Synthesis and Characterization of a Sterically Encumbered Unsymmetrical 9-Borafluorene, Its Pyridine Adduct, and Its Dilithium Salt

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The reaction of 2,6-(4-*t*-BuC_6H_4)$_2$$C_6H_3$Li with $BH_2Cl{\cdot}SMe_2$ in hexane or Et_2O solution affords the 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. Addition of pyridine gives the colorless crystalline adduct **1·py**. Compound **1** is readily reduced to the deep red heteroaromatic dianionic (μ_2-η^5,η^5-1-(4-*tert*-butylphenyl)-7-*tert*-butyl-9-(bis-2,6-(4-*tert*-butylphenyl)phenyl)-9-borafluorenyl)bis(diethyl ether)dilithium (**2**) with excess lithium powder in Et_2O solution. Reactions of the dianionic **2** with various metal salts leads to reduction of these salts, and bright yellow **1** is recovered in essentially quantitative yields. Compounds **1**, **1·py**, and **2** were characterized by ^1H, ^{13}C, and ^{11}B NMR spectroscopy and compounds **1·py** and **2** also by single-crystal X-ray diffraction.

Introduction

The synthesis of the first stable boratafluorene complex $[CpCo(C_5H_5BPh)]^+$ by Herberich et al.[1] in 1970 has sparked interest in boratabenzenes, boroles, and derivatives as potential replacements for the ubiquitous cyclopentadienyl ligand in organometallic compounds.[2] More recently, Ashe and Bazan[3−6] have successfully introduced these compounds as valuable ligands for “single-site” olefin polymerization catalysts. The most important feature of these systems is the ease of tuning the electronic properties by simply varying the exocyclic substituent on the boron atom. Steric properties can be affected by introducing different substituents around the ring system. Benzannulation (e.g., in the cases of indenyl or fluorenyl) is among the more common ways of increasing the size of the cyclopentadienyl ligand. Initial results from the groups of Ashe,[7] Bazan,[8] Herberich,[9] and Paetzhold[10] indicate that this concept can be successfully transferred to the boratabenzene and borole systems. However, the syntheses of 1- and 2-boranaphthalenes, 9-borafluorenes, and related compounds are still very demanding and not very practical for routine use. In the early 1960s, Köster and coworkers reported that 9-borafluorenes were formed upon thermolysis of 2-biphenyldialkylboranes,[11] and in 1973, Bickelhaupt and van Veen showed that the pyridine adduct of 2-biphenylborane could also be converted into the corresponding pyridine adduct of 9-borafluorene.[12] Both methods required temperatures of about 200 °C.

Assuming that a three-coordinate boron hydride species is the active intermediate in these ring-closure reactions, we set out to synthesize a series of base-free *m*-terphenylboranes, $[ArBH_2]_2$, and study their potential as precursors for unsymmetrical 9-borafluorenes via low-temperature C−H activation (eq 1). Unsymmetrical 9-borafluorenes such as the one shown in eq 1 could be of interest as ligands in catalytic systems.

Here, we report about the unexpected formation of the unsymmetrical 9-borafluorene **1** even below room temperature, the crystalline pyridine adduct **1·py**, and the reduction of **1** to the dianionic **2**.

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 Na/K alloy and

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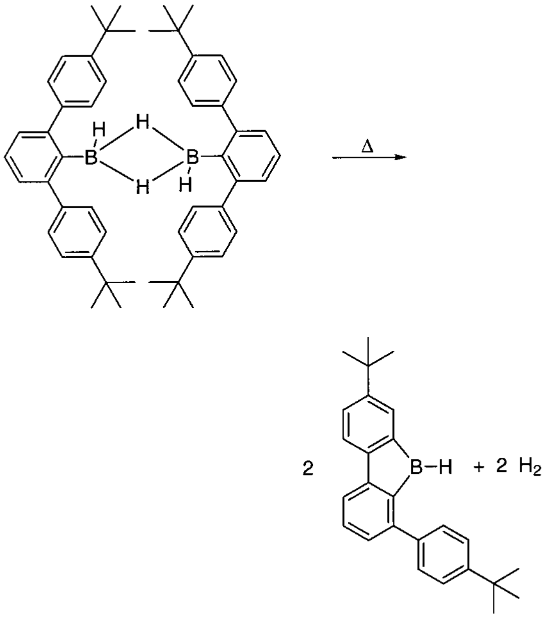

(1)

degassed twice prior to use. $BH_2Cl·SMe_2$, 4-*tert*-butylbromobenzene, 2-bromobiphenyl, *m*-dichlorobenzene, *n*-butyllithium (1.6 M in hexanes), lithium powder, $FeCl_2$, $FeBr_2$, $ZrCl_4$, $CpZrCl_3$, and $SnCl_2$ were obtained from commercial suppliers. $Cu(MeCN)PF_6$ was synthesized according to the literature.[13] ^1H and ^{13}C NMR spectra were recorded on a Varian Unity Plus 400 MHz spectrometer and ^{11}B NMR spectra on a Varian VXR 500S spectrometer. ^1H NMR chemical shift values were determined relative to the residual protons in C_6D_6 or $CDCl_3$ as internal reference (δ 7.15 or 7.26 ppm). ^{13}C NMR spectra were referenced to the solvent signals (δ 128.0 or 77.0 ppm). ^{11}B NMR spectra were referenced to a $CDCl_3$ solution of $BF_3·OEt_2$ as external standard (δ 0 ppm). UV–vis spectra were recorded on a Shimadzu UV-2401PC spectrophotometer. FAB mass spectra were measured with a VG ZAB-E mass spectrometer using 3-nitrobenzyl alcohol as the matrix material. Melting points were determined in Pyrex capillary tubes (sealed under nitrogen where appropriate) with a Mel-Temp apparatus and are uncorrected.

2,6-(4-*t*-BuC$_6$H$_4$)$_2$C$_6$H$_3$Br was synthesized according to a modification of the literature procedure[14] allowing for large-scale syntheses as described by Power et al.[15] after quenching with Br_2 at −15 °C instead of I_2 as a colorless crystalline solid (101 g, 53% yield). Mp: 145−9 °C. ^1H NMR (400 MHz, C_6D_6): 7.43 (d, *o*- or *m*-H (4-*t*-BuC$_6$H$_4$), 4H), $^3J_{HH}$ = 8.0 Hz, 7.31 (d, *o*- or *m*-H (4-*t*-BuC$_6$H$_4$), 4H), 7.17 (d, *m*-H, 2H), $^3J_{HH}$ = 7.4 Hz, 7.02 (t, *p*-H, 1H), 1.22 (s, Me, 18H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 150.3, 143.7, 139.1, 130.1 (*m*-C), 129.2 (*o*- or *m*-C, 4-*t*-BuC$_6$H$_4$), 126.8 (*p*-C), 124.8 (*o*- or *m*-C, 4-*t*-BuC$_6$H$_4$), 123.2 (*i*-C), 34.6 ($C(CH_3)_3$), 31.4 (CH_3).

1-(4-*tert*-Butylphenyl)-7-*tert*-butyl-9-(bis-2,6-(4-*tert*-butylphenyl)phenyl)-9-borafluorene·pyridine (1·py). A solution of 2,6-(4-*t*-BuC$_6$H$_4$)$_2$C$_6$H$_3$Br (2.41 g, 5.7 mmol) in hexanes (50 mL) was treated with *n*-butyllithium in hexanes (4.0 mL, 1.6 M, 6.4 mmol, 10% excess) with cooling in an ice bath. After ca. 10 min the ice bath was removed and the pale yellow reaction mixture was slowly warmed to room temperature and stirred for 1 h. The fine colorless precipitate was dissolved by heating to reflux for 2−3 min. After cooling to room temperature solvents were removed from the cloudy reaction mixture under reduced pressure. The resulting off-white solid was suspended in hexanes (50 mL) and cooled to −78 °C, and $BH_2Cl·SMe_2$ (0.67 mL, 6.4 mmol, 0.71 g) was added with a syringe. The reaction mixture was kept at −78 °C for 20 min, slowly warmed to room temperature, and stirred overnight (ca. 12 h). A color change to yellow commenced around 0 °C. Filtration and removal of the volatile materials afforded a bright yellow solid which contained ca. 75% **1** according to ^1H NMR spectroscopy. A portion of this solid (0.60 g) was dissolved in hexanes (15 mL) and treated with pyridine (0.2 mL, 0.19 g, 2.5 mmol), whereupon the color immediately faded and a small amount of a colorless precipitate formed. Filtration followed by concentration of the pale yellow filtrate to ca. 5−7 mL and storage at room temperature afforded large (2−3 mm) colorless crystals of **1·py** (0.23 g). Concentration of the mother liquor and cooling to −28 °C gave another 0.1 g of product. Yield: 54% (based on 2,6-(4-*t*-BuC$_6$H$_4$)$_2$C$_6$H$_3$Br). Anal. Calcd for $C_{57.75}H_{63.75}BN$: C, 88.62; H, 8.21; N, 1.79. Found: C, 88.36; H, 8.69; N, 1.98. Mp softens at 70 °C, changes color to yellow at 85−90 °C, melts with gas evolution at 125−140 °C. ^1H NMR (400 MHz, C_6D_6): 8.52 (s, br, 1H), 8.08 (s, br, 1H), 8.03 (s, br, 1H), 7.37 (t, 3H), J = 7.6 Hz, 7.19 (s, br, 4H), 6.81 (s, br, 2H), 6.69 (s, br, 2H), 6.53 (s, br, 1H), 6.13 (s, br, 1H), 5.61 (s, br, 1H), 5.52 (s, br, 1H), 1.41 (s, br, 9H), 1.34 (s, br, 9H), 1.30 (s, 9H), 0.98 (s, br, 9H). ^{11}B NMR (160.38 MHz, C_6D_6): 4.2 (s, br, $w_{1/2} \approx$ 1470 Hz).

Table 1. Determination of *K* for the Dissociation of 1·py

$m_{initial}$/mg	[**1·py**]/mol L^{-1}	[py]/mol L^{-1}	K = [**1**][py]/[**1·py**]/mol L^{-1}
6(1)	5.33×10^{-3}	3.50×10^{-3}	2.30×10^{-3}
10(1)	10.12×10^{-3}	4.60×10^{-3}	2.09×10^{-3}
16(1)	17.32×10^{-3}	6.23×10^{-3}	2.24×10^{-3}

Determination of the Dissociation Constant of 1·py. ^1H NMR spectra of three samples containing different amounts of **1·py** (6, 10, 16 mg) in C_6D_6 (0.88 mL) were collected at 20 °C, and the relative concentrations of free pyridine, [py], and of **1·py**, [**1·py**], were determined by integration of the signals at 8.52 (*o*-H, free pyridine) and 6.13 and 5.56 ppm (*p*- and *m*-H, coordinated pyridine in **1·py**). With [py] = [**1**] and $c_{initial}$= [**1·py**] + [py] the equilibrium constant K = 0.0022(5) mol L^{-1} was obtained (Table 1).

(μ_2-η^5,η^5-1-(4-*tert*-Butylphenyl)-7-*tert*-butyl-9-(bis-2,6-(4-*tert*-butylphenyl)phenyl)-9-borafluorenyl)bis(diethyl ether)dilithium (2). Lithium powder (high sodium, Aldrich, 0.31 g) was added to a −15 °C Et_2O solution (60 mL) of crude **1**, synthesized as above from 2,6-(4-*t*-BuC$_6$H$_4$)$_2$C$_6$H$_3$Br (2.79 g, 6.6 mmol). The reaction mixture, which turned dark green after a few minutes, was held at −15 °C for 30 min, slowly warmed to room temperature, filtered through a medium-porosity glass frit, and concentrated to ca. 10 mL. Small crystals began to form after a few minutes. Cooling to −28 °C for a day afforded a second crop of deep red, almost black crystals (1.20 g, 42% yield based on 2,6-(4-*t*-BuC$_6$H$_4$)$_2$C$_6$H$_3$Br). Anal. Calcd for $C_{60}H_{77}BLi_2O_2$: C, 84.29; H, 9.08. Found: C, 84.10; H, 8.81. Mp: 180−180 °C (dec with gas evolution and color change to yellow). ^1H NMR (400 MHz, C_6D_6): 8.15 (d, 1H, J = 0.8 Hz), 8.02 (d, 1H, J = 9.2 Hz), 7.97 (d, 1H, J = 8.0 Hz), 7.28 (s, br, 4H), 7.52 (d, 2H, J = 8.2 Hz), 7.31 (d, 2H, J = 8.2 Hz), 7.21, 7.20 (A_2B system, 3H, $J \approx$ 8 Hz), 7.02 (d, 4H, J = 8.4 Hz), 6.90 (dd, 1H, J = 9.2 Hz, 0.8 Hz), 6.84 (d, 1H, J = 6.4 Hz), 6.69 (dd, 1H, J = 8.0 Hz, 6.4 Hz), 2.50 (q, 8H, O*CH$_2$*, J = 7.2 Hz), 1.52 (s, 9H, *t*-Bu), 1.46 (s, 9H, *t*-Bu), 1.04 (s, 18H, *t*-Bu), 0.16 (t, 12 H, OCH$_2$*CH$_3$*, J = 7.2 Hz). $^{13}C\{^1H\}$ NMR (100.57 MHz, C_6D_6): 148.35, 147.46, 147.22, 147.19, 144.54, 143.15, 138.27, 128.97, 128.75, 128.65, 125.42, 125.09, 125.00, 123.41, 120.70, 120.02, 117.70, 113.39, 112.27, 111.93, 110.41, 66.37 (O*C*H$_2$), 34.89, 34.40, 34.15 (*C*(CH$_3$)$_3$), 32.27, 31.86, 31.31 (C(*C*H$_3$)$_3$), 13.50 (OCH$_2$*C*H$_3$). ^{11}B NMR (160.38 MHz, C_6D_6): 13.6 (s, br, $w_{1/2} \approx$ 430 Hz). ^7Li NMR (155.44 MHz, C_6D_6): −10.3 (s, $w_{1/2} \approx$ 20 Hz). UV–vis (hexanes): 380 nm (sh, ϵ = 5420), 435 nm (ϵ = 8450), 595 nm (ϵ = 1160).

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1-(4-*tert*-Butylphenyl)-7-*tert*-butyl-9-(bis-2,6-(4-*tert*-butylphenyl)phenyl)-9-borafluorene (1). $SnCl_2$ (0.16 g, 0.82 mmol) was added to a −78 °C solution of **2** (0.70 g, 0.82 mmol) in Et_2O (50 mL). The mixture was slowly warmed to room temperature. At a bath temperature of ca. −20 °C the deep red color of the solution began to fade and a fine dark solid began to precipitate. After stirring at room temperature for an additional 2 h the solvent was removed under reduced pressure and the remaining dark solid was extracted with hexanes (50 mL). After filtration through Celite and removal of the solvent under reduced pressure **1** was obtained in essentially quantitative yield as a bright yellow solid. Anal. Calcd for $C_{52}H_{57}B$: C, 90.15; H, 8.29. Found: C, 89.23; H, 8.69. Mp: 162−4 °C ^1H NMR (400 MHz, C_6D_6): 7.40 (d, 2H), J = 7.6 Hz, 7.35 (d, 4H), J = 8.4 Hz, 7.26 (t, 1H) J = 7.6 Hz, 7.26 (d, 1H), J = 7.6 Hz, 7.20 (dd, 1H), J = 7.2 Hz, 0.8 Hz, 7.15 (d, 2H), J = 8.0 Hz, 7.10 (dd, 1H), J = 7.6 Hz, 2.0 Hz, 7.05 (d, 1H), J = 2.0 Hz, 7.00 (d, 2H), J = 8.0 Hz, 6.95 (d, 4H), J = 8.4 Hz, 1.30 (s, 9H), 1.09 (s, 18H), 1.03 (s, 9H). $^{13}C\{^1H\}$ NMR (100.57 MHz, C_6D_6): 154.38, 150.70, 150.29, 149.67, 149.50, 149.33, 145.46, 140.93, 138.20, 134.64, 131.70, 129.87, 129.64, 129.43, 128.79, 128.74, 126.94, 125.18, 123.91, 119.14, 118.02, 34.46, 34.38, 34.33 ($C(CH_3)_3$), 31.49, 31.33, 31.30 ($C(CH_3)_3$). UV−vis (hexanes): 347 nm (ϵ = 6180), 428 nm (ϵ = 480). MS (FAB): *m/z* 692.7 (M^+).

Reactions of 2 with the Metal Salts $FeCl_2$, $FeBr_2$, $Cu(MeCN)_4PF_6$, $ZrCl_4$, and $CpZrCl_3$. A solution of **2** (ca. 0.5 mmol) in Et_2O or THF (10−20 mL) was added slowly to a −78 °C slurry of an equimolar amount of the metal salts in Et_2O or THF ($FeBr_2$). In the reaction of $Cu(MeCN)_4PF_6$ with **2**, 2 equiv of the copper salt was used. The mixture was kept at −78 °C for 1 h, slowly warmed to room temperature, and stirred for several hours. In the reactions involving the iron and copper salts a dark fine solid precipitated (magnetic in the iron salt reactions), and the supernatant solution was transparent brownish yellow. Removal of the solvent under reduced pressure followed by extraction with hexanes (20−30 mL), filtration, and removal of the solvent under reduced pressure afforded **1** in essentially quantitative yields. Actual isolated yields were lower due to mechanical losses. In the reactions involving the zirconium compounds deep red solutions were obtained whose NMR spectra where those of uncomplexed **1**. From these reaction mixtures **1** could be separated by addition of pyridine (0.1−0.2 mL) as **1·py** after change of solvent to hexanes and filtration.

X-ray Crystallography. Crystals of sufficient quality for single-crystal X-ray diffraction were obtained by crystallization from hexanes (**1·py**) or diethyl ether (**2**) at room temperature. Compound **1·py** was found to crystallize in two different modifications, **1·py·1/8C_6H_{14}** and **1·py·1/2C_6H_{14}**. The data set of the latter modification suffered from disorder problems and low data intensity. Due to these problems only the higher quality data of the modification **1·py·1/8C_6H_{14}** are the subject of the discussion in this paper, and information about the other data set is provided in the Supporting Information. Nevertheless, the metric parameters for **1·py** are essentially identical in both datasets.

Crystals of **1·py·1/8C_6H_{14}** 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.[16] The data for **1·py·1/8C_6H_{14}** were collected at 173(2) K on a Siemens P4 diffractometer using Mo Kα (λ = 0.71073 A) radiation. The data were corrected for Lorentz and polarization effects. An absorption correction was not applied since it was judged to be insignificant. The structure was solved by direct methods and refined by full-matrix least-squares procedures on F^2 using all reflections. The crystallographic programs employed were those of the SHELXTL program suite.[17] In the final refinement cycles all the non-hydrogen atoms were refined anisotropically, and all the hydrogen atoms were included in the refinement with idealized parameters except the hydrogen atoms belonging to the disordered hexane solvent molecule, which were not included in the refinement.

Table 2. Crystal Data and Structural Refinement Details for 1·py·1/8C_6H_{14} and 2

	1·py·1/8C_6H_{14}	**2**
empirical formula	$C_{57.75}H_{63.75}BN$	$C_{60}H_{77}BLi_2O_2$
fw	782.66	854.91
temp, K	173(2)	203(2)
wavelength, Å	0.71073	0.71073
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2(1)/c$
a, Å	15.9622(19)	13.4883(3)
b, Å	17.283(2)	35.4783(5)
c, Å	17.758(2)	12.2052(2)
α, deg	88.829(10)	90
β, deg	78.656(9)	114.3670(10)
γ, deg	87.525(10)	90
V, Å^3	4798.3(10)	5320.42(11)
Z	4	4
D_{calcd}, Mg/m^3	1.083	1.067
μ(Mo Kα), mm^{-1}	0.061	0.061
F(000)	1689	1856
cryst size, mm^3	0.64 × 0.56 × 0.52	0.33 × 0.20 × 0.10
cryst color and habit	colorless block	red needle
$2\theta_{max}$, deg	25.01	22.50
no. of observns	16 502	6878
no. of variables	1114	592
R1[a] [$I > 2\sigma(I)$]	0.0743	0.0882
wR2[b] [$I > 2\sigma(I)$]	0.1899	0.2012
goodness-of-fit on F^2	1.009	1.069
largest diff peak, e Å^{-3}	0.737	0.593

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = (\sum w||F_o| - |F_c||^2/\sum w|F_o|^2)^{1/2}$.

Crystals of **2** were treated similarly to those of **1·py** with the exception that they were removed from the flask inside a drybox. The data for **2** were collected at 203(2) K on a Siemens SMART 1000 diffractometer using Mo Kα (λ = 0.71073 A) radiation. The data were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied.[18] The structure was solved by direct methods and refined by full-matrix least-squares procedures on F^2 using all reflections. The crystallographic programs employed were those of the SHELXTL program suite.[17] Several *t*-Bu groups showed disorder and were modeled with refined occupancies. Six atoms were kept isotropic. One Et_2O molecule was disordered. Attempts to model the whole Et_2O molecule as disordered were unsatisfactory. The terminal CH_3 was modeled with two positions and the remaining atoms were left with large thermal parameters. The data were limited to 45° due to poor diffraction. In the final refinement cycles all the non-hydrogen atoms were refined anisotropically except six carbon atoms belonging to the disordered *t*-Bu groups, and all the hydrogen atoms were included in the refinement with idealized parameters. Some details of the data collections and refinements are given in Table 2, and selected bond distances and angles are listed in Tables 2 and 3. Further details are given in the Supporting Information.

Results and Discussion

Monosubstituted boranes $[RBH_2]_2$ can be obtained by the reaction of an organolithium compound RLi with

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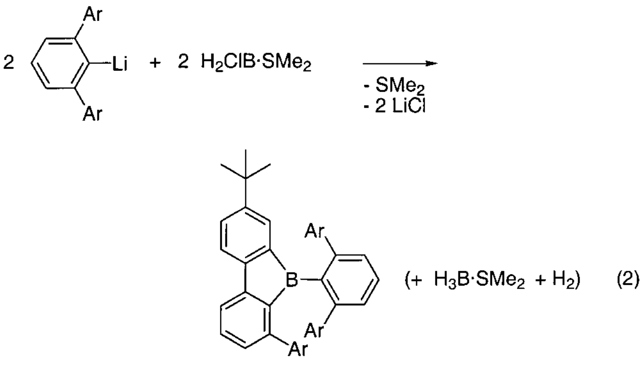
Table 3. Selected Bond Lengths (Å) for $1\cdot py\cdot 1/8C_6H_{14}$ and 2

$1\cdot py\cdot 1/8C_6H_{14}$		2	
B(1)−N(1)	1.638(3)	B(1)−C(1)	1.607(6)
B(1)−C(7)	1.638(4)	B(1)−C(27)	1.544(6)
B(1)−C(16)	1.640(4)	B(1)−C(38)	1.536(6)
B(1)−C(42)	1.645(4)	B(1)···Li(1)	2.317(9)
C(7)−C(8)	1.407(4)	Li(1)···C(38)	2.242(9)
C(8)−C(11)	1.468(4)	Li(1)···C(33)	2.247(9)
C(11)−C(16)	1.402(4)	Li(1)···C(32)	2.302(9)
B(2)−N(2)	1.641(3)	Li(1)···C(27)	2.328(9)
B(2)−C(64)	1.632(4)	B(1)···Li(2)	2.302(9)
B(2)−C(73)	1.645(4)	Li(2)···C(32)	2.250(9)
B(2)−C(99)	1.647(4)	Li(2)···C(33)	2.252(9)
C(64)−C(65)	1.409(3)	Li(2)···C(38)	2.253(8)
C(65)−C(68)	1.468(4)	Li(2)···C(27)	2.263(9)
C(68)−C(73)	1.414(4)	Li(1)−O(1)	1.915(8)
		Li(2)−O(2)	1.946(8)
		C(27)−C(32)	1.479(6)
		C(32)−C(33)	1.423(6)
		C(33)−C(38)	1.472(5)

dimethyl sulfide-stabilized $H_2ClB\cdot SMe_2$.[19] Indeed, the terphenyl-substituted species $[2,6\text{-}(o\text{-tol})_2C_6H_3BH_2]_2$ and $[2,6\text{-}Mes_2C_6H_3BH_2]_2$ (Mes = $2,4,6\text{-}Me_3C_6H_2$) have been synthesized according to this route.[20] However, when we now reacted $2,6\text{-}(4\text{-}t\text{-}BuC_6H_4)_2C_6H_3Li$ with $H_2ClB\cdot SMe_2$ in hexanes or diethyl ether at −78 °C followed by stirring at room temperature for ca. 12 h, no $[2,6\text{-}(4\text{-}t\text{-}BuC_6H_4)_2C_6H_3BH_2]_2$ was formed, but instead a bright yellow, fluorescing solution was obtained. The ^{1}H NMR spectrum of the crude product after removal of the solvent under reduced pressure indicated the presence of several compounds, with **1** (eq 2) being the main product (50−75%) as gauged by integration of the *tert*-butyl region of the spectrum.



(2)

(1) Ar = 4-*t*-BuC_6H_4
50-75% yield

Although the high solubility of **1** in hexanes, toluene, diethyl ether, or THF prevented the purification by crystallization, addition of a slight excess of pyridine caused a color change to almost colorless, and large colorless crystals of the adduct **1·py** formed after several days at room temperature. The structure of **1·py** was determined by X-ray crystallography (Figure 1) and will be discussed below.

The mechanism of the formation of **1** is not yet fully understood. The presence of donor solvents appears to suppress the formation of **1**. According to ^{1}H NMR spectroscopic investigations of the crude products, the yields of **1** are 70−75% in hexanes but only 50−53% in Et_2O solution. Attempts to perform the reaction in THF afforded only the protonated terphenyl substituent, i.e., the arene $2,6\text{-}(4\text{-}t\text{-}BuC_6H_4)_2C_6H_4$. In hexane and Et_2O solution the borafluorene formation (C−H activation) is facile and apparently commences even below room temperature (ca. 0−10 °C), as indicated by the appearance of the intense yellow color. This reaction provides a facile route to unsymmetrical 9-borafluorenes. We are currently studying the scope of this reaction.

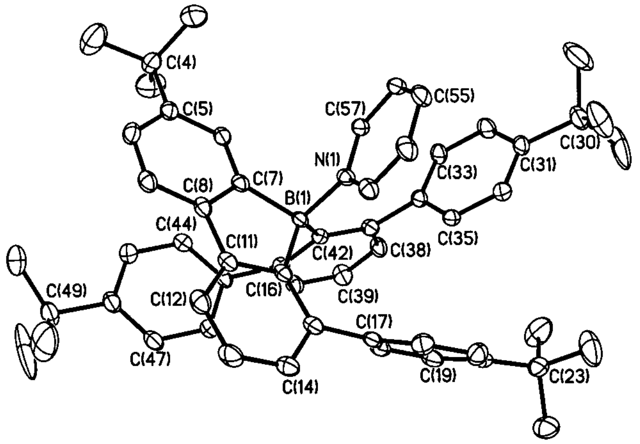


Figure 1. Thermal ellipsoid plot (30% probability ellipsoids) showing the molecular structure of one of the two independent molecules of **1·py**. Hydrogen atoms are omitted for clarity.

Table 4. Selected Bond Angles (deg) for $1\cdot py\cdot 1/8C_6H_{14}$ and 2

$1\cdot py\cdot 1/8C_6H_{14}$		2	
C(7)−B(1)−N(1)	101.76(19)	C(27)−B(1)−C(1)	126.6(4)
C(7)−B(1)−C(16)	98.9(2)	C(38)−B(1)−C(1)	130.3(4)
N(1)−B(1)−C(16)	107.1(2)	C(38)−B(1)−C(27)	103.0(3)
C(7)−B(1)−C(42)	116.4(2)	C(32)−C(27)−B(1)	108.6(3)
N(1)−B(1)−C(42)	114.2(2)	C(33)−C(38)−B(1)	109.2(3)
C(16)−B(1)−C(42)	116.5(2)	C(32)−C(33)−C(38)	109.5(3)
C(64)−B(2)−N(2)	101.13(19)	C(33)−C(32)−C(27)	109.6(3)
C(64)−B(2)−C(73)	99.09(19)		
N(2)−B(2)−C(73)	107.87(19)		
C(64)−B(2)−C(99)	115.2(2)		
N(2)−B(2)−C(99)	113.63(19)		
C(73)−B(2)−C(99)	117.8(2)		

Crystals of **1·py** contain two independent molecules and a disordered hexane molecule (with an occupancy of 0.25) per asymmetric unit. Some selected bond lengths and angles of both independent molecules are given in Tables 3 and 4. There are no large structural differences in the two independent molecules, and for brevity, only the parameters of one of the molecules are discussed here. The structure of **1·py** features a planar, unsymmetrically substituted 9-borafluorene unit. The boron atom is further coordinated to the *m*-terphenyl group $2,6\text{-}(4\text{-}t\text{-}BuC_6H_4)_2C_6H_3-$ and one pyridine in a distorted tetrahedral fashion. The B−N (1.638(4) Å) distance is somewhat elongated compared to those of the pyridine adduct of 9-chloro-9-borafluorene (d(B−N) = 1.612(3) Å)[21] and other pyridine adducts of boranes (see, e.g., $(C_6F_5)_3B\cdot(NC_5H_4(4\text{-}Me_2N)$, d(B−N) = 1.604 Å;[22] tetraethylbis(μ_2-2-(5-methyl)pyridyl)diborane, d(B−

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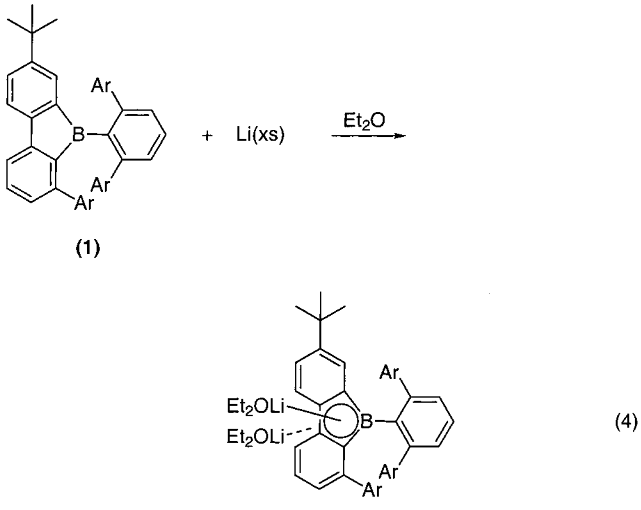
N) = 1.610 Å[23]). The B–C(aryl) distances (1.638(4)–1.645(4) Å) are within the range observed for four-coordinate organoboron compounds (*d*(B–C) = 1.59–1.65 Å).[24] The smallest angle at the boron atom is the internal C(7)–B(1)–C(16) angle with a value of 98.9(2)°, and the widest angles with values of 114.2(2)–116.5(2)° all involve the terphenyl substituent (i.e., C(42)). Further evidence for steric crowding is found in the short N(1)···C and C···C contacts between the pyridine and the C(31)–C(36) aromatic ring (e.g., N(1)···C(34) = 3.020 Å, N(1)···C(35) = 2.971 Å, C(57)···C(34) = 2.869 Å) as well as short C/B···C contacts between the borole unit and the C(43)–C(48) aromatic ring (e.g., B(1)···C(43) = 2.989 Å, C(7)···C(44) = 3.034 Å, C(16)···C(48) = 3.197 Å).

Consistent with the elongated B(1)–N(1) bond is the observation that dissolution of colorless **1·py** in hexanes or benzene affords bright yellow solutions, suggesting partial dissociation of the pyridine ligand according to eq 3.

$$\mathbf{1{\cdot}py} \rightleftharpoons \mathbf{1} + \mathrm{py} \qquad (3)$$

Similar equilibria have been observed for other sterically crowded boranes.[25] Determination of the relative concentration of **1·py** and pyridine in three samples of different concentrations using ^{1}H NMR spectroscopy gave the equilibrium constant $K = 2.2(0.5) \times 10^{-3}$ mol L^{-1}. However, attempts to remove the pyridine by distillation from a toluene solution of **1·py** or by vacuum distillation from melted **1·py** at 150–170 °C resulted in decomposition.

Boroles are readily reduced to the respective dianions owing in part to the empty p$_z$-orbital on the boron atom. Stirring of an Et$_2$O solution of crude **1** with excess lithium powder at −10 °C gave a dark green solution, which was concentrated to give deep red, almost black plates of **2** in moderate yields (eq 4).



(1)

(4)

(2) Ar = 4-*t*-BuC$_6$H$_4$

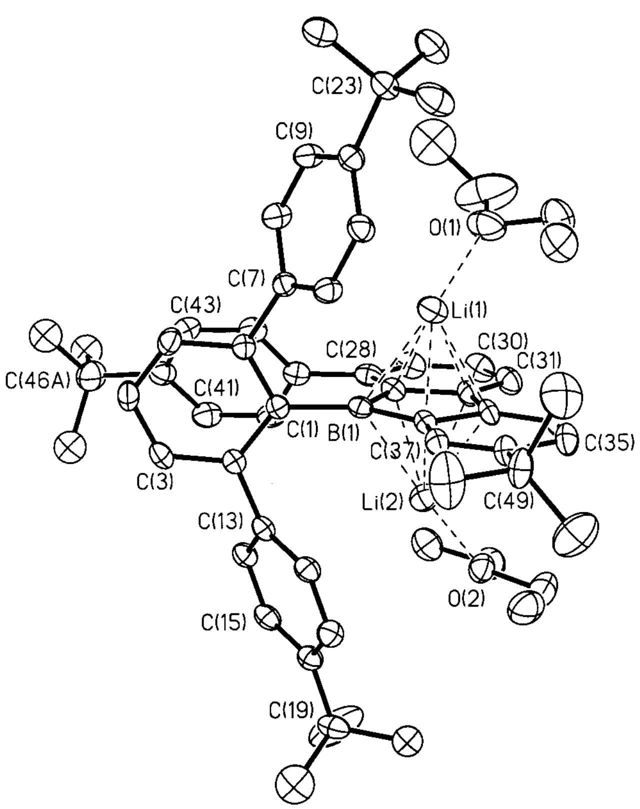


Figure 2. Thermal ellipsoid plot (30% probability ellipsoids) showing the molecular structure of **2**. Hydrogen atoms are omitted for clarity.

The structure of **2** (Figure 2) features a planar 9-boratafluorene unit. The coordination at the boron atom is distorted trigonal planar (∑(angles at boron) = 359.9°), with the narrow angle of 103.0(3)° being the internal C(27)–B(1)–C(38) angle of the boratafluorene. The two external angles are wider, with C(1)–B(1)–C(27) = 126.6° and C(1)–B(1)–C(38) = 130.3°. The two diethyl ether-solvated lithium cations are positioned almost symmetrically above and below the plane of the central C$_4$B ring of the boratafluorene unit. The Li···C distances range from 2.242(9) (Li(1)···C(38)) to 2.328(9) Å (Li(1)···C(27)) and average 2.280(36) and 2.254(5) Å for Li(1) and Li(2), respectively. The Li···B distances are slightly longer, with Li(1)···B(1) = 2.317(9) and Li···B(2) = 2.302(9) Å. Similar values have been reported for the related lithium salts of a 9-borafluorene,[26] a 2-benzoborole,[9] and two boroles.[27,28] The central ring of the terphenyl substituent is rotated 80.4° with respect to the boratafluorene plane so that the *m*-(4-*t*-BuC$_6$H$_4$) rings create pockets for the Li$^+$ cations. The interactions of the Li$^+$ cations with these rings are weak, with the shortest Li···C distances ranging from 2.82 (Li(2)···C(18)) to 3.04 Å (Li(1)···C(12)). However, the close proximity of these rings pushes the Li-coordinated Et$_2$O molecules away from the Li(1)···Li(2) axis by 35.9° (O(1)) and 39.3° (O(2)). The Li–O bond lengths with Li(1)–O(1) = 1.915(8) and Li(2)–O(2) = 1.946(8) Å are only slightly elongated by this interaction and are well within the range observed for organolithium compounds with Li$^+$–π-interactions.[26,29–32] The internal B–C distances

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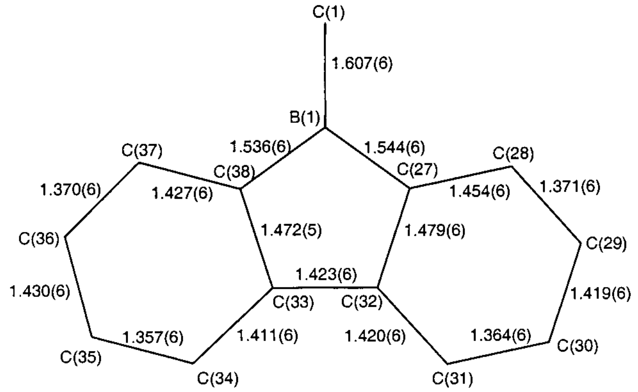
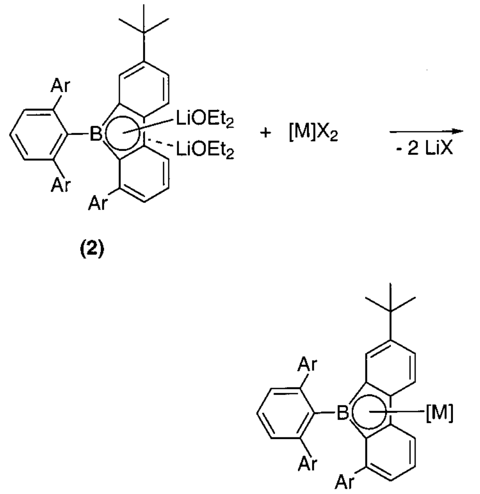


Figure 3. Schematic drawing of the 9-borafluorene core of **2** showing the bond lengths (Å).

B(1)−C(27) and B(1)−C(38) of 1.544(6) and 1.536(6) Å, respectively, are about 2−4% shorter than a typical B−C single bond (1.57−1.59 Å[33−35]), indicating some multiple bonding at the boron. The annulated aromatic rings are also slightly perturbed toward alternating elongated and shortened bonds, with the longest bonds belonging to the central C_4B ring (Figure 3). A similar distortion is found in related boratafluorene compounds[26] as well as in fluorenyl anions, albeit less pronounced in the latter species.[31,32,36−39]

The highfield shift of the CH_2 and CH_3 hydrogens of the coordinated Et_2O molecules in the ^1H NMR spectrum ($\delta_H = 2.50$ and 0.16 ppm) and that of the Li^+ cations in the ^7Li NMR spectrum ($\delta_{Li} = -10.3$ ppm) strongly suggest that the structure of **2** is maintained in C_6D_6 solution. The UV/vis spectrum displays two intensive bands in the visible region (435 nm ($\epsilon = 8450$), 595 nm ($\epsilon = 1160$)), which disappear upon oxidation to the neutral borafluorene **1**.

One of the exciting aspects of the dianionic complex **2** is the possibility to form transition metal complexes by metathesis reactions with transition metal halides (eq 5).



(5)

Ar = 4-*t*-BuC_6H_4, X = halide, [M] = complex fragment

Unfortunately, preliminary investigations showed that the reactions of **2** with the metal halide salts $ZrCl_4$, $CpZrCl_3$, $FeCl_2$, $FeBr_2$, and $Cu(MeCN)_4PF_6$ at low temperatures in diethyl ether or THF solutions only led to reduction of the metal halide salts, and the neutral species **1** could be recovered essentially quantitatively from these solutions. An analogous tendency to reduce metal salts rather than to form metal complexes was observed for the dianion of a tetra-*tert*-butyl-*s*-indacene.[40] However, given that it has not been possible so far to isolate pure **1** either by crystallization of the crude product of the reaction of 2,6-(4-*t*-$BuC_6H_4)_2C_6H_3$-Li with $H_2ClB{\cdot}SMe_2$ (vide supra) or by removal of the coordinated pyridine in **1·py**, the controlled oxidation of **2** by metal salts represents a viable route to uncomplexed **1**. We have found that using $SnCl_2$ in Et_2O at −78 °C as the oxidizing reagent affords **1** in essentially quantitative yields after a simple workup procedure (see also ref 41). Compound **1** is a bright yellow fluorescent solid which is very soluble in standard organic solvents. Solid **1** or solutions of **1** are stable toward short-time exposure to atmospheric oxygen and moisture. Interestingly, **1** decomposes when heated above ca. 100 °C. One explanation for the low thermal stability of **1** may be that the neutral 9-borafluorene is isoelectronic with the formally antiaromatic fluorenyl cation.[42−44] The reactivity of **1** and **2** toward a variety of main group and transition metal complexes is currently under investigation.

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Supporting Information Available: Crystallographic tables, numbering schemes, and unit cell plots for compounds $\mathbf{1{\cdot}py{\cdot}1/8C_6H_{14}}$, $\mathbf{1{\cdot}py{\cdot}1/2C_6H_{14}}$, and **2**. 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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