm (ε = 33775 L mol^{-1} cm^{-1}). $C_{28}H_{36}B_2ClN$ (443.67): C 76.82 (calcd. 75.80); H 7.99 (8.18); N 2.50 (3.16) %. MP: 160 °C.

Synthesis of 1,2-*para*-*N*,*N*-Dimethylaniline-1,2-(2,3,5,6-tetramethylphenyl) Diborane(4) (16): 1,2-Dibromodiduryl diborane(4) **12** (500 mg, 1.12 mmol, 1.0 equiv.) and (4-(dimethylamino)phenyl)lithium (419 mg, 3.14 mmol, 2.8 equiv.) were mixed as solids and dissolved in Et_2O (60 mL). Stirring was continued for two days. Removal of solvent and volatile species in vacuo was followed by filtration from hexane. Reducing the filtrate volume gives a yellow solution from which 110 mg (19 %) of diborane(4) **16** were obtained as yellow microcrystalline solid. **^{1}H NMR** (300.13 MHz, D_6D_6, 300K, TMS): δ = 8.21 (d, ^3J = 8.1 Hz, 4 H, Me_2N-Ph*H*), 6.95 (s, 2 H, Dur*H*), 6.53 (d, ^3J = 8.9 Hz, 4 H, Me_2N-Ph*H*), 2.45 [s, 12 H, (CH_3)$_2$N-Ph], 2.17 (s, 12 H, Dur-CH_3), 2.00 (br. s, 12 H, Dur-CH_3) ppm. **^{11}B NMR** (96.29 MHz, C_6D_6, 343 K, BF_3–Et_2O): δ = 87.1 ppm. **^{13}C NMR** (100.61 MHz, C_6D_6, 300K, TMS): δ = 153.8 (s, Me_2N-Ph$C_{quart.}$),150.0 (s, Dur$C_{quart.}$-B), 143.0 (s, Me_2N-Ph*C*H), 132.6, 132.1 (each s, Dur$C_{quart.}$Me), 131.3, (s, Me_2N-Ph$C_{quart.}$-B), 129.8 (s, Dur*C*H), 111.2 (s, Me_2N-Ph*C*H), 39.4 (s, (*C*H_3)$_2$N-Ph), 19.6, 19.6, (each s, Dur-*C*H_3) ppm. **UV/Vis** (hexane): λ_{max} = 341 nm (ε = 48225 L mol^{-1} cm^{-1}), 279 nm (ε = 13895 L mol^{-1} cm^{-1}), 244 nm (ε = 17130 L mol^{-1} cm^{-1}). $C_{36}H_{46}B_2N_2$ (528.40): C 81.87 (calcd. 81.83); H 8.80 (8.78); N 4.80 (5.30) %. MP: >230 °C.

Supporting Information (see footnote on the first page of this article): SI contains NMR, UV/Vis and Fluorescence spectra as well as crystallographic details.

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