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## Synthesis of bis(pyrrol-2-yl)arenes by Pd-catalyzed cross coupling

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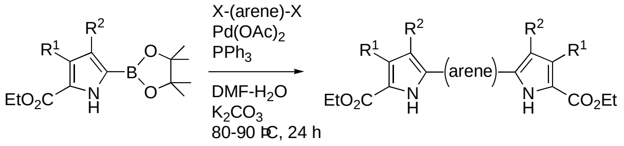

-(arene)- = 1,2-phenylene, 1,3-phenylene, 1,4-phenylene, 4,4'-biphenylene, 2,5-thienylene, 2,6-pyridylene, 9,10-anthracenylene, 2,7-fluorenylene, 2,7-(9-oxofluorenylene), 6,6'-(2,2'-bipyridylene)

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# Synthesis of bis(pyrrol-2-yl)arenes by Pd-catalyzed cross coupling

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**Abstract—** 2-Borylpyrrole was prepared from 2-iodopyrrole almost quantitatively and then reacted with dihaloarenes under typical reaction conditions of Suzuki-Miyaura cross coupling to give bis(pyrrol-2-yl)arenes in good yields, while the cross coupling reaction of 2-iodopyrrole with 1,4-phenylenebisboronic acid was susceptible to oxidative self-coupling to produce 4,4'-bis(pyrrol-2-yl)biphenyl as a byproduct. These bis(pyrrol-2-yl)arenes showed strong fluorescence.

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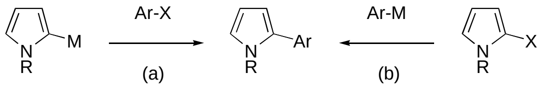
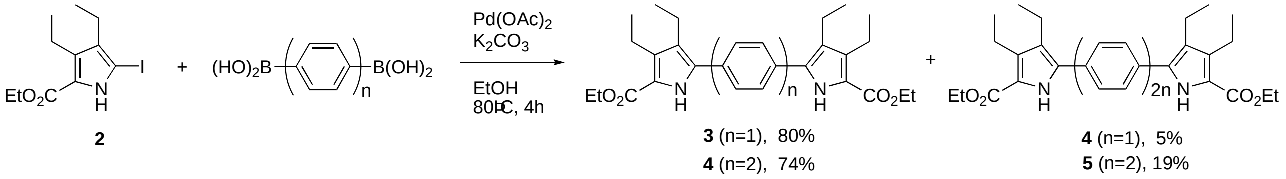
Organic materials containing pyrrole are of great interest and the application to $\pi$-conjugated polymers such as polypyrroles are well known.[1] Bis(pyrrol-2-yl)arenes have been regarded as useful monomers for electroactive polymeric material.[2] Another interesting application of bis(pyrrol-2-yl)arenes is their use as building blocks for expanded porphyrins.[3] In this context, various bipyrrole derivatives with an aromatic linker such as benzene, pyridine, furan, thiophene, and pyrrole have been reported.[4-6] The five-membered heteroaromatic linker between pyrroles was constructed by the cyclization of 1,4-bis(pyrrol-2-yl)-1,4-diketone.[4,5] On the other hand, pyrrole rings were constructed at both sides of the six-membered aromatic core to produce bis(pyrrol-2-yl)arenes.[6] However, these synthetic methods are not satisfactory in the synthesis of bipyrrolic compounds with various substituents.

The Pd-catalyzed cross coupling reaction is a straightforward synthetic method for arylpyrroles. Whereas arylation of N-unprotected pyrrole through C-H activation has recently been reported (Scheme 1. (a); R=M=H, X=halogen),[7] conventional Suzuki-Miyaura cross coupling reactions are favored practically in view of its wide applicability and milder reaction conditions.[8,9] There are two options of the reactant combination as shown in Scheme 1; (a) pyrrolylmetal and haloarene and (b) halopyrrole and arylmetal. While Pd-catalyzed reactions of N-unprotected halopyrrole and borylarene were frequently reported to give arylpyrroles (Scheme 1. (b); R=H, X=halogen, M=B(OR')$_2$),[8] the coupling reaction using N-unprotected borylpyrrole (Scheme 1. (a); R=H, X=halogen, M=B(OR')$_2$) has never been reported except a few examples.[9a] N-protected borylpyrroles have usually been employed in the protocol (a).[9b-i] Here, we will show convenient preparation of N-unprotected borylpyrrole and its successful applicatioin to the synthesis of bis(pyrrol-2-yl)arenes. The Pd-catalyzed cross coupling of N-unprotected borylpyrrole and dihaloarene was found to be much less susceptible to the oxidative self-coupling reaction in comparison with the reverse combination of halopyrrole and diborylarene.



**Scheme 1**. Pd-catalyzed cross coupling to 2-arylpyrrole.

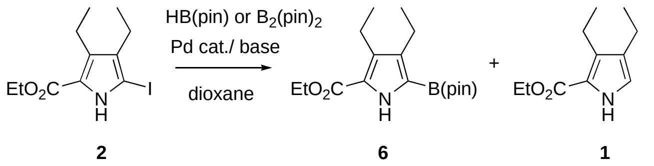
3,4-Dialkyl-2-ethoxycarbonylpyrrole **1** is the choice of pyrrole substrate in this paper since it is frequently used in the porphyrinoid synthesis.[10] It is well known that the ester substituent stabilizes pyrrole nucleus against oxidative degradation and is readily removed by the hydrolysis-decarboxylation procedure. When a mixture of 3,4-diethyl-2-ethoxycarbonyl-5-iodopyrrole **2** (2.0 mmol), 1,4-phenylenebisboronic acid (1.0 mmol), $K_2CO_3$ (6.6 mol), $Pd(OAc)_2$ (0.10 mmol), and $PPh_3$ (0.20 mmol) in ethanol (10 ml) was heated under argon for 24 h at reflux, 1,4-bis(pyrrol-2-yl)benzene **3**[11] was obtained in good yield. $^1$H NMR analysis after chromatographic purification showed that **3** (80% yield) was contaminated with a byproduct, 4,4'-bis(pyrrol-2-yl)biphenyl, **4**[11] (5% yield) originated from the self-coupling of the pyrrolylbenzeneboronic acid intermediate (Scheme 2). The compound **4** was identical with the major product of the similar Pd-catalyzed cross coupling reaction of **2** and 4,4'-biphenylenebisboronic acid. The major product **4** in 74% yield was also contaminated with a self-coupling product, bis(pyrrol-2-yl)quarterphenyl, **5** in 19% yield. The latter was characterized by the MS signal at 693.33 (theory for $C_{46}H_{48}N_2O_4 + H^+$: 693.37).



**Scheme 2**. Pd-catalyzed cross coupling reactions of 2-iodopyrrole **2** and arenebisboronic acid.

The purity of the bis(pyrrol-2-yl)arene is crucial if it is used to generate oligomers and polymers. Therefore, we examined the cross coupling of 2-borylpyrrole and diiodoarenes as a reverse combination in the hope of improving selectivity. 2-Borylpyrroles have been prepared by the reaction of N-Boc-protected 2-lithiopyrrole with alkoxyborane.[12] Ir-catalyzed direct borylation of pyrrole at the 2-position has recently been reported.[13] Since the latter reaction is restricted to sterically unhindered substrates and the former reaction needs protection-deprotection procedure, these methods would not be suitable for **1**. Thus, we have tried to convert **2** to 2-borylpyrrole **6** according to the procedure for Pd-catalyzed borylation of aromatic halides.[14] A mixture of **2** (4.6 mmol), pinacolborane (5.5 mmol), NEt$_3$ (11.5 mmol), and PdCl$_2$(PPh$_3$)$_2$ (0.23 mmol) in dioxane (20 ml) was heated at 60 ˚C for 3 h to give **6**[11] almost quantitatively. The amount of the dehalogenated product **1** was negligible under these reaction conditions. It is worthy of note that PdCl$_2$(PPh$_3$)$_2$ was much more effective than PdCl$_2$(dppf). The latter was reported to be the best catalyst for the borylation of ordinary aromatic iodide.[14a] Borylation with bispinacolatodiborane instead of pinacolborane did not work well in the case of **2** either as shown in Table 1.

**Table 1.** Pd-catalyzed borylation of iodopyrrole **2**.[a)]

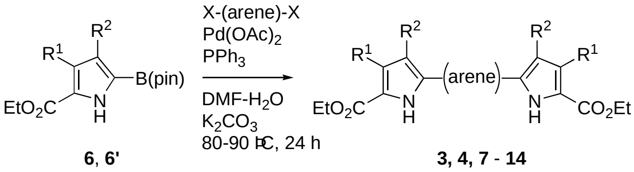


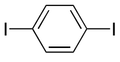
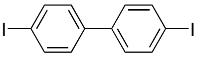
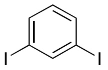
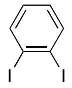
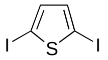
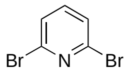
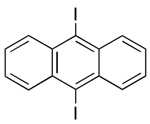
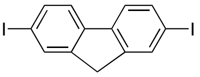
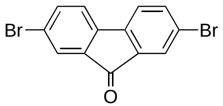
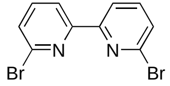
| entry | borane | Pd catalyst | base | time | yield (%)[b)] | |
|---|---|---|---|---|---|---|
| | | | | (h) | **6** | **1** |
| 1 | HB(pin) | PdCl$_2$(dppf) | Et$_3$N | 4 | 5 | 4 |
| 2 | HB(pin) | PdCl$_2$(PPh$_3$)$_3$ | Et$_3$N | 3 | 98 | 2 |
| 3 | B$_2$(pin)$_2$ | PdCl$_2$(dppf) | KOAc | 21 | 10 | 8 |
| 4 | B$_2$(pin)$_2$ | PdCl$_2$(PPh$_3$)$_3$ | KOAc | 2 | 12 | 2 |

[a] The molar ratio: **2**/borane/Pd/base = 1.0/1.2/0.05/2.5. [b] The yield was determined by $^1$H NMR.

2-Borylpyrrole **6** (3.0 mmol) after separating ammonium salts and most part of catalyst by filtration was subjected to the Suzuki-Miyaura cross coupling reaction with dihaloarenes (1.25 mmol) in the presence of Pd(OAc)$_2$ (0.13 mmol), PPh$_3$ (0.26 mmol), and K$_2$CO$_3$ (4.1 mmol) in DMF-H$_2$O (15-3 ml) at 80-90 ˚C for 5 h. The coupling products **3** and **4** free from the self-coupling byproducts were obtained in 69% and 92% yield from 1,4-diiodobenzene and 4,4'-diiodobiphenyl, respectively.

**Table 2.** Pd-catalyzed cross coupling of 2-borylpyrrole **6** and **6'** with dihaloarenes [a]



| X-(arene)-X | $R^1$ | $R^2$ | product | yield (%) |
|---|---|---|---|---|
|  | Et | Et | **3** | 69 |
|  | Et | Et | **4** | 92 |
|  | Et | Et | **7** | 84 |
|  | Et | Et | **8** | 81 |
|  | Et | Et | **9** | 70 |
|  | Et | Et | **10** | 74 |
|  | Me | i-Bu | **11** | 70 |
|  | Me | i-Bu | **12** | 92 |
|  | Me | i-Bu | **13** | 97 |
|  | Me | i-Bu | **14** | 76 |

Molar ratio: **6**(or **6'**)/dihaloarene/Pd(OAc)$_2$/PPh$_3$/K$_2$CO$_3$ = 2.4/1.0/0.10/0.20/3.3.

It has been shown that oxidative self-coupling of areneboronic acid is accelerated by dioxygen by way of diarylpalladium intermediate.[15] Probably because of the steric reason, double transmetallation of 2-borylpyrrole **6** to

Pd(II) seems to be suppressed, as compared with that of pyrrolylareneboronic acid as an intermediate in the cross coupling reaction of **2** and arenebisboronic acid. Facile formation of 2-borylpyrrole and its clean cross coupling reaction with dihaloarenes lead to a reliable synthetic procedure for bis(pyrrol-2-yl)arenes and bis(pyrrol-2-ly)heteroarenes. Table 2 summarizes the yields of the cross coupling reactions of **6** with *m*-diiodobenezene, *o*-diiodobenezene, 2,5-diiodothiophene, and 2,6-dibromopyridine to give the coupling products **7 – 10**. It is worthy of note that 1,2-bis(pyrrol-2-yl)benzene derivative could not be prepared by the pyrrole ring forming reaction starting from phthaloyl dichloride.[6a] 2-Borylpyrrole **6'** having a sterically demanding *iso*-butyl group was prepared similarly in more than 90% yield and then gave coupling products **11 – 14** in good yields.

The newly synthesized dipyrrolic compounds are fluorescent as shown in Figure 1 and the fluorescence intensity is very high in some cases. For example, the fluorescence efficiency of **4** in ethanol estimated relative to anthracene ($\Phi_F = 0.27$)[16] is 0.89. It is worthy of note that protonation at the pyridine nitrogen of **10** caused red shift of the absorption band from 352 nm to 432 nm and also of the fluorescence band from 392 nm to 490 nm.

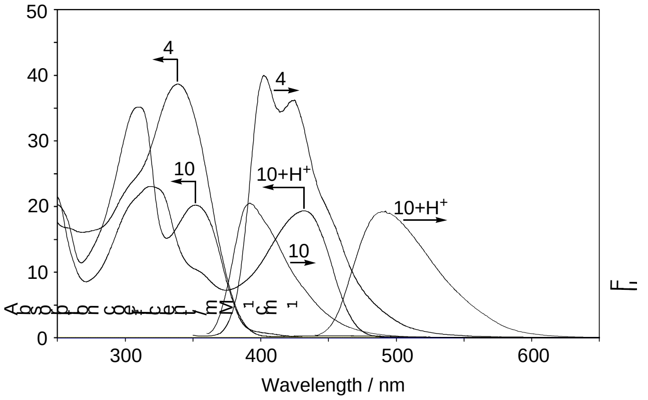


**Figure 1**. UV-vis absorption (left arrow) and emission spectra (right arrow) of **4**, **10**, and **10**+TFA in $CH_2Cl_2$ at room temperature. Emission spectra of **4** ($6.8\times10^{-8}$ mol/L), **10** ($2.0\times10^{-7}$ mol/L), and **10**+TFA ($2.0\times10^{-7}$ mol/L) were measured with the excitation at the absorption maxima at 339, 352, and 432 nm, respectively.

In summary, 2-borylpyrrole was readily prepared from 2-iodopyrrole and it was successfully applied to the synthesis of bis(pyrrol-2-yl)arenes by the Pd-catalyzed cross coupling with dihaloarenes. This is in contrast to the reverse combination of 2-halopyrrole and arenebisboronic acid that was found to be more susceptible to the oxidative self-coupling. In addition to good solubility owing to the alkyl substituents at the pyrrole-β positions, the strong fluorescence augments the utility of these bis(pyrrol-2-yl)arenes and bis(pyrrol-2-yl)heteroarenes as scaffolds for functional π-conjugated materials.

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11. 1,4-Bis(pyrrol-2-yl)benzene (**3**) Yield 69%. m.p. 208-210 °C. $^1$H NMR (400 MHz, δ-value, $CDCl_3$) 8.81 (br, 2H, NH), 7.53 (s, 4H, $C_6H_4$-linker), 4.35 (q, 4H, *J*=7.1 Hz, OC$H_2$Me), 2.81, 2.62 (q×2, 4H×2, *J*=7.4 and 7.5 Hz, C$H_2$Me), 1.38 (t, 6H, *J*=7.1 Hz, OCH$_2$*Me*), 1.22, 1.21 (t×2, 6H×2, CH$_2$*Me*, *J*=6.7 and 6.9 Hz). $^{13}$C NMR (100 MHz, δ, $CDCl_3$) 161.56, 134.40, 131.97, 131.62, 127.51, 124.27, 118.60, 60.01, 18.39, 17.49, 16.32, 15.87, 14.53. ESI-MS (found/calcd for $C_{28}H_{36}N_2O_4 + H^+$) 465.276/465.275. IR (cm$^{-1}$, in KBr pellet) 1666 (ν(CO)). Analysis calcd. for $C_{28}H_{36}N_2O_4$: C, 72.39; H, 7.81; N, 6.03. Found C, 72.36; H, 7.99; N, 5.63. 4,4'-Bis(pyrrol-2-yl)biphenyl (**4**) Yield 92%. m.p. 260 °C. $^1$H NMR (400 MHz, δ-value, $CDCl_3$) 8.84 (br, 2H, NH), 7.71, 7.56 (d×2, 4H×2, *J*=8.2 Hz, $(C_6H_4)_2$-linker), 4.36 (q, 4H, *J*=7.1 Hz, OC$H_2$Me), 2.82, 2.64 (q×2, 4H×2, *J*=7.5 and 7.6 Hz, C$H_2$Me), 1.39 (t, 6H, *J*=7.1 Hz, OCH$_2$*Me*), 1.23, 1.22 (t×2, 6H×2, CH$_2$*Me*, *J*=7.5 Hz). $^{13}$C NMR (100 MHz, δ, $CDCl_3$) 161.53, 139.35, 134.42, 132.07, 131.78, 127.65, 127.32, 124.24, 118.50, 60.00, 18.40, 17.51, 16.35, 15.88, 14.56. ESI-MS (found/calcd for $C_{34}H_{40}N_2O_4 + H^+$) 541.284/541.306. IR (cm$^{-1}$, in KBr pellet) 1656 (ν(CO)). Analysis calcd. for $C_{34}H_{40}N_2O_4$: C, 75.53; H, 7.46; N, 5.18. Found C, 75.41; H, 7.66; N, 5.09. 2-Borylpyrrole (**6**) $^1$H NMR (400 MHz, δ-value, $CDCl_3$) 9.17 (br, 1H, NH), 4.32 (q, 2H, *J*=7.1 Hz, OC$H_2$Me), 2.75, 2.65 (q×2, 2H×2, *J*=7.5 and 7.4 Hz, C$H_2$Me), 1.36 (t, 3H, *J*=7.2 Hz, OCH$_2$*Me*), 1.30 (s, 12H, Me), 1.15, 1.13 (t×2, 3H×2, CH$_2$*Me*, J=7.5 Hz). $^{13}$C NMR (100 MHz, δ, $CDCl_3$) 161.04, 138.12, 132.63, 122.26, 83.56, 59.91, 24.71, 18.14, 17.80, 17.30, 15.87, 14.44.
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