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Synthesis and properties of fluorescent organoboranes: triarylmethane-type dyes

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The syntheses and photochemical properties of the novel aminoaryldiarylboranes, **4**, which are isoelectronic with triarylmethane dyes, and also pyrrolyl- **8**, and indolyl-diarylboranes **11**, are described. The fluorescence spectra are strongly dependent on the solvent. The use of *o*-disubstituted arenes as stabilizing substituents at the boron atom leads to highly coloured solids which are stable to air and moisture. The structures of the triarylboranes **4a** and **b** were confirmed by X-ray analyses.

Introduction

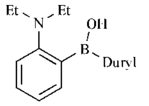
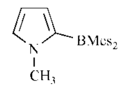
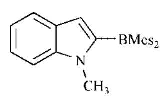
Polarized π-electron systems are important because they act as chromophores in organic dyes and, furthermore, are of interest as materials with non-linear optical properties used in opto-electronic techniques.[1] Usually, both electron donating and electron withdrawing groups are connected *via* aromatic or conjugated olefinic π-systems, resulting in an internal charge-transfer band in the UV-VIS area. In the frequently used triarylmethane dyes, conjugation is transferred over the central carbenium ion. Formally, such a carbenium ion is isoelectronic with an sp^2-hybridised boron atom[2] and replacement of the former by the latter should lead to a novel class of organic dyes.[3,4] As early as 1955, Wittig and Herwig reported the synthesis of tris[4-(*N*,*N*-dimethylamino)phenyl]borane and its interesting optical properties.[5] Further investigations showed that the stability towards nucleophilic attack could be increased by the introduction of two mesityl (2,4,6-trimethylphenyl) groups at the boron atom.[6] However, these studies were limited to 4-(*N*,*N*-dialkylamino)phenyl- and 4-(*N*,*N*-diarylamino)-phenyl-dimesitylboranes and no further investigations on different substituent patterns or aryl types have been reported.[7] As boranes are known to form complexes with Lewis bases, the possible solvent dependence of the UV and/or fluorescence spectra of these B–N-dyes could lead to interesting applications in the field of sensor molecules.

Results and discussion

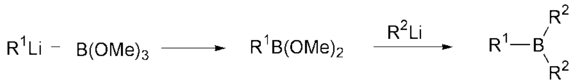
We now wish to report our results on the synthesis and properties of 2-(*N*,*N*-dialkylamino)phenyl- and 2-(*N*,*N*-diarylamino)phenyl-diarylboranes and 2-(*N*-alkylpyrrolyl)- and 2-(*N*-alkylindolyl)-diarylboranes. In order to develop a general approach to these triarylboranes, beginning with commercially available starting materials, we first synthesized the *N*-substituted arylboronic esters and then reacted them with the appropriate aryl anions.

Being Lewis acids, boranes form adducts with Lewis bases, such as amino groups, which are present intramolecularly in aminoaryldiarylboranes. Most boranes are decomposed in water in the presence of acids, bases or oxygen. However, sterically hindered boron substituents increase the stability of boranes towards nucleophilic attack. In preliminary experiments we examined the stability of the aminoaryldiarylboranes with respect to the steric hindrance of attack by oxygen and water. As a test system, we used 2-(*N*,*N*-dimethylamino)-phenylboronic acid dimethyl ester[8] and reacted it with different anions (Table 1, Scheme 1). The two mesityl and duryl (2,3,5,6-tetramethylphenyl) groups stabilize the resulting boranes independent of the nature of the third substituent.

Table 1 Optical properties and stability of **4a**–**e**, **5**, **8** and **11**

	R^3	R^4	R^5	UV-Vis λ_{max}/nm[a]	Fluorescence λ_{max}/nm[a]	Quantum yield ϕ
4a	Me	H	Mes	414.6[b]	488.4[b]	0.67[c]
4b	Me	H	Duryl	414.9[b]	488.1[b]	
4c	Et	H	Mes	415.6[b]	488.0[b]	0.89[c]
4d	Ph	H	Mes	386.9[b]	393.9[b]	
4e	Me	NMe_2	Mes	460.0[c]	603.0; 418.0[c]	
5				280.7[b]	406.9[b]	
8				327.4[c]	447.0[c]	0.20[c]
11				343.5[c]	458.0[c]	0.57[c]

[a] Only the longest wavelength is selected. [b] In isooctane. [c] In cyclohexane.



Scheme 1

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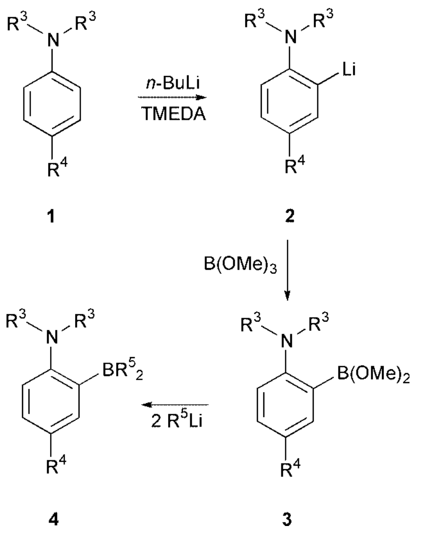
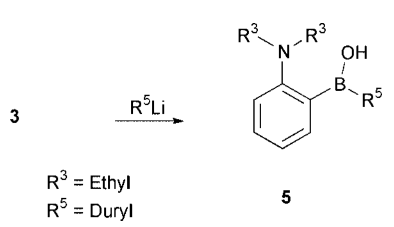
The preparation of *o*-borylated dialkylanilines can be easily performed by deprotonation of dialkylanilines (**1**) with strong bases, such as *n*-butyllithium, in the presence of TMEDA (*N*,*N*,*N′*,*N′*-tetramethylethylenediamine)[9] and subsequent reaction with $B(OMe)_3$ to give the boronic esters (**3**) (Scheme 2). In contrast to the usual hydrolysis workup to boronic acids, we either distilled the boronic acid ester directly from the reaction mixture or used it *in situ*. The introduction of two further substituents, R^5, to **4** succeeds in good yields by treatment with two equivalents of the corresponding lithium compound, R^5Li. Following this procedure, we were able to prepare a series of boranes (**4a–c, e**) with different alkyl groups, R^3, at the nitrogen and various aryl groups, R^5, at the boron atom. In order to evaluate the influence of the substituents on the properties of the resulting compounds (**4**), we introduced two phenyl groups at the amino group (**4d**), as well as an additional dimethylamino group in the *m*-position to the boron substituent (**4e**).[10] Whereas **4d** forms yellow crystals and behaves in a similar manner to **4a–c**, **4e** is a red solid that decomposes slowly in the presence of sunlight.



Scheme 2

Using only one equivalent of R^5Li in the conversion of **3**, after aqueous workup the borinic acid (**5**) could be isolated in moderate yield (Scheme 3). However, this reaction shows that a stepwise procedure to form triarylboranes with three different substituents at the boron atom is also possible.

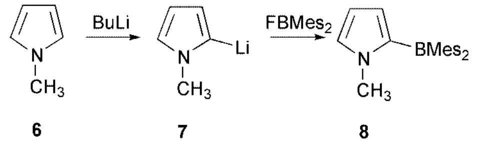


R^3 = Ethyl
R^5 = Duryl

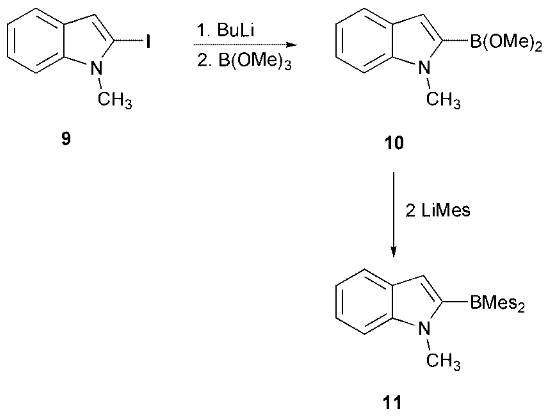
Scheme 3

The non-benzenoid pyrrole and indole groups incorporated into our work were borylated either by deprotonation, in the case of pyrrole,[11] or *via* halogen–metal exchange, in the case of indole.[12] In the final step compound **7** was treated with $FBMes_2$[13] to give the mixed triarylborane **8** (Scheme 4). The indole (**9**) was first transferred to the boronic ester (**10**), which was added to MesLi to give indol-2-yldimesitylborane (**11**) (Scheme 5). Both compounds **8** and **11** are stable in the presence of air and water and show a blue fluorescence. However, **8** is the only colourless aminoaryldiarylborane within our study.

Triarylboranes, in particular those with substituents in the *o*-position to the boron atom, are known to exist in a propeller-type conformation.[14] Accordingly, one might expect the aryl rings of the triarylboranes **4a–e**, **8** and **11** to be twisted out of the plane by about 50°.[15] However, the amino group in the neighbourhood of the boron atom favours conjugation that is at a maximum when B and N are in a planar conformation. As a direct intramolecular interaction is very unlikely,[16] we were interested in the structure and spectroscopic properties of **4a–e**, **8** and **11**.



Scheme 4



Scheme 5

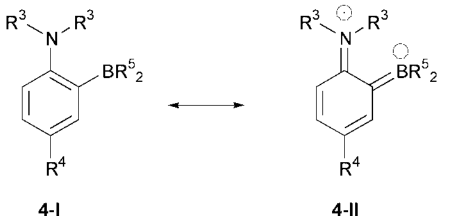


Fig. 1

Compared to carbon analogues, the main framework of **4a–e** is isoelectronic to triphenylmethane dyes. Their electronic structure could also be written in a mesomeric resonance formula, **4–II**, shown in Fig. 1. In fact, the 2-aminophenyldiarylboranes **4a–e** are coloured fluorescent solids. Further than the fundamental structural similarity between the triphenylmethane dyes and the newly developed compounds, **4a–e**, a detailed comparison proved difficult. The arene groups of common triphenylmethane dyes usually bear donating substituents in the *para*-position, whereas **4a–e** bear electron donating amino-groups in the *ortho*-position. Therefore, the structural, as well as electronic, properties of **4a–e**, which are largely influenced by the substituents, have no direct counterpart among the triphenylmethane dyes.

Solid-state parameters were derived from X-ray structure analysis of **4a** and **4b** (Table 2 and Fig. 2). In general, both structures are very similar, showing the expected propeller-type conformation (for reasons of clarity, we shall only discuss structure **4a**). However, the twisting of each aryl ring out of the reference plane is different, with 52 and 59° for the mesityl rings (which are oriented nearly orthogonal to each other), compared to only 31° for the 2-aminophenyl group, which is twisted towards the mesityl planes by 68 and 81°. The geometry at nitrogen is between tetrahedral and planarity with angles of $\angle C(15)N(1)C(24) = 118.65°$, $\angle C(15)N(1)C(25) = 119.31°$ and a dihedral angle $\angle C(24)N(1)C(25) = 112.21°$. Furthermore, the B–C bond length is slightly shorter to the 2-aminophenyl

Table 2 Crystal data[a]

Compound	**4a**	**4b**
Chemical formula	$C_{26}H_{32}BN$	$C_{28}H_{36}BN$
Formula weight	369.34	397.39
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$C2/c$
Final R factor ($I > 2\sigma(I)$)		
$R1$	0.0744	0.0717
$wR2$	0.2004	0.1794
Final R factor (all data)		
$R1$	0.1844	0.1391
$wR2$	0.2454	0.2180
Unit cell dimensions		
a/Å	28.728(20)	31.190(5)
b/Å	9.7130(10)	9.766(2)
c/Å	16.9970(10)	17.401(2)
β/°	105.95(2)°	111.053(7)°
V/Å^3	4560.2(32)	4946.4(13)
T/K	293	293
Z	8	8
Independent reflections (R_{int})	4459 (0.0202)	4381 (0.0497)

[a] CCDC reference number 188/265. See http://www.rsc.org/suppdata/p2/b0/b002184i/ for crystallographic files in .cif format.

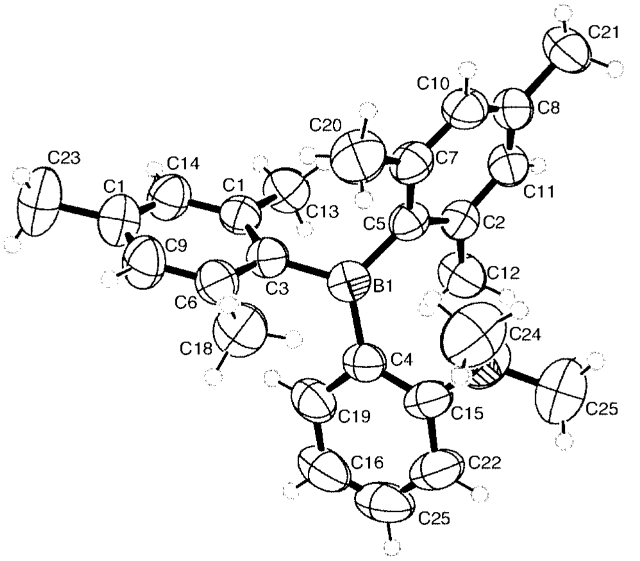
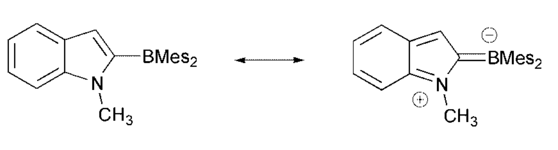


Fig. 2 Solid-state structure of **4a**. Selected distances (Å) and angles (°): BC(3), 1.573(5); BC(4), 1.555(6); BC(5), 1.593(5); C(4)C(15), 1.396(5); N(1)C(15), 1.415(5); N(1)C(24), 1.440(5); N(1)C(25), 1.444(5); ∠C(15)N(1)C(24), 118.65; ∠C(15)N(1)C(25), 119.31; ∠C(24)N(1)C(25), 112.21.



11-I **11-II**

Fig. 3

ring, with 155 pm compared to 157(9) pm to the mesityl rings. This structural finding can be interpreted in terms of the participation of the mesomeric form **4–II** to the valence-bond structure of **4**.

The pyrrole and indole derivatives, **8** and **11**, differ from **4a–e** in that the nitrogen is incorporated into an electron rich heterocycle. A mesomeric resonance structure must therefore be formulated using the whole ring system (Fig. 3). However, the participation of the dipolar **11–II** should also lead to a coloured and fluorescent compound.

In order to study the optical properties of **4a–e**, **5**, **8** and **11** in detail, we measured their UV and fluorescence spectra. While all compounds **4a–d**, **5**, **8** and **11** are stable in the solid state, kept in darkness for unlimited time, dilute solutions of **4a–e**, however, slowly undergo breaking of the boron–aminophenyl bond. This applies in particular for **4e**, which decomposes in solution within a few hours. With the exception of **4d**, **4e** and **5**, all the compounds show featureless, broad fluorescence emission spectra with maxima between 418 and 488 nm (isooctane or cyclohexane). Example quantum yields were measured for **4a**, **4c**, **8** and **11** (Table 1). The values range from 0.20 and 0.57 for pyrrole-type compounds **8** and **11** up to 0.67 and 0.89 for the triarylmethane-type dyes **4a** and **4c**. The polar excited states of **4a–e**, **8** and **11** are especially stabilized by polar solvents, as is shown by measuring the fluorescence spectra in different solvents. We observed a strong shift of the emission maxima *e.g*, for **4c** from 490 to 540 nm going from cyclohexane to DMSO, without any significant change in the excitation spectra.[17]

It is striking that, although **4d** incorporates two additional phenyl groups compared to **4a** and **4b**, the band of absorbance at the longest wavelength undergoes a hypsochromic shift (415→387 nm). Furthermore, the UV spectra, as well as the fluorescence spectra, of **4d** show a vibrational structure, which together suggest that the substituents at boron and the amino group have a non-coplanar arrangement of the C–B and the C–N bond due to steric hindrance. We are currently extending our study of the substituted derivatives of **4** and **11** and their spectroscopic properties *i.e.*, the fluorescence spectra in different solvents, durability of the excited states, and the quantum yields.

Experimental

All reactions were performed under a nitrogen atmosphere using the Schlenk technique. Hexane was distilled from sodium. Diethyl ether and THF were distilled from sodium benzophenone ketyl. *N,N,N′,N′*-Tetramethylethylenediamine (TMEDA) was dried over CaH_2 and distilled freshly before use. Chromatography was performed with mixtures of petroleum ether–diethyl ether, using Merck aluminium oxide 90, neutral (particle size 0.063–0.200 mm, activity III). All temperatures quoted are not corrected. Melting points were determined on a calibrated Büchi hot stage. NMR spectra were recorded on Bruker ARX 400 (400 MHz) and AC 200 F (200 MHz) spectrometers. Chemical shifts were reported relative to tetramethylsilane (^1H and ^{13}C) and $BF_3{\cdot}Et_2O$ (^{11}B). δ Values are given in ppm, J values in Hz. Multiplicities of ^{13}C NMR signals were determined by the DEPT sequence and are reported as follows: + for CH or CH_3, − for CH_2 and o for C. IR spectra were obtained using a Bruker Vector 22 FTIR instrument. UV spectra were recorded on a Perkin-Elmer 512. Fluorescence spectra were measured with a Hewlett Packard 8452A spectrometer and a Spex Fluorolog 2. Fluorescence lifetimes were obtained *via* time correlated single photon counting using a PRA flash lamp. The quantum yield ϕ was determined from the corrected fluorescence spectrum of the individual substances in diluted deoxygenated cyclohexane solution by using the flourescence standard 9,10-diphenylanthracene (DPA; Aldrich) in cyclohexane according to the literature procedure.[18] Mass spectra were obtained with a Hewlett Packard HP MS 5889 B instrument operating at 70 eV. The elemental analyses were performed by the Institute of Pharmaceutical Chemistry, University of Braunschweig.

General procedure 1 (GP 1) for the preparation of the 2-aminophenylboronic esters 3

To a solution of TMEDA (3.0 mL, 20.0 mmol) and BuLi (13.6 mL of a 1.6 M solution in hexane, 22.0 mmol) in hexane (50 mL) was added the *N,N*-dialkyl- or *N,N*-diphenylaminobenzene (20 mmol) at 0 °C, and the mixture was stirred at room temperature for 12 h. Subsequently, the anion suspension was added *via* a Teflon tube to a −78 °C solution of B(OMe)$_3$ (2.5 mL, 22 mmol) in hexane (10 mL). The mixture was warmed to room temperature and stirred for 8 h.

Compounds 3a–b. The solution was separated from precipitated LiOMe and the solvents distilled slowly under reduced pressure. The product was first flash distilled at 1 Torr and finally purified by a precision distillation (20 cm Vigreux) at the same pressure and stored under nitrogen.

Compounds 3c–d. The solution was separated from precipitated LiOMe and used without further purification.

2-(*N*,*N*-Dimethylamino)phenylboronic acid dimethyl ester (3a). Yield 2.5 g (65%), bp 70 °C/1 Torr. δ_H (200 MHz; CDCl$_3$) 2.85 (6 H, s, NCH$_3$), 3.64 (6 H, s, OCH$_3$), 6.75–6.90 (2 H, m, ArH), 7.19–7.28 (2 H, m, ArH); δ_C (50.3 MHz; CDCl$_3$) 43.8 (+, NCH$_3$), 52.3 (+, OCH$_3$), 114.7 (+), 119.2 (+), 129.2 (o), 129.6 (+), 132.8 (+), 155.3 (o); δ_B (128.4 MHz; CDCl$_3$) 30.6; *m*/*z* (EI) 193 (M$^+$, 15%), 178 (25), 146 (32), 120 (100), 77 (63). $C_{10}H_{16}NBO_2$ (193.1): calcd. C 62.22, H 8.35, N 7.26; found C 62.63, H 8.14, N 7.20%.

2-(*N*,*N*-Diethylamino)phenylboronic acid dimethyl ester (3b). Yield 2.0 g (45%), bp 76 °C/1 Torr. δ_H (200 MHz; CDCl$_3$) 1.05 (6 H, t, ^3J 7, CH$_2$C*H*$_3$), 3.11 (4 H, q, ^3J 7, NCH$_2$), 3.56 (6 H, s, OCH$_3$), 6.72–6.93 (2 H, m, ArH), 7.09–7.23 (2 H, m, ArH); δ_C (50.3 MHz; CDCl$_3$) 12.3 (+, CH$_2$*C*H$_3$), 46.9 (−, *C*H$_2$CH$_3$), 52.9 (+, OCH$_3$), 118.2 (+), 120.6 (+), 129.0 (+), 132.7 (+), 134.8 (o), 153.7 (o); δ_B (128.4 MHz; CDCl$_3$) 30.2; *m*/*z* (EI) 221 (M$^+$, 16%), 206 (80), 192 (100), 176 (79), 160 (66), 134 (62). $C_{12}H_{20}NBO_2$ (221.1): calcd. C 65.19, H 9.12, N 6.33; found C 65.53, H 9.18, N 6.21%.

General procedure 2 (GP 2) for the preparation of the 2-aminophenyldiarylboranes (4)

To an ice cold solution of the aryl bromide (10.0 mmol) in diethyl ether (20 ml) was added BuLi (6.9 mL of a 1.6 M solution in hexane, 11.0 mmol), and the mixture was stirred for 2 h at room temperature. Subsequently, the boronic ester (5.0 mmol), either in diethyl ether (10 mL) or from the reaction mixture of GP 1, was added to the anion suspension within 1 h. After stirring for 12 h, the mixture was hydrolysed with brine (30 mL), extracted with diethyl ether (2 × 20 ml) and dried with Na$_2$SO$_4$. The diethyl ether was distilled off and the residue chromatographed on Al$_2$O$_3$ with petroleum ether–diethyl ether (5:1).

2-(*N*,*N*-Dimethylamino)phenyldimesitylborane (4a). Bromomesitylene (1.95 g, 10.0 mmol) was treated with **3a** (960 mg, 5.0 mmol) to give 1.40 g (76%) **4a** as yellow crystals, $R_f = 0.07$; mp 144 °C. Single crystals of **4a** were obtained by recrystallization from pentane. ν_{max}/cm^{-1} (KBr) 3002, 2917, 1605, 1581, 1468, 1236, 849, 834; λ_{max} (isooctane/nm) 414.6 (lg (ε/dm^3 mol^{-1} cm^{-1}) 3.53), 315.4 (4.04), 256.4 (4.26), 203.1 (4.78); fluorescence (excitation at 315 nm): λ_{max} (isooctane/nm) 488.4; δ_H (200 MHz; C$_6$D$_6$) 2.11 (12 H, s, ArCH$_3$), 2.18 (6 H, s, ArCH$_3$), 2.45 (6 H, s, NCH$_3$), 6.55–6.61 (1 H, m, ArH), 6.76 (4 H, s, MesH), 6.69–6.81 (1 H, m, ArH), 7.11–7.19 (1 H, m, ArH), 7.49–7.61 (1 H, m, ArH); δ_C (50.3 MHz; C$_6$D$_6$) 19.9 (+, ArCH$_3$), 22.1 (+, ArCH$_3$), 43.6 (+, NCH$_3$), 113.4 (+), 118.4 (+), 126.5 (o), 127.5 (+), 127.9 (o), 132.2 (+), 136.7 (o), 137.2 (+), 139.5 (o), 157.9 (o); δ_B (128.4 MHz; CDCl$_3$) 70.5; *m*/*z* (EI) 369 (M$^+$, 50%), 354 (100), 324 (20), 234 (22), 204 (88). $C_{26}H_{32}BN$ (369.4): calcd. C 84.55, H 8.73, N 3.79; found C 84.23, H 8.23, N 4.15%.

2-(*N*,*N*-Dimethylamino)phenylbis(2,3,5,6-tetramethylphenyl)-borane (4b). 1-Bromo-2,3,5,6-tetramethylbenzene (2.13 g, 10.0 mmol) was treated with **3a** (960 mg, 5.0 mmol) to give 1.29 g (65%) **4b** as yellow crystals, $R_f = 0.08$; mp 154 °C. ν_{max}/cm^{-1} (KBr) 2923, 2854, 1583, 1556, 1456, 1263, 1021, 797; λ_{max} (isooctane/nm) 414.9 (lg (ε/dm^3 mol^{-1} cm^{-1}) 3.51), 316.2 (3.96), 252.6 (4.15), 201.6 (4.71); fluorescence (excitation at 315 nm): λ_{max} (isooctane/nm) 488.1; δ_H (200 MHz; C$_6$D$_6$) 2.15 (24 H, br s, ArCH$_3$), 2.43 (6 H, s, NCH$_3$), 6.61–6.83 (2 H, m, ArH), 7.00 (2 H, s, ArH), 7.14–7.33 (1 H, m, ArH), 7.65–7.78 (1 H, m, ArH); δ_C (50.3 MHz; C$_6$D$_6$) 20.8 (+, Ar*C*H$_3$), 45.1 (+, NCH$_3$), 116.2 (+), 120.5 (+), 126.1 (o), 127.7 (+), 132.8 (+), 133.7 (o), 134.1 (o), 136.7 (+), 139.9 (o), 159.8 (o); δ_B (128.4 MHz; CDCl$_3$) 72.5; *m*/*z* (EI) 398 (M$^+$+1, 100%), 383 (20), 352 (23), 264 (22). $C_{28}H_{36}BN$ (397.4): calcd. C 84.62, H 9.13, N 3.52; found C 84.36, H 9.26, N 3.15%.

2-(*N*,*N*-Diethylamino)phenyldimesitylborane (4c). Bromomesitylene (1.95 g, 10.0 mmol) was treated with **3b** (960 mg, 5.0 mmol) to give 1.43 g (72%) **4c** as yellow crystals, $R_f = 0.07$; mp 124 °C. ν_{max}/cm^{-1} (KBr) 2978, 2916, 1605, 1556, 1468, 1431, 1274, 1236, 849, 834, 754; λ_{max} (isooctane/nm) 415.6 (lg (ε/dm^3 mol^{-1} cm^{-1}) 3.57), 315.1 (4.08), 256.5 (4.30), 202.9 (4.84); fluorescence (excitation at 315 nm): λ_{max} (isooctane/nm) 488.0; δ_H (200 MHz; C$_6$D$_6$) 0.65 (6 H, t, ^3J 7, CH$_2$C*H*$_3$), 2.09 (6 H, s, ArCH$_3$), 2.17 (12 H, s, ArCH$_3$), 2.77–3.01 (4 H, br s, C*H*$_2$CH$_3$), 6.51–6.75 (2 H, m, ArH), 6.77 (4 H, s, MesH), 7.14–7.22 (1 H, m, ArH), 7.45–7.52 (1 H, m, ArH); δ_C (50.3 MHz; CDCl$_3$) 11.7 (+, CH$_2$*C*H$_3$), 21.7 (+, ArCH$_3$), 23.8 (+, ArCH$_3$), 48.3 (−, NCH$_2$), 117.9 (+), 120.7 (+), 127.4 (o), 127.9 (+), 133.4 (+), 138.5 (+), 138.6 (o), 141.4 (o), 143.5 (o), 158.1 (o); δ_B (128.4 MHz; CDCl$_3$) 71.0; *m*/*z* (EI) 398 (M$^+$+1, 44%), 382 (85), 324 (20), 262 (43), 204 (52), 133 (100). $C_{28}H_{36}BN$ (397.4): calcd. C 84.62, H 9.13, N 3.52; found C 84.70, H 9.40, N 3.40%.

2-(*N*,*N*-Diphenylamino)phenyldimesitylborane (4d). Bromomesitylene (1.95 g, 10.0 mmol) was treated with 5 mmol from the reaction mixture of **3c** to give 570 mg (23% over both steps) **4d** as yellow crystals, $R_f = 0.06$; mp 204 °C. λ_{max} (isooctane/nm) 386.9 (lg (ε/dm^3 mol^{-1} cm^{-1}) 4.24), 368.6 (4.08), 291.1 (3.91), 280.5 (3.85), 251.4 (4.93), 204.3 (4.86); fluorescence (excitation at 280 nm): λ_{max} (isooctane/nm) 393.9; δ_H (200 MHz; C$_6$D$_6$) 2.19 (12 H, s, ArCH$_3$), 2.31 (6 H, s, ArCH$_3$), 6.67–7.24 (14 H, m, ArH), 8.05–8.21 (4 H, m, ArH); δ_C (50.3 MHz; CDCl$_3$) 21.9 (+, ArCH$_3$), 24.0 (+, ArCH$_3$), 117.9 (+), 120.8 (+), 125.0 (+), 128.1 (+), 128.7 (o), 129.1 (+), 131.3 (+), 133.6 (+), 137.9 (+), 139.8 (o), 141.4 (o), 142.4 (o), 143.5 (o), 147.6 (o); δ_B (128.4 MHz; CDCl$_3$) 70.0; *m*/*z* (EI) 493 (M$^+$, 6%), 373 (100), 253 (11), 245 (10). $C_{36}H_{36}BN$ (493.5): calcd. C 87.57, H 7.35, N 2.84; found C 87.41, H 7.73, N 2.44%.

2,5-Bis(*N*,*N*-dimethylamino)phenyldimesitylborane (4e). Bromomesitylene (1.95 g, 10.0 mmol) was treated with 5 mmol from the reaction mixture of **3d** to give 290 mg (14%) **4e** as red crystals, $R_f = 0.05$; mp = 65.0 °C. λ_{max} (hexane/nm) 460.0 (lg (ε/dm^3 mol^{-1} cm^{-1}) 3.42), 260.0 (4.10), 216.0 (4.80); fluorescence (excitation at 324 nm): λ_{max} (cyclohexane/nm) 603.0 (rel. int. 1.0), 418.0 (0.47); fluorescence lifetime (cyclohexane, λ_{Ex} 322 nm, λ_{Em} 550 nm): τ 11.9 ns; δ_H (200 MHz; C$_6$D$_6$) 2.31 (6 H, s, ArCH$_3$), 2.42 (12 H, s, ArCH$_3$), 2.61 (6 H, s, NCH$_3$), 2.62 (6 H, s, NCH$_3$), 6.66–7.08 (2 H, m, ArH), 6.89 (4 H, s, MesH), 7.15–7.14 (1 H, m, ArH); δ_C (50.3 MHz; CDCl$_3$) 21.7 (+, ArCH$_3$), 23.9 (+, ArCH$_3$), 41.5 (+, NCH$_3$), 46.6 (−, NCH$_3$), 116.6 (+), 118.3 (+), 118.9 (+), 127.7 (+), 129.1 (o), 137.9 (o), 138.4 (o), 141.2 (o), 147.2 (o), 151.2 (o); δ_B (128.4 MHz; CDCl$_3$) 75.0; *m*/*z* (EI) 412 (M$^+$, 100%), 397 (20), 382 (27), 247 (48). $C_{28}H_{37}BN_2$ (412.4): calcd. C 81.54, H 9.04, N 6.79; found C 81.70, H 9.40, N 6.92%.

2-(*N*,*N*-Diethylamino)phenyl-2,3,5,6-tetramethylphenylborinic acid (5)

To an ice cold solution of 1-bromo-2,3,5,6-tetramethylbenzene (1.06 g, 5.0 mmol) in diethyl ether (10 mL) was added BuLi (3.5

mL of a 1.6 M solution in hexane, 5.5 mmol), and the mixture was stirred for 2 h at room temperature. Subsequently, a solution of **3b** (1.10 g, 5.0 mmol) in diethyl ether (5 mL) was added to the anion suspension over 1 h. After stirring for 12 h, the mixture was hydrolysed with brine (30 mL) and extracted with diethyl ether (2 × 20 mL) and dried with Na_2SO_4. The diethyl ether was distilled off and the residue chromatographed on Al_2O_3 using petroleum ether–diethyl ether (5:1) as solvent ($R_f = 0.21$), giving 650 mg (42%) **5** as yellow crystals, mp 124 °C. λ_{max} (isooctane/nm) 445.4 (lg (ε/dm^3 mol^{-1} cm^{-1}) 0.64), 426.5 (0.77), 416.8 (0.80), 411.5 (1.11), 376.7 (0.99), 363.4 (0.95), 354.0 (0.87), 280.7 (3.06), 272.8 (3.10), 223.1 (4.26); fluorescence (excitation at 280 nm): λ_{max} (isooctane/nm) 406.9; δ_H (200 MHz; C_6D_6) 0.95 (6 H, t, ^3J 7.5, CH_2CH_3), 2.19 (6 H, s, $ArCH_3$), 2.30 (6 H, s, $ArCH_3$), 2.66 (4 H, q, ^3J 7.5, CH_2CH_3), 6.83–6.7.14 (4 H, m, ArH), 7.50–7.62 (1 H, m, ArH), 13.48 (1 H, s, OH); δ_C (50.3 MHz; $CDCl_3$) 13.2 (+, CH_2CH_3), 19.9 (+, $ArCH_3$), 20.1 (+, $ArCH_3$), 51.6 (−, NCH_2), 122.9 (+), 127.0 (+), 127.5 (o), 128.7 (+), 131.8 (o), 132.6 (+), 133.5 (o), 135.1 (o), 139.5 (o), 157.1 (o); δ_B (128.4 MHz; $CDCl_3$) 47.9; *m/z* (EI) 309 (M^+, 44%), 221 (35), 160 (55), 147 (100), 121 (72). $C_{20}H_{28}BNO$ (309.3): calcd. C 77.61, H 9.13, N 4.53; found C 77.34, H 9.25, N 4.45%.

(*N*-Methylpyrrol-2-yl)dimesitylborane (8)

At −78 °C, to a solution of *N*-methylpyrrole (1.60 g, 20.0 mmol) in diethyl ether (10 mL) was added BuLi (6.9 mL of a 1.6 M solution in hexane, 11.0 mmol) and the mixture was stirred 8 h at room temperature. Subsequently, the solution was cooled to −78 °C and a solution of fluorodimesitylborane (2.68 g, 10.0 mmol) in THF (10 mL) was added. After stirring for 12 h, the mixture was hydrolysed with brine (30 mL), extracted with diethyl ether (2 × 20 mL) and dried with Na_2SO_4. The solvents were distilled off and the residue was chromatographed on Al_2O_3 using petroleum ether–diethyl ether (5:1) as solvent ($R_f = 0.3$), giving 1.41 g (43%) **8** as colourless crystals, mp 138 °C. λ_{max} (cyclohexane/nm) 327.4 (lg (ε/dm^3 mol^{-1} cm^{-1}) 4.64), 245.2 (4.07), 222.8 (4.96), 209.8 (4.83); fluorescence (excitation at 327 nm): λ_{max} (cyclohexane/nm) 447.0; fluorescence lifetime (cyclohexane, λ_{Ex} 322 nm, λ_{Em} 448 nm): τ 10.3 ns; δ_H (200 MHz; C_6D_6) 2.31 (12 H, s, $ArCH_3$), 2.38 (6 H, s, $ArCH_3$), 3.12 (3 H, s, NCH_3), 6.32 (1 H, dd, ^3J 3.8, 2.2, pyrrole H), 6.66 (1 H, t, ^3J 2.2, pyrrole H), 6.85–7.10 (5 H, m, ArH); δ_C (50.3 MHz; $CDCl_3$) 21.6 (+, $ArCH_3$), 22.8 (+, $ArCH_3$), 36.5 (+, NCH_3), 110.7 (+), 128.7 (+), 129.1 (+), 132.9 (+), 138.3 (o), 138.6 (o), 140.8 (o), 141.8 (o); δ_B (128.4 MHz; $CDCl_3$) 61.1; *m/z* (EI) 329 (M^+, 100%) 314 (70), 248 (95), 209 (75), 105 (32). $C_{23}H_{28}BN$ (329.3): calcd. C 83.83, H 8.57, N 4.25; found C 83.85, H 8.73, N 4.03%.

(*N*-Methylindol-2-yl)dimesitylborane (11)

At −78 °C, to a solution of **9** (260 mg, 1.0 mmol) in diethyl ether (10 mL) BuLi (0.7 mL of a 1.6 M solution in hexane, 1.1 mmol) was added and the mixture warmed up to room temperature. The solution was separated from the precipitated LiOMe and added to a freshly prepared suspension of 2.2 mmol MesLi, prepared from bromomesitylene (400 mg, 2.2 mmol) and BuLi (1.4 mL of a 1.6 M solution in hexane, 2.2 mmol). The mixture was stirred for 8 h, hydrolysed with brine (30 ml), extracted with diethyl ether (2 × 20 mL) and dried with Na_2SO_4. The solvents were distilled off and the residue was chromatographed on Al_2O_3 using petroleum ether as solvent ($R_f = 0.3$), giving 90 mg (23% over both steps) of **11** as yellow crystals, mp 188 °C. λ_{max} (cyclohexane/nm) 343.5 (lg (ε/dm^3 mol^{-1} cm^{-1}) 4.27), 250.7 (3.90), 226.5 (4.55), 205.3 (4.74); fluorescence (excitation at 346 nm): λ_{max} (cyclohexane/nm) 458.0; fluorescence lifetime (cyclohexane, λ_{Ex} 340 nm, λ_{Em} 448 nm): τ 11.4 ns; δ_H (200 MHz; C_6D_6) 2.25 (6 H, s, $ArCH_3$), 2.34 (12 H, s, $ArCH_3$), 3.39 (3 H, s, NCH_3), 6.88 (4 H, s, ArH), 7.08–7.40 (4 H, m, ArH), 7.55–7.77 (1 H, m, ArH); δ_C (50.3 MHz; $CDCl_3$) 18.4 (+, $ArCH_3$), 21.4 (+, $ArCH_3$), 32.1 (+, NCH_3), 110.8 (+), 119.7 (+), 120.6 (+), 123.7 (+), 125.6 (+), 126.8 (o), 127.8 (o), 128.7 (+), 129.2 (o), 136.9 (o), 139.1 (o), 140.6 (o); δ_B (128.4 MHz; $CDCl_3$) 64.0; *m/z* (EI) 379 (M^+, 65%), 364 (70), 258 (21), 244 (100), 119 (19). $C_{27}H_{30}BN$ (379.4): calcd. C 85.43, H 7.97, N 3.69; found C 85.66, H 8.02, N 3.43%.

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