

Iron-Mediated Direct Arylation of Unactivated Arenes**

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The scientific importance and commercial value of biaryl compounds is illustrated by their presence in a vast array of natural products, pharmaceuticals, agrochemicals, and materials.^[1] Various highly efficient direct syntheses of these compounds have been reported. Of these approaches, transition-metal-catalyzed reactions constitute one of the predominant strategies.^[2] In such reactions, the coupling between an organometallic reagent and an aryl halide or pseudohalide is commonly involved.^[3] However, this method requires pre-modification of the substrate to form the aryl halide, and the overall process is neither atom-economical nor green. The metal-catalyzed direct arylation, through C–H bond activation, has consequently received considerable attention as an efficient method of biaryl synthesis.^[4] In recent years, significant progress has been made in direct arylation using complexes of Pd,^[5] Rh,^[6] Ru,^[7] and other metals.^[8] However, the development of cheap, environmentally benign alternative catalysts is still a challenge. Consequently, iron, as an inexpensive, readily available, and environmentally friendly transition metal, has attracted much attention in the field of cross-coupling,^[9,10] and the iron-catalyzed transformation of C–H bonds has emerged as a valuable method in organic synthesis. For these reasons, we envisaged the application of iron complexes to the direct arylation of unactivated arenes.

Recently, Bolm and co-workers have reported an efficient iron-catalyzed Sonogashira reaction^[10a] and various iron-catalyzed cross-coupling arylations by carbon–heteroatom bond formation.^[10b–c] Nakamura and co-workers have reported iron-catalyzed direct arylation at C–H bonds.^[11a] In their studies, zinc salts and a large excess of aryl Grignard reagents were required for the reactions, which needed to be carried out under strictly anhydrous conditions, and the types of substrates were limited.^[11b] Nevertheless, these results provide a significant starting point in the development of iron-catalyzed direct arylation reactions. Herein, we report the development of a novel iron-mediated direct arylation of

unactivated arenes with arylboronic acids. These facile reactions offer good functional group compatibility, and all reagents are moisture stable with low toxicity.^[12]

For initial optimization of the reaction conditions, the coupling of 4-bromophenylboronic acid and benzene was selected as a model reaction system. The results are summarized in Table 1. The first attempted reactions, in air, with FeCl₃, 1,5,7,10-tetraazacyclododecane (cyclen) as a ligand,

Table 1: Iron-mediated C-arylation of benzene with 4-bromophenylboronic acid (**1a**).^[a]

Entry	[Fe]	Ligand	Base	Additive	Yield of 2a [%]
1	FeCl ₃	none	K ₃ PO ₄	none	trace
2	FeCl ₃	cyclen	K ₃ PO ₄	none	trace
3	FeCl ₃	cyclen	K ₃ PO ₄	pyrazole	54
4	FeCl ₃ ·6 H ₂ O	cyclen	K ₃ PO ₄	pyrazole	57
5	Fe ₂ (SO ₄) ₃ ·7 H ₂ O	cyclen	K ₃ PO ₄	pyrazole	82
6	Fe(NO ₃) ₃ ·9 H ₂ O	cyclen	K ₃ PO ₄	pyrazole	69
7	FeC ₂ O ₄ ·2 H ₂ O	cyclen	K ₃ PO ₄	pyrazole	32
8 ^[b]	Fe ₂ (SO ₄) ₃ ·7 H ₂ O	TMEDA	K ₃ PO ₄	pyrazole	trace
9 ^[b]	Fe ₂ (SO ₄) ₃ ·7 H ₂ O	en	K ₃ PO ₄	pyrazole	16
10 ^[b]	Fe ₂ (SO ₄) ₃ ·7 H ₂ O	proline	K ₃ PO ₄	pyrazole	trace
11	Fe ₂ (SO ₄) ₃ ·7 H ₂ O	terpyridine	K ₃ PO ₄	pyrazole	trace
12	Fe ₂ (SO ₄) ₃ ·7 H ₂ O	cyclen	K ₂ CO ₃	pyrazole	61
13	Fe ₂ (SO ₄) ₃ ·7 H ₂ O	cyclen	CS ₂ CO ₃	pyrazole	trace
14	Fe ₂ (SO ₄) ₃ ·7 H ₂ O	cyclen	K ₃ PO ₄	imidazole	63
15	Fe ₂ (SO ₄) ₃ ·7 H ₂ O	cyclen	K ₃ PO ₄	triazole	39
16 ^[c]	Fe ₂ (SO ₄) ₃ ·7 H ₂ O	cyclen	K ₃ PO ₄	pyrazole	trace
17 ^[d]	Fe ₂ (SO ₄) ₃ ·7 H ₂ O	cyclen	K ₃ PO ₄	pyrazole	83

[a] Reaction conditions (unless otherwise stated): benzene (5 mL), **1a** (1.0 equiv), [Fe] (1.0 equiv), ligand (1.0 equiv), base (4.0 equiv), additive (2.0 equiv), 80°C, 48 h, under air. [b] 2.0 equivalents of ligand were used. [c] Reaction under nitrogen. [d] Reaction under oxygen. cyclen = 1,4,7,10-tetraazacyclododecane; en = 1,2-ethylenediamine; TMEDA = *N,N,N',N'*-tetramethylethylenediamine.

and K₃PO₄ as base (Table 1, entries 1 and 2), afforded no arylation product. Addition of pyrazole to the reaction system led to the desired product **2a** in 54 % yield (Table 1, entry 3). In our reaction, pyrazole is a necessary additive to ensure good results, but its role remains unclear. Studies on this and the entire mechanism are currently in progress. Notably, no Suzuki-type product or homo-coupling byproduct of the arylboronic acid was obtained. The same reaction using of FeCl₃·6H₂O provided **2a** in almost the same yield (Table 1, entry 4), indicating that the presence of water in the iron salt had little effect on the reaction. By changing the iron salt hydrate in the reaction, the arylation product **2a** was obtained

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in varying yields ranging from 32 to 82 % (Table 1, entries 5–7). On testing the effect of the ligand (Table 1, entries 8–11), we discovered that reactions using en as ligand provided **2a** in low yields, whereas those with other ligands, or without the use of a ligand, gave only trace amounts of desired product. The use of other bases and additives also resulted in lower yields (Table 1, entries 12–15). We also carried out the reactions under atmospheres of nitrogen and oxygen. Only trace product was obtained under nitrogen, and little difference was found between the reaction carried out under oxygen and that carried out under air (Table 1, entries 16 and 17). These results indicate that O₂ is a required sacrificial oxidant for the coupling.

We then evaluated the scope of the cross-coupling of benzene with various arylboronic acids under optimized conditions. The results are summarized in Table 2. The reactions between benzene and substituted arylboronic acids with different electronic properties, using Fe₂(SO₄)₃·7H₂O, cyclen, K₃PO₄, and pyrazole under air, gave the expected products in mostly good yields. However, substituents at the *ortho* position of the arylboronic acids significantly compromised the reaction, and only trace products were obtained (Table 2, entries 4 and 7), indicating

that the reaction system is sensitive to steric effects. The reaction of benzene with 4-carboxyphenylboronic acid afforded the cross-coupling product in negligible yield (Table 2, entry 13), indicating that the acidity of the substrate damaged the reaction system.

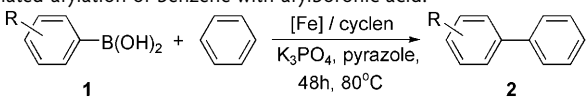
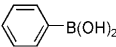
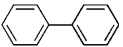
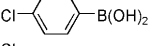
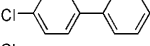
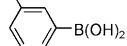
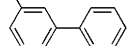
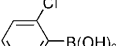
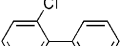
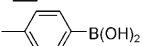
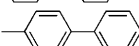
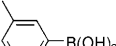
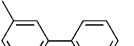
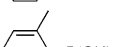
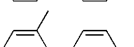
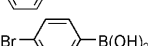
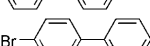
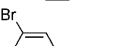
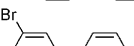
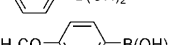
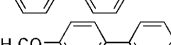
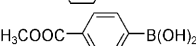
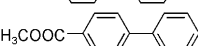
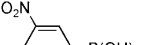
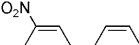
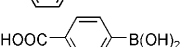
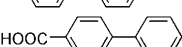
Subsequently, we studied the iron-mediated cross-coupling between phenylboronic acid and several simple unactivated arenes. The results are listed in Table 3. For mono-substituted benzenes, electron-withdrawing groups apparently benefit the reaction (Table 3, entries 1–3). For chlorobenzene, the regioisomeric coupling products were obtained in a total yield of 82 % (Table 3, entry 2). Reaction temperature also had an obvious effect. For substrate **3e**, the steric hindrance from two *ortho* substituents led to a yield of only 10 % at 110 °C. However, by raising the reaction temperature to 130 °C, the yield was increased to 64 %. GC and ¹H NMR spectroscopy were used to determine the composition of regioisomeric product mixtures. Interestingly, the results indicated that the C–H bonds *ortho* to the substituents, despite a higher degree of steric hindrance (Table 3, entry 7), displayed highest reactivity (Table 3, entries 1–3, 6, and 7).

Studies into the mechanism of iron-catalyzed cross-coupling reactions have evolved at a comparatively slow

pace, and it remains unclear.^[9d] The results of reactions carried out under nitrogen and oxygen atmospheres (Table 1, entries 16 and 17) indicate that oxygen is a required sacrificial oxidant for the coupling. The isotope effect of the reaction was determined by applying the standard conditions to the reaction of 4-methylphenylboronic acid (**1f**) with equimolar amounts of benzene and [D₆]benzene (see the Supporting Information). The reaction yielded **2f** and the deuterated product with a molar ratio of 3:2, giving a *k_H*/*k_D* value of 1.5; this suggests that C–H bond activation is the rate-determining step.^[13] 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO, 20 mol %) was then added to the iron-mediated reaction between phenylboronic acid and benzene, to act as a radical scavenger; it had no effect on the yield, suggesting that no radical species participates in the coupling process.^[5]

In summary, we have developed a novel method to prepare biaryl compounds through iron-mediated direct arylation. In comparison with previously reported systems, the reagents used in these reactions were easily handled and had low toxicity. Commercially available arenes were used directly and were

Table 2: Iron-mediated arylation of benzene with arylboronic acid.^[a]

			
Entry	Arylboronic acid 1	Product 2	Yield [%]
1	 1b	 2b	83
2	 1c	 2c	66
3	 1d	 2d	73
4	 1e	 2e	trace
5	 1f	 2f	62
6	 1g	 2g	65
7	 1h	 2h	trace
8	 1a	 2a	82
9	 1i	 2i	55
10	 1j	 2j	62
11	 1k	 2k	31
12	 1l	 2l	51
13	 1m	 2m	trace

[a] Reaction conditions: benzene (4 mL), arylboronic acid (1.0 equiv), Fe₂(SO₄)₃·7H₂O (1.0 equiv), cyclen (1.0 equiv), K₃PO₄ (4.0 equiv), pyrazole (2.0 equiv), 80 °C, 48 h, under air.

Table 3: Iron-mediated arylation of arenes with benzenboronic acid.^[a]

$\text{C}_6\text{H}_5\text{B(OH)}_2 + \text{C}_6\text{H}_4\text{R} \xrightarrow[\text{K}_3\text{PO}_4, \text{pyrazole, 48h, 110}^\circ\text{C}]{[\text{Fe}] / \text{cyclen}} \text{C}_6\text{H}_4\text{R-C}_6\text{H}_5$					
Entry	Arene 3	Product 4	Yield [%]	Ratio of regioisomers	
1			38	<i>o/m/p</i> = 50:19:31 ^[b]	
2			82	<i>o/m/p</i> = 57:24:19 ^[c]	
3			56	<i>o/m/p</i> = 55:26:19 ^[c]	
4			29	—	
5			10 (64) ^[d]	—	
6			25	4f-1/4f-2 = 58:42 ^[b]	
7			28	4g-1/4g-2/4g-3 = 40:49:11 ^[b]	

[a] Reaction conditions (unless otherwise stated): arene (4 mL), benzenboronic acid (1.0 equiv), $\text{Fe}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$ (1.0 equiv), cyclen (1.0 equiv), K_3PO_4 (4.0 equiv), pyrazole (2.0 equiv), 110°C, 48 h, under air. [b] The ratio of the regioisomers was determined by ^1H NMR spectroscopy. [c] The ratio of the regioisomers was determined by GC. [d] Value in parentheses refers to reaction carried out at 130°C.

easily recovered after the reactions. The reaction worked well in coupling a series of substituted phenylboronic acids with simple unactivated arenes. Further studies to elucidate the mechanism and to expand the synthetic scope of this reaction are currently underway.

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