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

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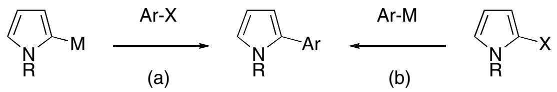
Abstract—2-Borylpyrrole was prepared from 2-iodopyrrole almost quantitatively and then reacted with dihaloarenes under typical reaction conditions of Suzuki–Miyaura cross coupling to give bis(pyrrol-2-yl)arenes in good yields, while the cross coupling reaction of 2-iodopyrrole with 1,4-phenylenebisboronic 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.

Organic materials containing pyrrole are of great interest and their application to π-conjugated polymers such as polypyrroles is well known.[1] Bis(pyrrol-2-yl)arenes have been regarded as useful monomers for electroactive polymeric materials.[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 for a few examples.[9a] N-Protected borylpyrroles have usually been employed in the protocol (a).[9b–i] Here, we will show a convenient preparation of N-unprotected borylpyrrole and its successful application 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 a pyrrole substrate in this letter since it is frequently used in the porphyrinoid synthesis.[10] It is well known that the ester substituent stabilizes the 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

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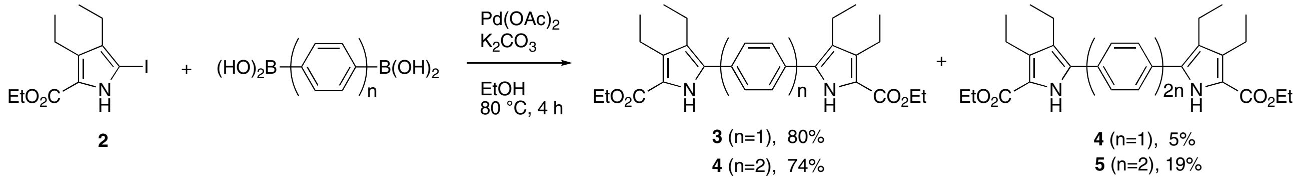


Scheme 2. Pd-catalyzed cross coupling reactions of 2-iodopyrrole **2** and arenebisboronic acid.

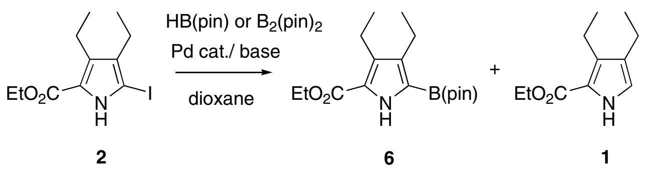
for 24 h at reflux, 1,4-bis(pyrrol-2-yl)benzene **3**[11] was obtained in good yield. ^{1}H NMR analysis after chromatographic purification showed that **3** (80% yield) was contaminated with a byproduct, 4,4′-bis(pyrrol-2-yl)biphenyl, **4**[11] (5% yield) originated from the self-coupling of the pyrrolylbenzeneboronic acid intermediate (Scheme 2). 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).

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.

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_2CO_3 (4.1 mmol) in DMF–H_2O (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.

It has been shown that the 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

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

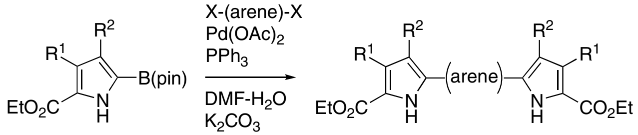


Entry	Borane	Pd catalyst	Base	Time (h)	Yield[b] (%)	
					6	**1**
1	HB(pin)	$PdCl_2$(dppf)	Et_3N	4	5	4
2	HB(pin)	$PdCl_2(PPh_3)_2$	Et_3N	3	98	2
3	$B_2(pin)_2$	$PdCl_2$(dppf)	KOAc	21	10	8
4	$B_2(pin)_2$	$PdCl_2(PPh_3)_2$	KOAc	2	12	2

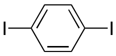
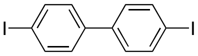
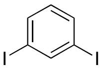
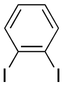
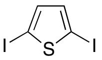
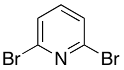
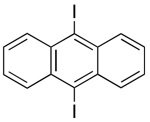
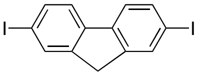
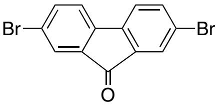
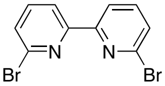
[a] The molar ratio: **2**/borane/Pd/base = 1.0/1.2/0.05/2.5.

[b] The yield was determined by ^{1}H NMR.

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



6, **6'** → **3, 4, 7 - 14**

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

[a] Molar ratio: **6** (or **6′**)/dihaloarene/$Pd(OAc)_2$/PPh_3/K_2CO_3 = 2.4/1.0/0.10/0.20/3.3.

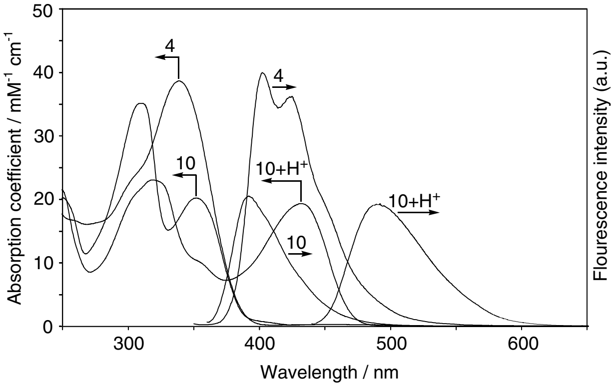


Figure 1. UV–vis absorption (left arrow) and emission spectra (right arrow) of **4**, **10**, and **10** + TFA in CH_2Cl_2 at room temperature. Emission spectra of **4** (6.8×10^{-8} mol/L), **10** (2.0×10^{-7} mol/L), and **10** + TFA (2.0×10^{-7} mol/L) were measured with the excitation at the absorption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

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.

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%. Mp 208–210 °C. ^{1}H NMR (400 MHz, δ-value, $\mathrm{CDCl_3}$) 8.81 (br, 2H, NH), 7.53 (s, 4H, $\mathrm{C_6H_4}$-linker), 4.35 (q, 4H, $J = 7.1$ Hz, $\mathrm{OC}\mathit{H}_2\mathrm{Me}$), 2.81, 2.62 (q × 2, 4H × 2, $J = 7.4$ and 7.5 Hz, $\mathrm{C}\mathit{H}_2\mathrm{Me}$), 1.38 (t, 6H, $J = 7.1$ Hz, $\mathrm{OCH_2}\mathit{Me}$), 1.22, 1.21 (t × 2, 6H × 2, $\mathrm{CH_2}\mathit{Me}$, $J = 6.7$ and 6.9 Hz). ^{13}C NMR (100 MHz, δ, $\mathrm{CDCl_3}$) 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 $\mathrm{C_{28}H_{36}N_2O_4 + H^+}$) 465.276/465.275. IR (cm^{-1}, in KBr pellet) 1666 (ν(CO)). Anal. Calcd for $\mathrm{C_{28}H_{36}N_2O_4}$: 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%. Mp 260 °C. ^{1}H NMR (400 MHz, δ-value, $\mathrm{CDCl_3}$) 8.84 (br, 2H, NH), 7.71, 7.56 (d × 2, 4H × 2, $J = 8.2$ Hz, $\mathrm{(C_6H_4)_2}$-linker), 4.36 (q, 4H, $J = 7.1$ Hz, $\mathrm{OC}\mathit{H}_2\mathrm{Me}$), 2.82, 2.64 (q × 2, 4H × 2, $J = 7.5$ and 7.6 Hz, $\mathrm{C}\mathit{H}_2\mathrm{Me}$), 1.39 (t, 6H, $J = 7.1$ Hz, $\mathrm{OCH_2}\mathit{Me}$), 1.23, 1.22 (t × 2, 6H × 2, $\mathrm{CH_2}\mathit{Me}$, $J = 7.5$ Hz). ^{13}C NMR (100 MHz, δ, $\mathrm{CDCl_3}$) 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 $\mathrm{C_{34}H_{40}N_2O_4 + H^+}$) 541.284/541.306. IR (cm^{-1}, in KBr pellet) 1656 (ν(CO)). Anal. Calcd for $\mathrm{C_{34}H_{40}N_2O_4}$: 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, $\mathrm{CDCl_3}$) 9.17 (br, 1H, NH), 4.32 (q, 2H, $J = 7.1$ Hz, $\mathrm{OC}\mathit{H}_2\mathrm{Me}$), 2.75, 2.65 (q × 2, 2H × 2, $J = 7.5$ and 7.4 Hz, $\mathrm{C}\mathit{H}_2\mathrm{Me}$), 1.36 (t, 3H, $J = 7.2$ Hz, $\mathrm{OCH_2}\mathit{Me}$), 1.30 (s, 12H, Me), 1.15, 1.13 (t × 2, 3H × 2, $\mathrm{CH_2}\mathit{Me}$, $J = 7.5$ Hz). ^{13}C NMR (100 MHz, δ, $\mathrm{CDCl_3}$) 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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