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Boron-Dipyrromethene-Functionalized Hemilabile Ligands as "Turn-On" Fluorescent Probes for Coordination Changes in Weak-Link Approach Complexes

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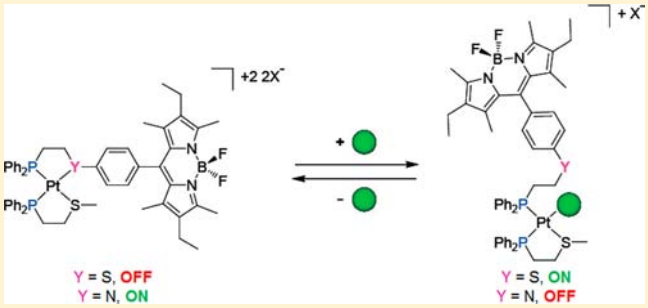
Supporting Information

ABSTRACT: Herein we report a new class of hemilabile ligands with boron-dipyrromethene (Bodipy) fluorophores that, when complexed to Pt(II), can signal changes in coordination mode through changes in their fluorescence. The ligands consist of phosphino-amine or phosphino-thioether coordinating moieties linked to the Bodipy's meso carbon via a phenylene spacer. Interestingly, this new class of ligands can be used to signal both ligand displacement and chelation reactions in a fluorescence "turn-on" fashion through the choice of weakly binding heteroatom in the hemilabile moiety, generating up to 10-fold fluorescence intensity increases. The Pt(II) center influences the Bodipy emission efficiency by regulating photoinduced electron transfer between the fluorophore and its meso substituent. The rates at which the excited Bodipy-species generate singlet oxygen upon excitation suggest that the heavy Pt(II) center also influences Bodipy's emission efficiency by affecting intersystem crossing from the Bodipy excited singlet to excited triplet states. This signaling strategy provides a quantitative read-out for changes in coordination mode and potentially will enable the design of new molecular systems for sensing and signal amplification.



INTRODUCTION

The weak-link approach (WLA) is a coordination-chemistry-based strategy for the synthesis of supramolecular structures that can be reversibly toggled between different geometries via ligand displacement reactions at transition metal structural regulatory sites using small molecule analytes.[1−3] Through the synthetic incorporation of catalysts whose activities depend on their position and orientation within these frameworks, the WLA has been employed to regulate various catalytic properties, including turnover rate and enantioselectivity.[4,5] This kind of control over a catalyst offers potential for sensing and signal amplification applications since the coordination of an analyte can result in an output that is amplified by the catalyst in an ELISA-[6] or PCR-like fashion.[7] In these systems, sensing and signal amplification are possible since the sensing analytes produce changes in coordination mode of the WLA complexes that significantly affect their functionality.

A useful strategy to signal structural changes[8−15] and binding events[16−24] in functional molecular and supramolecular systems is to incorporate fluorescent signaling units, due to the sensitivity of the fluorescence output and the number of ways these outputs can be analyzed (e.g., changes in spectral features, emission intensity, fluorescence lifetimes, and fluorescence anisotropy). Herein we explore a new strategy of incorporating boron-dipyrromethene (Bodipy) fluorophores into hemilabile ligands for the signaling of coordination changes in WLA complexes (Scheme 1). When complexed to Pt(II), these novel ligands create active structures that can be toggled with small molecules or elemental anions between significantly different fluorescent states and therefore represent new synthons for the WLA that can be utilized, in principle, for both stoichiometric and catalytically amplified sensing strategies. Bodipy was chosen because its high molar absorption coefficient and fluorescence quantum yield, and the variety of approaches to modulate the latter make it an appealing signaling unit.[25−29] In particular, Bodipy has been used for the construction of a wide variety of fluorescence switches since photoinduced electron transfer (PeT) between the fluorophore and its meso substituent can be regulated deliberately via coordination chemistry to either enhance or quench its fluorescence.[30−32] In the case of Pt(II) complexes, we show that displacement of the Pt−S bond in a phosphino-thioether (P,S) hemilabile moiety attached to the Bodipy meso carbon via a phenylene spacer (eq 1, Scheme 1) impedes PeT, and a fluorescence "turn-on" signal ensues. Similarly, "turn-on" fluorescence signaling of the opposite coordination event, ligand chelation, is possible by utilizing phosphino-amine (P,N) hemilabile moieties in place of P,S (eq

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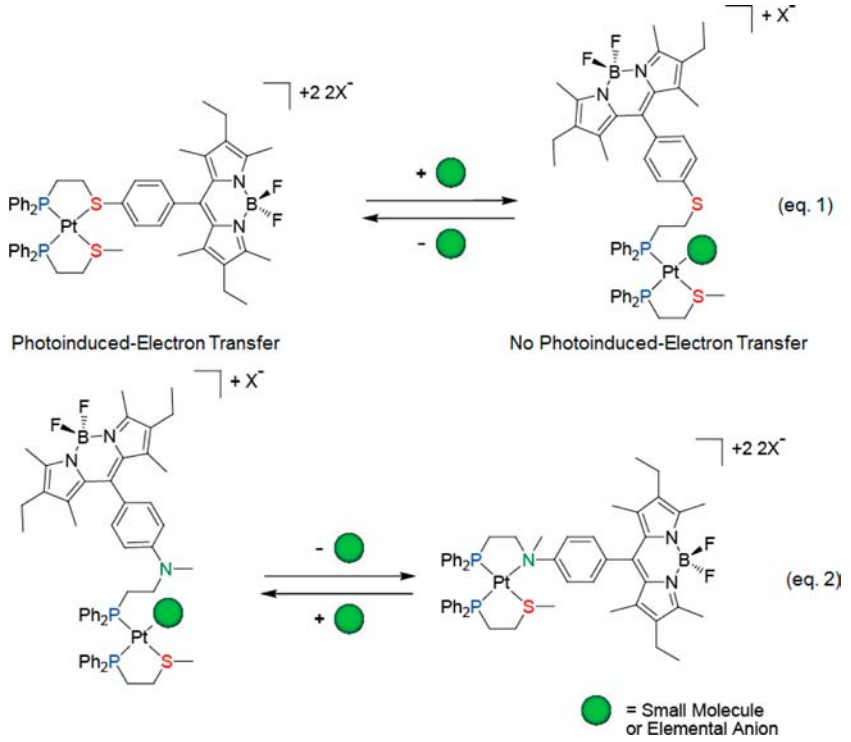
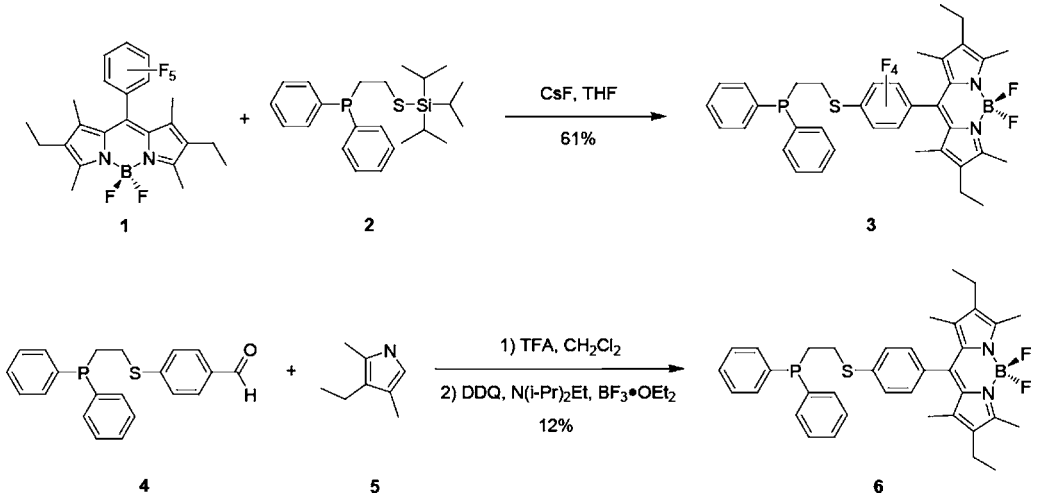
Scheme 1. Novel Bodipy-Functionalized Hemilabile Ligands Can Be Used for Signaling Changes in Coordination Mode via Variations in the Bodipy Fluorescence Emission[a]



[a]Both ligand displacement (eq 1) and chelation (eq 2) reactions can be signaled in a fluorescence "turn-on" fashion through the choice of heteroatom (S or N) in the hemilabile moiety.

Scheme 2. Synthesis of P,S-Bodipy Ligands 3 and 6



2, Scheme 1). In all examples studied, the Pt(II) structural regulatory site directly affects the photophysics of Bodipy by interacting with the meso substituent, thus establishing a quantifiable signaling methodology for coordination changes. In addition, all data suggest that the Pt(II) center may further modulate the fluorescence emission efficiency of Bodipy via the heavy atom effect (HAE),[33,34] since coordination changes vary the distance between the fluorophore and the metal cation. By exploring the fluorescence signaling of coordination changes in model WLA coordination complexes, we establish a general Bodipy-containing hemilabile ligand class that can be incorporated into supramolecular WLA systems and potentially used for sensing and signal amplification applications.

RESULTS AND DISCUSSION

Synthesis. In order to access "turn-on" fluorescence signaling of both ligand chelation and partial displacement reactions, we synthesized a set of novel Bodipy-containing hemilabile ligands in which the nature and electron donating abilities of the weakly coordinating heteroatom in the hemilabile moiety are varied (Schemes 2 and 3).

P,S-Bodipy ligands **3** and **6**, which differ in the electron donating ability of the sulfur based on the presence of electron

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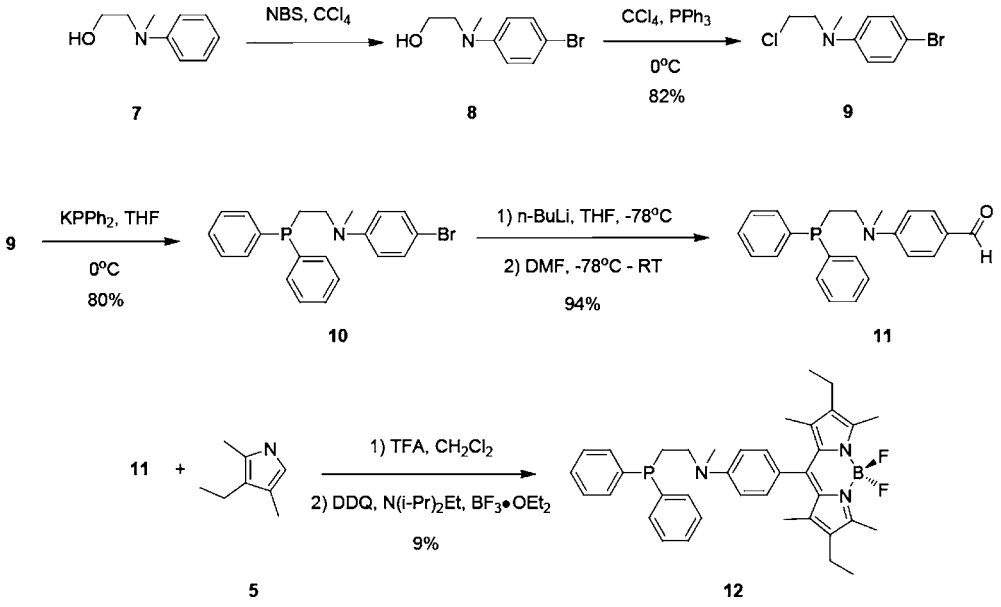
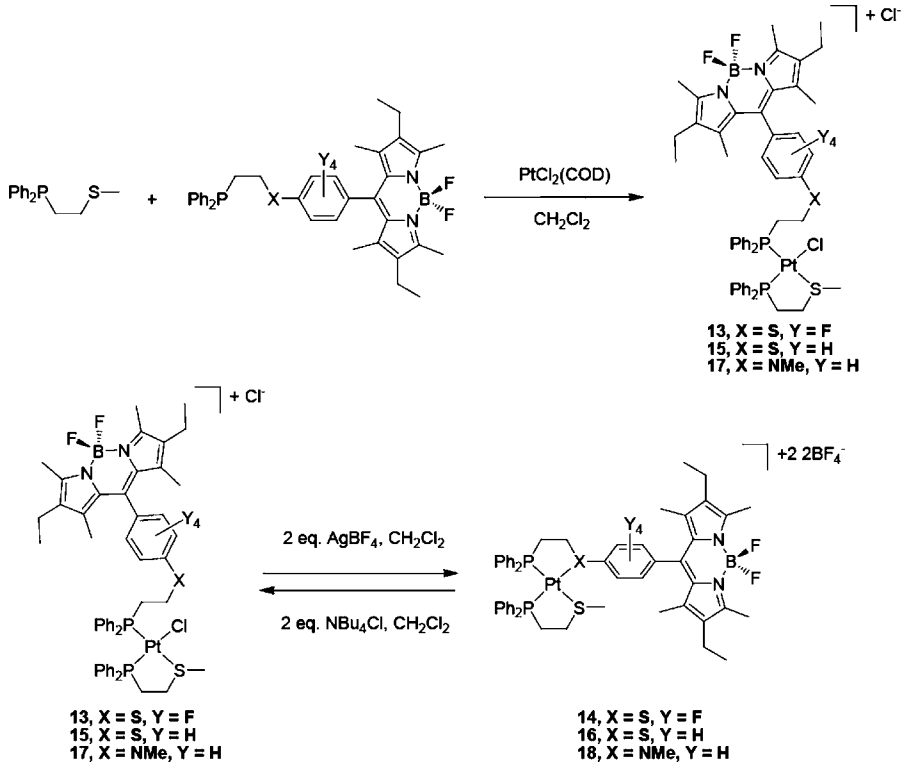
Scheme 3. Synthesis of P,N-Bodipy Ligand 12



Scheme 4. Formation of Heteroligated Pt(II) Complexes and Reversible Toggling Between Semiopen (Bottom Left) and Closed (Bottom Right) Coordination Modes



withdrawing fluorine atoms on the meso phenyl ring, were synthesized via two different approaches (Scheme 2). Ligand **3** was obtained via nucleophilic aromatic substitution of the para fluorine in compound **1** by a thiomethoxide nucleophile generated *in situ* upon deprotection of **2** in tetrahydrofuran (THF).[35] P,S-Bodipy ligand **6**, on the other hand, was obtained in a one pot reaction starting with benzaldehyde **4** and a sequence of steps involving an acidic Knoevenagel condensation with cryptopyrrole **5** catalyzed by trifluoroacetic acid (TFA),[36] oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), and treatment with N(*i*-Pr)$_2$Et and excess BF_3·OEt_2. Ligands **3** and **6** were isolated after purification as analytically pure substances, which exhibit diagnostic $^{31}P\{^1H\}$ NMR resonances at δ −16.6 and δ −16.7, respectively.

The synthesis of P,N-Bodipy ligand **12** involves five synthetic steps from commercially available 2-(methylanilino)ethanol **7** in 5.5% overall yield (Scheme 3). First, electrophilic bromination of the aromatic ring in amine **7** with *N*-bromosuccinimide (NBS) provided **8**. Next, the chloride derivative **9** was obtained via the Appel reaction, and the S_N2

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reaction of **9** with potassium diphenylphosphide yielded **10**. The installation of a formyl unit to give **11** was accomplished via lithium-halogen exchange with n-butyl lithium (*n*-BuLi) followed by treatment with *N*,*N*-dimethylformamide (DMF). Finally, the target P,N-Bodipy **12** was obtained via reaction of **11** with cryptopyrrole **5** under similar conditions used to generate P,S-Bodipy **6**. Ligand **12** was isolated as an analytically pure solid after recrystallization of the crude product mixture from a 1:1 mixture of CH_2Cl_2/hexanes ($^{31}P\{^1H\}$ NMR signal: δ −20.5).

Bodipy-containing ligands were incorporated into model WLA complexes that also contain a nonfunctionalized P,S ligand to highlight the potential to integrate other functional moieties relevant for sensing and signal amplification into the system studied herein. Note that although 2-(diphenylphosphino)ethyl-methyl-thioether (P,S-Me) is used as a proof-of-concept example, in our previous work, we have shown that this ligand can be replaced with a wide variety of isoelectronic structures that have pendant groups consisting of recognition (i.e., hydrogen-bonding groups)[4] and catalytic moieties (i.e., metallosalens, metalloporphyrins).[2] The generation of Pt(II) semiopen complexes **13**, **15**, and **17** was accomplished via sequential addition of P,S-Me and the appropriate Bodipy-containing ligand to a dichloromethane solution of dichloro(1,4-cyclooctadiene)platinum(II) (Scheme 4). In all cases, this resulted in the formation of monocationic complexes in which P,S-Me is chelated to the metal center, and the Bodipy-functionalized ligand is coordinated through the phosphorus only. In the case of complexes containing P,S-Bodipy ligands, the formation of semiopen complexes **13** and **15** was confirmed by the two characteristic set of $^{31}P\{^1H\}$ NMR resonances arising from the coordination of chelated P,S-Me (**13**, δ 43.1, J_{P-P} = 14 Hz, J_{P-Pt} = 3478 Hz; **15**, δ 43.6, J_{P-P} = 14 Hz, J_{P-Pt} = 3515 Hz) and P-bound P,S-Bodipy ligands (**13**, δ 8.9, J_{P-P} = 13 Hz, δ 9.0, J_{P-Pt} = 3199 Hz; **15**, J_{P-P} = 13 Hz, J_{P-Pt} = 3168 Hz).[37] In the case of semiopen complex **17** containing P,N-Bodipy ligand **12**, the $^{31}P\{^1H\}$ NMR spectrum shows two sets of resonances centered at δ 43.8 (J_{P-P} = 15 Hz, J_{P-Pt} = 3515 Hz) and 6.6 (J_{P-P} = 13 Hz, J_{P-Pt} = 3141 Hz), consistent with a chelated P,S-Me ligand and P-bound P,N-Bodipy ligand.[37]

The semiopen complexes were quantitatively converted to their closed forms via chloride abstraction with 2 equiv of $AgBF_4$ in dichloromethane. The chelation of the P,S-Bodipy ligands in complexes **14** and **16** was confirmed by the two characteristic sets of signals in their $^{31}P\{^1H\}$ NMR (**14**, δ 46.6, J_{P-P} = 13 Hz, J_{P-Pt} = 3093 Hz and δ 46.2, J_{P-P} = 13 Hz, J_{P-Pt} = 3290 Hz; **16**, δ 46.3 J_{P-P} = 13 Hz, J_{P-Pt} = 3165 Hz and δ 45.8 J_{P-P} = 13 Hz, J_{P-Pt} = 3100 Hz), indicative of two nonequivalent, chelated phosphine ligands. Similarly, chelation of P,N-Bodipy ligand to give closed complex **18** was confirmed by $^{31}P\{^1H\}$ NMR resonances at δ 37.9 (J_{P-P} = 16 Hz, J_{P-Pt} = 3397 Hz) and 31.0 (J_{P-P} = 15 Hz, J_{P-Pt} = 3183 Hz), which are highly diagnostic of two chelated phosphines trans to sulfur and nitrogen moieties, respectively.[37] Complexes **13**−**18** were also characterized by ^1H, $^{11}B\{^1H\}$, ^{19}F NMR spectroscopy and mass spectrometry (see Experimental Section). Closed complexes **14**, **16**, and **18** can be quantitatively converted back to their semiopen forms, **13**, **15**, and **17**, respectively, via addition of 2 equiv of tetrabutylammonium chloride in CH_2Cl_2, highlighting the ability of the complexes to toggle reversibly between the semiopen and closed coordination modes.

Structures of Complexes 13 and 14. Single crystals of compounds **13** and **14** suitable for X-ray analysis were grown by slow diffusion of pentane into CH_2Cl_2 solutions of the respective complexes (Figure 1). The solid-state structures are

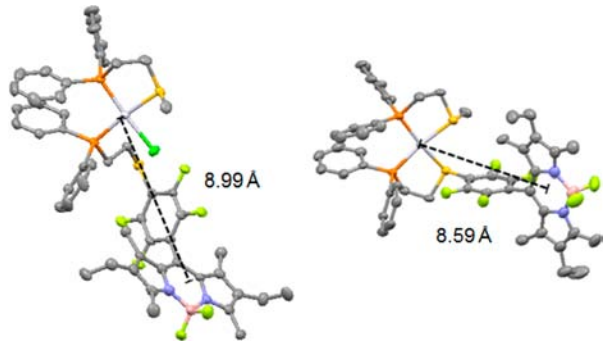

Figure 1. Crystal structures of **13** (left) and **14** (right) drawn with 50% thermal ellipsoid probability. The distances between the center of the Bodipy moiety and the Pt(II) center were measured from the crystal structures. Hydrogen atoms and counterions were omitted for clarity.

consistent with the assignments of the structures in solution, displaying Pt(II) square planar centers with phosphine ligands coordinated in a cis-fashion in both **13** and **14**. In the case of **13**, P,S-Bodipy ligand **3** is coordinated to the Pt(II) center through the phosphorus only, displaying a Pt−P bond length of 2.279 Å. The distance between the metal center and the center of the Bodipy moiety is 8.99 Å, and the angle between the Bodipy plane and the plane of the meso phenyl ring is 83.02°. In the case of closed complex **14**, P,S-Bodipy **3** is chelated to the Pt(II) center with a bite angle of 85.19° and the Pt−P and Pt−S bond lengths are 2.278 and 2.354 Å, respectively. The angle between the planes of the Bodipy and the meso phenyl ring is slightly lower (83.15°) compared to that observed in **13**, demonstrating that changes in coordination mode at the Pt(II) center do not appreciably change geometric factors of the dye that affect its photophysics.[38] However, the distance between the center of the Bodipy moiety and the heavy Pt(II) center in **14** is lowered by 0.4 to 8.6 Å, relative to **13**. The degree of spin−orbit coupling facilitated by the heavy atom center is highly distance dependent,[33,34] and thus, the variation in Bodipy-Pt(II) distances upon changes in coordination mode can affect the Bodipy fluorescence efficiency through intersystem crossing in addition to PeT. Even though the distances in solution may be different from those observed in the solid state, the structures in Figure 1 highlight that changes in the degree of intersystem crossing may also play a role in the differences in quantum yield between semiopen and closed complexes.

Fluorescence Efficiency Regulation. The steady-state luminescence properties of the novel Bodipy-functionalized hemilabile ligands **3**, **6**, and **12**, and their respective Pt(II) complexes, were measured in dichloromethane (Table 1).[39] P,S-Bodipy ligands **3** and **6** display steady-state quantum yields of 91% and 84%, respectively, which are within the same magnitude of reported values for phenyl (77% in acetonitrile) and tetrafluorophenyl (99% in acetone) meso-substituted Bodipys.[40,41] These results confirm that substitution of Bodipy in the meso position with P,S hemilabile moieties does not enable significant PeT between the Bodipy excited state and the meso substituent in the free ligands. Conversely, the presence

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Table 1. Spectral Parameters and Quantum Yields for Bodipy-Containing Hemilabile Ligands and their Respective Pt(II) Complexes[a]

compd	λ_{abs} (max/nm)	λ_{abs} (max/nm)	$\Delta\lambda$ (nm)	ϕ_f
3	544	558	14	0.91
13	540	556	16	0.76
14	547	561	14	0.16
6	527	541	14	0.83
15	527	541	14	0.64
16	277	541	14	0.15
12	525	541	16	0.066
17	525	544	19	0.031
18	525	543	18	0.32

[a]Fluorescence quantum yields for **3**, **13**, and **14** were calculated in DCM at room temperature using sulforhodamine B in ethanol as a standard (λ_{ex} = 505 nm). For all other compounds, rhodamine 6G in ethanol at room temperature was used as a standard (λ_{ex} = 505 nm).

of an aniline moiety on the meso position in **12** results in a Bodipy species with a much lower quantum yield (6.6%). As expected on the basis of literature precedent, PeT from the electron rich aniline substituent to the excited Bodipy efficiently quenches the fluorophore's luminescence.[42,43]

The fluorescence of P,S- and P,N-Bodipy ligands was similarly measured after the ligands were incorporated into semiopen and closed Pt(II) complexes (**13**–**18**). When incorporated into semiopen complexes, the quantum yields of P,S-Bodipy **3** and **6** decrease to 76% in **13** and 64% in **15**, respectively, with minimal absorbance profile changes (see SI). However, a more dramatic reduction of quantum yields was observed upon formation of closed complexes **14** and **16**. Complex **14** displays a fluorescence quantum yield of 16%, and **16** displays a similar steady-state emission efficiency of 15%. Therefore, the P,S-Bodipy ligands exhibit "turn-on" florescence behavior upon substitution-induced breaking of the Pt–S bond.

In the case of P,N-Bodipy ligand **12**, incorporation into semiopen Pt(II) complex **17** also results in a moderate decrease of the fluorophore's quantum yield to 3.1%. However, formation of closed complex **18** results in a fluorescence quantum yield of 32%, a 10-fold increase relative to semiopen complex **17**. The lack of profile changes observed in the emission and absorbance spectra of P,N-Bodipy and its Pt(II) complexes indicates that the Bodipy moieties in **12**, **17**, and **18** fluoresce from their locally excited singlet state, and that there are no emissive charge transfer decay pathways (see SI).[31] We can thus ascribe the changes in fluorescence quantum yield to the stabilization of meso centered orbitals via chelation to Pt(II), which makes reductive PeT decay less favorable, as observed in the majority of aniline substituted Bodipy transition metal sensors.[25,31] This is further supported by the fact that the nature of the fluorescence switch can be reversed by simply reducing the electron density on the meso phenyl ring upon exchanging the N moiety for an S group. It is thus likely that coordination through the sulfur in complexes **14** and **16** lowers the energy of meso-centered orbitals to the extent that oxidative PeT effectively diminishes the fluorescence quantum yield (see Computational Section, SI). Hence, P,S or P,N-Bodipy ligands can be used to create complexes that signal ligand displacement or ligand chelation reactions, respectively, both in a fluorescence "turn-on" fashion. In all cases, the Pt(II) center directly affects the interaction between the fluorophores and their meso substituents via changes in coordination mode of the hemilabile ligands. Thus, inclusion of Bodipy in WLA

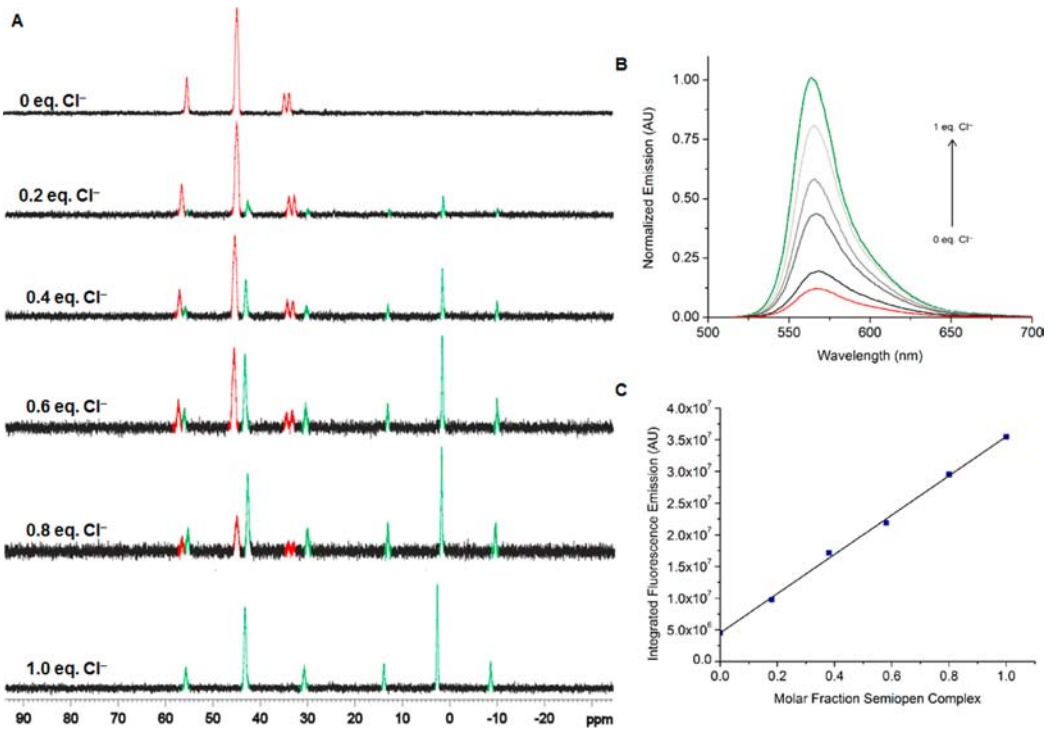

Figure 2. Addition of tetrabutylammonium chloride to **14** results in quantitative formation of **13**. (A) ^{31}P NMR spectroscopy shows structural changes arising from toggling from closed complex **14** (red) to semiopen complex **13** (green). (B) Fluorescence emission from the mixture increases upon addition of chloride up to 1 equiv. (C) Correlation between molar fractions of semiopen complex determined by NMR spectroscopy and integrated fluorescence shows a linear relationship between the two variables.

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systems provides a fluorescence output that is directly generated by the structural regulatory site, and that can be toggled between florescence "turn-on" or "turn-on" upon chelation to Pt(II) simply through the choice of weakly binding heteroatom.

Quantitative Signaling of Coordination Changes. To enable the use of Bodipy as a signaling unit for coordination changes in functional WLA systems, it is paramount to establish the ability of hemilabile Bodipy ligands to signal these changes in a quantitative fashion. Toward this end, we studied a system in which the effector for the coordination changes interacts directly with the structural regulatory metal center (Figure 2 and Scheme 4). In particular, coordination changes were effected as tetrabutylammonium chloride was added into closed complex **14** in dichloromethane, and the reaction mixture was monitored spectroscopically. Variations in fluorescence signals throughout the titration were correlated with the ^{31}P NMR spectrum of the mixture since this characterization technique has been used previously to quantitatively track coordination mode changes in WLA systems.[37,44] While the Bodipy absorbance centered at 544 nm only shifts slightly as **14** is converted to **13**, the integration of the Bodipy emission profile is directly proportional to the fraction of semiopen complex present as determined by ^{31}P NMR spectroscopy (Figure 2). Therefore, changes in fluorescence emission provide a quantitative read-out for determining the fraction of semiopen complex in a given sample.

Role of Heavy Atom Effect. Several studies have been carried out in which heavy atoms, such as chalcogens[45] and halides,[46] are placed at different positions around and in proximity to the Bodipy core to populate its excited triplet state. This has also been shown in molecular arrays in which the Bodipy excited states interact with a transition metal coordination complex leading to the population of excited triplet states.[47,48] Among other factors, the degree of spin−orbit coupling is dependent on the distance between the fluorophore and the heavy atom. As shown in Figure 1, a variation in distance between Bodipy and the heavy Pt(II) is observed in the solid state structures of **13** and **14**. In addition, all of the semiopen complexes in this study display lower quantum yields than their corresponding free ligands in solution (see Table 1). These observations suggest that the modulation of PeT processes might not be the only way in which the model WLA fluorescence switches operate, but intersystem crossing into triplet excited states may also diminish emission from the Bodipy excited singlet state.[49]

The presence of nonemissive excited triplet states can be detected indirectly though their ability to generate singlet oxygen, which in turn can degrade a variety of organic substrates.[50,51] We thus assessed the changes in the degree of intersystem crossing based on coordination mode by exciting an oxide-protected version of ligand **3** (**3′**), semiopen complex **13**, and closed complex **14**, and observing the effect excitation has on the oxidation of diphenylbenzofuran (DPBF) by reactive oxygen species.[51] In particular, the photoactivated degradation of DPBF was tracked by observing the disappearance of the characteristic band centered at 414 nm in its absorbance profile upon excitation of the Bodipy species at 545 nm.[51] As shown in Figure 3, we were able to observe a 1.2-fold oxidation rate increase upon excitation of semiopen complex **13** relative to the oxygen-protected ligand **3′**. Furthermore, the relative rate of oxidation is increased by 1.7-fold when the Bodipy in closed complex **14** is excited. The changes in catalytic degradation rates thus suggest that intersystem crossing to a triplet manifold upon irradiation is increased by the proximity to the Pt(II) heavy atom. Therefore, the 4.5-fold fluorescence decrease in **14** relative to **13** is likely the combined result of the excited singlet state of Bodipy undergoing PeT to the meso substituent and intersystem crossing to an excited triplet state, two pathways which are enabled by the Pt(II) structural regulatory center.

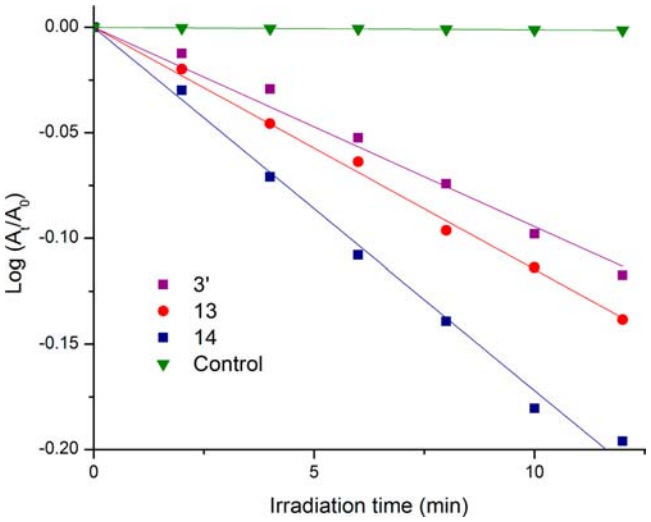

Figure 3. Variation in DPBF absorbance at 414 nm upon excitation at 545 nm in 90 × 10^{-5} M solutions with 5 × 10^{-5} M oxidized ligand **3′** (purple squares), semiopen complex **13** (red circles), closed complex **14** (blue squares), and no Bodipy species (green triangles). Absorbance values were normalized to 1 using the initial value prior to irradiation.

CONCLUSION

A new class of Bodipy-functionalized hemilabile ligands has been developed in which the nature of the weakly coordinating heteroatom is deliberately varied to allow for fluorescence "turn-on" signaling of both ligand chelation and partial displacement reactions. The ligands display high quantum yields, even when in physical proximity to heavy Pt(II) centers, and the changes in emission intensity upon coordination changes are greater than those observed for other fluorophores previously studied in the context of WLA complexes, such as anthracene and pyrene.[52,53] This new class of Bodipy-functionalized ligands will allow for fluorescence signaling in a broader array of sensing strategies amenable to the WLA. For instance, P,S-Bodipy ligands can be used to signal the binding of small molecule analytes that displace the Pt−S bond upon coordination to WLA complexes. Conversely, P,N-Bodipy ligands can be employed to signal recognition events that result in the displacement of a receptor ligand by the Bodipy-functionalized chelating moiety. Further, since the coordination changes studied herein also result in variations in the degree of intersystem crossing from the Bodipy excited singlet state, this study offers the potential to utilize WLA constructs as triplet sensitizers switches for photo-oxidation processes relevant to the production of small molecules and photodynamic therapy.

EXPERIMENTAL SECTION

General Methods. Phosphino-heteroatom ligands were prepared and stored using standard Schlenk techniques under an inert nitrogen atmosphere, unless noted otherwise. The synthesis of Pt(II) complexes and their manipulations and characterization were performed under

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ambient conditions. All solvents used for synthesis and physical measurements were purchased as HPLC grade and thoroughly degassed with a stream of argon gas prior to use. HPLC grade dichloromethane used for photodegradation measurements of diphenylbenzofuran was not degassed. Deuterated solvents were purchased from Cambridge Isotope Laboratories and were degassed with a stream of argon prior to usage. Freshly distilled pyrrole was used for the synthesis of all Bodipy species, and $N(i\text{-}Pr)_2Et$ amine was distilled over potassium hydroxide prior to use. Dichloro(1,4-cyclooctadiene)platinum(II) was purchased from Strem Chemicals Inc. and was used as received. All other chemicals were used as received from Aldrich Chemical Co.

All NMR spectra were recorded on a Bruker Avance 400 MHz. ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to residual proton and carbon resonances in the deuterated solvents. $^{11}B\{^1H\}$ NMR spectra were referenced to neat $BF_3{\cdot}OEt_2$. $^{19}F\{^1H\}$ NMR spectra were referenced to $CFCl_3$ in $CDCl_3$. ^{31}P /$^{31}P\{^1H\}$ NMR spectra were referenced to an 85% H_3PO_4 aqueous solution. All chemical shifts are reported in ppm.

UV−vis absorption measurements were performed in a Varian Cary 50 Bio spectrophotometer utilizing 10 mm cell-path quartz cuvettes (VWR). Fluorescence measurements and photoexcitation experiment were performed with a Horiba Jovin-Yvonne Fluorolog fluorimeter. Quantum yield values were determined from the comparative method using sulforhodamine B or rhodamine 6G in ethanol as standards. Each quantum yield value was derived from the least-squares fit of a fluorescence emission versus concentration curve using seven dilutions yielding r^2 values of 0.99. Photoexcitation experiments were performed under constant stirring and power outputs of 0.2 mW. Electrospray ionization mass spectra (ESI-MS) were recorded on a Micromas Quatro II triple quadrapole mass spectrometer.

Synthesis. *P,S-Bodipy (**3**).* Pentafluorophenyl Bodipy **1**[41] (3.85 g, 8.19 mmol) and P,S-TIPS **2** (3.29 g, 8.19 mmol) were dissolved in THF (40 mL), and cesium fluoride was added (3.80 g, 25.0 mmol). After stirring for 20 h at room temperature, the mixture was washed with water, and extracted with CH_2Cl_2 (2 × 100 mL). Drying under $MgSO_4$ and solvent evaporation yielded a dark red oil. Silica-gel column chromatography (9:1 v/v, petroleum ether/ethyl acetate as eluent) afforded the product as a red solid with a green-golden luster (3.48 g, 61% yield). ^1H NMR (400.16 MHz, 25 °C, CD_2Cl_2): δ 7.38 (m, 10H), 3.11 (m, 2H), 2.51 (s, 6H), 2.34 (q, J_{H-H} = 8 Hz, 4H), 2.32 (m, 2H), 1.46 (s, 6H), 1.01 (t, J_{H-H} = 8 Hz, 6H). $^{13}C\{^1H\}$ NMR (100.63 MHz, 25 °C, CD_2Cl_2): δ 156.0 (s), 148.7 (d, J_{C-F} = 14 Hz), 146.2 (d, J_{C-F} = 14 Hz), 145.0 (d, J_{C-P} = 16 Hz), 142.7 (d, J_{C-F} = 33 Hz), 137.3 (d, J_{C-P} = 11 Hz), 136.9 (s), 134.0 (s), 132.5 (d, J_{C-P} = 19 Hz), 130.0 (s), 128.9 (s), 128.6 (d, J_{C-P} = 7 Hz), 122.0 (s), 31.1 (d, J_{C-P} = 25 Hz), 28.9 (d, J_{C-P} = 16 Hz), 16.9 (s), 14.2 (s), 12.4 (s), 10.6 (s). $^{31}P\{^1H\}$ NMR (161.98 MHz, 25 °C, CD_2Cl_2): δ −16.6 (s). ^{19}F NMR (376.49 MHz, 25 °C, CD_2Cl_2): δ −133.0 (q, J_{F-F} = 11 Hz, 2F), −141.3 (q, J_{F-F} = 11 Hz, 2F), −146.2 (q, J_{F-B} = 33 Hz, 2F). $^{11}B\{^1H\}$ NMR (128.38 MHz, 25 °C, CD_2Cl_2): δ −0.05 (t, J_{B-F} = 33 Hz). ESIMS (m/z): Calcd 697 $[M]^+$. Found 697.

*P(O),S-Bodipy (**3′**).* Ligand **3** (25.0 mg, 0.0359 mmol) was dissolved in CH_2Cl_2 (4 mL), and the solution was stirred while exposed to air under illumination from a UV lamp (λ = 360 nm, 0.16 W) for 12 h. The solution volume was then reduced to 1 mL, and pentane was added to precipitate the oxide. The product was then isolated as a red solid with a green-golden luster via vacuum filtration (21.0 mg, 82%). ^1H NMR (400.16 MHz, 25 °C, CD_2Cl_2): δ 7.45−7.82 (m, 10H), 3.25 (m, 2H), 2.54 (m, 2H), 2.51 (s, 6H), 2.34 (q, J_{H-H} = 8 Hz, 4H), 1.48 (s, 6H), 1.01 (t, J_{H-H} = 8 Hz, 6H). $^{13}C\{^1H\}$ NMR (100.63 MHz, 25 °C, CD_2Cl_2): δ 156.6 (s), 137.2 (d, J_{C-F} = 15 Hz), 134.6 (d, J_{C-P} = 23 Hz), 133.3 (s), 132.8 (s), 132.6 (s), 132.5 (s), 132.3 (s), 131.2 (d, J_{C-P} = 11 Hz), 131.0 (d, J_{C-P} = 9 Hz), 129.5 (s), 129.3 (d, J_{C-P} = 12 Hz), 115.7 (s), 31.4 (d, J_{C-P} = 66 Hz), 27,8 (s), 17.4 (s), 14.7 (s), 12.9 (s), 11.1 (s). $^{31}P\{^1H\}$ NMR (161.98 MHz, 25 °C, CD_2Cl_2): δ 28.9 (s). ^{19}F NMR (376.49 MHz, 25 °C, CD_2Cl_2): δ −133.2 (q, J_{F-F} = 11 Hz, 2F), −141.3 (q, J_{F-F} = 11 Hz, 2F), −145.9 (q, J_{F-B} = 33 Hz, 2F). $^{11}B\{^1H\}$ NMR (128.38 MHz, 25 °C, CD_2Cl_2): δ −0.05 (t, J_{B-F} = 33 Hz). ESIMS (m/z): Calcd 713 $[M]^+$. Found 713.

*P,S-Bodipy (**6**).* Benzaldehyde **4** (2.00 g, 5.71 mmol) and pyrrole **5** (1.46 g, 12.0 mmol) were dissolved in CH_2Cl_2 (600 mL), and trifluoroacetic acid was added (800 μL). After stirring at room temperature for 1.5 h, DDQ (1.30 g, 5.71 mmol) was slowly added as a powder under a stream of nitrogen, and the mixture was stirred for another 45 min. $N(i\text{-}Pr)_2Et$ (6.00 mL, 34.3 mmol) was added dropwise, and after 5 min $BF_3{\cdot}OEt_2$ (5.65 mL, 45.7 mmol) was slowly added. After 1 h the mixture was filtered through a pad of silica, washed with water, and dried under $MgSO_4$. Solvent evaporation *in vacuo* yielded a dark red oil. Silica-gel column chromatography (9:1 v/v, petroleum ether/ethyl acetate as eluent) afforded the product as a red solid with a green luster (428 mg, 12% yield). ^1H NMR (400.16 MHz, 25 °C, CD_2Cl_2): δ 7.80−7.30 (m, 12H), 7.01 (d, J_{H-H} = 8 Hz, 2H), 3.05 (m, 2H), 2.50 (s, 6H), 2.37 (m, 2H), 2.32 (q, J_{H-H} = 8 Hz, 4H), 1.32 (s, 6H), 1.00 (t, J_{H-H} = 8 Hz, 6H). $^{13}C\{^1H\}$ NMR (100.63 MHz, 25 °C, CD_2Cl_2): δ 153.7 (s), 139.7 (s), 138.43 (s), 137.9 (d, J_{C-P} = 14 Hz), 137.1 (s), 133.3 (s), 133.0 (s), 132.6 (d, J_{C-P} = 18 Hz), 130.7 (s), 129.6 (s), 128.9 (s), 128.8 (s), 128.5 (d, J_{C-P} = 7 Hz), 29.9 (d, J_{C-P} = 23 Hz), 28.0 (d, J_{C-P} = 16 Hz), 16.9 (s), 14.3 (s), 12.2 (s), 11.6(s). $^{31}P\{^1H\}$ NMR (161.98 MHz, 25 °C, CD_2Cl_2): δ −16.7 (s). ^{19}F NMR (376.49 MHz, 25 °C, CD_2Cl_2): δ −146.2 (q, J_{F-B} = 33 Hz). $^{11}B\{^1H\}$ NMR (128.38 MHz, 25 °C, CD_2Cl_2): δ 0.14 (t, J_{B-F} = 33 Hz). ESIMS (m/z): Calcd 625 $[M]^+$. Found 625.

*N-(4-Bromophenyl)-N-(2-chloro)-N-methylamine (**9**).* To a 2-(methylanilino)ethanol (7.04 g, 46.6 mmol) solution in CCl_4 (60 mL) was added N-bromosuccinimide (8.29 g, 46.6 mmol) as a powder at 0 °C while stirring vigorously. After stirring overnight at room temperature, the mixture was filtered and passed through a pad of silica using CH_2Cl_2 as eluent. The resulting yellow solution of amine **8** was shown to be pure by TLC and was used for the subsequent reaction without further purification. To the solution of amine **8** in CCl_4/CH_2Cl_2 (100 mL) were added triphenylphosphine (12.2 g, 46.6 mmol) and molecular sieves at 0 °C. After stirring overnight at room temperature, the mixture was filtered, washed with water, and extracted with CH_2Cl_2. The solution was dried under $MgSO_4$, and the solvent was removed *in vacuo*. The crude oil was dissolved in a minimal amount of CH_2Cl_2 and passed through a pad of silica, first using 5:1 v/v, hexanes/CH_2Cl_2, and then CH_2Cl_2 as eluents. The fraction eluted with CH_2Cl_2 was concentrated in vacuo to give **9** as a dark yellow oil, which was used for the following synthetic step without further purification (9.50 g, 82% yield over two steps). ^1H NMR (400.16 MHz, 25 °C, CD_2Cl_2): δ 7.31 (d, J_{H-H} = 8 Hz, 2H), 6.63 (d, J_{H-H} = 8 Hz, 2H), 3.71 (t, J_{H-H} = 8 Hz, 2H), 3.47 (t, J_{H-H} = 8 Hz, 2H), 2.98 (s, 3H).

*P,N-Bromobenzene (**10**).* Amine **9** (4.49 g, 18.1 mmol) was dissolved in THF (30 mL) and chilled to −78 °C. $KPPh_2$ (33.9 mL, 0.5 M solution in THF, 18.1 mmol) was added dropwise, and the solution was left to warm up to room temperature. After stirring overnight, the solvent was removed *in vacuo*, and the mixture was extracted with water and CH_2Cl_2. The solution was dried under $MgSO_4$, and the solvent was removed *in vacuo*. Silica-gel column chromatography (1:1 v/v, hexanes/CH_2Cl_2) afforded the product as a white solid (5.74 g, 80%). ^1H NMR (400.16 MHz, 25 °C, CD_2Cl_2): δ 7.56−7.28 (m, 12H), 7.23 (d, J_{H-H} = 8 Hz, 2H), 6.46 (d, J_{H-H} = 7 Hz, 2H), 3.40 (m, 2H), 2.86 (s, 3H), 2.30 (m, 2H). $^{13}C\{^1H\}$ NMR (100.63 MHz, 25 °C, CD_2Cl_2): δ 148.1 (s), 138.7 (d, J_{C-P} = 14 Hz), 133.1 (d, J_{C-P} = 19 Hz), 132.1 (s), 129.2 (s), 129.0 (d, J_{C-P} = 7 Hz), 114.4 (s), 49.9 (d, J_{C-P} = 25 Hz), 38.4 (s), 25.3 (d, J_{C-P} = 15 Hz). $^{31}P\{^1H\}$ NMR (161.98 MHz, 25 °C, CD_2Cl_2): δ −20.7. ESIMS (m/z): Calcd 398 $[M]^+$. Found 398.

*P,N-Benzaldehyde (**11**).* A solution of **10** (3.00 g, 7.54 mmol) in THF (40 mL) was chilled to −78 °C, and *n*-BuLi (3.15 mL, 2.5 M solution in THF, 7.87 mmol) was added dropwise over 5 min. The solution was left to stir at −78 °C for 45 min, and DMF (7.00 mL, 90.8 mmol) was added dropwise. After stirring overnight at room temperature, the reaction was quenched with water (5 mL), washed with LiCl(aq) and water, and extracted with CH_2Cl_2. The solution was dried under $MgSO_4$, and the solvent was removed in vacuo to give the pure product as a thick yellow oil (2.46 g, 94% yield). ^1H NMR (400.16 MHz, 25 °C, CD_2Cl_2): δ 9.70 (s, 1H), 7.64 (d, J_{H-H} = 9 Hz,

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2H), 7.42 (m, 10H), 6.55 (d, J_{H-H} = 9 Hz, 2H), 3.53 (m, 2H), 2.99 (s, 3H), 2.39 (m, 2H). $^{13}C\{^1H\}$ NMR (100.63 MHz, 25 °C, CD_2Cl_2): δ 190.1 (s), 153.3(s), 138.4 (d, J_{C-P} = 13 Hz), 133.1 (d, J_{C-P} = 19 Hz), 132.1 (s), 129.4 (d, J_{C-P} = 11 Hz), 129.0 (s), 125.8 (s), 111.5 (s), 49.7 (d, J_{C-P} = 25 Hz), 38.5 (s), 25.9 (d, J_{C-P} = 15 Hz). $^{31}P\{^1H\}$ NMR (161.98 MHz, 25 °C, CD_2Cl_2): δ −20.8 (s). ESIMS (*m*/*z*): Calcd 347 $[M]^+$. Found 347.

*P,N-Bodipy (**12**).* The synthesis and purification procedure for **12** was carried out entirely in a glovebox under oxygen- and water-free conditions. Benzaldehyde **11** (2.00 g, 5.76 mmol) and pyrrole **5** (1.48 g, 12.1 mmol) were dissolved in CH_2Cl_2 (600 mL), trifluoroacetic acid was added (800 μL), and the solution was stirred at room temperature for 1.5 h. DDQ (1.31 g, 5.75 mmol) was added slowly as a powder, and after 45 min N(*i*-Pr)$_2$Et (6.05 mL, 34.6 mmol) was added dropwise. After 5 min, BF_3·OEt_2 (5.70 mL, 46.1 mmol) was slowly added, and the mixture was left to stir for 1 h. The whole reaction mix was then passed through two large pads of silica, first using CH_2Cl_2 and then hexanes/CH_2Cl_2 (2:1, v/v) as eluents. Most of the CH_2Cl_2 was removed *in vacuo*, and the solution was left overnight at 0 °C. The product was isolated *via* vacuum filtration and washed with hexanes which gave a red microcrystalline solid (322 mg, 9% yield). ^1H NMR (400.16 MHz, 25 °C, CD_2Cl_2): δ 7.60−7.30 (m, 10H), 7.00 (d, J_{H-H} = 8 Hz, 2H), 6.61 (d, J_{H-H} = 8 Hz, 2H), 3.52 (m, 2H), 2.93 (s, 3H), 2.48 (s, 6H), 2.37 (m, 2H), 2.33 (q, J_{H-H} = 7 Hz, 4H), 1.40 (s, 6H), 0.99 (t, J_{H-H} = 7 Hz, 6H). $^{13}C\{^1H\}$ (100.63 MHz, 25 °C, CD_2Cl_2): δ 152.8 (s), 148.9 (s), 141.8 (s), 138.7 (s), 138.1 (d, J_{C-P} = 13 Hz), 132.6 (d, J_{C-P} = 19 Hz), 131.3 (s), 129.0 (s), 128.7 (s), 128.4 (d, J_{C-P} = 5 Hz), 122.7 (s), 112.4 (s), 49.4 (d, J_{C-P} 14 Hz), 37.7 (s), 24.9 (d, J_{C-P} 15 Hz), 16.9 (s), 14.3 (s), 12.1 (s), 11.7 (s). $^{31}P\{^1H\}$ NMR (161.98 MHz, 25 °C, CD_2Cl_2): δ −20.5 (s). ^{19}F NMR (376.49 MHz, 25 °C, CD_2Cl_2): δ −146.2 (q, J_{F-B} = 33 Hz). $^{11}B\{^1H\}$ NMR (128.38 MHz, 25 °C, CD_2Cl_2): δ 0.05 (t, J_{B-F} = 33 Hz). ESIMS (*m*/*z*): Calcd 622 $[M]^+$. Found 622.

General Procedure for the Generation of Semiopen Complexes. A solution of P,S-Me (26.1 mg, 0.100 mol) in 3 mL of CH_2Cl_2 was added dropwise to a solution of dichloro(1,4-cyclooctadiene)platinum-(II) (37.4 mg, 0.100 mmol) in 3 mL of CH_2Cl_2. The solution was left to stir at room temperature for 5 min, and a solution of Bodipy-functionalized ligand (1.00 equiv, 0.100 mmol) in 3 mL of CH_2Cl_2 was added. The solvent volume was reduced to approximately 1 mL *in vacuo*, and the product was then precipitated out of solution with hexanes. The product was then isolated *via* vacuum filtration and washed with hexanes to afford the semiopen complex (*in situ* $^{31}P\{^1H\}$ NMR yields = quantitative, isolated yields >95%).

General Procedure for the Generation of Closed Complexes. Semiopen complex (0.100 mmol) was dissolved in 2 mL of CH_2Cl_2, and $AgBF_4$ (40.9 mg, 2.10 equiv, 0.210 mmol) was added. The mixture was left to stir vigorously in the dark for 15 min. The mixture was filtered and the solvent volume reduced to approximately 1 mL in vacuo. The product was then precipitated out of solution with hexanes and collected via filtration to yield the closed complex (*in situ* $^{31}P\{^1H\}$ NMR yields = quantitative, isolated yields >95%).

*[PtCl(κ$_2$-P,S-Me)(P,S-Bodipy)]Cl (**13**).* $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ $^{31}P\{^1H\}$ NMR (161.98 MHz, 25 °C, CD_2Cl_2): δ 43.1 (d, J_{P-P} = 14 Hz, J_{P-Pt} = 3478 Hz, 1P), 8.9 (d, J_{P-P} = 13 Hz, J_{P-Pt} = 3199 Hz, 1P). ^1H NMR (400.16 MHz, 25 °C, CD_2Cl_2): δ 8.40−7.00 (m, 20H), 3.50−2.00 (m, 21H), 1.50−0.80 (m, 12H). ^{19}F NMR (376.49 MHz, 25 °C, CD_2Cl_2): δ −146.1 (q, J_{F-B} = 34 Hz), −140.5 (q, J_{F-B} = 11 Hz), −131.8 (q, J_{F-B} = 11 Hz). $^{11}B\{^1H\}$ NMR (128.38 MHz, 25 °C, CD_2Cl_2): δ 0.26 (t, J_{B-F} = 33 Hz). MS (ESI): *m*/*z* calcd for $C_{52}H_{53}BClF_6N_2P_2PtS_2$ $[M-Cl]^+$: 1187. Found: 1187.

*[Pt(κ$_2$-P,S-Me)(κ$_2$-P,S-Bodipy)]2BF$_4$ (**14**).* $^{31}P\{^1H\}$ NMR (161.98 MHz, 25 °C, CD_2Cl_2): δ 46.6 (d, J_{P-P} = 13 Hz, J_{P-Pt} = 3093 Hz, 1P), 46.2 (d, J_{P-P} = 13 Hz, J_{P-Pt} = 3290 Hz, 1P). ^1H NMR (400.16 MHz, 25 °C, CD_2Cl_2): δ 8.10−7.00 (m, 20H), 4.20−1.20 (m, 27H), 1.01 (t, J_{H-H} = 8 Hz, 6H). ^{19}F NMR (376.49 MHz, 25 °C, CD_2Cl_2): δ −127.4 (q, J_{F-F} = 11 Hz), −135.5 (q, J_{F-F} = 11 Hz), −146.0 (q, J_{F-B} = 33 Hz), −150.2 (s). $^{11}B\{^1H\}$ NMR (128.38 MHz, 25 °C, CD_2Cl_2): δ −0.70 (t, J_{B-F} = 32 Hz), −2.23 (s). MS (ESI): *m*/*z* calcd for $C_{52}H_{53}B_2F_{10}N_2P_2PtS_2$ $[M - BF_4]^+$: 1239. Found: 1239.

*[PtCl(κ$_2$-P,S-Me)(P,S-Bodipy)]Cl (**15**).* $^{31}P\{^1H\}$ NMR (161.98 MHz, 25 °C, CD_2Cl_2): δ 43.6 (d, J_{P-P} = 14 Hz, J_{P-Pt} = 3515 Hz, 1P), 9.0 (d, J_{P-P} = 13 Hz, J_{P-Pt} = 3168 Hz, 1P). ^1H NMR (400.16 MHz, 25 °C, CD_2Cl_2): δ 8.22−6.78 (m, 24H), 4.0−0.5 (m, 33H). ^{19}F NMR (376.49 MHz, 25 °C, CD_2Cl_2): δ −146.2 (q, J_{F-B} = 34 Hz). $^{11}B\{^1H\}$ NMR (128.38 MHz, 25 °C, CD_2Cl_2): δ 0.11 (t, J_{B-F} = 33 Hz). MS (ESI): *m*/*z* calcd for $C_{52}H_{57}BClF_2N_2P_2PtS_2$ $[M - Cl]^+$: 1115. Found: 1115.

*[Pt(κ$_2$-P,S-Me)(κ$_2$-P,S-Bodipy)]2BF$_4$ (**16**).* $^{31}P\{^1H\}$ NMR (161.98 MHz, 25 °C, CD_2Cl_2): δ 46.3 (d, J_{P-P} = 13 Hz, J_{P-Pt} = 3165 Hz, 1P), 45.8 (d, J_{P-P} = 13 Hz, J_{P-Pt} = 3100 Hz, 1P). ^1H NMR (400.16 MHz, 25 °C, CD_2Cl_2): δ 8.43−6.71 (m, 24H), 4.25−0.41 (m, 33H). ^{19}F NMR (376.49 MHz, 25 °C, CD_2Cl_2): δ −146.1 (q, J_{F-B} = 34 Hz), −150.5 (s). $^{11}B\{^1H\}$ NMR (128.38 MHz, 25 °C, CD_2Cl_2): δ 0.11 (t, J_{B-F} = 33 Hz), −1.37 (s). MS (ESI): *m*/*z* calcd for $C_{52}H_{57}B_2F_6N_2P_2PtS_2$ $[M-BF_4]^+$: 1167. Found: 1167.

*[PtCl(κ$_2$-P,S-Me)(P,S-Bodipy)]Cl (**17**).* $^{31}P\{^1H\}$ NMR (161.98 MHz, 25 °C, CD_2Cl_2): δ 43.8 (d, J_{P-P} = 15 Hz, J_{P-Pt} = 3515 Hz, 1P), 6.6 (d, J_{P-P} = 13 Hz, J_{P-Pt} = 3141 Hz, 1P). ^1H NMR (400.16 MHz, 25 °C, CD_2Cl_2): δ 7.93−6.85 (m, 24 H), 3.94−0.68 (m, 36H). ^{19}F NMR (376.49 MHz, 25 °C, CD_2Cl_2): δ −146.2 (q, J_{F-B} = 34 Hz). $^{11}B\{^1H\}$ NMR (128.38 MHz, 25 °C, CD_2Cl_2): δ 0.16 (t, J_{B-F} = 34 Hz). MS (ESI): *m*/*z* calcd for $C_{53}H_{60}BClF_2N_3P_2PtS$ $[M - Cl]^+$: 1112. Found: 1112.

*[Pt(κ$_2$-P,S-Me)(κ$_2$-P,S-Bodipy)]2BF$_4$ (**18**).* $^{31}P\{^1H\}$ NMR (161.98 MHz, 25 °C, CD_2Cl_2): δ 37.9 (d, J_{P-P} = 16 Hz, J_{P-Pt} = 3397 Hz, 1P), 31.0 (d, J_{P-P} = 15 Hz, J_{P-Pt} = 3183 Hz, 1P). ^1H NMR (400.16 MHz, 25 °C, CD_2Cl_2): δ 8.18−6.86 (m, 24H), 4.19−0.40 (m, 37H). ^{19}F NMR (376.49 MHz, 25 °C, CD_2Cl_2): δ −146.2 (q, J_{F-B} = 34 Hz), −150.9 (s). $^{11}B\{^1H\}$ NMR (128.38 MHz, 25 °C, CD_2Cl_2): δ 0.13 (t, J_{B-F} = 34 Hz), −1.50 (s). MS (ESI): *m*/*z* calcd for $C_{53}H_{60}B_2F_6N_3P_2PtS$ $[M - BF_4]^+$: 1164. Found: 1164.

X-ray Crystallography. Crystallographic data are displayed in the Supporting Information (Table S1). Single crystals were mounted using oil (Infineum V8512) on a glass fiber. All measurements were made on a CCD area detector with graphite monochromated Cu KR radiation. Data were collected using Bruker APEXII detector and processed using APEX2 from Bruker. All structures were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in idealized positions, but not refined. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-97.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

NMR, absorbance, and emission spectra of compounds **3**, **6**, **12**, and **13**−**18**; X-ray diffraction crystallographic data for complexes **13** and **14** in crystallographic table and CIF forms; and theoretical modeling of a model P,S-Bodipy ligand. This material is available free of charge via the Internet at http://pubs.acs.org.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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