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Unsymmetrical 9-Borafluorenes via Low-Temperature C−H Activation of *m*-Terphenylboranes

Rudolf J. Wehmschulte,* Armando A. Diaz, and Masood A. Khan

Department of Chemistry and Biochemistry, University of Oklahoma, 620 Parrington Oval, Room 208, Norman, Oklahoma 73019

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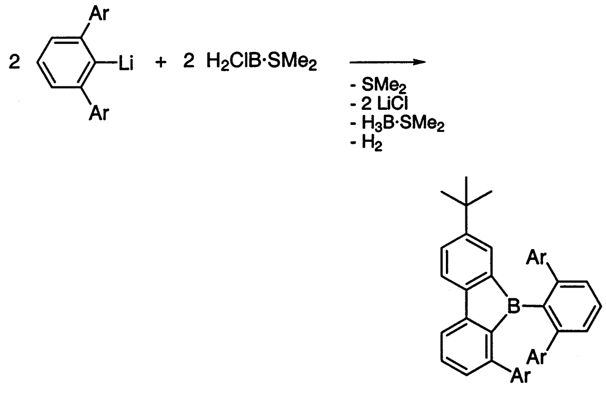
The reaction of 2,6-(4-*t*-$BuC_6H_4)_2C_6H_3Li$ and with $H_2ClB{\cdot}SMe_2$ or $HCl_2B{\cdot}SMe_2$ in hexane solution afforded the *m*-terphenyl-substituted unsymmetrical 9-borafluorene 1-(4-*tert*-butylphenyl)-7-*tert*-butyl-9-(bis-2,6-(4-*tert*-butylphenyl)phenyl)-9-borafluorene, **1**, in good to moderate yields. The related reaction of 2,6-(3,5-$Me_2C_6H_3)_2C_6H_3Li$ with $BH_2Cl{\cdot}SMe_2$ or $BHCl_2{\cdot}SMe_2$ in toluene solution gave 1-(3,5-dimethylphenyl)-6,8-dimethyl-9-(bis-2,6-(3,5-dimethylphenyl)phenyl)-9-borafluorene, **3**. Compounds **1** and **3** are air-stable fluorescent solids. The reactions of 2,6-(2-$MeC_6H_4)_2C_6H_3Li$ or 2,6-$Mes_2C_6H_3Li$ (which possess either two or no *o*- and *o*″-hydrogens) with $H_2ClB{\cdot}SMe_2$ gave the primary boranes [2,6-(2-$MeC_6H_4)_2C_6H_3$-$BH_2]_2$, **4**, and [2,6-$Mes_2C_6H_3BH_2]_2$, **5**, respectively. Quenching of the reaction of 2,6-(4-*t*-$BuC_6H_4)_2C_6H_3Li$ with $H_2ClB{\cdot}SMe_2$ after 1.5 h with pyridine resulted in the isolation of the primary borane [2,6-(4-*t*-$BuC_6H_4)_2C_6H_3BH_2]_2$, **2**, as the pyridine adduct **2**·py, which after thermolysis at 190 °C gave 1-(4-*tert*-butylphenyl)-7-*tert*-butyl-9-borafluorene·pyridine, **7**·py. Heating a C_6D_6 solution of **4** to 60−70 °C led to C−H activation and formation of a 1:1 adduct of monomeric **4** and 1-(2-methylphenyl)-5-methyl-9-borafluorene, **12**. Reaction of 2 equiv of 2,6-(4-*t*-$BuC_6H_4)_2C_6H_3Li$ with $H_2ClB{\cdot}SMe_2$ in hexane solution followed by addition of THF gave the very crowded diterphenyl borate [2,6-(4-*t*-$BuC_6H_4)_2C_6H_3]_2B(\mu\text{-}H)_2Li(THF)_2]_2$, **11**, which can be converted to **1** by simple addition of water. Prolonged exposure of **1** to concentrated aqueous HCl led to B−C bond cleavage and formation of the sterically very crowded diterphenylborinic acid [2,6-(4-*t*-$BuC_6H_4)_2C_6H_3]_2BOH$, **15**. All compounds have been characterized by ^1H, ^{13}C, and ^{11}B NMR spectroscopy and mass spectrometry, and compounds **1**, **4**, and **11** have also been characterized by single-crystal X-ray crystallography.

Introduction

In an effort to explore the coordination properties of unsymmetrical 9-borafluorenes as potential alternatives to the ubiquitous cyclopentadienide-based ligand systems,[1] we discovered 9-borafluorene formation via a remarkably facile intramolecular C−H activation even below room temperature.[2] The reaction of 2,6-(4-*t*-$BuC_6H_4)_2C_6H_3Li$ with $H_2ClB{\cdot}SMe_2$ afforded the sterically encumbered terphenyl-substituted 9-borafluorene **1** in yields of up to 75% (eq 1).



(1)

1

Ar = 4-*t*-BuC_6H_4

Typically, the synthesis of 9-borafluorenes requires either *o,o*′-biphenylmercury compounds,[3] which are highly toxic, or temperatures of at least 150 °C in thermolysis reactions of 2-biphenyldialkylboranes.[4] Thus, 9-borafluorene formation via a low-temperature C−H activation involving an intermediate primary borane [2,6-(4-*t*-$BuC_6H_4)_2C_6H_3BH(\mu\text{-}H)]_2$, **2**, constitutes a significant improvement with respect to the previous methods. Furthermore, the steric protection brought on by the bulky *m*-terphenyl substituent in 9-borafluorene **1** leads to enhanced stability. For example, **1** is even

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* Corresponding author. Fax: +1 405 325 6111. E-mail: rjwehmschulte@ou.edu.

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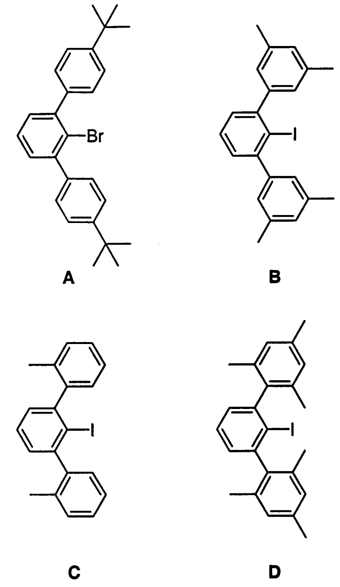
Scheme 1



stable toward brief exposure to concentrated aqueous HCl. In the doubly reduced form of **1** the lithium cations are positioned above and below the five-membered borole ring in an almost symmetrical fashion. They are further protected by weak interactions with the flanking 4-*t*-BuC_6H_4 groups of the *m*-terphenyl substituent.[2] Transition metals are expected to be coordinated in a similar manner. In fact, preliminary spectroscopic data of a $Cr(CO)_3$-containing complex of **1** are in agreement with this coordination mode.[5] Other potential applications of air-stable, bright yellow-green fluorescent 9-borafluorenes could be as fluoride ion sensors[6] or electronic materials such as chromophores in organic LEDs.[7] Therefore, we have further investigated the scope of the 9-borafluorene formation from readily available *m*-terphenyl precursors. We have prepared three additional *m*-terphenyl compounds which differ in the substitution pattern of the *o*- and *o''*-aromatic rings (Scheme 1). Here, we report on the reactions of the *m*-terphenyllithium compounds derived from the precursors **A** to **D** with $H_2ClB\cdot SMe_2$ or $HCl_2B\cdot SMe_2$ to afford either 9-borafluorenes or primary boranes $[TerphBH(\mu\text{-}H)]_2$ (Terph = *m*-terphenyl). Furthermore, we have investigated the reaction of 2,6-(4-*t*-$BuC_6H_4)_2C_6H_3$-Li with $H_2ClB\cdot SMe_2$ in more detail. The results of thermolysis reactions of the new primary boranes $[2,6\text{-}(2\text{-}MeC_6H_4)_2C_6H_3BH(\mu\text{-}H)]_2$, **4**, and $[2,6\text{-}Mes_2C_6H_3BH(\mu\text{-}H)]_2$, **5**, are also presented.

Results and Discussion

We have previously reported that the reaction of 2,6-(4-*t*-$BuC_6H_4)_2C_6H_3Li$ with $H_2ClB\cdot SMe_2$ in hexanes afforded the sterically encumbered borafluorene **1** in up to 50−75% yield.[2] Similarly, the corresponding reaction of 2,6-(3,5-$Me_2C_6H_3)_2C_6H_3Li$ with $H_2ClB\cdot SMe_2$ afforded the terphenyl-substituted 9-borafluorene **3**, albeit in lower yields (eq 2).

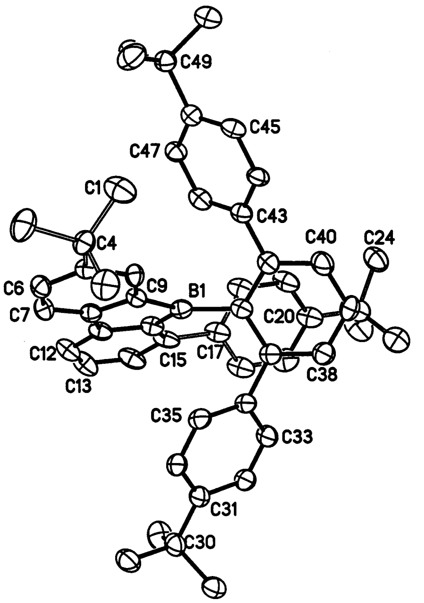
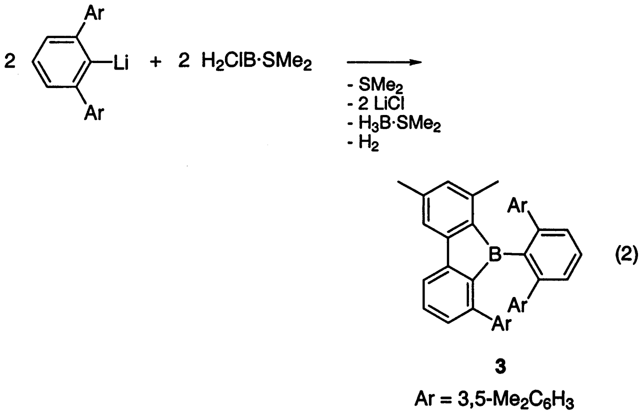


Figure 1. Thermal ellipsoid plot (30% probability ellipsoids) showing the molecular structure of **1**. Hydrogen atoms are omitted for clarity.



Whereas the high solubility of **1** in standard organic solvents prevents the isolation of **1** by crystallization from the reaction mixture (vide infra), **3** is less soluble in hexanes or Et_2O and can be isolated by this method. Both compounds are bright yellow-green fluorescent, air- and moisture-stable solids. 9-Borafluorenes are isoelectronic with the formally antiaromatic fluorenyl cation $C_{13}H_9^+$.[8−10] To assess the extent of π-electron delocalization and antiaromaticity on the metric parameters of the borafluorene ring system, a crystal structure analysis of **1** was undertaken. The structure of **1** (Figure 1) features an unsymmetrical, essentially planar 9-borafluorene core with the boron being slightly pushed out of the borafluorene plane due to close C−C contacts involving the C(37)−C(42) and the C(17)−C(22) aromatic rings: C(17)···C(37) = 3.502 Å, C(17)···C(42) = 3.424 Å, C(22)···C(42) = 3.230 Å. The geometry at

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Table 1. Crystal Data and Structural Refinement Details for 1, 4, and 11

	1	4	11
emp formula	$C_{52}H_{57}B$	$C_{40}H_{38}B_2$	$C_{60}H_{76}BLiO_2$
fw	692.79	540.32	846.96
T, K	173(2)	173(2)	103(2)
wavelength, Å	0.71073	0.71073	0.71073
cryst syst	monoclinic	triclinic	orthorhombic
space group	$P2(1)/c$	$P\bar{1}$	$P2(1)2(1)2(1)$
a, Å	14.400(3)	11.2756(14)	12.3136(8)
b, Å	20.794(5)	11.298(2)	15.1506(10)
c, Å	15.672(5)	12.691(2)	27.4491(18)
α, deg	90	77.854(12)	90
β, deg	115.900(13)	88.050(9)	90
γ, deg	90	86.787(12)	90
V, Å^3	4221.5(19)	1577.7(4)	5120.9(6)
Z	4	2	4
D_{calcd}, Mg/m^3	1.090	1.137	1.099
μ(Mo K$_\alpha$), mm^{-1}	0.061	0.063	0.063
F(000)	1496	576	1840
cryst size, mm^3	0.64 × 0.44 × 0.34	0.36 × 0.32 × 0.24	0.32 × 0.24 × 0.16
cryst color and habit	yellow plate	colorless prism	colorless plate
$2\theta_{\max}$, deg	46.00	48.48	53.00
no. of observns	5836	5034	10595
no. of variables	547	399	596
$R_1{}^a$ [$I>2\sigma(I)$]	0.0830	0.0580	0.0389
$wR_2{}^b$ [$I>2\sigma(I)$]	0.1677	0.1236	0.0903
goodness-of-fit on F^2	1.058	1.056	1.029
largest diff peak, e Å^{-3}	0.279	0.202	0.229

^{a} $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR_2 = (\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2)^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1

B(1)−C(9)	1.573(6)	C(16)−B(1)−C(9)	103.5(4)
B(1)−C(16)	1.556(7)	C(16)−B(1)−C(42)	128.3(4)
B(1)−C(42)	1.575(7)	C(9)−B(1)−C(42)	127.9(4)
C(8)−C(9)	1.391(6)	C(8)−C(9)−B(1)	107.7(4)
C(8)−C(11)	1.472(6)	C(9)−C(8)−C(11)	111.4(4)
C(11)−C(16)	1.434(6)	C(16)−C(11)−C(8)	109.4(4)
		C(11)−C(16)−B(1)	107.4(4)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 4

B(1)−C(13)	1.574(4)	C(13)−B(1)−H(1)	123(2)
B(1)−H(1)	1.11(3)	C(13)−B(1)−H(2)	108(2)
B(1)−H(2)	1.22(3)	C(13)−B(1)−H(3)	115.5(12)
B(1)−H(3)	1.27(3)	H(1)−B(1)−H(2)	111(2)
B(1)···B(2)	1.787(5)	H(1)−B(1)−H(3)	107(2)
B(2)−C(33)	1.575(4)	H(2)−B(1)−H(3)	87(2)
B(2)−H(2)	1.22(3)	C(33)−B(2)−H(2)	114(2)
B(2)−H(3)	1.24(3)	C(33)−B(2)−H(3)	115.8(12)
B(2)−H(4)	1.07(3)	C(33)−B(2)−H(4)	120(2)
		H(2)−B(2)−H(3)	88(2)
		H(2)−B(2)−H(4)	105(2)
		H(3)−B(2)−H(4)	109(2)

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 11

B(1)−C(16)	1.643(2)	C(16)−B(1)−C(42)	111.44(12)
B(1)−C(42)	1.645(2)	C(16)−B(1)−H(1)	113.1(8)
B(1)−H(1)	1.175(14)	C(16)−B(1)−H(2)	108.3(8)
B(1)−H(2)	1.180(14)	C(42)−B(1)−H(1)	108.6(8)
Li(1)−H(1)	1.851(14)	C(42)−B(1)−H(2)	109.9(8)
Li(1)−H(2)	1.852(14)	H(1)−B(1)−H(2)	105.3(11)
Li(1)−(O1)	1.906(3)	H(1)−Li(1)−H(2)	60.8(7)
Li(1)−O(2)	1.903(3)	O(1)−Li(1)−O(2)	104.61(15)

the boron atom is distorted trigonal planar. The B−C bond lengths (Table 2) with values of 1.556(7), 1.573(6), and 1.575(7) Å are typical for B−C$_{\text{aryl}}$ bonds found in other three-coordinate aryl boranes (e.g., 1.589(5) and 1.571(3) Å in Ph$_3$B,[11] 1.574(4) and 1.565(7) Å in [2,6-(MeO)$_2$C$_6$H$_3$]$_3$B,[12] and 1.579(2) and 1.580(3) Å in Mes$_3$B[13]) and 9-borafluorenes (e.g., 1.592(6) and 1.588(6) Å in 9-*N*,*N*-(di-*tert*-butylboryl)methyl-9-borafluorene[14] and 1.556(4) and 1.549(3) Å in 9-pentafluorophenyloctafluoro-9-borafluorene[15]). Due to the 9-borafluorene structure constraints, the internal C(9)−B(1)−C(16) angle with a value of 103.5(4)° is significantly smaller than the other two C−B−C angles with values of 128.3(4)° and 127.9(4)°. Very similar values were observed for the two aforementioned 9-borafluorenes[14,15] and, interestingly, also for the doubly reduced dilithium salt of **1**, **1**·2LiOEt$_2$.[2] The terphenyl substituent is rotated out of the 9-borafluorene plane by 65° and the central C(37)−C(42) ring is almost parallel to the C(17)−C(22) aromatic ring. With the exception of the C(11)−C(16) bond distance of 1.434(6) Å, which may be caused by minor disorder problems, the metric parameters indicate only little distortion and thus little antiaromaticity, and thus the 9-borafluorene group may be best described as a substituted biphenyl.

Contrary to the results above, the reaction of 2,6-(2-MeC$_6$H$_4$)$_2$C$_6$H$_3$Li and 2,6-Mes$_2$C$_6$H$_3$Li[16] (Mes = 2,4,6-Me$_3$C$_6$H$_2$) with H$_2$ClB·SMe$_2$ afforded the expected primary boranes [2,6-(2-MeC$_6$H$_4$)$_2$C$_6$H$_3$BH(μ-H)]$_2$, **4**, and [2,6-Mes$_2$C$_6$H$_3$BH(μ-H)]$_2$, **5**, in moderate to good yields (eq 3).

$$2\ \text{TerphLi} + 2\ \text{BH}_2\text{Cl}\cdot\text{SMe}_2 \longrightarrow [\text{TerphBH}(\mu\text{-H})]_2 + 2\ \text{LiCl} + 2\ \text{SMe}_2 \qquad (3)$$

Terph = 2,6-(2-MeC$_6$H$_4$)$_2$C$_6$H$_3$, **4**
2,6-Mes$_2$C$_6$H$_3$, **5**

Both compounds are colorless solids that are stable toward brief exposure to air. The structure of **4** was confirmed by X-ray diffraction as a dimer with bridging hydrogens (Figure 2). The B−C, B−H$_{\text{term}}$, and B−H$_{\text{bridg.}}$ bond distances with average values of 1.574(4), 1.09(3), and 1.24(3) Å, respectively, are slightly shorter than those observed for [MeBH(μ-H)]$_2$[17] or [(Me$_3$Si)$_3$CBH(μ-H)]$_2$,[18] and the B···B separation in **4** with a value of 1.787(5) Å lies between those reported for [MeBH(μ-H)]$_2$ or [(Me$_3$Si)$_3$CBH(μ-H)]$_2$. The terphenyl substituents are rotated 71.9° with respect to each other, which may be a result of steric repulsion considering that the related dimeric aluminum hydrides [2,6-Mes$_2$C$_6$H$_3$AlH(μ-H)]$_2$ and [2,6-Trip$_2$C$_6$H$_3$AlH(μ-H)]$_2$ (Trip = 2,4,6-*i*-Pr$_3$C$_6$H$_3$)[19] feature an almost parallel alignment of the terphenyl substituents. Contrary to the situation in solution only one isomer is found in the solid state of **4**. Here, all methyl groups are pointed outward. The internal H−B−H angles are relatively narrow, with values of 87-

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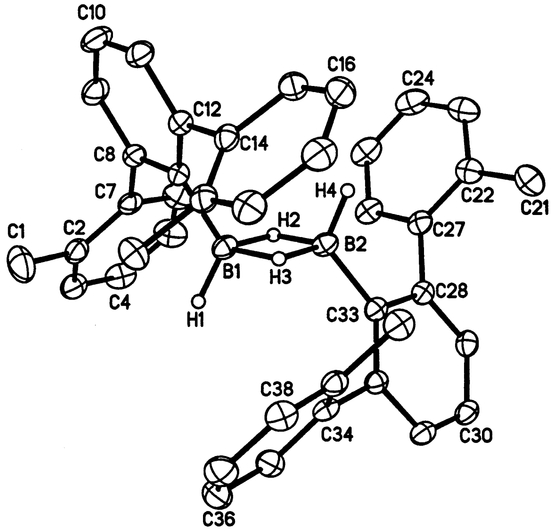


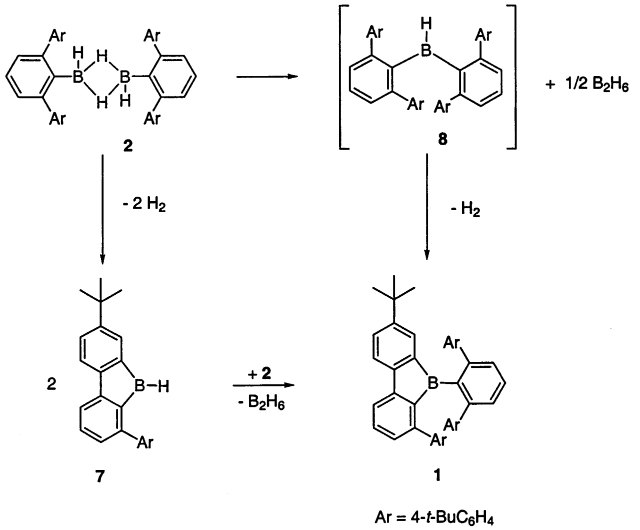
Figure 2. Thermal ellipsoid plot (30% probability ellipsoids) showing the molecular structure of **4**. Hydrogen atoms except of those bound to boron are omitted for clarity.

(2)° and 88(2)°, whereas the external C−B−H angles with values of 123(2)° and 120(2)° are significantly wider. The dimeric structures of **4** and **5** are maintained in solution, which is evidenced by the occurrence of separate ^{1}H NMR signals for the terminal and bridging hydrides. Furthermore, the ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **4** are complicated due to the presence of several isomers which originate in the different orientations the *o*-tolyl groups can assume with respect to each other.

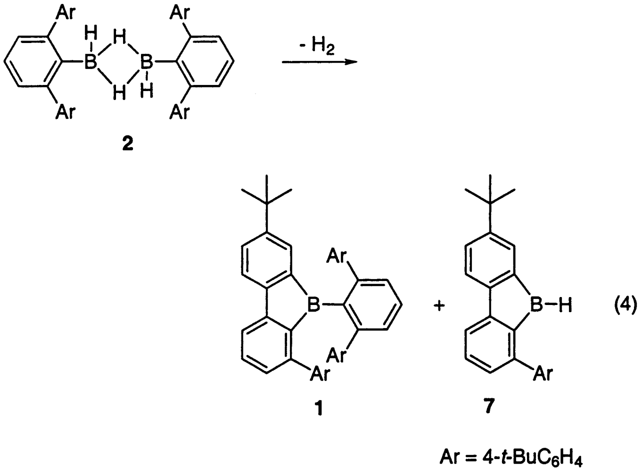
The formation of the terphenyl-9-borafluorenes **1** and **3** instead of the corresponding primary boranes $[2,6\text{-}(4\text{-}t\text{-}BuC_6H_4)_2C_6H_3BH(\mu\text{-}H)]_2$, **2**, and $[2,6\text{-}(3,5\text{-}Me_2C_6H_3)_2\text{-}C_6H_3BH(\mu\text{-}H)]_2$, **6**, in the reaction of $2,6\text{-}(4\text{-}t\text{-}BuC_6H_4)_2\text{-}C_6H_3Li$ or $2,6\text{-}(3,5\text{-}Me_2C_6H_3)_2C_6H_3Li$ with $H_2ClB\cdot SMe_2$ is remarkable due to two factors: (i) the facile activation of an aromatic C−H bond by a primary borane $ArBH_2$ and (ii) the ease of the aryl migration despite the large size of the aryl substituent. To better understand the factors that govern the borafluorene formation, the reaction of $2,6\text{-}(4\text{-}t\text{-}BuC_6H_4)_2C_6H_3Li$ with $H_2ClB\cdot SMe_2$ was investigated in greater detail.

If the reaction is stopped after only 1.5 h by removal of the volatile materials under reduced pressure, the main product observed in the residue is the primary borane $[2,6\text{-}(4\text{-}t\text{-}BuC_6H_4)_2C_6H_3BH(\mu\text{-}H)]_2$, **2**. Compounds **1**·py, $H_3B\cdot SMe_2$, and $LiBH_4$ have been identified among the other products by ^{1}H and ^{11}B NMR spectroscopy after addition of excess pyridine. Redissolution of a portion of the crude product in hexanes followed by addition of pyridine afforded, after workup, the adduct **2**·py as a pale yellow crystalline solid. Contrary to uncomplexed **2**, the adduct **2**·py is stable at room temperature with respect to C−H activation. Indeed, heating to the melting point (165 °C) is required before a gas evolution and formation of the 9-borafluorene **7**·py is observed. This corresponds well with Bickelhaupt's report of the synthesis of the parent 9-borafluorene·py by thermolysis of the pyridine adduct 2-biphenylborane·py at 260 °C.[20]

Scheme 2



After stirring a hexane solution of crude **2** (synthesized as above) at room temperature for 3 days essentially all of **2** was consumed, and the main products were the 9-borafluorenes **1** and **7** (eq 4). These could be separated and isolated as pyridine adducts by fractional crystallization in the presence of excess pyridine.



The formation of **7** may be explained by C−H activation of one of the *o*- or *o''*-aromatic hydrogens in **2**. Unfortunately, these results do not explain the formation of **1**, for which there are several possible pathways, two of which are discussed below (Scheme 2): **7** reacts with **2** to give **1** and B_2H_6 or **2** rearranges to form B_2H_6 and the very crowded diterphenyl borane $[2,6\text{-}(4\text{-}t\text{-}BuC_6H_4)_2C_6H_3]_2BH$ (**8**), which readily undergoes C−H activation to afford **1**. The fact that **8** has not yet been isolated or detected by spectroscopic techniques suggests either that **8** is very short-lived or that it is not an intermediate in the formation of **1**. The isolation of the borafluorene **9**, an analogue of **7**, as the pyridine adduct **9**·py from the reaction of $2,6\text{-}(3,5\text{-}Me_2C_6H_3)_2C_6H_3Li$ with $H_2ClB\cdot SMe_2$ indicates that both compounds **1** and **3** may be formed by the same mechanism.

The terphenyl-9-borafluorenes **1** and **3** can also be synthesized by the reaction of 2 equiv of $2,6\text{-}(4\text{-}t\text{-}BuC_6\text{-}H_4)_2C_6H_3Li$ or $2,6\text{-}(3,5\text{-}Me_2C_6H_3)_2C_6H_3Li$ with

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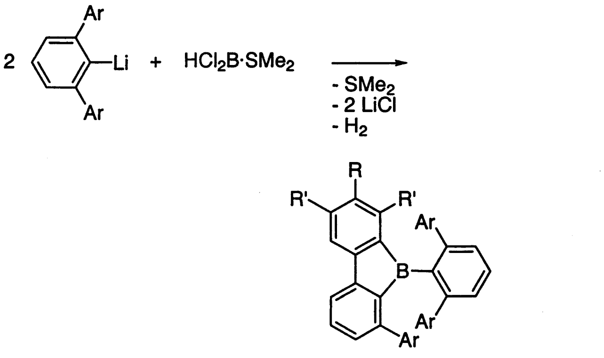
[20] Veen, R. v.; Bickelhaupt, F. *J. Organomet. Chem.* **1973**, *47*, 33−38.

$HCl_2B{\cdot}SMe_2$ (eq 5).

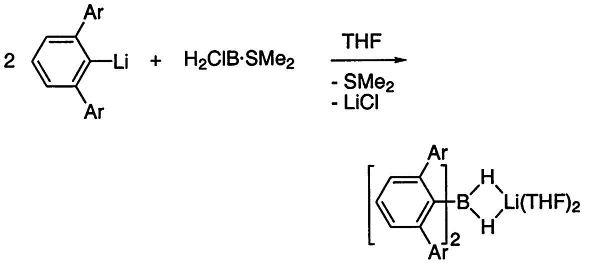


(5)

Ar = 4-*t*-BuC$_6$H$_4$, R = *t*-Bu, R' = H, **1**
3,5-Me$_2$C$_6$H$_3$, R = H, R' = Me, **3**

Although the reaction mechanism is not known at this time, it seems likely that the very crowded diterphenyl boranes [2,6-(4-*t*-BuC$_6$H$_4$)$_2$C$_6$H$_3$]$_2$BH, **8**, and [2,6-(3,5-Me$_2$C$_6$H$_3$)$_2$C$_6$H$_3$]$_2$BH, **10**, may be intermediates.

In an effort to evaluate the potential role of a diterphenylborate Terph$_2$BH$_2$Li as a possible intermediate in the formation of **1** and **3** as well as an alternative access to the very crowded **8**, 2 equiv of 2,6-(4-*t*-BuC$_6$H$_4$)$_2$-C$_6$H$_3$Li was reacted with $H_2ClB{\cdot}SMe_2$ according to eq 6.



(6)

11, Ar = 4-*t*-BuC$_6$H$_4$

The ^{11}B NMR spectrum of the crude product indicated the formation of the [2,6-(4-*t*-BuC$_6$H$_4$)$_2$C$_6$H$_3$]$_2$BH$_2^-$ anion with a triplet at −20.0 ppm and a B−H coupling constant of 73 Hz. Attempts to isolate this species by crystallization from hexanes were unsuccessful, but the THF-solvated compound [2,6-(4-*t*-BuC$_6$H$_4$)$_2$C$_6$H$_3$]$_2$B(μ-H)$_2$Li(THF)$_2$, **11**, was eventually obtained in the form of small pale yellow needles after addition of THF to the hexanes solution of the crude product. The crystal structure (Figure 3) shows that there is remarkably little distortion despite the large size of the terphenyl substituents. The terphenyl groups are rotated with respect to each other so that they adopt an approximate staggered arrangement of the flanking aryl groups and also generate a cleft large enough to accommodate the lithium cation and the two THF molecules. This results in an almost parallel alignment of the C(43)−C(48) with the C(11)−C(16) aromatic ring and the C(37)−C(42) with the C(15)−C(10) aromatic ring with C···C distances not below 3.456 Å, with the exception of C(8)···C(42) and C(16)···C(43), with values of 3.066 and 3.083 Å, respectively. The geometry at the boron center is essentially tetrahedral with only minor deviations from the ideal 109.5° angles with C(16)−B(1)−C(42) = 111.44(12)°, H(1)−B(1)−H(2) = 105.3(11)°, and C(16)−B(1)−H(1) = 113.1(8)°. Similarly the B−C distances with values of 1.643(2) Å for B(1)−C(16) and 1.645(2) Å for B(1)−C(42) are typical for four-coordinate B−C$_{\text{aryl}}$ distances.[21] The lithium cation is solvated by two THF molecules and the two bridging hydrides in a distorted tetrahedral fashion in which the long Li−H distances (compared to the B−H distances) lead to a narrow H(1)−Li(1)−H(2) angle of 60.8(7)°. With the exception of the close aryl···aryl interactions the structure of **11** corresponds closely to that of Mes$_2$B(μ-H)$_2$Li(DME).[22] It should also be noted that diterphenyl compounds are quite rare and have so far been limited to a few gallium and indium species.[23−25] The steric crowding in these species is expressed in the wide C$_{\text{ipso}}$−M−C$_{\text{ipso}}$ angles with values ranging from 134.4° to 153.3°.

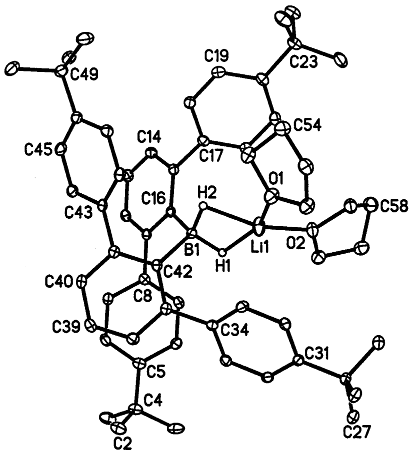


Figure 3. Thermal ellipsoid plot (30% probability ellipsoids) showing the molecular structure of **11**. Hydrogen atoms except of those bound to boron are omitted for clarity.

Compound **11** is stable in solution under anhydrous and anaerobic conditions and decomposes only at its melting point of 190−198 °C with gas evolution and color change to yellow. Thus, its role as an intermediate in the formation of **1** may be ruled out, but its existence supports our proposal that the diterphenylboranes **8** and **10** may be intermediates in the formation of **1** and **3** according to eq 5. To generate **8**, borate **11** was reacted with Me$_3$SiCl or H$_2$O in C$_6$D$_6$ solution in analogy with the synthesis of Trip$_2$BH[26] or [Mes*AlH$_2$]$_2$[27] from the corresponding borate or alanate. Whereas no reaction was observed between **11** and Me$_3$SiCl even after 24 h at room temperature, the reaction of **11** with water led to a gentle gas evolution, which was accompanied by a gradual color change from pale yellow to bright yellow fluorescent. The formation of **1** was verified by ^{1}H NMR spectroscopy, but no signals attributable to **8** were detected. Thus, we propose that the reaction of **11** with H$_2$O leads to the formation of **8**, which immediately

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(21) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1−S19.

(22) Hooz, J.; Akiyama, S.; Cedar, F. J.; Bennett, M. J.; Tuggle, R. M. *J. Am. Chem. Soc.* **1974**, *96*, 274−276.

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(24) Crittendon, R. C.; Li, X.-W.; Su, J.; Robinson, G. H. *Organometallics* **1997**, *16*, 2443−2447.

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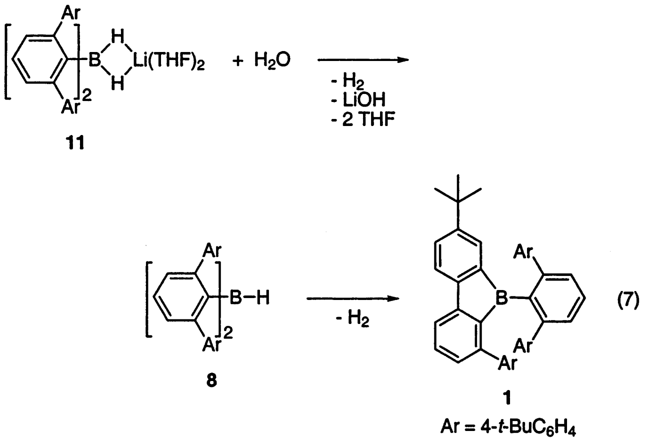
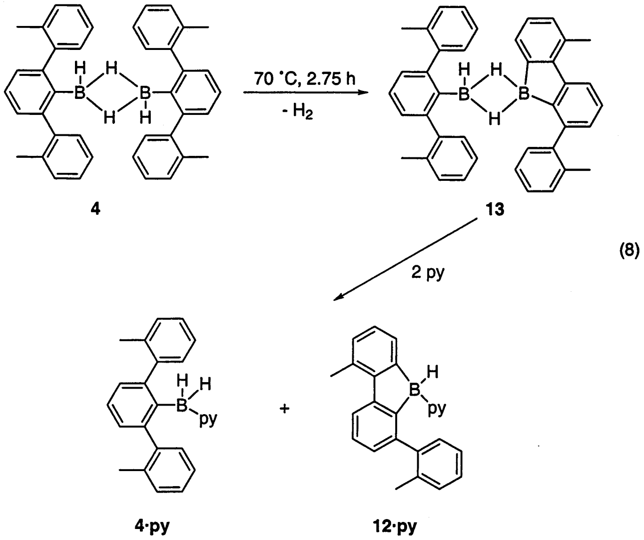
(27) Wehmschulte, R. J.; Power, P. P. *Inorg. Chem.* **1994**, *33*, 5611−5612.

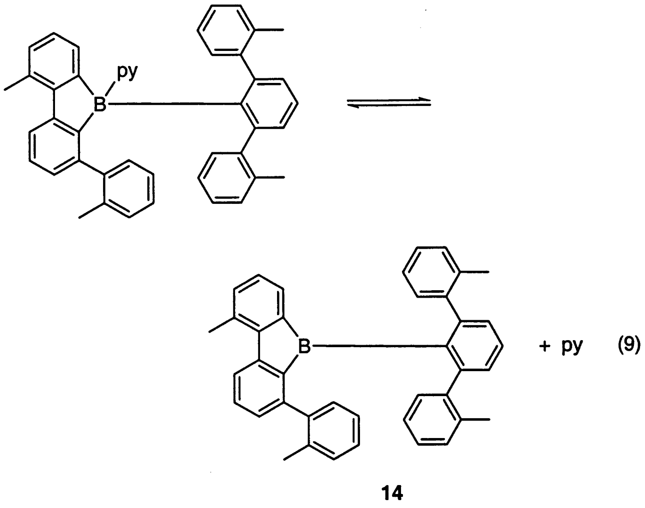
rearranges to **1** (eq 7).



Thermolysis Reactions. To gain further insight into the formation of **1** and **3** and also to explore the scope of the 9-borafluorene formation via C–H activation, the thermolysis of the primary boranes **4** and **5** was investigated. Heating of both compounds to their respective melting points led to gas evolution and the formation of mixtures of compounds. Thermolysis of a C_6D_6 solution of **4** at 68–71 °C for ca. 2.75 h resulted in the disappearance of the ^{1}H NMR signals of **4** and a color change of the solution to yellow. The ^{11}B NMR spectrum shows two signals of equal intensity at 24.1 and 12.1 ppm. Addition of excess pyridine significantly simplified the methyl region of the ^{1}H NMR spectrum, and the signals were identified as belonging to a 1:1 mixture of **4**·py and the 9-borafluorene **12**·py by comparison with original samples (see Experimental Section for the synthesis of **4**·py and **12**·py). The same reaction also occurs at room temperature, albeit much more slowly. It takes approximately five months for the disappearance of the ^{1}H NMR signals of **4** from a sample of **4** kept in C_6D_6 solution at room temperature in a sealed NMR tube. No further reaction is observed under these conditions. On the basis of these findings we propose the initial product of the thermolysis to be the dimer **13**, consisting of one monomer each of **4** and **12** (eq 8). Addition of pyridine cleaves the B–H–B bridges and afforded the observed 1:1 mixture of **4**·py and the 9-borafluorene **12**·py.



Further heating of the C_6D_6 solution of **13** at 74–78 °C for 4 days led to the gradual disappearance of the ^{1}H NMR signals at 1.70 and 1.81 associated with **13**. In addition, formation of hydrogen ($\delta_H = 4.47$ ppm)[28] and a color change to yellow fluorescent, which appears to be characteristic for 9-borafluorenes,[2,4] were observed. The ^{11}B NMR spectrum displayed two new signals of approximately equal intensity at 28.6 and 0.0 ppm. Addition of 4-(dimethylamino)pyridine (DMAP, a stronger base than pyridine) resulted in the disappearance of these peaks and the appearance of two new signals at −2.5 and −12.5 ppm, respectively. In a separate experiment in which a more dilute sample was thermolyzed and pyridine was added instead of DMAP, a broad singlet at 7.3 and a quartet at −10.7 ($J_{B-H} = 99$ Hz) were observed in the ^{11}B NMR spectrum. The latter signal is probably due to H_3B·py,[29] whereas the chemical shift of the former signal corresponds with the one found for **1**·py. In both cases the ^{1}H NMR spectra showed only severely broadened signals, in accordance with the equilibrium given in eq 9.



Attempts to isolate **14** or its pyridine or DMAP adducts have not yet been successful, in part due to the difficulty of determining the completion of the thermolysis and the high solubility of the products in aliphatic or aromatic solvents.

Although the bond strengths of benzylic C–H bonds are lower than those for aromatic C–H bonds (85 kcal/mol for $C_6H_5CH_2$–H vs 110 kcal/mol for C_6H_5–H[30]), no reaction took place when **5** was heated to ca. 130 °C in C_7D_8 solution in a sealed NMR tube. Gas evolution, however, was observed when neat **5** was heated to its melting point, but only a complicated mixture was detected via ^{1}H NMR spectroscopy. Whereas the mechanism for the C–H activation in the *m*-terphenyl borane compounds discussed earlier is not known, the fact that **5** does not undergo C–H activation under mild conditions suggests that an electrophilic attack of the Lewis acidic boron center on the aromatic ring system may be an important step in this reaction.

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[29] Nöth, H.; Wrackmeyer, B. *Chem. Ber.* **1974**, *107*, 3070–3088.

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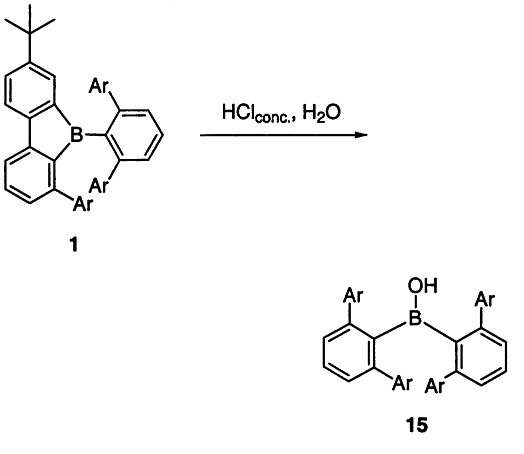
Stability and Purification of 1 and Synthesis of 15. Due to its very high solubility in common organic solvents, **1** could not be isolated by crystallization from the reaction mixture. We have previously shown that the doubly reduced dianionic **1**·2LiOEt$_2$ is readily oxidized by various metal salts, and pure **1** can be obtained from these reactions.[2] However, this method requires the prior synthesis and isolation of the highly air- and moisture-sensitive **1**·2LiOEt$_2$. Previous work has also shown that the air-stable pyridine adduct **1**·py can be isolated from the reaction mixture containing **1** and pyridine by crystallization and that the pyridine was not bound very tightly.[2] As **1**·py is sensitive toward elevated temperatures, removal of the coordinated pyridine by distillation was not feasible. We then investigated the trapping of pyridine by a strong acid and found ca. 6 M aqueous HCl suitable. Addition of 2 to 3 equiv of HCl to an Et$_2$O solution of **1**·py at room temperature led to an immediate brightening of the yellow color of the Et$_2$O phase and a colorless solid formed in the aqueous phase. Separation of the Et$_2$O phase, followed by exchange of the solvent to petroleum ether and subsequent drying over MgSO$_4$, afforded pure **1** after removal of the solvent under reduced pressure. Activated Al$_2$O$_3$ may also be used to remove the pyridine, but up to 50% loss of **1** occurred due to its apparent strong adsorption on alumina. Prolonged exposure (1 week) of **1**·py to concentrated aqueous HCl in the presence of air led to cleavage of one of the B−C bonds of the 9-borafluorene unit and the formation of the diterphenyl borinic acid [2,6-(4-*t*-BuC$_6$H$_4$)$_2$C$_6$H$_3$]$_2$BOH (**15**) (eq 10).



1

15

(10)

Ar = 4-*t*-BuC$_6$H$_4$

Unfortunately, the crystals of **15** were not suitable for X-ray crystallography, but a crowded structure similar to **11** or [2,6-Ph$_2$C$_6$H$_3$]$_2$GaI[25] is expected.

Summary

Terphenyl-substituted unsymmetrical 9-borafluorenes are readily available at or below room temperature by the reaction of TerphLi with either H$_2$ClB·SMe$_2$ or HCl$_2$B·SMe$_2$ provided the terphenyl substituent possesses four *o*- and *o*″-hydrogens. If only two of these hydrogens are available, as in the case of substituent **C**, the primary borane [2,6-(2-MeC$_6$H$_4$)$_2$C$_6$H$_3$BH(μ-H)]$_2$ (**4**) can be isolated, and C−H activation to afford the 9-borafluorene requires elevated temperatures (ca. 60−70 °C). Investigations of the reaction of 2,6-(4-*t*-BuC$_6$H$_4$)$_2$C$_6$H$_3$Li with H$_2$ClB·SMe$_2$ and the thermolysis of **4** indicate that the primary boranes **2** and **4** react to give the 9-borafluorenes **7** and **12** and, in a second step, undergo ligand migration to give **1** and **14**. 9-Borafluorenes **1** and **3** can also be prepared by the reaction of 2 equiv of TerphLi with HCl$_2$B·SMe$_2$, in which case the very crowded diterphenyl boranes **8** and **10** are the most likely intermediates. The (short-lived) existence of **8** is further supported by the isolation of the diterphenylborate **11** and its conversion into **1** upon addition of H$_2$O. Compounds **1** and **3** are air-stable and fluorescent. A study to exploit these properties for application as, for example, fluoride sensor is under way.

Experimental Section

General Procedures. All work was performed under anaerobic and anhydrous conditions by using either modified Schlenk techniques or an Innovative Technologies drybox. Solvents were freshly distilled under N$_2$ from sodium, potassium, or sodium/potassium alloy and degassed twice prior to use. H$_2$ClB·SMe$_2$, HCl$_2$B·SMe$_2$, and *n*-butyllithium (1.6 M in hexanes) were obtained from commercial suppliers. Compounds **1**,[2] **1**·py,[2] 2,6-(4-*t*-BuC$_6$H$_4$)$_2$C$_6$H$_3$Br,[2] 2,6-(2-MeC$_6$H$_4$)$_2$-C$_6$H$_3$I,[31] 2,6-(3,5-Me$_2$C$_6$H$_3$)$_2$C$_6$H$_3$I,[32,33] and 2,6-Mes$_2$C$_6$H$_3$I[16] were synthesized according to literature methods.[34,35] NMR spectra were recorded on a Varian Mercury 300 MHz, a Varian Unity Plus 400 MHz, or a Varian VXR-500S spectrometer, and ^{1}H NMR chemical shift values were determined relative to the residual protons in C$_6$D$_6$ or C$_7$D$_8$ as internal reference (δ = 7.15 or 2.09 ppm). ^{13}C NMR spectra were referenced to the solvent signal (δ = 128.0 or 20.4 ppm) and ^{11}B NMR spectra to an external solution of F$_3$B·OEt$_2$ in CDCl$_3$. Infrared spectra were recorded in the range 4000−200 cm^{-1} as a Nujol mull between CsI plates using a Nicolet Nexus 470 FTIR spectrometer. UV−vis spectra were recorded on a Shimadzu UV-2401PC spectrophotometer and fluorescence spectra on a Shimadzu RF5301 spectrofluorimenter. FAB mass spectra were measured with a VG ZAB-E mass spectrometer using 3-nitrobenzyl alcohol as the matrix material, electron impact mass spectra with a Finnigan MAT Polaris spectrometer, and electrospray mass spectra with a Micromass Q-ToF spectrometer. Melting points were determined in Pyrex capillary tubes (sealed under nitrogen where appropriate) with a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed at Complete Analysis Laboratories Inc. in Parsippany, NJ.

1-(4-*tert*-Butylphenyl)-7-*tert*-butyl-9-(bis-2,6-(4-*tert*-butylphenyl)phenyl)-9-borafluorene·pyridine (1·py). Method A: see ref 2. Method B: A solution of 2,6-(4-*t*-BuC$_6$H$_4$)$_2$C$_6$H$_3$-Br (3.90 g, 9.25 mmol) in hexanes (50 mL) was treated with a hexane solution of *n*-BuLi (6.3 mL, 10.1 mmol, 1.6 M) at 0 °C. The ice bath was removed after 10 min, and the mixture was allowed to warm to room temperature. After 1 h the off-white suspension was briefly heated to reflux and then cooled to room temperature. The volatile material was removed under reduced pressure (0.05 Torr), and the resulting solid was suspended in hexanes (50 mL). The resulting suspension was cooled to −78 °C, and H$_2$ClB·SMe$_2$ (0.53 mL, 4.6 mmol) was added via syringe. No reaction was observed. The reaction mixture was slowly warmed to room temperature and stirred

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overnight to afford a cloudy yellow fluorescent solution. After filtration through a medium-porosity frit the volatile materials were removed under reduced pressure (0.05 Torr) to give a bright yellow solid. After redissolution in hexanes (70 mL) pyridine (1.5 mL, 18.5 mmol) was added, whereupon the color immediately faded and the solution became slightly cloudy. Warming to 40−50 °C for a few minutes resulted in a clear, pale brown solution. Cooling to −30 °C for two weeks afforded colorless crystals that were covered with a small amount of an oily substance. Recrystallization from hexanes at room temperature for 1 day afforded well-shaped crystals of **1**·py (0.87 g). An additional batch (0.87 g) was obtained from the concentrated mother liquor of the first crop. Yield: 49%.

Purification of 1. A solution of **1**·py (0.81 g, 1.05 mmol) in Et_2O (40 mL) was treated with ca. 1 mL of HCl_{conc}. The yellow solution became cloudy immediately and clarified after a few minutes. The bright yellow Et_2O phase was decanted from the aqueous phase and dried with $MgSO_4$ (30 min). After filtration and removal of the solvent under reduced pressure the resulting yellow glassy solid was redissolved in petroleum ether (40 mL) and stirred again with $MgSO_4$ (1 h). Filtration followed by removal of the solvent under reduced pressure afforded pure **1**. Yield: 86%. Crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent from a concentrated solution of **1** in Et_2O (ca. 200 mg in 2 mL). Fluorescence spectrum (hexanes): emission: 495, 515 nm; excitation: 316, 390, 436, 451 nm.

Reaction of 2,6-(4-*t*-$BuC_6H_4)_2C_6H_3Li$ with $H_2ClB·SMe_2$. Freshly prepared 2,6-(4-*t*-$BuC_6H_4)_2C_6H_3Li$ (from 2,6-(4-*t*-$BuC_6H_4)_2C_6H_3Br$ (4.15 g, 9.85 mmol), as above) was suspended in Et_2O (50 mL), and $H_2ClB·SMe_2$ (1.12 mL, 10.8 mmol) was added via syringe at 0 °C. The reaction mixture was kept at 0 °C for ca. 45 min and then slowly warmed to 5−10 °C, whereupon the color changed to yellow. The volatile material was removed under reduced pressure, and the resulting yellow, glassy solid was stored at −30 °C.

2,6-(4-*t*-$BuC_6H_4)_2C_6H_3BH_2·C_5H_5N$ (2·py). A sample (2 g) of the crude product from the reaction of 2,6-(4-*t*-$BuC_6H_4)_2C_6H_3$-Br with $H_2ClB·SMe_2$ (vide supra) was dissolved in hexanes (40 mL), and the resulting cloudy (LiCl) yellow solution was treated with pyridine (1 mL). The color faded immediately, and after 1.5 h some fine, colorless needles formed. The supernatant liquid was decanted and cooled to −28 °C for 2 days to give colorless needles of **2**·py (0.25 g). A second batch (0.15 g) was obtained by recrystallization of the needles that had formed just after the pyridine addition. Mp: 165−166 °C (with gas evolution). ^1H NMR (300 MHz, C_6D_6): 7.55 (d, J = 8.4 Hz, *o*- or *m*-H(4-*t*-BuC_6H_4), 4H), 7.50 (m, *o*-H(py), 2H), 7.46 (d, J = 7.4 Hz, *m*-H, 2H), 7.33 (t, J = 7.4 Hz, *p*-H, 1H), 7.19 (d, J = 8.4 Hz, *o*- or *m*-H(4-*t*-BuC_6H_4), 4H), 6.36 (m, *p*-H(py), 1H), 5.90 (m, *m*-H(py), 2H), 4.08 (s, br, $w_{1/2}$ = 180 Hz, BH, 2H), 1.24 (s, CH_3, 18 Hz). $^{13}C\{^1H\}$ NMR (100.57 MHz, C_6D_6): 149.19, 147.98, 147.01, 144.42, 137.00, 129.98, 128.77, 125.92, 124.34, 123.63, 34.34 ($C(CH_3)_3$), 31.61 (CH_3). ^{11}B NMR (160.38 MHz, C_6D_6): −5.4 (s, br), $w_{1/2} \approx 420$ Hz. IR: 2417(m), 2361(sh), 2338(m), 2296(sh) cm^{-1}, ν (BH). MS (EI, 70 eV, 210 °C): *m/z* 431.2 ($M^+ - H_2$, 16), 416.2 ($M^+ - H_2 -$ Me, 23), *m/z* 352.2 ($M^+ - H_2 -$ py, 76), *m/z* 337.3 ($M^+ - H_2 -$ Me − py, 100).

2,6-(3,5-$Me_3C_6H_3)_2C_6H_3Li$. A solution of 2,6-(3,5-Me_3C_6-$H_3)_2C_6H_3I$ (4.40 g, 10.7 mmol) in hexanes (45 mL) was treated with *n*-butyllithium (6.9 mL, 11.0 mmol, 1.6 M in hexanes) at 0 °C. The ice bath was removed, and the pale yellow reaction mixture was stirred overnight. A small amount of colorless solid was separated, and the clear, pale yellow solution was pumped to dryness to afford an off-white solid. Yield: 95%. ^1H NMR (C_6D_6, 300 MHz): 7.47 (d, J = 7.2 Hz, *m*-H, 2H), 7.31 (t, J = 7.2 Hz, *p*-H, 1H), 7.20 (s, *o*-H(3,5-$Me_3C_6H_3$), 4H), 6.58 (s, 20 (s, *p*-H(3,5-$Me_3C_6H_3$), 2H), 2.00 (s, CH_3, 12H). $^{13}C\{^1H\}$ NMR (75.45 MHz, C_6D_6): 152.22, 147.78, 140.08, 128.55, 126.32, 124.66, 124.14, 21.25 (CH_3). ^7Li NMR (C_6D_6, 155.44 MHz): 1.95 (s).

1-(3,5-Dimethylphenyl)-6,8-dimethyl-9-(bis-2,6-(3,5-dimethylphenyl)phenyl)-9-borafluorene (3). Method A: H_2-$ClB·SMe_2$ (0.64 mL, 6.1 mmol) was added slowly via syringe to a suspension of 2,6-(3,5-$Me_3C_6H_3)_2C_6H_3Li$ (1.79 g, 6.1 mmol) in hexanes (50 mL) at −78 °C. After 5 min the dry ice bath was removed and the reaction mixture was warmed to room temperature and stirred overnight to give a cloudy, bright yellow solution. After filtration the volatile material was distilled off under reduced pressure. The remaining yellow oil was extracted with hexanes (40 mL) to afford a yellow solution and **3** as a yellow-green solid that did not dissolve. Yield (based on 2,6-(3,5-$Me_3C_6H_3)_2C_6H_3Li$): 21%. Anal. Calcd for $C_{44}H_{41}B$: C, 91.02; H, 7.12. Found: C, 90.87; H, 6.98. Mp: 148−152 °C. ^1H NMR (C_6D_6, 300 MHz): 7.42 (d, J = 7.2 Hz, *m*-H, 2H), 7.29 (dd, J = 7.2 Hz, 1.2 Hz, 1H), 7.24 (t, J = 7.2 Hz, *p*-H, 1H), 7.19 (s, *o*-H(3,5-$Me_2C_6H_3$), 4H), 7.08 (s, 1H), 7.03 (t, J = 7.2 Hz, 1H), 6.92 (dd, J = 7.2 Hz, 1.2 Hz, 1H), 6.84 (s, 2H), 6.69 (s, 1H), 6.53 (s, 2H), 6.36 (s, 1H), 2.08 (s, CH_3, 6H), 1.99 (s, CH_3, 3H), 1.98 (s, CH_3, 12H), 1.92 (s, CH_3, 3H). $^{13}C\{^1H\}$ NMR (75.45 MHz, C_6D_6): 153.13, 152.68, 149.25, 144.88, 144.23, 143.62, 143.10, 141.60, 137.69, 136.14, 132.88, 131.43, 130.79, 129.40, 128.52, 126.71, 126.11, 117.98, 117.94, 21.94, 21.71, 21.36, 20.55. UV−vis (CH_2Cl_2): 353 nm (ϵ = 6140), 410 nm (ϵ = 430). Fluorescence spectrum (THF): emission: 505 nm; excitation: 314, 380(sh), 433 nm. MS (EI, 70 eV): *m/z* 580.1 (M^+, 100).

Method B: $HCl_2B·SMe_2$ (0.23 mL, 1.9 mmol) dissolved in hexanes (7−8 mL) was added dropwise via cannula to a suspension of 2,6-(3,5-$Me_3C_6H_3)_2C_6H_3Li$ (1.12 g, 3.8 mmol) in toluene (30 mL) at −78 °C. The reaction mixture was slowly warmed to room temperature and stirred overnight (ca. 12 h). After filtration the yellow fluorescent solution was pumped to dryness and the remaining yellow solid was extracted with hexanes (45 mL) to leave the essentially hexane-insoluble **3** behind (0.31 g). After concentration of the supernatant liquid to 15−20 mL and subsequent cooling to −30 °C for 1 day an additional crop of **3** was obtained (0.02 g). Yield: 29%.

2,6-(2-$MeC_6H_4)_2C_6H_3Li$. A suspension of 2,6-(2-$MeC_6H_4)_2$-C_6H_3I (3.88 g, 10.1 mmol) in hexanes (50 mL) was treated with *n*-butyllithium (6.9 mL, 11.0 mmol, 1.6 M in hexanes) at 0 °C. After initial partial clarification of the solution a fine, colorless solid began to precipitate. The reaction mixture was warmed to room temperature and stirred overnight (ca. 12 h). The fine, colorless solid was collected on a glass frit and dried under reduced pressure. Yield: 87%. ^1H NMR(C_6D_6, 400 MHz): 7.12 (m, ArH, 5H), 6.92 (m, ArH, 6H), 2.06 (s, Me, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): 176.5 (br, *i*-C), 151.4, 146.3, 136.8 (quaternary carbons), 131.8, 127.6, 127.4, 127.3, 124.4, 20.9 (Me).

[2,6-(2-$MeC_6H_4)_2C_6H_3BH(\mu$-H)]$_2$ (4). $H_2ClB·SMe_2$ (0.92 mL, 8.8 mmol, 0.98 g) was added via syringe to a suspension of 2,6-(2-$MeC_6H_4)_2C_6H_3Li$ (2.34 g, 8.8 mmol) in hexanes (50 mL) at −78 °C. The mixture was slowly warmed to room temperature and stirred for 4 h, whereupon the color changed to pale yellow, and a fine colorless precipitate formed. After filtration and removal of the volatile materials under reduced pressure the pale yellow solid was redissolved in hexanes (5 mL). Cooling to −28 °C for 3 days afforded small colorless crystals (1.36 g). A second batch of larger crystals was obtained from the concentrated mother liquor (ca. 1−2 mL) after 1 day at room temperature. Yield: 1.47 g (61%). Anal. Calcd for $C_{40}H_{38}B_2$: C, 88.91; H, 7.09. Found: C, 88.45; H, 6.99. Mp: softens at 105 °C, melts with gas evolution at 120−125 °C, and turns yellow. ^1H NMR (400 MHz, C_6D_6): 7.03−6.83 (m, aromatic H, 22H), 3.75 (s, broad, $w_{1/2} \approx 260$ Hz, B-H, 2H), 1.89, 1.88, 1.83, 1.82, 1.754, 1.749 (*o*-Me, 12H, rel intensity: 0.07: 0.13:0.23:0.34:0.09:0.14), 1.52 (s, br, $w_{1/2} \approx 80$ Hz, B-H, 2H). ^{11}B NMR (160.38 MHz, C_6D_6): 19.8 (s, br), $w_{1/2} \approx 460$ Hz. MS (FAB, 3NBA matrix): *m/z* 269.1 ($M^+/2 -$ H). IR: 2513 cm^{-1} (m), ν(BH).

$2,6\text{-}(2\text{-MeC}_6H_4)_2C_6H_3BH_2\cdot py$ (4·py). Pyridine (0.18 mL, 2.2 mmol) was added to a solution of **8** (0.30 g, 0.55 mmol) in hexanes (30 mL) at room temperature to give a colorless cloudy solution. After 2 h stirring **4**·py was isolated by removal of the volatile materials under reduced pressure as a colorless powder. Mp: 128 °C. ^{1}H NMR (300 MHz, C_6D_6): 7.48 (m, *o*-H(py), 2H), 7.23 (m, 4H), 7.11 (m, 3H), 6.96 (m, 4H), 6.29 (m, *p*-H(py), 1H), 5.94 (m, *m*-H(py), 2H, 3.5 (s, br, $w_{1/2} = 250$ Hz, B-H, 2H), 2.44 and 2.07 (s, Me, 6H, syn and anti). ^{13}C{^{1}H} NMR (75.45 MHz, C_6D_6): 148.54. 148.25, 147.08, 147.03, 146.89, 146.77, 137.60, 137.35, 136.63, 130.67, 129.72, 129.40, 128.96, 126.32, 126.24, 126.29, 125.71, 125.15, 124.91, 123.90, 123.81, 21.18, 20.99. ^{11}B NMR (160.38 MHz, C_6D_6): −6.1 (s, br), $w_{1/2} \approx 320$ Hz. IR: 2338(m), 2345(m). MS (EI, 70 eV): *m/z* 349.2 (M^+, 44), 347.2 ($M^+ - H_2$, 38), 268.1 ($M^+ - H_2 -$ py, 100).

$[2,6\text{-Mes}_2C_6H_3BH(\mu\text{-H})]_2$ (5). A solution of $[2,6\text{-Mes}_2C_6H_3\text{Li}]_2$ (0.90 g, 1.4 mmol) in Et_2O (30 mL) was treated with $H_2ClB\cdot SMe_2$ (0.29 mL, 2.8 mmol, 0.31 g) at −78 °C. The clear, colorless solution was held at −78 °C for an hour and then slowly warmed to room temperature, whereupon a fine, colorless precipitate formed. After stirring for an additional 2 h at room temperature the mixture was filtered through a medium-porosity glass frit. Volatile materials were removed from the filtrate under reduced pressure, and the remaining pale yellow viscous oil was extracted with ca. 70 mL of hexanes. Filtration followed by concentration to ca. 50 mL and cooling to −28 °C overnight afforded large (2−3 mm) colorless crystals. Yield: 0.49 g (54%). Anal. Calcd for $C_{48}H_{54}B_2$: C, 88.35; H, 8.34. Found: C, 88.16; H, 8.46. Mp: turns opaque at ca. 150 °C and melts with gas evolution at 235−240 °C. ^{1}H NMR (400 MHz, C_6D_6): 7.13 (t, *p*-H, 2H), $^3J_{HH}$= 8.0 Hz, 6.84 (d, *m*-H, 4H), 6.82 (s, *m*-H(Mes), 8H), 3.36 (s, br, $w_{1/2} \approx 270$ Hz, B-H, 2H), 2.23 (s, *p*-Me, 12H), 1.80 (s, *o*-Me, 24H), 0.95 (s, br, $w_{1/2} \approx 95$ Hz, B-H, 2H), ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): 146.3, 140.4, 136.1, 135.6, 129.4 (*p*-C), 128.5 (*m*-C(Mes)), 127.4 (*m*-C), 21.2 (*p*-Me), 20.6 (*o*-Me). ^{11}B NMR (160.38 MHz, C_6D_6): 17.6 (s, br), $w_{1/2} \approx 290$ Hz. IR: 2546 cm^{-1} (m), ν (BH). MS (EI, 70 eV): *m/z* 652.0 (M^+, 17), 326.1 ($M^+/2$, 70), 324.1 ($M^+/2 - H_2$, 100).

1-(4-*tert*-Butylphenyl)-7-*tert*-butyl-9-borafluorene·pyridine (7·py). Method A: The remainder (ca. 2 g) of the crude product from the reaction of $2,6\text{-}(4\text{-}t\text{-BuC}_6H_4)_2C_6H_3Br$ with $H_2ClB\cdot SMe_2$ (vide supra) was dissolved in hexanes (40 mL), and the resulting cloudy (LiCl) yellow solution was stirred at room temperature for 3 days, filtered, and treated with pyridine (1 mL). The fine precipitate was redissolved by gentle warming (40 °C). After standing at room temperature for 1 day a yellow-orange oil separated, which was shown to be a mixture of mainly **7**·py and some **2**·py. Cooling of the supernatant liquid to −28 °C afforded pure **7**·py in the form of small crystalline spheres (0.1 g). Removal of the solvent from the mother liquor resulted in a pale yellow glassy solid, which was impure **1**·py.

Method B: A Schlenk flask charged with **2**·py (0.075 g, 0.17 mmol) was placed into a 190 °C preheated oil bath. The crystals began to melt after approximately 1 min with gentle gas evolution. The gas evolution stopped after 2 min, leaving a pale yellow liquid behind, which solidified into a pale yellow glass after cooling to room temperature. Anal. Calcd for $C_{31}H_{34}BN$: C, 86.30; H, 7.94. Found: C, 86.35; H, 8.03. Mp: 113−115 °C. ^{1}H NMR(C_6D_6, 400 MHz): 7.97 (d, $J = 8.0$ Hz, 1H), 7.93 (d, $J = 7.6$ Hz, 1H), 7.77 (s, 1H), 7.74 (m, *o*-H(py), 2H), 7.53 (d, $J = 8.0$ Hz, *o*- or *m*-H(4-*t*-BuC_6H_4), 2H), 7.47 (m, 2H), 7.33 (d, $J = 7.6$ Hz, 1H), 7.02 (d, $J = 8.0$ Hz, *o*- or *m*-H(4-*t*-BuC_6H_4), 2H), 6.35 (m, *p*-H(py), 1H), 5.93 (m, *m*-H(py), 2H), 4.75 (s, br, $w_{1/2} = 195$ Hz, 1H), 1.36 (s, CH_3, 9H), 1.18 (s, CH_3, 9H). ^{13}C{^{1}H} NMR (100.57 MHz, C_6D_6): 150.37, 148.91, 148.34, 147.50, 146.74, 145.05, 142.38, 138.66, 128.85, 128.09. 126.44, 124.55, 124.42, 124.18, 119.62, 118.50, 34.82 ($C(CH_3)_3$), 34.29 ($C(CH_3)_3$), 31.96 (CH_3), 31.56 (CH_3). ^{11}B NMR (160.38 MHz, C_6D_6): 7.6 (s, br), $w_{1/2} \approx 350$ Hz. IR: 2312(w). MS (EI, 70 eV, 225 °C): *m/z* 431.2 (M^+, 48), 416.2 (M^+ Me, 100), *m/z* 352.2 ($M^+ -$ py, 61), *m/z* 337.3 ($M^+ -$ Me − py, 96).

1-(3,5-Dimethylphenyl)-6,8-dimethyl-9-borafluorene·pyridine (9·py). Pyridine (1.0 mL, 12.2 mmol) was added to the yellow mother liquor (50 mL) obtained in the synthesis of **3** according to method A. Concentration to 10−15 mL followed by cooling to −30 °C for 3 days afforded a small amount of a colorless solid (70 mg) and a yellow oil. The colorless solid was identified as pure **9**·py, whereas the oil was found to be impure **9**·py. Mp: 162−167 °C. ^{1}H NMR (C_6D_6, 300 MHz): 7.92 (dd, $J = 7.5$ Hz, 0.9 Hz, 1H), 7.70, (s, 1H), 7.69 (m, *o*-H(py), 2H), 7.42 (t, $J = 7.5$ Hz, 1H), 7.27 (dd, $J = 7.5$ Hz, 0.9 Hz), 7.08 (s, *o*-H(3,5-$Me_2C_6H_3$), 2H), 6.93 (s, 1H), 6.67 (s, 1H), 6.39 (m, *p*-H(py), 1H), 5.93 (m, *m*-H(py), 2H), 4.59 (s, br, $w_{1/2} = 190$ Hz, B-H, 1H), 2.43 (s, CH_3, 3H), 2.13 (s, CH_3, 3H), 2.07 (s, 3,5-$(CH_3)_2C_6H_3$, 3H). ^{13}C{^{1}H} NMR (75.45 MHz, C_6D_6): 150.20, 150.02, 146.62, 145.33, 145.10, 139.05, 138.43, 136.62, 136.44, 128.56, 127.60, 127.21, 127.03, 126.53, 124.01, 118.60, 118.33, 21.92, 21.32 (3,5-$(CH_3)_2C_6H_3$), 21.27. ^{11}B NMR (160.38 MHz, C_6D_6): −1.0 (s, br), $w_{1/2} \approx 350$ Hz. IR: 2341(m). MS (EI, 70 eV): *m/z* 375.3 (M^+, 100), 296.1 ($M^+ -$ py, 99).

$[2,6\text{-}(4\text{-}t\text{-BuC}_6H_4)_2C_6H_3]_2B(\mu\text{-H})_2Li[O(CH_2CH_2)_2]_2$ (11). $H_2ClB\cdot SMe_2$ (0.21 mL, 0.22 g, 2.0 mmol) was added dropwise via syringe to a suspension of $2,6\text{-}(4\text{-}t\text{-BuC}_6H_4)_2C_6H_3Li$ (1.40 g, 4.0 mmol) in hexanes at −78 °C. The mixture was kept at this temperature for 1 h, warmed to room temperature, and stirred for 18 h to give a pale yellow cloudy solution. After filtration the clear yellow filtrate was concentrated to ca. 2 mL and cooled to − 40 °C for 2 days. As no crystals were obtained, the remaining solid was distilled off under reduced pressure, and the resulting yellow glass was redissolved in hexanes (30 mL). THF (2 mL) was added, and a fluffy colorless precipitate formed immediately. Partial dissolution of the precipitate by gentle warming with a heatgun (ca. 40−50 °C) for 2−3 min followed by slow cooling to room temperature afforded **11** as fine, colorless to pale yellow needles. Yield: 22%. Mp: 190−198 °C with gas evolution and color change to yellow fluorescent. ^{1}H NMR (300 MHz, C_6D_6): 7.32 (s, *o*- and *m*-H, 16H), 7.02 (m, *p*- and *m*- H, 6H), 3.18 (s, br, OCH_2, 8H), 2.17 (q, 1:1:1:1 rel int, J_{H-B}= 73 Hz, B-H, 2H), 1.39 (s, CH_3, 36H), 1.23 (s, br, CH_2, 8H). ^{13}C{^{1}H} NMR (75.45 MHz, C_6D_6): 148.27, 147.16, 146.26, 129.50, 128.47, 124.02, 123.25, 68.49 (OCH_2), 34.60 ($C(CH_3)_3$), 32.06 (CH_3), 25.60 (CH_2). ^{11}B NMR (160.38 MHz, C_6D_6): −20.0 (t, $J = 73$ Hz, $w_{1/2} = 27$ Hz). FTIR (CsI plates, mineral oil): 2234(m), 2210(m), 2168(m) cm^{-1}.

1-(2-Methylphenyl)-5-methyl-9-borafluorene·pyridine (12·py). A Schlenk flask was charged with **4**·py (0.065 g) and placed into a 200 °C oil bath. After 2 min the powder began to melt, and a minute later a smooth gas evolution commenced from the yellow liquid which stopped after about 2 min. After cooling to room temperature the melt solidified into a yellow glass. Anal. Calcd for $C_{25}H_{22}BN$: C, 86.47; H, 6.39. Found: C, 86.23; H, 6.50. Mp: 74−78 °C. ^{1}H NMR (300 MHz, C_6D_6): 8.09 (d, $J = 7.8$ Hz, 1H), 7.75 (s, br, 0.5H), 7.42 (m, 4H), 7.10 (m, 4.5H), 6.96 (t, $J = 7.8$ Hz, 1H), 6.68 (s, br, 0.5H), 6.45 (s, br, 2H), 6.27 (s, br, 0.5H), 5.96 (s, br, 2H), 4.25 (s, br, $w_{1/2} \approx 230$ Hz, B-H, 1H), 2.80 (s, CH_3, 3H), 2.45 and 1.45 (s, br, Me, 3H in 0.55:0.45 ratio). ^{13}C{^{1}H} NMR (75.45 MHz, C_6D_6): 146.55, 138.56, 132.62, 131.37, 130.44, 129.90, 128.96, 126.52, 126.14, 125.77, 125.67, 124.29, 122.96, 23.24, 20.81, 20.14. ^{11}B NMR (160.38 MHz, C_6D_6): −0.6 (s, br), $w_{1/2} \approx 300$ Hz. IR: 2351(m). MS (EI, 70 eV): *m/z* 347.1 (M^+, 70), 268.2 ($M^+ -$ py, 75).

$[2,6\text{-}(4\text{-}t\text{-BuC}_6H_4)_2C_6H_3]_2BOH$ (15). A solution of **1**·py (0.41 g, 0.53 mmol) in Et_2O (30 mL) was treated with concentrated HCl (1 mL) to give a cloudy solution. No significant color change was observed after 6 days at room temperature. As a sample taken at this time contained still mainly unreacted **1**, additional HCl (1 mL) was added and stirring was continued for another week, whereupon the color faded. The Et_2O phase was decanted from the aqueous phase, and the solvent was distilled off under reduced pressure (ca. 400 Torr). The remaining pale yellow oil was dissolved in petroleum ether (40 mL) and dried over $MgSO_4$. Removal of the solvent at reduced pressure (ca. 400 Torr) afforded **15** as a colorless solid, which was recrystallized from petroleum ether (30 mL) at −30 °C for one week to give small colorless needles. Yield: 17%. Anal. Calcd for $C_{52}H_{59}BO$: C, 87.86; H, 8.37. Found: C, 87.93; H, 8.52. Mp: 193−197 °C. ^{1}H NMR (300 MHz, $CDCl_3$): 7.24 (d, $J = 8.7$ Hz, *o*-or *m*-H(4-*t*-BuC_6H_4), 8H), 7.12 (d, $J = 8.7$ Hz, *o*-or *m*-H(4-*t*-BuC_6H_4), 8H), 7.06 (t, $J = 7.2$ Hz, *p*-H, 2H), 6.88 (d, $J = 7.2$ Hz, *m*-H, 4H), 5.94 (s, B-OH, 1H), 1.33 (s, Me, 36H). $^{13}C\{^1H\}$ NMR (75.45 MHz, $CDCl_3$): 148.84, 146.86, 140.69, 129.18, 128.79, 128.08, 124.35, 34.47 ($C(CH_3)_3$), 31.35 (CH_3). ^{11}B NMR (160.38 MHz, $CDCl_3$): 47 (s, br, $w_{1/2} = 1500$ Hz). IR: 3537 (m), ν(O−H). MS (EI, 70 eV, 270 °C): *m*/*z* 485.2 ($M^+ - 4\ CH_2C(CH_3)_2 - H$, 75).

X-ray Crystallography. Crystals of **1** were obtained by slow evaporation of a concentrated Et_2O solution of **1** at room temperature. Crystals were removed from the Schlenk tube under a stream of N_2-gas and immediately covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber, and immediately placed in the low-temperature nitrogen stream.[36] The data for **1** and **4** were collected at 173(2) K on a Siemens P4 diffractometer, and those for **11** at 103(2) K on a Bruker Apex diffractometer using Mo Kα ($\lambda = 0.71073$ A) radiation. The data were corrected for Lorentz and polarization effects. Absorption corrections were not applied for **1** and **4** but for **11** by a multiscan method from equivalent reflections. The structures were solved by direct methods using the SHELXTL system[37] and refined by full-matrix least-squares on F^2 including all reflections. All the non-hydrogen atom were refined anisotropically, and all the hydrogen atoms were included in the refinement with idealized parameters with the exception of the hydrogen atoms attached to the B atoms in the structures of **4** and **11**, which were located in the difference map and refined isotropically. The *tert*-butyl group C(24)−C(26) in **1** displayed rotational disorder and was refined using split occupancies of 0.70 for C(24)−C(26) and 0.30 for C(24A)−C(26A). Some details of the crystal data and refinement are given in Table 1, and selected bond distances and angles are listed in Tables 2, 3, and 4. Further details are given in the Supporting Information.

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Supporting Information Available: Crystallographic tables, numbering schemes, and unit cell plots for compounds **1**, **4**, and **11**. Data are also given as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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