

Reactivity of Aryldimesitylboranes under Suzuki-Miyaura Coupling Conditions

Nan Wang, Zachary M. Hudson, and Suning Wang*

Department of Chemistry, Queen's University, 90 Bader Lane, Kingston, Ontario, Canada K7L 3N6

Received July 13, 2010

Sterically protected triarylboron compounds such as $BMes_2(Ar)$ have important applications in organic optoelectronic devices and chemical sensors. Furthermore, the Suzuki–Miyaura cross-coupling reaction is the most commonly used method for building the π skeletons of such conjugated materials. We have found that $BMes_2(Ar)$ can also be a highly active and effective coupling partner under typical Suzuki–Miyaura coupling conditions. For $BMes_2(p-Br-Ph)$, self-coupling leads to the formation of oligomers $Mes_2B-(Ph)_n$ –Mes, where the products with n = 1 (1), 2 (2), 3 (3), 4 (4) have been isolated and fully characterized. Examination of cross-coupling reactions of $BMes_2(Ph)$ with various aryl bromides has established the generality of $BMes_2(Ar)$ as a coupling partner.

Triarylboron compounds are an attractive class of materials for optoelectronic applications due to the empty p_{π} orbital on the boron center. This feature allows them to act as excellent electron acceptors, and such compounds have been successfully developed as anion sensors,¹ nonlinear optical materials,² and luminescent or electron-transporting compounds for organic light-emitting diodes (OLEDs).³ However, the empty p_{π} orbital also leaves these compounds susceptible to nucleophilic attack and hydrolysis.

In 1972, Williams and co-workers reported that two mesityl groups (Mes = 2,4,6-trimethylphenyl) were sufficient to provide an unusual degree of stability to arylboranes, preventing the attack of most nucleophiles.⁴ On the basis of this design, a great many molecular and polymeric materials have since been synthesized containing the aryldimesitylboron moiety which are in general very stable toward hydrolysis. Only very small

(2) (a) Collings, J. C.; Poon, S. Y.; Droumaguet, C. L.; Charlot, M.; Katan, C.; Palsson, L. O.; Beeby, A.; Mosely, J. A.; Kaiser, H. M.; Kaufmann, D.; Wong, W. Y.; Blanchard-Desce, M.; Marder, T. B. *Chem. Eur. J.* **2009**, *15*, 198. (b) Entwistle, C. D.; Marder, T. B. *Chem. Mater.* **2004**, *16*, 4574. (c) Entwistle, C. D.; Marder, T. B. *Angew. Chem.*, *Int. Ed.* **2002**, *41*, 2927. (d) Yuan, Z.; Collings, J. C.; Taylor, N. J.; Marder, T. B.; Halet, J. F. *J. Solid State Chem.* **2000**, *154*, 5. (e) Yuan, Z.; Entwistle, C. D.; Collings, J. C.; Albesa-Jové, D.; Batsanov, A. S.; Howard, J. A. K.; Taylor, N. J.; Kaiser, H. M.; Kaufmann, D. E.; Poon, S. Y.; Wong, W. Y.; Jardin, C.; Fathallah, S.; Boucekkine, A.; Halet, J. F.; Marder, T. B. *Chem. Eur. J.* **2006**, *12*, 2758 and references therein.

(3) (a) Noda, T; Shirota, Y. J. Am. Chem. Soc. 1998, 120, 9714–9715.
(b) Noda, T; Ogawa, H.; Shirota, Y. Adv. Mater. 1999, 11, 283. (c) Li, F.; Jia, W.-L.; Wang, S.; Zhao, Y.; Lu, Z.-H. J. Appl. Phys. 2008, 103, 034509/1.
(d) Zhou, G. J.; Ho, C. L.; Wong, W. Y; Wang, Q.; Ma, D. G.; Wang, L. X.; Lin, Z. Y; Marder, T. B.; Beeby, A. Adv. Funct. Mater. 2008, 18, 499.
(e) Hudson, Z. M.; Sun, C.; Helander, M. G.; Amarne, H.; Lu, Z.-H.; Wang, S. Adv. Funct. Mater., 2010, in press. (f) Hudson, Z. M.; Wang, S. Acc. Chem. Res. 2009, 42, 1584 and references therein.

(4) Doty, J. C.; Babb, B.; Grisdale, P. J.; Glogowski, M.; Williams, J. L. R. J. Organomet. Chem. 1972, 38, 229.

© 2010 American Chemical Society

anions, such as fluoride and cyanide, are capable of overcoming the steric bulk of the mesityl groups to bind to the boron center, forming the basis of their use as chemical sensors.^{1d} Hydroxide ions have also been found to be able to bind to the boron center of aryldimesitylboron compounds, but the binding constants are considerably weaker than those of fluoride ions.^{1b}

The synthesis of such π -conjugated materials commonly makes use of metal-catalyzed carbon–carbon bond formation reactions, such as Stille, Negishi, Suzuki–Miyaura, and Sonogashira couplings.⁵ Among these, the Suzuki–Miyaura coupling reaction is arguably the most common for the formation of arene–arene bonds, due to its broad scope and lack of toxic byproducts. However, we have recently discovered that under the basic conditions required for typical Suzuki coupling reactions, the association of hydroxide with the boron center of a triarylboron compound is significant enough to allow this group to act as the transmetalation coupling partner of a Suzuki-type reaction under Pd(0) catalysis, despite the steric bulk of the mesityl groups. The details of our findings are reported herein.

Results and Discussion

Self-Coupling of Bromophenyldimesitylborane. The involvement of protected triarylboron in cross-coupling reactions was first observed during our attempts to react *p*-bromophenyldimesitylborane with *p*-carboxamidephenylboronic acid by Suzuki–Miyaura coupling. Despite repeated attempts, the desired product was never isolated. However, we reproducibly obtained and isolated a series of oligomers by chromatography and crystallization, containing dimesitylboron and mesityl groups bound to an oligophenylene linker (Scheme 1).

To further understand this result, a series of control experiments were designed and investigated as shown in Table 1. Since the coupling reactions with benzamide and

^{*}To whom correspondence should be addressed. E-mail: suning.wang@ chem.queensu.ca.

 ⁽a) Yamaguchi, S.; Akiyama, S.; Tamao, K. J. Am. Chem. Soc. 2001, 123, 11372. (b) Kim, Y.; Gabbaï, F. P. J. Am. Chem. Soc. 2009, 131, 3363. (c) Sun, Y.; Ross, N.; Zhao, S.-B.; Huszarik, K.; Jia, W.-L.; Wang, R.-Y.; Macartney, D.; Wang, S. J. Am. Chem. Soc. 2007, 129, 7510.
 (d) Hudnall, T. W.; Chiu, C.-W.; Gabbaï, F. P. Acc. Chem. Res. 2009, 388 and references therein.

^{(5) (}a) Miyaura, N. Adv. Met.-Org. Chem. **1998**, 6, 187 and references therein. (b) Suzuki, A. J. Organomet. Chem. **1999**, 576, 147 and references therein. (c) McGlacken, G. P.; Fairlamb, I. J. S. Eur. J. Org. Chem. **2009**, 24, 4011 and references therein. (d) Hartwig, J. Organotransition Metal Chemistry: From Bonding to Catalysis; University Science Books: Sausalito, CA, 2010.





3-methylbenzamide gave the same result, it was clear that the p-Br-B(Mes)₂-benzene compound alone was responsible for the observed coupling. Indeed, when the amide coupling partner was removed from the reaction entirely, the same mixture of oligomeric products was obtained. It appeared as though the dimesitylborane was undergoing self-coupling, with transmetalation of either a mesityl group to the bromine site or a bromophenyl group, which allows for further coupling to form the observed mesityl-capped oligomers.

While 2-4 were isolated only in 1-4% yields, compound 1 was isolated in moderate yield (28%, assuming that one *p*-Br– BMes₂-benzene produces one molecule of 1). Nonetheless, the formation of compound 1 requires the consumption of two molecules of Mes₂B-Ph-Br, one as an aryl bromide and the other as a transmetalation reagent, most likely in the form of a borate formed by reaction with a hydroxyl group in the Pd -catalyzed cycle, as shown in Scheme 2. Because of this and the fact that 1 is not the only product, the actual isolated yield of 1 can be considered to be at least 56%. Such significant formation of self-coupling products from a sterically protected triarylborane substrate is highly unusual. The low yields of the oligomers are understandable, since they require the starting material Mes₂B– Ph–Br to undergo multiple and repetitive Suzuki–Miyaura cycles, as illustrated in Scheme 2.

Scheme 2. Catalytic Cycles for the Formation of Compounds 1-4 and the Corresponding Intermediates (n = 1, 2, 3, ...)



All four compounds were characterized by ¹H NMR, mass spectrometry, and spectroscopic analysis. Compounds 1–3 were also examined by UV–vis and fluorescence spectroscopy. These compounds are all fluorescent in solution, exhibiting only a small red shift in emission maximum on lengthening of the π conjugation (λ_{max} 376, 383, and 386 nm for 1–3). A similar trend is observed in the absorption spectra, with the wavelength of the low-energy band maximum increasing from 1 (316 nm) to 2 (331 nm) to 3 (337 nm), as expected for a more highly conjugated π -skeleton (see the Supporting Information). Most interestingly, the

Table 1. Formation of Arylborane Phenylene Oligomers^a



^{*a*} Reagents and conditions: *p*-Br–(BMes₂)–benzene (1 equiv), substrate (1.2 equiv), Pd(PPh₃)₄ (5%), K_2CO_3 (5 equiv, 1 M in H₂O) in toluene/EtOH/H₂O (2/1/1 v/v), 80 °C, reflux, 16 h.

fluorescence quantum yield markedly increases with increasing conjugation length, with values of 0.22 for 1, 0.43 for 2, and near unity (~1) for 3. This may be attributed to the increased π conjugation of the molecule and the increased contribution from the polyphenyl linker to the emission.

The structures of compounds 1-3 were determined by singlecrystal X-ray diffraction analysis and are shown in Figure 1. The structure of **3** is considerably out of coplanarity, which may be attributed to intermolecular interactions in the crystal lattice. As shown in Figure 2, there are significant intermolecular edgeon $\pi-\pi$ interactions between the triphenyl linkers and the interactions between the methyl protons and the phenyl ring are evident. In addition, molecules of **3** are all oriented in a parallel manner along the same direction in the lattice.

The use of anionic aryl borates as coupling partners has been reported previously, most commonly making use of NaBPh₄ due to the relatively poor stability of BPh₃.⁶ This reagent may be used with a palladium catalyst to transfer an aryl group in much the same manner as, for example, phenylboronic acid. It should also be noted that there are a small number of examples of Suzuki coupling reactions carried out on dimesitylboryl-containing substrates that were indeed successful, though low yields were often problematic.⁷ Clearly, the reactivity of the aryl halide, aryl borate, and catalyst together determine the product distribution in each reaction, and as such the dimesitylboron group

^{(6) (}a) Qin, W.; Yasuike, S.; Kakusawa, N.; Sugawara, Y.; Kawahata, M.; Yamaguchi, K.; Kurita, J. J. Organomet. Chem. 2008, 693, 109.
(b) Rahman, O.; Kihlberg, T.; Langstroem, B. Eur. J. Org. Chem. 2004, 3, 474. (c) Yao, T.; Larock, R. C. J. Org. Chem. 2003, 68, 5936. (d) Kakino, R.; Yasumi, S.; Shimizu, I.; Yamamoto, A. Bull. Chem. Soc. Jpn. 2002, 75, 137.
(e) Ciattini, P. G.; Morera, E.; Ortar, G. Tetrahedron Lett. 1992, 33, 4815.





Figure 1. Crystal structures of 1 (top), 2 (middle), and 3 (bottom).

does not always participate in coupling reactions. For example, we have recently reported a Suzuki coupling route to dual-emissive silane compounds containing triarylboron, which can be achieved using the highly active Pd(OAc)₂/SPhos catalyst.⁸ When Pd(PPh₄)₃ was used, however, this same reaction was not successful.

Cross-Coupling of B(Ph)Mes₂ with Aryl Bromide. In order to more clearly demonstrate the role of the boron center in these coupling reactions, a second series of control experiments were designed in which B(Ph)Mes₂, which lacks the bromine functionality, was used as one of the coupling partners. First, B(Ph)Mes₂ was reacted with 3.2 equiv of bromobenzene for 16 h using 1 M K₂CO₃ as base (Table 2, entry 1). Mesitylbenzene and biphenyl were isolated from this reaction in 23% and 17% yields, respectively, showing some preference for the biphenyl product, since a 2:1 product ratio would be expected in the absence of any selectivity. However, in this case the total conversion of starting materials (40%) was relatively low. In order to increase the

Figure 2. (top) Diagram showing the closest intermolecular contact distances of **3**. (bottom) Crystal lattice packing diagram showing the stacking of molecules of **3**.

conversion of the starting materials, the reaction was repeated using 2 M NaOH as base in place of K_2CO_3 (entry 2). After 16 h, this reaction produced mesitylbenzene and biphenyl in 61% and 25% yields, respectively, indicating that the coupling of the mesityl groups is slightly favored under more basic conditions. To once again firmly establish the role of each coupling partner (entry 3), this reaction was repeated using *p*-bromoethylbenzene, where the coupling products *p*-ethylmesitylbenzene and 4-ethylbiphenyl were obtained in a ratio similar to those in entry 2, and 4,4'diethylbiphenyl was not observed, establishing that coupling does indeed occur between the aryl halide and aryl borate.

Interestingly, no reaction was observed between bromobenzene and trimesitylborane (entry 4). This indicates that the steric barrier offered by three pairs of *o*-methyl groups is sufficient to protect these materials from reaction in this manner, while two pairs clearly are not.

Since many triarylboron-based materials include a boron moiety attached to a pyridine heterocycle, and the electronegativity of the heterocycle makes the boron center more susceptible to nucleophilic attack by groups such as hydroxide, the generality of our observations was further tested using 5-(dimesitylboryl)-2-phenylpyridine, an N,C-chelate ligand recently reported by our group,⁹ as a coupling partner (entry 5). The reaction of (dimesitylboryl)-2-phenylpyridine with 2.2 equiv of *p*-bromoethylbenzene resulted in the isolation of 55% *p*-ethylmesitylbenzene and 45% pyridine coupling product (Table 2) with a high conversion yield of the

^{(7) (}a) Huh, J. O.; Do, Y.; Lee, M. H. Organometallics 2008, 27, 1022.
(b) Sakuda, E.; Funahashi, A.; Kitamura, N. Inorg. Chem. 2006, 45, 10670.
(c) Jia, W.-L.; Moran, M. J.; Yuan, Y.-Y.; Lu, Z.-H.; Wang, S. J. Mater. Chem. 2005, 15, 3326. (d) Jia, W.-L.; Bai, D.-R.; McCormick, T.; Liu, Q. D.; Motala, M.; Wang, R. Y.; Seward, C.; Tao, Y.; Wang, S. Chem. Eur, J. 2004, 10, 994.

⁽⁸⁾ Hudson, Z. M.; Zhao, S.-B.; Wang, S. Chem. Eur. J. 2009, 15, 6131.

⁽⁹⁾ Rao, Y.-L.; Wang, S. Inorg. Chem. 2009, 48, 7698.



^{*a*} Reagents and conditions: Pd(PPh₃)₄ (5%), component 1 (1 equiv), toluene/EtOH/H₂O (2/1/1 v/v), 80 °C, reflux 16 h. Legend for entries 1–5: (a) component 2 (3.2 equiv), K₂CO₃ (5 equiv, 1 M in H₂O); (b) component 2 (3.2 equiv), NaOH (5 equiv, 2 M in H₂O); (c) component 2 (2.2 equiv), K₂CO₃ (5 equiv, 1 M in H₂O).

B(Ph)Mes₂ starting material. This demonstrates the higher selectivity/reactivity of the phenylpyridine—B bond, as the electron-withdrawing pyridine moiety results in a weaker B–C bond; were the reactivity of the pyridyl and mesityl groups the same, a 2:1 ratio of *p*-ethylmesitylbenzene and pyridine coupling product would again be expected. The relatively weak Mes₂B–C(py) bond was also supported by our observation that the cleavage of the Mes₂B–C(py) bond occurs usually at ~80 °C in solution while the Mes₂-B–C(aryl) bond cleavage usually does not occur until ~100 °C. The low stability of the B–py bond may be explained by the decreased electron donation of py to the B center, compared to that of a phenyl.

Several key conclusions can be drawn from these results. First, in the presence of aqueous base and a Pd(0) catalyst, sterically protected triarylboranes such as dimesitylarylboron compounds are susceptible to reaction in much the same manner as traditional aryl boronates and can produce coupling products of its pendant aryl groups. This demonstrates that, in principle, a species of the form BMes₂(Ar) may be used in a Suzuki–Miyaura coupling reaction with an aryl halide, in much the same manner as a boronic acid or ester could be used in a 1:1 ratio.

Perhaps more importantly, however, we have shown that while Suzuki–Miyaura coupling reactions are one of the most common methods for the synthesis of π -conjugated materials, these reactions are best avoided when the substrate contains a triarylboron group. We note, however, that such reactions are possible using a sufficiently bulky or active catalyst. Furthermore, the lack of reactivity of trimesitylborane indicates that materials which include three pairs of *o*-methyl groups, such as tridurylboranes (duryl = 2,3,5,6-tetramethylphenyl) can tolerate Suzuki coupling conditions.

For the synthesis of typical dimesitylboron compounds, however, it is preferable to employ alternative methods such as Stille or Negishi coupling; these methods avoid basic conditions when a palladium catalyst is used, and numerous successful examples have been reported for them.^{3d,10}

Experimental Section

General Experimental Information. All reactions were carried out under a nitrogen atmosphere with standard Schlenk techniques. All starting materials were purchased from Aldrich Chemical Co. and used without further purification. Reagentgrade solvents were used without further purification. NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer. High-resolution mass spectra were obtained from a Waters/Micromass GC-TOF EI-MS spectrometer. Quantum yields were measured using the optically dilute method relative to an anthracene standard ($\Phi = 0.36$). 1-Bromo-4-dimesitylboron benzene,¹¹ dimesitylboron benzene,¹¹ and 5-(dimesitylboryl)-2-phenylpyridine⁹ were synthesized according to previously reported procedures.

X-ray Diffraction Analysis. Single crystals of the oligomers were mounted on glass fibers for data collection. Data were collected on a Bruker Apex II single-crystal X-ray diffract-ometer with graphite-monochromated Mo K α radiation, operating at 50 kV and 30 mA and at 180 K. Data were processed on a PC with the aid of the Bruker SHELXTL software package (version 5.10) and corrected for absorption effects. All structures were solved by direct methods.

Synthesis of Arylborane Phenylene Oligomers. *p*-Br–BMes₂– benzene (0.60 mmol, 243 mg), Pd(PPh₃)₄ (0.03 mmol, 35 mg), and K₂CO₃ (3.0 mmol, 414 mg) were added to a 50 mL Schlenk flask with a stir bar and condenser. A toluene/ethanol/water mixture (v/v/v, 6 mL/3 mL/3 mL) was stirred and purged with nitrogen for 1 h, and then the mixed solvents were transferred to the reaction flask via cannula. The mixture was stirred at 80 °C for 16 h and then cooled to room temperature and concentrated in vacuo. The residue was partitioned between water and CH₂Cl₂ and the aqueous layer separated and extracted with dichloromethane (3 × 15 mL). The combined organic layers were dried over MgSO₄, concentrated, and purified on silica gel (hexanes as the eluent).

4-Dimesitylboron-1-mesitylbenzene (1). ¹H NMR (400 MHz, CDCl₃, 298.0 K, δ , ppm): 7.59 (d, J = 7.9 Hz, 2H), 7.16 (d, J = 7.9 Hz, 2H), 6.97 (s, 2H), 6.87 (s, 4H), 2.36 (s, 3H), 2.35 (s, 6H), 2.08 (s, 12H), 2.03 (s, 6H). ¹³C{¹H} NMR (100 MHz, CDCl₃, δ , ppm): 144.9, 141.9, 140.8, 138.9, 138.6, 137.2, 136.7, 136.4, 135.6, 128.9, 128.2, 128.0, 23.4, 21.2, 21.0, 20.6. HRMS: calcd for C₃₃H₃₇B[M]⁺ m/z 444.3078, found 444.2994. Yield: 28%.

4-Dimesitylboron-4'-mesitylbiphenyl (2). ¹H NMR (400 MHz, CDCl₃, 298.0 K, δ , ppm): 7.75 (d, J = 8.2 Hz, 2H), 7.68 (d, J = 8.2 Hz, 2H), 7.64 (d, J = 8.2 Hz, 2H), 7.25 (d, J = 8.2 Hz, 2H), 6.98 (s, 2H), 6.86 (s, 4H), 2.36 (s, 3H), 2.34 (s, 6H), 2.07 (s, 12H), 2.06 (s, 6H). ¹³C{¹H} NMR (100 MHz, CDCl₃, δ , ppm): 144.5, 144.0, 141.8, 140.8, 140.7, 138.7, 138.6, 138.5, 137.1, 136.7, 136.0, 129.8, 128.2, 128.1, 127.1, 126.4, 23.5, 21.2, 21.0, 20.8. HRMS: calcd for C₃₉H₄₁B[M]⁺ m/z 520.3308, found 520.5031. Yield: 4%.

4-Dimesitylboron-4'-mesitylterphenyl (3). ¹H NMR (400 MHz, CDCl₃, 298.0 K, δ , ppm): 7.78 (s, 4H), 7.73 (d, J = 8.2 Hz, 2H), 7.69 (d, J = 8.5 Hz, 2H), 7.64 (d, J = 8.2 Hz, 2H), 7.26 (d, J = 8.2 Hz, 2H), 6.99 (s, 2H), 6.87 (s, 4H), 2.36 (s, 3H), 2.35 (s, 6H), 2.08 (s, 6H), 2.07 (s, 12H). HRMS: calcd for C₄₅H₄₅B[M]⁺ m/z 596.3700, found: 596.2096. Yield: trace (ca. 2%).

^{(10) (}a) Bai, D.-R.; Liu, X.-Y.; Wang, S. Chem. Eur. J. 2007, 13, 5713.
(b) Liu, X.-Y.; Bai, D.-R.; Wang, S. Angew. Chem., Int. Ed. 2006, 45, 5475.
(c) Sun, Y.; Wang, S. Inorg. Chem. 2010, 49, 4394.

⁽¹¹⁾ Jia, W. L.; Bai, D. R.; McCormick, T.; Liu, Q. D.; Motala, M.; Wang, R.; Seward, C.; Tao, Y.; Wang, S. *Chem. Eur. J.* **2004**, *10*, 994.

4-Dimesitylboron-4'-mesitylquaterphenyl (4). ¹H NMR (400 MHz, CDCl₃, 298.0 K, δ , ppm): 7.78 (s, 8H), 7.74 (d, J = 8.2 Hz, 2H), 7.66 (d, J = 8.2 Hz, 2H), 7.64 (d, J = 8.2 Hz, 2H), 7.77 (d, J = 8.2 Hz, 2H), 6.99 (s, 2H), 6.87 (s, 4H), 2.37 (s, 3H), 2.35 (s, 6H), 2.09 (s, 6H), 2.07 (s, 12H). HRMS: calcd for C₅₁H₄₉B-[M]⁺ m/z 672.4014, found 672.2162. Yield: trace (ca. 1%).

Typical Suzuki–Miyaura Coupling of Dimesitylboranes. Method 1. Dimesityl(phenyl)borane (0.6 mmol, 196 mg), bromobenzene (2.0 mmol, 0.21 mL), Pd(PPh₃)₄ (5%, 0.030 mmol, 34 mg), and K_2CO_3 (3.0 mmol, 414 mg) were added to a 50 mL Schlenk flask with stir bar and condenser. A toluene/ethanol/water mixture (v/v/v, 6 mL/3 mL/3 mL) was stirred and purged with nitrogen for 1 h, and then the mixed solvents were transferred to the reaction flask via cannula. The mixture was stirred at 80 °C for 16 h and then cooled to room temperature and concentrated in vacuo. The residue was partitioned between water and CH₂Cl₂, and the aqueous layer was separated and extracted with dichloromethane (3 × 15 mL). The combined organic layers were dried over MgSO₄, concentrated, and purified on silica gel (hexanes as eluent). The two coupling products 2,4,6-trimethyl-1,1'-biphenyl and biphenyl were identified by proton NMR.

Method 2. Aryldimesitylborane (0.6 mmol), aryl halide (2.0 mmol), Pd(PPh₃)₄ (5%, 0.030 mmol, 34 mg), and NaOH (3.0 mmol, 120 mg) were added to a 50 mL Schlenk flask with a stir bar and condenser. A toluene/ethanol/water mixture (v/ v/v, 3 mL/1.5 mL/1.5 mL) was stirred and purged with nitrogen for 1 h, and then the mixed solvents were transferred to the reaction flask via cannula. The mixture was stirred at 80 °C for 16 h and then cooled to room temperature and concentrated in vacuo. The residue was partitioned between water and CH₂Cl₂, and the aqueous layer was separated and extracted with dichloromethane (3 × 15 mL). The combined organic layers were dried over MgSO₄, concentrated, and purified on silica gel (hexanes as the eluent).

1-Ethyl-4-mesitylbenzene. ¹H NMR (400 MHz, CDCl₃, 298.0 K, δ , ppm): 7.36 (d, J = 7.6 Hz, 2H), 7.18 (d, J = 7.9 Hz, 2H),

7.06 (s, 2H), 2.83 (q, J = 7.6 Hz, 2H), 2.45 (s, 3H), 2.14 (s, 6H), 1.41 (t, J = 7.6 Hz, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃, δ , ppm): 142.2, 139.0, 138.2, 136.2, 136.0. 129.1, 128.0, 127.7, 28.5, 21.0, 20.8, 15.4. HRMS: calcd for C₁₇H₂₀ *m*/*z* 225.1643, found 225.1640.

5-(p-Ethylphenyl)phenylpyridine. 5-(Dimesitylboryl)-2-phenylpyridine (0.37 mmol, 150 mg), 1-bromo-4-ethylbenzene (0.77 mmol, 0.1 mL), Pd(PPh₃)₄ (5%, 0.02 mmol, 22 mg), and NaOH (1.86 mmol, 74 mg) were added to a 50 mL Schlenk flask with stir bar and condenser. A toluene/ethanol/water mixture (v/v/v, 12 mL/4 mL/4 mL) was stirred and purged with nitrogen for 1 h, and then the mixed solvents were transferred to the reaction flask via cannula. The mixture was stirred at 80 °C for 16 h and then cooled to room temperature and concentrated in vacuo. The residue was partitioned between water and CH₂Cl₂, and the aqueous layer was separated and extracted with dichloromethane $(3 \times 15 \text{ mL})$. The combined organic layers were dried over MgSO₄, concentrated, and purified on silica gel (hexanes as the eluent). Yield: 45%. ¹H NMR $(400 \text{ MHz}, \text{CDCl}_3, 298.0 \text{ K}, \delta, \text{ppm})$: 8.93 (d, J = 2.2 Hz, 1H), 8.04 (d, J = 7.3 Hz, 2H), 7.94 (dd, J = 8.2 Hz, J = 2.2 Hz, 1H),7.79 (d, J = 8.2 Hz, 1H), 7.56 (d, J = 8.0 Hz, 2H), 7.49 (t, J =7.6 Hz, 2H), 7.42 (t, J = 7.6 Hz, 1H), 7.93 (d, J = 8.0 Hz, 2H), 2.72 (q, J = 7.6 Hz, 2H), 1.29 (t, J = 7.6 Hz, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃, δ, ppm): 155.7, 147.8, 144.2, 139.0, 134.8, 132.4, 130.8, 128.8, 128.7, 128.6, 126.8, 126.7, 120.2, 28.5, 15.5. HRMS: calcd for $C_{19}H_{17}N[M]^+ m/z$ 259.1361, found 259.1362.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council for financial support.

Supporting Information Available: Figures giving absorption and fluorescence spectra of compounds 1-3 and CIF files giving crystallographic data for 1-3. This material is available free of charge via the Internet at http://pubs.acs.org.