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# Iron-Mediated Direct Suzuki−Miyaura Reaction: A New Method for the *ortho*-Arylation of Pyrrole and Pyridine

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## ABSTRACT

**The first example of an iron-mediated direct Suzuki−Miyaura reaction between N-heterocyclic compounds and arylboronic acids is described, and both electron-rich and electron-deficient heteroarenes can be successfully used for the coupling reaction.**

The coupling between an aryl halide and an organic boronic acid, known as the Suzuki−Miyaura reaction,[1] is one of the most valuable synthetic processes for the construction of C−C bonds. This reaction was used to produce biaryl compounds, which have numerous applications in the construction of natural products, pharmaceuticals, agrochemicals, and materials.[2] Since the discovery of the Suzuki−Miyaura reaction, boronic acids have been developed as powerful reagents for C−C bond formation due to their nontoxicity, stability, and compatibility with most functional groups.[3] On the other hand, many organic halides and pseudohalides, including aryl halides and aryl sulfonates,[4] were developed as electrophiles for this reaction. However, this method requires premodification of the substrate to form the electrophiles, and the overall process is neither atom-economical nor green. In recent years, a significant breakthrough was obtained in the direct Suzuki−Miyaura reaction using complexes of Pd and Ru,[5] which is an ideal and green method to construct C−C bonds through direct functionalization of C−H bonds. However, the requirements of directing group, expensive catalysts, and relatively low yields limit the application of this method.

Iron is one of the most abundant metals on the Earth. Owing to its low cost, availability, and environmental benignity, iron has attracted much attention in the field of C−C cross coupling reactions.[6,7] However, the application

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of iron catalysis on the C−C bond formation through C−H bond functionalization remains a challenge.[8] In this respect, we have recently reported the iron-mediated direct arylation of unactivated arenes.[9] Although a stoichiometric amount of iron was used and less regioselectivity was obtained therein, such work afforded a novel protocol for the direct Suzuki−Miyaura reaction. On the basis of our previous studies, we present herein a convenient and easily handled iron-mediated direct Suzuki−Miyaura reaction for the regioselective 2-arylation of N-heterocyclic compounds. Nevertheless, some challenges for the reaction exist, such as: (1) the regioselectivity of the reaction; (2) the reactivity of electron-deficient heteroarenes; (3) the toleration for free amine on the heterocycle.[10]

Our previous studies showed that the formation of a proper iron−macrocyclic polyamine (MCPA, Figure 1) complex plays a key role in this type of reaction. Thus, we first optimized the reaction conditions including the types of iron salt and MCPA ligand in a model reaction between phenylboronic acid and pyrrole (15 mmol as slovent), and the results are summarized in Table 1. Under the optimized conditions for the iron-mediated direct arylation of unactivated arenes we reported earlier,[9] no arylation product was detected (entry 1). Fortunately, we found that the desired cross-coupling product could be obtained in 27% yield (entry 2) without the addition of base or other additives. This result encouraged us to find an appropriate combination of the iron−MCPA complex for the reaction. After screening of several iron sources (entries 2−8), Fe(II) oxalate was found to be the most efficient salt, and 47% yield of desired product was obtained in $FeC_2O_4$-present reaction (entry 5). Further $FeC_2O_4$-mediated reactions focused on the screening of MCPA ligands were studied. The reactions employing four different MCPA ligands gave desired product in low to good yields (entries 5 and 9−11). The best result was achieved in the reaction using pyridine-containing **L2** as the MCPA ligand, and 81% yield was obtained (entry 9). More importantly, almost the same result was found in the reaction using decreased amounts of iron and MCPA ligand (0.2 equiv, entry 12), indicating that the iron complex could catalyze the reaction. It is noteworthy that phenol was found as a main byproduct in the reactions employing Fe−**L1** and Fe−**L3**, but only trace phenol was detected in the reaction under optimized conditions employing Fe−**L2**. Furthermore, only trace product was obtained when the reaction was carried out under nitrogen (entry 13), indicating that oxygen is an indispensable oxidant for the coupling. To exclude the possibility that the trace other metal impurity would catalyze the reaction,[11] we did the control experiment using ultrapure $FeC_2O_4 \cdot 2H_2O$ (99.999%) as catalyst. We were pleased that

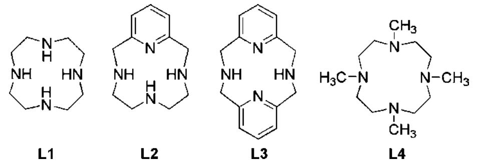
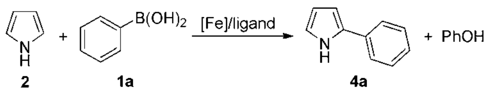


**Figure 1.** Macrocyclic polyamine (MCPA) ligands studied here.

**Table 1.** Iron-Catalyzed C-2 Arylation of Pyrrole with Phenylboronic Acid[a]



| entry | [Fe] | ligand | yield of **4a** [%][b] | yield of PhOH [%][b] |
|---|---|---|---|---|
| 1[c] | $Fe_2(SO_4)_3 \cdot 7H_2O$ | **L1** | 0 | N.D.[f] |
| 2 | $Fe_2(SO_4)_3 \cdot 7H_2O$ | **L1** | 27 | N.D. |
| 3 | $FeCl_3$ | **L1** | <10 | N.D. |
| 4 | $FeCl_3 \cdot 6H_2O$ | **L1** | <10 | N.D. |
| 5 | $FeC_2O_4 \cdot 2H_2O$ | **L1** | 47 | 17 |
| 6 | $FeCl_2$ | **L1** | 18 | N.D. |
| 7 | $Fe_2(CO)_9$ | **L1** | 17 | N.D. |
| 8 | $Fe_2O_3$ | **L1** | 25 | N.D. |
| 9 | $FeC_2O_4 \cdot 2H_2O$ | **L2** | 81 (68)[d] | trace |
| 10 | $FeC_2O_4 \cdot 2H_2O$ | **L3** | 64 | 10 |
| 11 | $FeC_2O_4 \cdot 2H_2O$ | **L4** | 18 | N.D. |
| 12[e] | $FeC_2O_4 \cdot 2H_2O$ | **L2** | 80 (66)[d] | trace |
| 13[g] | $FeC_2O_4 \cdot 2H_2O$ | **L2** | trace | N.D. |
| 14[h] | $FeC_2O_4 \cdot 2H_2O$ | **L2** | 80 | N.D. |

[a] Reaction conditions (unless otherwise stated): pyrrole (15 mmol), **1a** (0.2 mmol), [Fe] (1.0 equiv), ligand (1.0 equiv), 130 °C, 10 h, under air. [b] Yield determined by GC analysis with the use of *n*-dodecane as an internal standard. [c] With $K_3PO_4$ (4.0 equiv), pyrazole (2.0 equiv). [d] The data in parentheses are isolated yields. [e] [Fe] (0.2 equiv), ligand (0.2 equiv). [f] N.D.: not determined. [g] Reaction under nitrogen. [h] 99.999% $FeC_2O_4 \cdot 2H_2O$.

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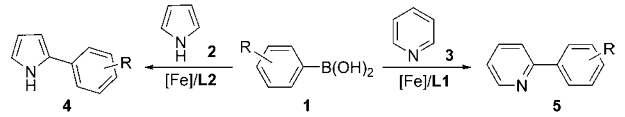
almost the same yield was obtained (entry 14). Moreover, such a reaction catalyzed by various trace impurities in $FeC_2O_4{\cdot}2H_2O$ (99.999%) has also been performed, and no product was detected, indicating that this reaction is not likely to be catalyzed by metal contaminants (see Supporting Information for details).

The substrate scope was subsequently investigated under the optimized conditions. The results of direct Suzuki–Miyaura reactions between a variety of substituted arylboronic acids and pyrrole catalyzed by Fe–**L2** are summarized in Table 2 (entries 1–14). Moderate to good yields were obtained in most reactions without the formation of 3-arylation products. Electron-withdrawing substituents might benefit the reaction (entries 7, 11, and 12), while the electron-donating group might show inhibition effects (entries 9 and 10). Some *ortho*-substituted arylboronic acids also gave moderate yields of 2-arylation product **4** in spite of the steric hindrance (entries 3 and 6).

**Table 2.** Iron-Catalyzed Arylation of N-Heterocyclic Compounds with Arylboronic Acid[a]



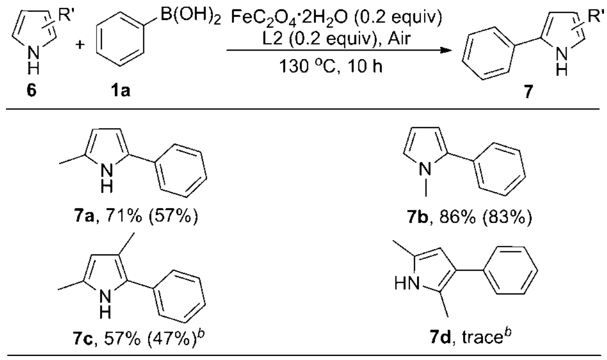
| entry | R | product | yield (%)[b] |
|---|---|---|---|
| 1 | H (**1a**) | (**4a**) | 80 (66) |
| 2 | 3-Cl (**1b**) | (**4b**) | 71 (61) |
| 3 | 2-Cl (**1c**) | (**4c**) | 56 (45) |
| 4 | 4-$CH_3$ (**1d**) | (**4d**) | 55 (43) |
| 5 | 3-$CH_3$ (**1e**) | (**4e**) | 67 (59) |
| 6 | 2-$CH_3$ (**1f**) | (**4f**) | 47 (36) |
| 7 | 4-Br (**1g**) | (**4g**) | 84 (67) |
| 8 | 4-F (**1h**) | (**4h**) | 63 (52) |
| 9 | 4-$OCH_3$ (**1i**) | (**4i**) | 28 (17) |
| 10 | 4-$CH(CH_3)_2$ (**1j**) | (**4j**) | 32 (23) |
| 11 | 4-$COOCH_3$ (**1k**) | (**4k**) | 83 (70) |
| 12 | 3-$NO_2$ (**1l**) | (**4l**) | 84 (67) |
| 13 | Nap-2 (**1m**) | (**4m**) | 61 (42) |
| 14 | 3,5-diF (**1n**) | (**4n**) | 73 (52) |
| 15[c] | H (**1a**) | (**5a**) | 41, o/(m + p) = 80:20[d] |
| 16[c] | 4-$COOCH_3$ (**1k**) | (**5k**) | 45, o/(m + p) = 95:5[d] |
| 17[c] | 4-Br (**1g**) | (**5g**) | 26, o/(m + p) = 90:10[d] |
| 18[c] | 3-$NO_2$ (**1l**) | (**5l**) | 42, o/(m + p) = 80:20[d] |

[a] Reaction conditions: pyrrole (15 mmol), **1** (0.2 mmol), $FeC_2O_4{\cdot}2H_2O$ (0.2 equiv), **L2** (0.2 equiv), 130 °C, 10 h, under air. [b] Yield determined by GC analysis with the use of *n*-dodecane as an internal standard. The data in parentheses are isolated yields. [c] Pyridine (1 mL), acetic acid (1 mL), **1** (0.2 mmol), $FeCl_3{\cdot}6H_2O$ (0.5 equiv), **L1** (0.5 equiv), 110 °C, 10 h, under air. [d] The ratio of regioisomers was determined by GC.

The iron-mediated cross-coupling between arylboronic acids and pyridine was also studied. As an electron-deficient heteroarene, pyridine is rarely arylated through direct and selective C–H arylation.[12] Herein, in the presence of the Fe–cyclen combination, high regioselective (*ortho*-) products in moderate yields could be obtained from the direct arylation of pyridine (Table 2, entries 15–18). This method provides a new protocol for the direct arylation of electron-deficient heteroarenes. Some further studies about the reaction of pyridine are now in progress.

Reactions of some substituted pyrroles with phenylboronic acid were investigated with the present iron catalytic system (Scheme 1). It was found that the substituted pyrrole was phenylated at the 2-position with excellent regioselectivity to give the desired product in moderate to good yields. Using α,α-disubstituted pyrrol such as 2,5-dimethyl-1*H*-pyrrole as substrate (Scheme 1, **7d**), only trace phenylated product was obtained, while a mass of dimeric pyrrole was produced. These results further proved that this catalyst system has excellent regioselectivity to the active 2-position of pyrrole.

**Scheme 1.** Iron-Catalyzed Arylation of Substituted Pyrroles with Phenylboronic Acid[a,b]



[a] Yield determined by GC analysis with the use of *n*-dodecane as an internal standard. The data in parentheses are isolated yields. [b] Reaction under 150 °C.

As there is a lack of mechanistic details about iron-catalyzed cross-couplings through C–H bond activation, we carried out preliminary mechanistic studies to have an insight into the mechanism of this iron-catalyzed direct arylation. The reaction was unaffected by the addition of free radical scavenger TEMPO (20%), suggesting that no free radical intermediate was involved in the reaction. In addition, oxygen was found to be indispensable for the coupling because only trace product was obtained when the reaction was carried out under nitrogen. It is known that iron species with terminal oxo ligands can be formed via reactive iron complexes with dioxygen,[13] and the Suzuki–Miyaura reaction is able to be

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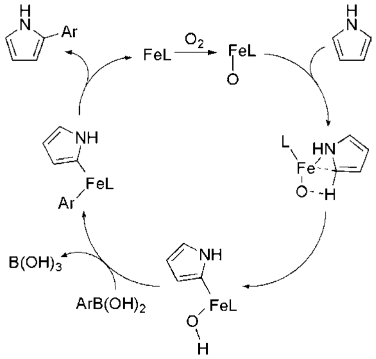
catalyzed by the oxo−metal complex in the absence of a base.[14] To find out the effective catalytic species, we utilized ESI-MS to monitor the reaction process. The consecutive formation of iron complex Fe−**L2** and oxoiron species FeO−**L2** was clearly observed by HRMS (Figure S2, Supporting Information (SI)).[15] Further, the formation of oxoiron could also be detected by UV/vis spectroscopy (Figure S3 and S4, SI).[15] These findings suggested that the oxoiron complex might be the most probable active species in the reaction.[16]

Two different pathways are possible for the C−H bond cleavage step, namely, oxidative addition and $\sigma$-bond metathesis. DFT calculations were utilized to study this step. Results showed that the transferable hydrogen on the pyrrole should move to the oxygen of the oxoiron complex without any tendency to form an iron-hydride intermediate, indicating the C−H activation by $\sigma$-bond metathesis. On the basis of these results, we speculated that the reaction started with the oxidation of an iron complex to form oxoiron species derived from oxygen, followed by an electrophilic attack of the oxoiron complex on C-2 position of heteroarenes with the assistance of a heteroatom. After subsequent deprotonation, a tertiary complex consisting of iron, heterocycle, and MCPA ligand was formed. Thereafter, in the presence of arylboronic acid, transmetalation and elimination of the iron complex would provide the desired product (Scheme 2).

**Scheme 2.** Proposed Catalytic Cycle of the Coupling[a]



[a] L = ligand.

To further understand the mechanism of the iron-catalyzed direct Suzuki−Miyaura reaction, open-shell DFT calculations were carried out to give a qualitative similar mechanistic picture of the reaction for the quartet and sextet state. The energy diagrams of the reaction are depicted in Figure 2.[15] Analyses of the reaction energy profiles indicated that the quartet was the lowest spin state in the major part of the reaction. The largest energy barriers on the potential energy surface (PES) were predicted to be 130.9 and 126.6 kJ/mol for the quartet and sextet state, representing the rate-determining step of the formation of metallo-benzene moiety via TS3.

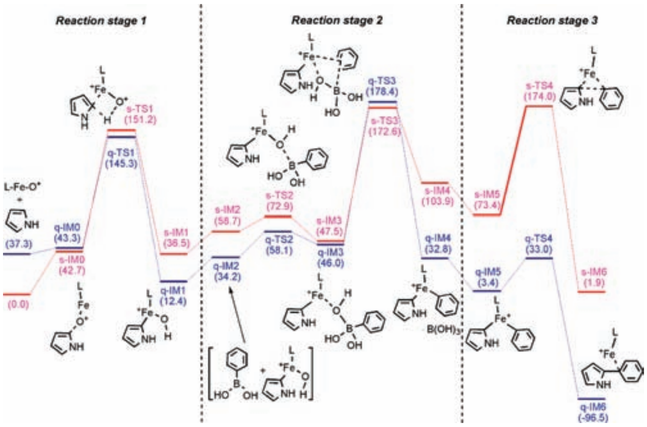


**Figure 2.** Free-energy diagrams of the Suzuki reaction calculated at the B3LYP(PCM)/6-311+G(d,p) level. The relative energies (in kJ/mol) are listed in parentheses. (The blue curve represents the quartlet surface, the red one represents the sextet surface.)

In conclusion, we developed a novel iron catalyst system for the regioselective arylation of N-heterocyclic compounds. Both electron-rich and electron-deficient heteroarenes can be successfully used for the coupling reaction. To the best of our knowledge, this is the first example of an iron-mediated direct Suzuki−Miyaura reaction between N-heterocyclic compounds and arylboronic acids. Additionally, preliminary mechanistic studies suggest that the oxoiron compound is the catalytically active species for this reaction. A full catalytic cycle of the iron-catalyzed direct Suzuki−Miyaura coupling between pyrrole and phenylboronic acid has been analyzed by means of DFT calculation, and an unprecedented catalytic C−H activation process of N-heteroaromatics by iron is revealed. Further studies to elucidate the mechanism and to expand the synthetic scope of this reaction are currently under investigation.

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**Supporting Information Available:** Experimental procedures, synthetic and spectroscopic data for various compounds, and supplementary spectral data. This material is available free of charge via the Internet at http://pubs.acs.org.

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