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Perfluoroaryl-Substituted Boron Dipyrrinato Complexes

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A methodology for the incorporation of fluoroaryl groups into boron dipyrrinato complexes (modified BODIPY dyes) is reported. Two hexaalkylated dipyrrinato ligands with either H or CH_3 occupying the meso position were employed; when they were treated with fluoroaryl haloboranes in the presence of a weak base, the title compounds were prepared in good to excellent yields. The structures of seven derivatives were determined using X-ray crystallography, and their spectroscopic, photophysical, and redox properties are compared.

Introduction

Dipyrrinato complexes incorporating boron (BODIPY, $\mathbf{LBF_2}$, Scheme 1)[1] are used in various applications such as biological labeling,[2] dye lasers,[3] and ion sensing[4] because of their favorable photophysical characteristics. These dyes exhibit high absorptivity and generally fluoresce with excellent efficiency; furthermore, they demonstrate a high level of photostability. Synthetic procedures have been developed to install a variety of functional groups at different positions on the dipyrrinato core in order to further improve their stability and/or finely tune their photo- and electrochemical properties.[5,6]

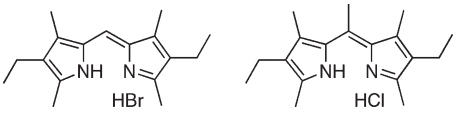
Despite their useful properties, areas for improvement remain. Specifically, known BODIPY dyes generally exhibit small Stokes shifts. Various strategies to address this issue have been employed, the most successful being the development of cassettes in which a strongly absorbing group is attached to the BODIPY core.[1] Recently, researchers have also begun to explore the substitution of the fluoride ligand(s) to produce new BODIPY dyes with aryl,[7] alkynyl,[8] and alkoxy[9] substituents on boron in an effort to modulate the Stokes shift.[10] To this end, we became interested in substituting the fluoride substituents with highly electron withdrawing pentafluorophenyl groups[11] and investigating the properties of the resulting derivatives. We expected the new complexes to be particularly stable due to the chemical inertness of perfluorinated groups.

In this paper, a synthetic method for preparing mono- and bis-substituted perfluorinated aryl BODIPY dyes is described, using two dipyrrinato ligands that differ by the presence or absence of a methyl group at the 8-position (meso) (Chart 1). The scope and limitations of the method, which may be generalizable to other BODIPY derivatives, are discussed.

Results and Discussion

Synthesis. Ziessel and co-workers prepared B-aryl functionalized BODIPY dyes by reaction of $\mathbf{L^{Me}BF_2}$ with aryl Grignard or aryllithium reagents to afford the mono- and bis-aryl derivatives, respectively.[7] Accordingly, reaction of $\mathbf{L^{Me}BF_2}$ with C_6F_5MgBr[12] yielded the mono-C_6F_5 complex **1-L^{Me}**, albeit in a moderate isolated yield of 40% (Scheme 1), similar to that achieved by Ziessel for the C_6H_5-substituted analogue.[7] Use of 2 equiv of the (fluoroaryl)lithium reagent C_6F_5Li[13] produced only small amounts (5−10%) of the desired bis-pentafluorophenyl complex **2-L^{Me}**, in contrast with the 34% yield obtained for the analogous bis-phenyl complex.[7] The lack of stability of the (fluoroaryl)lithium

Chart 1



L^{H}·HBr L^{Me}·HCl

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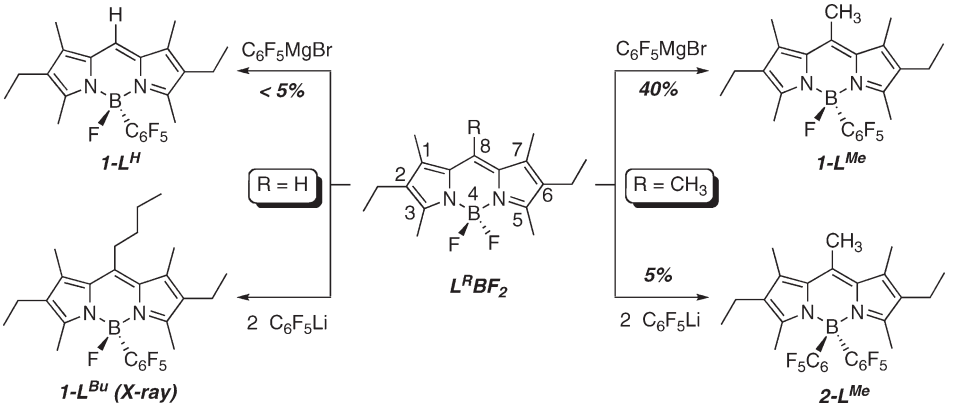
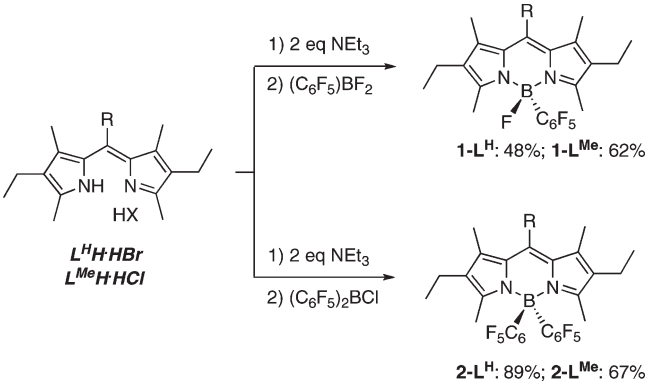
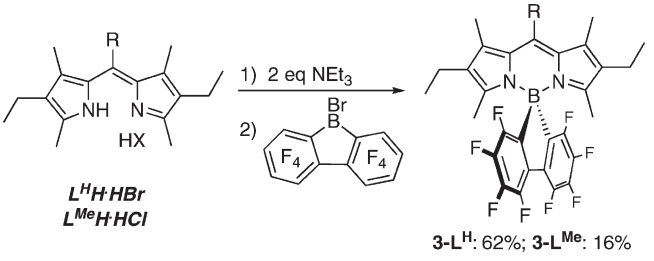
Scheme 1



Scheme 2



Scheme 3



reagents[14] at temperatures above −40 °C may be behind the poor yields in these reactions.

This approach was even less successful for $\mathbf{L^HBF_2}$, where the meso H substituent of the boron difluorodipyrrinato complex has previously been suspected of being susceptible to deprotonation.[8d] Thus, when $\mathbf{L^HBF_2}$ was treated with C_6F_5MgBr, the isolated yield of the mono-C_6F_5 complex **1-L^H** was significantly lower (less than 5%) than that found for the $\mathbf{L^{Me}}$ derivative. Moreover, the reaction with 2 equiv of C_6F_5Li gave the monofluoro-substituted complex **1-L^{Bu}** in small amounts as the only isolated product (Scheme 1). The structure of **1-L^{Bu}** and the presence of the *meso*-butyl group was confirmed using X-ray crystallography (see the Supporting Information for details). Here, the second equivalent of C_6F_5Li presumably deprotonates the meso position, and subsequent butylation occurs via reaction with ^{n}BuBr, the byproduct formed in the preceding step involving generation of C_6F_5Li from C_6F_5Br and ^{n}BuLi. Substitution of the meso proton by lithio reagents has previously been suggested to account for the low yields obtained in the preparation of boron-substituted alkynyl derivatives.[8d] Clearly, this synthetic route is not viable for the preparation of the desired boron perfluoroaryl dipyrrinato compounds, and thus higher yielding approaches were sought.

To do this, we turned to the use of perfluoroaryl haloborane reagents such as $C_6F_5BF_2$[15] and $(C_6F_5)_2BCl$[13] to prepare **1-L** and **2-L**, respectively (Scheme 2). A similar strategy has been used to prepare bis-alkyl-substituted BODIPYs.[16] In this methodology, only a mild base is required to neutralize and sequester the HX (X = Br, Cl, F) byproducts of complex formation. Thus, the addition of a haloborane to a solution of $\mathbf{L^H}$ or $\mathbf{L^{Me}}$ and triethylamine immediately gave dark red solutions that fluoresced yellow under irradiation with a UV lamp. The isolated yields of compounds **1-L** and **2-L** prepared via this route were significantly higher than those obtained using the previous methodology, confirming the convenience of this synthetic strategy, provided that suitable $Ar_{3-n}BX_n$ (n = 1, 2) reagents are available. Moreover, the crude products are cleaner, thereby simplifying the purification procedure to involve either a short chromatographic column or even filtration through a silica plug. The lower yields for the reactions producing mono-C_6F_5 compounds **1-L** by this method have two causes. One has to do with the difficulty in handling the $C_6F_5BF_2$ reagent,

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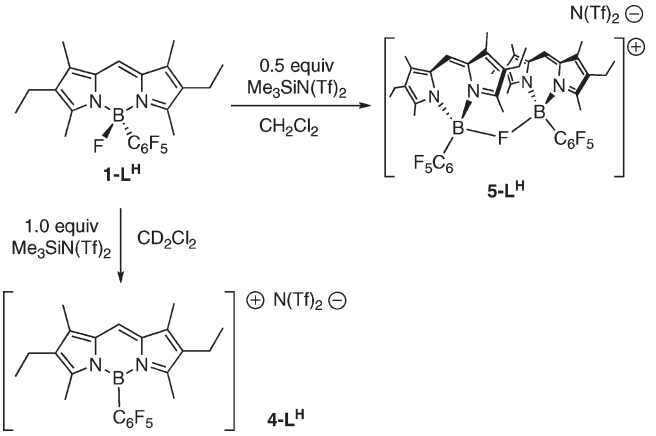
which is a highly volatile, air- and moisture-sensitive liquid.[15] The other is that detectable amounts (up to 15%) of L^RBF_2 complexes (produced via loss of C_6F_5H) are observed, indicating that this is a competing process using the $C_6F_5BF_2$ reagent.

This methodology can be employed to prepare perfluoroaryl BODIPY derivatives that would be challenging to prepare via a Grignard or aryllithium-based methodology.[7] For example, preparation of the spiro BODIPY complexes **3-L** (Scheme 3) would first require dilithiation or two successive lithiations of a 2,2′-dihaloperfluorobiphenyl derivative[17] followed by LiF elimination of the L^RBF_2 BODIPY precursor. The higher temperatures necessary (i.e., room temperature)[7] for the latter step preclude the use of an unstable dilithio perfluorobiphenyl reagent. However, using the perfluorinated 9-bromoborafluorene $C_{12}F_8BBr$[17] in the methodology of Scheme 2 rapidly gave the desired products as depicted in Scheme 3, demonstrating the applicability of this strategy to other haloboranes. The reason for the low yield observed for **3-L^{Me}** is not clear but may be related to tautomerization of the dipyrrin to the vinyl dipyrrole.[18]

Monitoring these reactions using NMR spectroscopy shows that, upon mixing an equimolar amount of L^H·HBr with $(C_6F_5)_2BCl$ or $C_{12}F_8BBr$, an adduct between the haloborane and the ligand was quantitatively formed. Upfield shifts of the ^{11}B NMR resonances to 2.3 and −1.9 ppm for $(C_6F_5)_2BCl$ or $C_{12}F_8BBr$, respectively, as well as changes in the ^1H and ^{19}F NMR chemical shifts, were consistent with the assignment of these orange, non-fluorescent intermediates as Lewis acid/base complexes between the haloboranes and L^H·HBr. Upon subsequent addition of 2 equiv of NEt_3 to the NMR tube, signals for the final/isolated products were rapidly observed.

Characterization. NMR Spectroscopy and Mass Spectrometry. All compounds were characterized using multinuclear NMR ^1H, ^{11}B, $^{13}C\{^1H\}$, and ^{19}F spectroscopy, in $CDCl_3$ solvent; in the L^H series, ^{15}N NMR spectroscopy was also examined. The resonances most affected by structural variations at boron are those for the methyl substituents, and the meso-proton resonances in the L^H derivatives. In general, the resonances of the methyl groups move upfield as the Lewis acidity of the haloborane starting material increases. An opposite but less significant trend is observed for the meso proton of the **L^H** derivatives; while the chemical shifts of the meso proton for **1-L^H** and **2-L^H** are essentially identical (7.08 and 7.07 ppm, respectively), the resonance of this proton is shifted downfield for **3-L^H** (7.23 ppm). It has been previously observed that the electron density at boron influences the chemical shift of that particular proton (i.e., an electron-deficient boron center will move this signal to lower fields).[19] The ^{15}N chemical shifts for compounds **1**, **2**, and **3-L^H** of −193.1, −198.3, and −204.8 ppm, respectively,[20] also reflect the trend in increasingly Lewis acidic boron centers and are generally consistent with

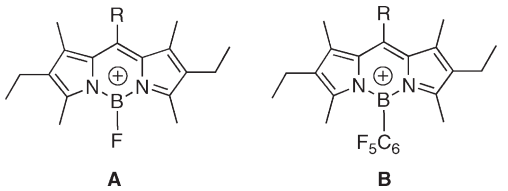
Scheme 4



chemical shifts found for other BF_2 dipyrrinato complexes.[21]

The $^{11}B\{^1H\}$ signal for all compounds is found around 0 ppm, as expected for neutral, tetracoordinated boron compounds.[22] In compounds **1**, a $^1J_{BF}$ coupling of ∼60 Hz was resolved, unlike in the unfluorinated mono-aryl complexes previously reported.[7] In the ^{19}F NMR spectra, the B*F* signal of compounds **1** is broadened due to further coupling with the ortho fluorine atoms ($^{19}F-^{19}F$ COSY) of the $B-Ar_F$ groups and the BF coupling constant could not be extracted from these spectra.

The compounds were also characterized using mass spectrometric techniques (ESI or EI), and the analyses of the spectra for compounds **1-L^R** and **2-L^R** revealed informative fragmentation patterns. For example, detection of BODIPY borenium ions[19,23] **A** (*m*/*z* 285.1 and 298.8, for R = H, Me, respectively) and **B** (*m*/*z* 433.0 and 446.7) in the positive ion ESI mode suggests that loss of the pentafluorophenyl anion ($C_6F_5^-$) is facile from both families of compounds;



indeed, this anion was observed (*m*/*z* 166.8) in negative ion mode. The absence of **B** in the spectra of compounds **1** suggests that loss of the pentafluorophenyl anion is more facile than loss of F^-, as expected, due to the greater stability of $C_6F_5^-$ versus fluoride. Because of the chelation of the Ar^F group in compounds **3**, borenium ion formation is not observed when these compounds are subjected to mass ESI spectrometric analysis; instead, losses of various alkyl groups (methyl and ethyl) from the dipyrrinato core constitute the dominant fragmentation pathways.

The viability of **A** and **B** was confirmed with separate synthetic experiments; ion **A** has previously been fully

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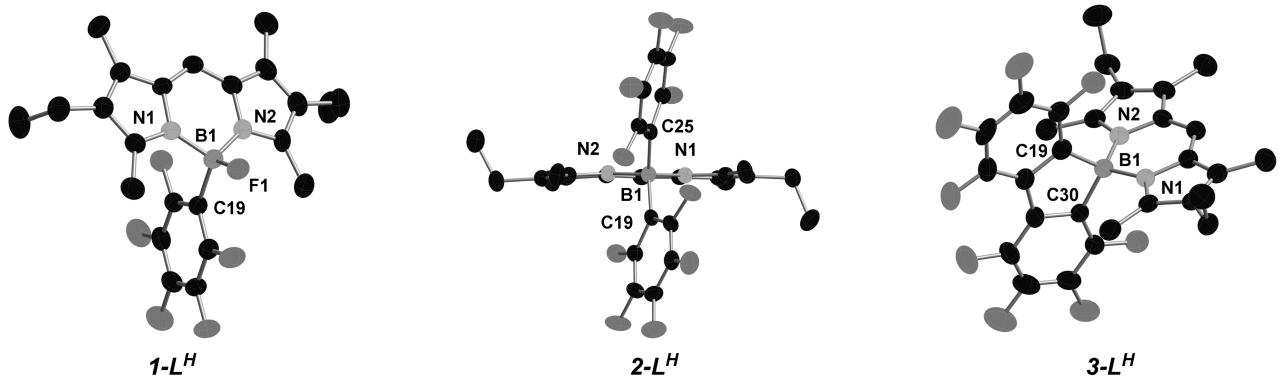

Figure 1. Thermal ellipsoid diagrams (50%) of compounds **1-L^{H}**−**3-L^{H}**. Selected metrical parameters can be found in Table 1.

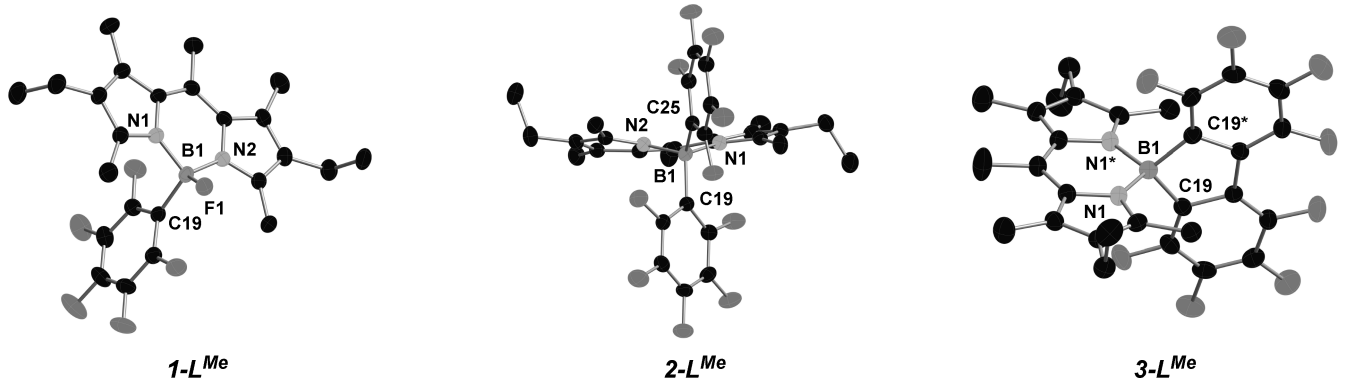

Figure 2. Thermal ellipsoid diagrams (50%) of compounds **1-L^{Me}**−**3-L^{Me}**. Selected metrical parameters can be found in Table 1.

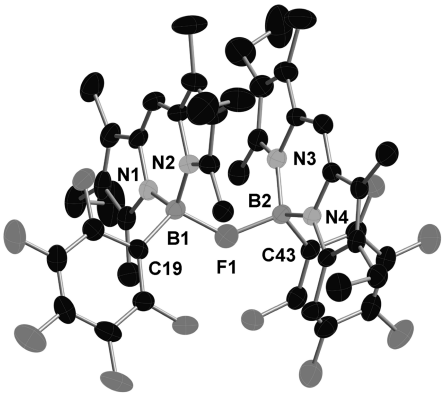

Figure 3. Thermal ellipsoid (50%) diagram of the cationic portion of **5-L^{H}**. Selected bond distances (Å): B(1)−F(1), 1.566(5); B(2)−F(1), 1.576(5); B(1)−N(1), 1.532(5); B(1)−N(2), 1.524(5); B(2)−N(3), 1.528(5); B(2)−N(4), 1.537(5); B(1)−C(19), 1.635(6); B(2)−C(43), 1.636(5). Selected bond angle (deg): B(1)−F(1)−B(2), 131.7(3).

Table 1. Selected Bond Distance (Å) and Angle (deg) Data for 1-L^{R}−3-L^{R}

	B−F	B−N	B−C	N−B−N	C−B−C
1-L^{H}	1.400(3)	1.555(3)	1.646(3)	106.90(17)	
		1.556(3)			
2-L^{H}		1.588(2)	1.664(3)	106.82(14)	115.99(14)
		1.575(3)	1.662(3)		
3-L^{H}					
cis		1.558(5)	1.623(5)	107.2(3)	97.7(3)
		1.566(5)	1.625(6)		
trans		1.552(5)	1.620(6)	107.7(3)	97.0(3)
		1.560(5)	1.631(5)		
1-L^{Me}	1.410(3)	1.545(3)	1.650(3)	106.31(16)	
		1.541(3)			
2-L^{Me}		1.557(2)	1.667(2)	105.47(13)	116.19(13)
		1.575(2)	1.645(2)		
3-L^{Me}		1.561(3)	1.631(3)	106.8(2)	98.0(2)
		1.561(3)	1.631(3)		

characterized as its $[B(C_6F_5)_4]^-$ salt,[19a] while **B** was generated as its $N(Tf)_2^-$ salt (**4-L^{H}**), as shown in Scheme 4. The borenium ion **4-L^{H}** was not isolated, but its NMR spectroscopic features are consistent with its proposed formulation, particularly the broad ^{11}B resonance at 19 ppm. When only $^1/_2$ equiv of the $Me_3SiN(Tf)_2$ reagent was employed, the Lewis acidic boron center in **4-L^{H}** was quenched by the remaining $^1/_2$ equiv of **1-L^{H}** to form a fluoride-bridged dimer, **5-L^{H}**, which was characterized by NMR spectroscopy and X-ray crystallography (see below). Together, the mass spectrometric data and the synthetic chemistry suggest the viability of a larger family of borenium ions beyond those we recently reported.[19a]

Structures. Compounds **1-L^{R}**−**3-L^{R}** and **5-L^{H}** were obtained as crystalline materials, and X-ray crystallographic analysis was performed on the seven derivatives (Figures 1−3 and Table 1). The structures of compounds **1**−**3** display similar features, including a distorted-tetrahedral geometry at the boron center, an essentially planar dipyrrinato core (including boron), and generally similar, unremarkable bond distances for bonds to boron. The dipyrrinato core was found to be more distorted in the **L^{Me}** derivatives; DFT and semiempirical calculations on different LBF_2 compounds have shown that methylation of the 1- and

Table 2. Electronic Spectroscopic Data for Compounds 1−3

	λ_{max} (nm)[a]	λ_{max} (nm)[b]	λ_{max} (nm)[c]	ε_{max} (M^{-1} cm^{-1})[b]	λ_{flu} (nm)[b]	Stokes shift (cm^{-1})[b]	Φ_{flu}[b]	τ_{flu} (ns)[b]
1-L^{H}	534	532	527	55 586	541	313	0.78	7.0
2-L^{H}	528	527	523	66 410	544	593	0.65	7.3
3-L^{H}	529	527	522	29 641	533	213	0.67	7.3
1-L^{Me}	524	521	517	28 417	540	675	0.61	6.6
2-L^{Me}	525	523	519	25 563	566	1452	0.34	3.9
3-L^{Me}	519	518	514	37 660	537	646	0.92	7.0

[a] Recorded in deoxygenated cyclohexane solution. [b] Recorded in deoxygenated dichloromethane solution. [c] Recorded in deoxygenated acetonitrile solution.

7-positions of the dipyrrinato core in LBF_2 induces distortion of the central C_3N_2B ring because of the steric interaction with the *meso*-methyl group.[24] The ethyl groups for **1**−**3** are mainly arranged transoid to each other with respect to the dipyrrin plane, with the exception of **1-L^{H}** (cisoid) and **3-L^{H}** (both conformations are found in two independent molecules in the unit cell). The spatial orientations of the ethyl groups are probably governed by packing effects, wherein dipyrrin−dipyrrin or Ar^F−Ar^F interactions are balanced.

The molecular structure of dimeric **5-L^{H}** is shown in Figure 3, along with selected metrical data; the $N(Tf)_2$ counterion is not shown. The cation shown can be viewed as a Lewis acid/base adduct between **1-L^{H}** and **4-L^{H}**, although the B(1)−F(1)−B(2) bridge is essentially symmetric in terms of the boron−fluorine distances observed. The angle subtended at the bridging fluorine is 131.7(3)°, and the two dipyrrinato moieties are twisted about the B(1)−F(1)−B(2) plane to minimize steric repulsions. The two C_6F_5 groups are similarly rotated away from each other in this conformation.

Photophysical and Electrochemical Properties. Absorption and emission spectra of all derivatives show the usual characteristics of BODIPY dyes;[5] the data are summarized in Table 2 ,and typical spectra are given in Figures S2 and S3 (Supporting Information) for L^H and L^{Me} complexes, respectively. The most intense absorption is centered at ∼525 nm and is associated with the $S_0 \rightarrow S_1$ (HOMO−LUMO) transition; in addition, a less intense $S_0 \rightarrow S_2$ absorption at 360 nm is observed; emission occurs at ∼540 nm. The energy of the maximum absorption and emission is red-shifted by 5 nm in comparison with the parent aryl compounds;[7] the Stokes shift remains constant and small for all derivatives, except **2-L^{Me}**. The quantum yields, obtained using rhodamine 6G as a standard, vary somewhat with the nature of the perfluoroaryl substitution at boron. In the **L^{Me}** series, mono-fluorides **1** are more efficient emitters than the bis-perfluoroaryls **2**, meaning that $C_6F_5^-$ offers more degrees of freedom for dissipating energy than does F^-. However, the chelating nature of the 9-borafluorene unit rigidifies this biaryl unit and compounds **3** deliver the highest quantum yield of the series. The values for the **L^{H}** derivatives are more consistent and do not obviously show this trend.

The absorption characteristics for compounds **1**−**3** suggest that the perfluoroaryl-substituted BODIPY complexes possess an optical band gap similar to that of their nonfluorinated aryl derivatives. However, electrochemical data show that the energies of the HOMO and LUMO orbitals were altered by the presence of the more electronegative fluorinated aryl groups. Cyclic voltammetry experiments were conducted, and all compounds showed a reversible one-electron oxidation and reduction process (Table 3). The $E_{1/2}$ values for both processes are 0.25 V more positive than for their aryl counterparts, as expected from the presence of the perfluoroaryl group. The observed good agreement between the optical and electrochemical band gaps confirms that these processes are dipyrrinato ligand centered.[7] In addition to the reversible processes described above, compounds **2-L^{H}** and **3-L^{H}** exhibit additional electrochemical activity at intermediate potentials that are likely due to decomposition of the radical cations formed upon oxidation.[25]

Table 3. Electrochemical Data for Compounds 1−3

	$E_{1/2}$ (V)		
	$L^{\bullet+}/L$	$L/L^{\bullet-}$	HOMO−LUMO gap (eV)[a]
1-L^{H}	+1.05	−1.32	2.19
2-L^{H}	+1.03	−1.41	2.25
3-L^{H}	+1.01	−1.50	2.25
1-L^{Me}	+1.04	−1.42	2.27
2-L^{Me}	+1.01	−1.50	2.32
3-L^{Me}	+1.07	−1.46	2.31

[a] Measured at onset.

In conclusion, six BODIPY complexes incorporating fluoroaryl groups at the boron center were synthesized using a novel methodology which complements that developed for synthesizing nonfluorinated analogues. Electronic spectroscopy indicates that these perfluoroaryl-substituted boron dipyrrinato complexes exhibit behavior consistent with related compounds but that they are more electrochemically stable toward oxidation.

Experimental Section

General Procedures and Equipment. All operations were performed under a purified argon atmosphere using glovebox or vacuum line techniques. Toluene and hexanes solvents were dried and purified by passing through activated alumina and then vacuum-distilled from Na/benzophenone. NEt_3 and CH_2Cl_2 were dried over and distilled from CaH_2. Silica gel column chromatography was carried out on Geduran Silica 60 silica gel (particle size 40−63 μm). All NMR spectra were recorded in dry, oxygen-free $CDCl_3$ on Bruker AMX-300 MHz, DRX-400 MHz, and AVANCE 500 MHz spectrometers (operating at 300 and 400 MHz (^{1}H), 128 MHz (^{11}B), 75 MHz (^{13}C), 50.67 MHz (^{15}N), and 282 or 376 MHz (^{19}F)) at 25 °C, unless indicated. Chemical shifts are reported in ppm relative to residual solvent signal (^{1}H and $^{13}C\{^1H\}$), $BF_3\cdot OEt_2$ ($^{11}B\{^1H\}$), and C_6F_6 (^{19}F) standards. The labeling scheme

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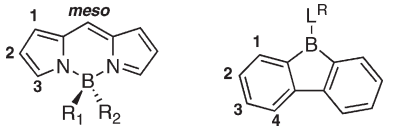
shown below is utilized in making the ^{1}H and ^{19}F NMR spectroscopic assignments:



Low-resolution mass spectra were obtained using a Bruker Esquire 3000 spectrometer operating in electrospray ionization (ESI) mode or using a Finnigan MAT SSQ7000 operating at 70 eV in electron impact (EI) mode. Fluorescence spectra were obtained using Yvon-Jobin and Cary Eclipse spectrophotometers with excitation and emission set to a 1.0 nm bandpass, and UV−visible spectra were obtained using Cary 100 Bio and 1E spectrophotometers operating in double-beam mode. Fluorescence quantum yield values were measured in CH_2Cl_2 and reported relative to rhodamine 6G in methanol ($\Phi_{flu} = 0.80$).[26] Fluorescence lifetime experiments were performed using a Jobin Yvon Fluorolog Tau-3 lifetime system spectrophotometer using Ludox solution (aqueous suspension of colloidal silica with zero lifetime) as a light-scattering standard and a 500 nm filter. The lifetime experiments were performed at an excitation wavelength of 530 nm, with interleave processing, and modeled using Δ_{phase} and $\Delta_{modulation}$ values of 0.5 and 0.05, respectively. Electrochemical studies were performed using an EG&G Model 283 potentiostat with a three-electrode cell: a platinum-wire auxiliary electrode, a silver-wire pseudoreference electrode, and a platinum-disk working electrode. Solutions were comprised of 1 mM test compound and 0.1 M [nBu$_4$N][PF$_6$] as the supporting electrolyte in 5 mL of dry, deoxygenated CH_2Cl_2. All $E_{1/2}$ values were referenced internally to [Cp$_2$Co][PF$_6$] ($E_{1/2} = -0.87$ V in CH_2Cl_2 (vs SCE)). X-ray crystallographic analyses were performed on suitable crystals coated in Paratone oil and mounted on a Nonius Kappa CCD diffractometer. Crystals were grown by dissolving samples in a minimum of CH_2Cl_2 and layering with hexanes, unless otherwise noted. Elemental analyses were performed using a Perkin-Elmer Model 2400 Series II analyzer by Johnson Li (University of Calgary). The solvent mixtures are given in volume/volume (v/v) ratio.

Materials. $(C_6F_5)_2BCl$,[13] $BrB(C_{12}F_8)$,[17] 2,8-diethyl-1,3,7,9-tetramethyldipyrrin hydrobromide ($L^HH\cdot HBr$),[20] 2,8-diethyl-1,3,7,9-tetramethyldipyrrin hydrochloride ($L^HH\cdot HCl$),[20] and 2,8-diethyl-1,3,5,7,9-pentamethyldipyrrin hydrochloride ($L^{Me}H\cdot HCl$)[27] were prepared according to literature procedures. $C_6F_5BF_2$[15] was synthesized according to a modified preparation where the product was not isolated from CH_2Cl_2 solvent and was instead used as a solution. [Me$_3$Si][N(SO$_2$CF$_3$)$_2$] was purchased from TCI America and used as received. The concentration of the solution was obtained by ^{19}F NMR by using α,α,α-trifluorotoluene as internal standard.

Synthesis of 1-L^H. $L^HH\cdot HBr$ (11 mg, 0.038 mmol) was dissolved in CH_2Cl_2 (10 mL), and NEt_3 (10 μL, 0.076 mmol). After the mixture was stirred for 15 min at room temperature, a CH_2Cl_2 solution of $C_6F_5BF_2$ (0.038 mmol) was added dropwise with stirring. After 15 min, volatiles were removed in vacuo and the compound was purified using column chromatography on silica (hexanes/toluene 3/2) to afford an orange solid: Yield: 8 mg (0.018 mmol, 48%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.08 (s, 1 H, H-*meso*), 2.34 (q, 4 H, $J = 7.6$ Hz, 2-CH_2CH$_3$), 2.21 (s, 6 H, 1-CH$_3$), 2.20 (s, 6 H, 3-CH$_3$), 1.03 (t, 6 H, 2-CH$_2$CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 154.3 (C3), 136.5 (C1), 132.3 (q), 131.7 (C2), 119.1 (C-*meso*), 17.3 (2-CH_2CH$_3$), 14.5 (2-CH$_2$$CH_3$), 12.2 (3-CH$_3$), 9.4 (1-CH$_3$), pentafluorophenyl carbons were not observed. ^{11}B{^{1}H} NMR ($CDCl_3$, 128 MHz): δ 0.23 (d, $^1J_{BF} = 59$ Hz). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −135.9 (m, 2 F, *o*-F), −157.3 (t, 1 F, $J = 20$ Hz, *p*-F), −163.8 (broad, 3 F, *m*-F and B*F*). EI (*m*/*z* (nature of peak, relative intensity)): 452.0 ([M]$^+$, 46), 285.1 ([M − C$_6$F$_5$]$^+$, 100). Anal. Calcd for $C_{23}H_{23}N_2BF_6$: C, 61.08; H, 5.13; N, 6.19. Found: C, 61.14; H, 5.20; N, 6.02.

Synthesis of 2-L^H. To a solution of $L^HH\cdot HBr$ (40 mg, 0.14 mmol) in CH_2Cl_2 (15 mL) was added triethylamine (40 μL, 0.28 mmol), and the solution was stirred for 15 min. A solution of $(C_6F_5)_2BCl$ (52 mg, 0.14 mmol) in CH_2Cl_2 (15 mL) was added, and the mixture was stirred for 15 min. Volatiles were removed in vacuo, and the red solution was passed through a plug of silica (CH_2Cl_2/hexanes 3/2) to yield the desired compound (73 mg, 0.12 mmol, 89%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.07 (s, 1 H, H-*meso*), 2.36 (q, 4 H, $^3J_{HH} = 7.6$ Hz, 2-CH_2CH$_3$), 2.21 (s, 6 H, 1-CH$_3$), 1.89 (s, 6 H, 3-CH$_3$), 1.02 (t, 6 H, 2-CH$_2$CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): 154.6 (C3), 136.6 (C1), 132.4 (q), 132.2 (C2), 119.3 (C-*meso*), 17.6 (2-CH_2CH$_3$), 14.4 (2-CH$_2$$CH_3$), 13.4 (3-CH$_3$), 9.4 (1-CH$_3$), pentafluorophenyl carbons were not observed. ^{11}B{^{1}H} NMR ($CDCl_3$, 128 MHz): −5.53 (s). ^{19}F NMR ($CDCl_3$, 282 MHz): −133.4 (m, 4 F, *o*-F), −156.7 (t, 2 F, $^3J_{FF} = 20$ Hz, *p*-F), 163.4 (m, 4 F, *m*-F). UV−vis (CH_2Cl_2; λ, nm (ε, M^{-1} cm^{-1})): 527 (66 410), 368 (5897), 295 (4017). EI (*m*/*z* (nature of peak, relative intensity)): 600.0 ([M]$^+$, 81), 433.0 ([M − C$_6$F$_5$]$^+$, 100). Anal. Calcd for $C_{29}H_{23}N_2BF_{10}$: C, 58.02; H, 3.86; N, 4.67. Found: C, 58.00; H, 3.91; N, 4.46.

Synthesis of 3-L^H. To a solution of $L^HH\cdot HBr$ (36 mg, 0.12 mmol) in CH_2Cl_2 (10 mL) was added triethylamine (34 μL, 0.24 mmol), and the solution was stirred for 15 min. A solution of $BrB(C_{12}F_8)$ (44 mg, 0.12 mmol) in CH_2Cl_2 (10 mL) was added, and the mixture was stirred for 15 min. Volatiles were removed in vacuo, and the red solution was passed through a plug of silica (toluene/hexanes 3/2), to yield the desired compound (42 mg, 0.075 mmol, 62%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.23 (s, 1 H, H-*meso*), 2.30 (q, 4 H, $^3J_{HH} = 7.5$ Hz, 2-CH_2CH$_3$), 2.26 (s, 6 H, 1-CH$_3$), 1.54 (s, 6 H, 3-CH$_3$), 0.99 (t, 6 H, 2-CH$_2$CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): 153.1 (C3), 135.8 (C1), 132.4 (q), 132.1 (C2), 119.7 (C-*meso*), 17.4 (2-CH_2CH$_3$), 14.6 (2-CH$_2$$CH_3$), 11.9 (3-CH$_3$), 9.5 (1-CH$_3$), pentafluorophenyl carbons were not observed. ^{11}B{^{1}H} NMR ($CDCl_3$, 128 MHz): −2.23 (s). ^{19}F NMR ($CDCl_3$, 282 MHz): −134.3 (m, 2 F, F1), −135.7 (m, 2 F, F4), −155.0 (m, 4 F, F2,3). UV−vis (CH_2Cl_2; λ, nm (ε, M^{-1} cm^{-1})): 527 (29 641), 380 (156), 281 (6396), 236 (7176). CI (*m*/*z* (nature of peak, relative intensity)): 563 ([M + H]$^+$, 100). Anal. Calcd for $C_{29}H_{23}N_2BF_8$: C, 61.94; H, 4.12; N, 4.98. Found: C, 61.84; H, 3.87; N, 4.63.

Synthesis of 1-L^{Me}. To a solution of $L^{Me}H\cdot HCl$ (20 mg, 0.065 mmol) in CH_2Cl_2 (10 mL) was added triethylamine (18 μL, 0.13 mmol) was added, and the solution was stirred for 15 min. A solution of $C_6F_5BF_2$ in CH_2Cl_2 (0.065 mmol) was slowly added with a syringe, and the red solution was stirred for 15 min. Volatiles were removed in vacuo, and the solid was purified by column chromatography on silica (hexanes/toluene, 3/2) to yield the desired compound (19 mg, 0.041 mmol, 62%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.69 (s, 3 H, CH$_3$-*meso*), 2.38 (s, 6 H, 1-CH$_3$), 2.35 (q, 4 H, $^3J_{HH} = 7.3$ Hz, 2-CH_2CH$_3$), 2.21 (s, 6 H, 3-CH$_3$), 1.01 (t, 6 H, 2-CH$_2$CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): 151.5 (C3), 140.3 (C-*meso*), 136.1 (C1), 132.4 (C2), 131.7 (q), 17.1 (CH$_3$-*meso*), 14.9 (2-CH$_2$$CH_3$), 14.5 (2-$CH_2CH_3$ or 1-CH$_3$), 12.2 (2-CH_2CH$_3$ or 1-CH$_3$), 12.1 (3-CH$_3$), pentafluorophenyl carbons were not observed. ^{11}B{^{1}H} NMR ($CDCl_3$, 128 MHz): −0.20 (d, $^1J_{BF} = 63$ Hz). ^{19}F NMR ($CDCl_3$, 282 MHz): −135.7 (m, 2 F, *o*-F), −157.5 (t, 1 F, $^3J_{FF} = 20$ Hz, *p*-F), −162.9 (broad, 1 F, B*F*), −163.9 (m, 2 F, *m*-F). UV−vis (CH_2Cl_2); λ, nm (ε, M^{-1} cm^{-1})): 521 (28 417), 362 (3000), 288 (7667), 265 (1025). ESI$^-$ (*m*/*z* (nature of peak, relative intensity)): 464.57 ([M − H]$^-$, 100), 166.78 ([C$_6$F$_5$]$^-$,

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62). Anal. Calcd for $C_{24}H_{25}N_2BF_6$: C, 61.82; H, 5.40; N, 6.01. Found: C, 61.57; H, 5.47; N, 5.66.

Synthesis of 2-L^{Me}. To a solution of L^{Me}H·HCl (40 mg, 0.13 mmol) in CH_2Cl_2 (15 mL) was added triethylamine (36 μL, 0.26 mmol), and the solution was stirred for 15 min. A solution of $(C_6F_5)_2BCl$ (49 mg, 0.13 mmol) in CH_2Cl_2 (15 mL) was added, and the mixture was stirred for 15 min. Volatiles were removed in vacuo, and the crude solid was purified by column chromatography on silica (hexanes/toluene, 3/2) to yield the desired compound (53 mg, 0.086 mmol, 67%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.61 (s, 3 H, CH_3-*meso*), 2.36 (q, 4 H, $^3J_{HH}$ = 7.6 Hz, 2-CH_2CH$_3$), 2.35 (s, 6 H, 1-CH$_3$), 1.82 (s, 6 H, 3-CH$_3$), 1.00 (t, 6 H, 2-CH$_2$CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): 152.1 (C3), 140.2 (C-*meso*), 136.2 (C1), 132.8 (C1 or q), 132.6 (C1 or q), 18.1 (CH_3-*meso*), 17.4 (2-*C*H$_2$CH$_3$), 14.8 (2-CH$_2$*C*H$_3$), 14.5 (1-CH$_3$), 13.7 (3-CH$_3$), pentafluorophenyl carbons were not observed. ^{11}B{^{1}H} NMR ($CDCl_3$, 128 MHz): −6.00 (s). ^{19}F NMR ($CDCl_3$, 282 MHz): −134.6 (m, 4 F, *o*-F), −156.9 (t, 2 F, $^3J_{FF}$ = 20 Hz, *p*-F), −163.6 (m, 4 F, *m*-F). UV−vis (CH_2Cl_2; λ, nm (ε, M^{-1} cm^{-1})): 523 (25 563), 368 (1625), 304 (5000). ESI$^-$ (*m*/*z* (nature of peak, relative intensity)): 612.92 ([M − H]$^-$, 100), 166.91 ([C_6F_5]$^-$, 33). Anal. Calcd for $C_{30}H_{25}N_2BF_{10}$: C, 58.65; H, 4.10; N, 4.56. Found: C, 58.65; H, 4.15; N, 4.50.

Synthesis of 3-L^{Me}. To a solution of L^{Me}H·HCl (41 mg, 0.13 mmol) in CH_2Cl_2 (15 mL) was added triethylamine (36 μL, 0.26 mmol), and the solution was stirred for 15 min. A solution of $BrB(C_{12}F_8)$ (51 mg, 0.13 mmol) in CH_2Cl_2 (15 mL) was added, and the mixture was stirred for 15 min. Volatiles were removed in vacuo, and the remaining solid was purified by column chromatography on silica (toluene/hexanes, 3:2) to yield the desired compound (12 mg, 0.021 mmol, 16%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.78 (s, 3 H, CH_3-*meso*), 2.42 (s, 6 H, 1-CH$_3$), 2.30 (q, 4 H, $^3J_{HH}$ = 7.5 Hz, 2-CH_2CH$_3$), 1.53 (s, 6 H, 3-CH$_3$), 0.96 (t, 6 H, 2-CH$_2$CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): 150.1 (C3), 140.9 (C-*meso*), 135.4 (C1), 132.8 (C2), 132.2 (q), 17.8 (CH_3-*meso*), 17.3 (2-*C*H$_2$CH$_3$), 14.9 (2-CH$_2$*C*H$_3$ or 1-CH$_3$), 14.8 (2-CH$_2$*C*H$_3$ or 1-CH$_3$), 12.0 (3-CH$_3$), pentafluorophenyl carbons were not observed. ^{11}B{^{1}H} NMR ($CDCl_3$, 128 MHz): −2.51 (s). ^{19}F NMR ($CDCl_3$, 282 MHz): −134.4 (m, 2 F, 1-F), −135.8 (m, 2 F, 4-F), −155.1 (m, 4 F, 2-F and 3-F). UV−vis (CH_2Cl_2; λ, nm (ε, M^{-1} cm^{-1})): 518 (52 885), 368 (4167), 271 (19 551), 233 (32 212). EI (*m*/*z* (nature of peak, relative intensity)): 576.2 ([M]$^+$, 100), 561.2 ([M − CH$_3$]$^+$, 49), 547 ([M − C$_2$H$_5$]$^+$, 36). Anal. Calcd for $C_{30}H_{25}N_2BF_8$: C, 62.52; H, 4.37; N, 4.86. Found: C, 62.35; H, 4.46; N, 4.68.

Generation of 4-L^{H}. 1-L^{H} (13 mg, 0.03 mmol) was loaded in a NMR tube, and a CD_2Cl_2 solution of $[Me_3Si][N(SO_2CF_3)_2]$ (10 mg, 0.03 mmol in 0.4 mL) was added. The tube was capped with a rubber septum, and NMR spectra were acquired. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 7.59 (s, 1H, H-*meso*), 2.41 (q, 4 H, $^3J_{HH}$ = 7.6 Hz, 2-CH_2CH$_3$), 2.38 (s, 6 H, 3-CH$_3$), 2.06 (s, 6 H, 1-CH$_3$), 1.07 (t, 6H, 2-CH$_2$CH_3), 0.22 (d, 9 H, (CH_3)$_3$SiF, $^2J_{SiH}$ = 7.4 Hz). ^{13}C{^{1}H} NMR (CD_2Cl_2, 100 MHz): 158.5 (C3), 138.4 (C2), 135.3 (C1), 122.4 (C-*meso*), 17.8 (2-*C*H$_2$CH$_3$), 14.1 (2-CH$_2$*C*H$_3$), 13.8 (3-CH$_3$), 10.9 (1-CH$_3$), quaternary and pentafluorophenyl carbons were not observed. ^{11}B{^{1}H} NMR (CD_2Cl_2, 128 MHz): 19.1 (broad). ^{19}F NMR (CD_2Cl_2, 376 MHz): −79.3 (6 F, CF_3), −131.5 (broad, 2 F, *o*-F), −149.2 (broad, 1 F, *p*-F), −159.2 (broad, 2 F, *m*-F). EI (*m*/*z* (nature of peak, relative intensity)): 433.25 ([M]$^+$, 100).

Synthesis of 5-L^{H}. To a CH_2Cl_2 solution of **1-L^{H}** (62 mg, 0.14 mmol in 10 mL) was added a solution of $[Me_3Si][N(SO_2CF_3)_2]$ (24 mg, 0.07 mmol) in 5 mL of CH_2Cl_2 dropwise with stirring. The solution immediately turned dark blue and was stirred for a further 15 min. Volatiles were removed in vacuo, and the solid was dried. X-ray-quality crystals were grown from a CH_2Cl_2/hexanes solution to afford **5-L^{H}** as purple crystals (70 mg, 0.06 mmol, 86%). ^{1}H NMR (CD_2Cl_2, 400 MHz, 278 K): δ 7.67 (s, 1H, H-*meso*), 2.39 (q, 4 H, $^3J_{HH}$ = 7.6 Hz, 2-CH_2CH$_3$), 2.39 (s, 6 H, 3-CH$_3$), 2.01, (s, 6 H, 1-CH$_3$), 1.50 (t, 6H, 2-CH$_2$CH_3). ^{13}C{^{1}H} NMR (CD_2Cl_2, 100 MHz): 155.8 (C3), 134.4 (C1), 134.0 (q), 121.8 (C2), 118.6 (C-*meso*), 17.8 (2-*C*H$_2$CH$_3$), 14.4 (2-CH$_2$*C*H$_3$), 13.6 (3-CH$_3$), 10.2 (1-CH$_3$), pentafluorophenyl carbons were not observed. ^{11}B{^{1}H} NMR (CD_2Cl_2, 128 MHz, 278 K): 24.33 (broad). ^{19}F NMR (CD_2Cl_2, 282 MHz): −79.2 (6 F, CF_3), −130.3 (broad, *o*-F), −147.2 (broad, *p*-F), −157.8 (broad, *m*-F), the bridging F was not observed.

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Supporting Information Available: CIF files giving crystallographic data for compounds **1-L^{Bu}**, **1-L^{H}**, **2-L^{H}**, **3-L^{H}**, **1-L^{Me}**, **2-L^{Me}**, **3-L^{Me}**, and **5-L^{H}** and figures giving excitation and emission spectra for compounds **1-L$^{H/Me}$**−**3-L$^{H/Me}$**. This material is available free of charge via the Internet at http://pubs.acs.org.