JOC Note

Palladium-Catalyzed Direct C-2 Arylation of Indoles with Potassium Aryltrifluoroborate Salts

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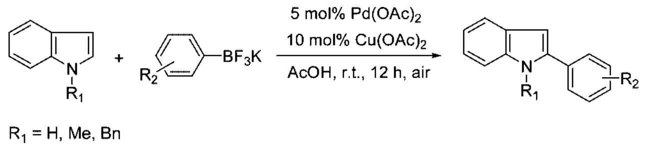

Mild conditions have been developed to achieve Pd(OAc)$_2$-catalyzed regioselective cross-coupling between indoles and potassium aryltrifluoroarylborates in the presence of Cu(OAc)$_2$ in acetic acid at room temperature. A variety of potassium aryltrifluoroborates selectively undergo the direct arylation across indoles and afford 2-aryl indoles in moderate to good yields.

The C-arylated indoles are found in many natural products and pharmaceuticals and are the important building blocks of bioactive molecules.[1] The main way to obtain C-arylated indoles is the palladium-catalyzed cross-coupling of functionalized heteroarenes (e.g., boronates or halides) with activated arenes (halogenation, metalation).[2] Although these methods have provided the efficient routes to these compounds, the requirement for preactivating the reaction components to their halides, silicon, tin, or boron derivatives is costly and inefficient. More recently, considerable attention has been given to the direct arylation via cross-coupling of aromatic (sp^2) C−H bonds with activated arenes, which allows for carbon−carbon bond formation without the need for prior functionalization of one of the coupling partners.[3,4] The aryl halides were first pioneered as the coupling partners of direct C-arylation of indoles with rhodium and palladium catalysts,[5,6] and the subsequent studies showed that [Ph-I-Ph]BF$_4$ underwent oxidative arylation efficiently with indoles under mild reaction conditions.[7] More recently, Shi and co-works reported that aryl boronic acids were good coupling partners with the direct C-arylation of indoles in the presence of palladium catalysts in an atmosphere of oxygen.[8] Aryl boronic acids have been studied extensively in Suzuki−Miyaura reactions,[9] and the use of organotrifluoroborate salts as an alternative to organoboronic acids in the Suzuki−Miyaura reaction and other coupling reactions has been well developed by Molander and others.[10,11] These salts can be readily prepared through a variety of one-pot synthetic routes from readily available starting materials or by the addition of KHF$_2$ to a wide variety of organoboron intermediates.[12] By taking advantage

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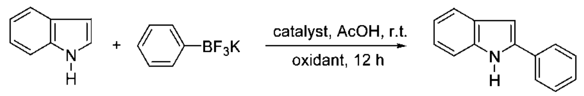
TABLE 1. Effect of Catalysts and Oxidants[a]



entry	catalyst (mol %)	oxidant	yield (%)[b]
1	Pd(OAc)$_2$ (5%)	(PhCO$_2$)$_2$	n.r.
2	Pd(OAc)$_2$ (5%)	mCPBA	trace
3	Pd(OAc)$_2$(5%)	H$_2$O$_2$	n.r.
4	Pd(OAc)$_2$(5%)	*t*-BuOOH	15[c]
5	Pd(OAc)$_2$(5%)	*t*-BuOOBu-*t*	25[c]
6	Pd(OAc)$_2$(5%)	K$_2$S$_2$O$_8$	72
7	Pd(OAc)$_2$(5%)	oxone	63
8	Pd(OAc)$_2$(5%)	O$_2$	71
9	Pd(OAc)$_2$(5%)	air	62
10	Pd(OAc)$_2$(5%)/Cu(OAc)$_2$ (10%)	air	81
11	Pd(OAc)$_2$ (5%)/Cu(OAc)$_2$ (10%)	N$_2$	10[c]
12	PdCl$_2$(5%)/Cu(OAc)$_2$ (10%)	air	20[c]
13	Pd(dba)$_2$ (5%)/Cu(OAc)$_2$ (10%)	air	65
14	Pd(OTFA)$_2$(5%)/Cu(OAc)$_2$ (10%)	air	53
15	Pd(OAc)$_2$ (5%)/Cu(OAc)$_2$ (100%)	N$_2$	10[c]

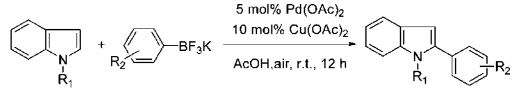
[a] Reaction conditions: indole (0.5 mmol), potassium phenyltrifluoroborate (0.75 mmol), Cu(OAc)$_2$ (10 mol %), Pd(OAc)$_2$ (5 mol %), room temperature, 12 h. [b] Isolated yields based on indole. [c] GC yields based on indole.

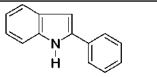
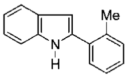
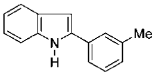
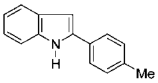
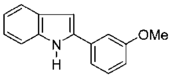
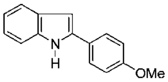
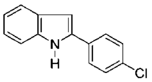
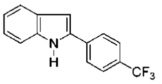
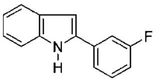
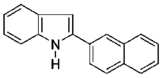
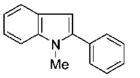
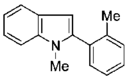
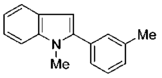
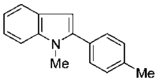
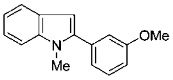
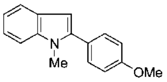
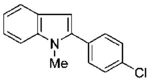
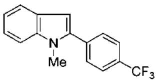
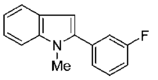
of the attractive features of organotrifluoroborate salts, we report here an efficient and regioselective method for the C-arylation of indoles with potassium trifluoroborate salts in the presence of palladium catalyst. The oxidants were proved to be crucial for the success of the reaction, and the reactions can be performed in the absence of ligands without any precautions with regard to the exclusion of air and moisture.

Our initial efforts toward direct coupling of the C−H bond of indole with potassium phenyltrifluoroborate focused on the use of oxidants (Table 1, entries 1−10). We first used the previous oxidants described for arylation of 2-phenylpyridines with aryl iodides by us,[13] such as benzoyl peroxide, *m*-chloroperbenzoic acid, and hydrogen peroxide, but in this case they were inactive (Table 1, entries 1−3). Other peroxides including 2-hydroperoxy-2-methylpropane and 2-(*tert*-butylperoxy)-2-methylpropane afforded the desired coupling product, but in very low yields (Table 1, entries 4 and 5). Potassium peroxydisulfate and oxone showed an obvious effect on the coupling reaction and moderate yields were achieved (Table 1, entries 6 and 7). It should be noted that a 62% yield was obtained for the coupling reaction in the presence of air, while oxygen provided the higher yield (Table 1, entries 8 and 9). Considering that oxygen is relatively hard to handle, 10 mol % Cu(OAc)$_2$ was added as cocatalyst for the reaction in air. It was found that the rate of the coupling reaction was significantly improved and the best yields were obtained (Table 1, entry 10). The reaction was sluggish in nitrogen (Table 1, entry 11). When PdCl$_2$, Pd(dba)$_2$,and Pd(OTFA)$_2$ were used, the yields decreased (Table 1, entries 12−14). The homocoupling product from potassium phenyltrifluoroborate was observed on a small scale, and could be easily isolated by column chromatography.

Further investigations of efficiency and scope of the method were performed and the Pd(OAc)$_2$/Cu(OAc)$_2$ was proved to be an active catalyst for the direct C−H bond coupling of indoles with potassium aryltrifluoroborates in air (Table 2).As shown in Table 2, in most cases, good results were obtained for the

TABLE 2. Palladium-Catalyzed Direct Arylation of Indole with Potassium Aryltrifluoroborate Salts[a]



Entry	R$_1$	R$_2$	Product	Yield (%)[b]
1	H	H		81 (71)
2	H	2-Me		36 (20)
3	H	3-Me		70 (59)
4	H	4-Me		65 (55)
5	H	3-OMe		70 (62)
6	H	4-OMe		38 (22)[c]
7	H	4-Cl		62 (45)
8	H	4-CF$_3$		35 (28)[d]
9	H	3-F		33 (22)[d]
10	H	2-naph		70 (63)
11	Me	H		78 (71)
12	Me	2-Me		82 (75)
13	Me	3-Me		86 (73)
14	Me	4-Me		71 (66)
15	Me	3-OMe		83 (69)
16	Me	4-OMe		78 (70)
17	Me	4-Cl		60 (55)
18	Me	4-CF$_3$		45 (38)[d]
19	Me	3-F		42 (33)[d]

[a] Reaction conditions: indole (0.5 mmol), potassium aryltrifluoroborate salts (0.75 mmol), Cu(OAc)$_2$ (10 mol %), Pd(OAc)$_2$ (5 mol %), room temperature, 12 h. [b] Isolated yields based on indole. The yield with arylboronate acids as substrates is in parentheses. [c] The homocoupling product from potassium 4-methoxylphenyl trifluoroborate was 54%. [d] Cu(OAc)$_2$ (100 mol %) was used.

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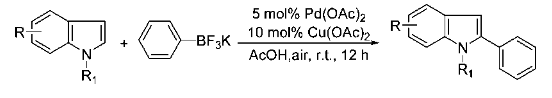
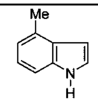
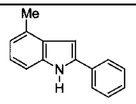
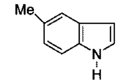
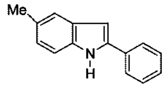
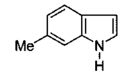
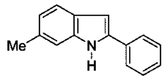
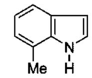
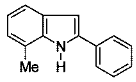
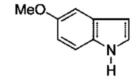
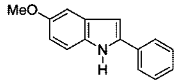
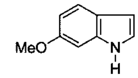
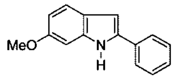
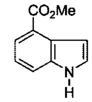
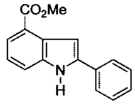
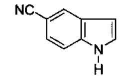
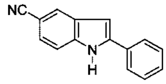
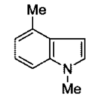
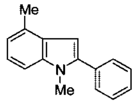
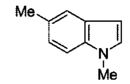
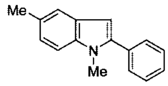
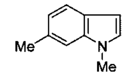
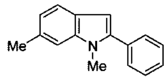
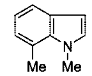
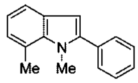
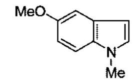
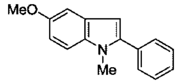
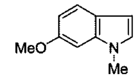
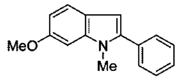
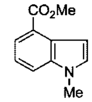
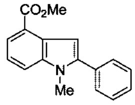
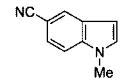
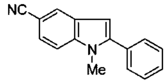
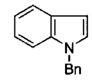
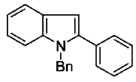
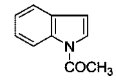
(13) Cheng, K.; Zhang, Y. H.; Zhao, J. L.; Xie, C. S. *Synlett* **2008**, 1325–1330.

TABLE 3. Direct Arylation of Various Substituted Indoles with PhBF$_3$K[a]



Entry	Indole	Product	Yield (%)[b]
1			55
2			68
3			64
4			53
5			74
6			46
7			30 [c]
8			35 [c]
9			85
10			82
11			84
12			80
13			72
14			68
15			33 [c]
16			36 [c]
17			74
18		-	

[a] Reaction conditions: indoles (0.5 mmol), potassium phenyltrifluoroborate (0.75 mmol), Cu(OAc)$_2$ (10 mol %), Pd(OAc)$_2$ (5 mol %), room temperature, 12 h. [b] Isolated yields based on indole. [c] Cu(OAc)$_2$ (100 mol %) was used.

potassium trifluoroarylborates with an electron-donating group in the aromatic ring (Table 2, entries 1−6). However, the homocoupling of potassium 4-methoxylphenyltrifluoroborate was very fast and a 54% isolated yield of this byproduct was obtained, which led to the decrease of yield of desired cross-coupling product (Table 2, entry 6). Potassium aryltrifluroborate with ortho substitutent delivered the corresponding arylated indole in poor yield (Table 2, entry 2), illustrating that the steric hindrance played a role in the reaction. The presence of strong electron-withdrawing groups such as −F and −CF$_3$ in the aromatic ring of aryltrifluoroborate salts led to lower efficiency even with 100 mol % Cu(OAc)$_2$ (Table 2, entries 8 and 9), while a moderate yield was obtained for potassium 4-chlorophenyltrifluoroborate (Table 2, entry 6). Potassium 2-naphthalenyltrifluoroborate carried out the reaction smoothly and a 70% yield was afforded (Table 2, entry 10). In the case of 1-methyl-1*H*-indoles, the efficiency was generally enhanced in respect to that of free indoles (Table 2, entries 11−19). In particular, the coupling of sterically hindered potassium trifluoroborates was feasible, as exemplified by the reaction of potassium 2-methylphenyltrifluoroborate with 1-methyl-1*H*-indole to give arylated product in 82% yield (Table 2, entry 12), which is consistent with the results reported by Shi using aryl boronic acids.[8] The potassium aryltrifluoroborates need not be in excess for electron-rich indoles and potassium aryltrifluoroborates, but an excess is required for electron-deficient indoles and potassium aryltrifluoroborates. We also examined the reactivity of aryl boronic acids and found that the aryl boronic acids were less efficient than the corresponding potassium aryltrifluoroborates under the reaction conditions (Table 2, yield in parentheses).[14] However, only a trace of the desired product was observed by the analysis of GC-MS for 3-methylindole, and 2-methylindole was inactive.

The substituent groups on the indoles influenced the direct arylation reactions as summarized in Table 3. Indoles containing strongly electron-withdrawing substituents exhibited lower yields to the arylation than their electron-rich counterparts. For example, the yields of −CN- and −CO$_2$Et-substituted indoles were considerably depressed in contrast to Me- and MeO-substituted indoles (Table 3, entries 1−8). Again, the N-substituted indoles were more reactive than the free (N−H) indoles (Table 3, entries 9−16), and *N*-benzylindole was well tolerated (Table 3, entry 17). In contrast, *N*-acetylindole was inactive to the reaction (Table 3, entry 18).

The reaction mechanism is not clear currently. In the study of palladium-catalyzed alkenylation of indoles, Gaunt and co-workers found that the selectivity of C2- and C3-alkenylated indoles was strongly influenced by solvents, and acidic reaction conditions favor C2-alkenylation production.[15] They proposed that the deprotonation of palladation intermediate **1** at C3 would be slowed at acidic conditions, which could allow the migration of C3→C2 to form the intermediate **2** (Scheme 1). The mechanism studies by Sames et al. also revealed that the first electrophilic substitution of the indole ring at C3-position followed by a C3 → C2 migration (Scheme 1, intermediate **1** to **2**) was the most probable pathway for the selective C2-arylation in the direct palladium-catalyzed arylation of indoles.[6f] In our experiment, the electron-rich indoles are more reactive

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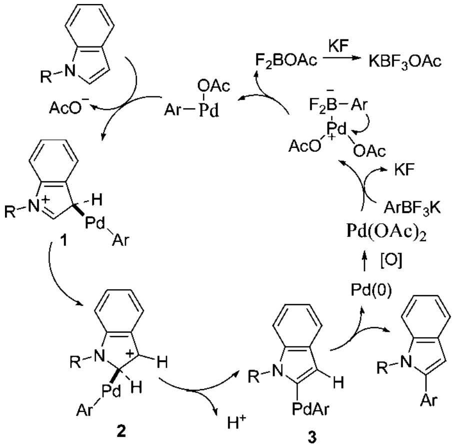
(14) (a) Batey, R. A.; Thadani, A. N.; Smil, D. V. *Org. Lett.* **1999**, *1*, 1683–1686. (b) Batey, R. A.; Thadani, A. N.; Smil, D. V.; Lough, A. J. *Synthesis* **2000**, 990–998. (c) Molander, G. A.; Elia, M. D. *J. Org. Chem.* **2006**, *71*, 9198–9202.

(15) Grimser, N. P.; Gauntlett, C.; Godfrey, C. R. A.; Gaunt, M. J. *Angew. Chem., Int. Ed.* **2005**, *44*, 3125–3129.

SCHEME 1. Proposed Mechanism for the Direct Arylation of Indoles with $ArBF_3K$



than the electron-deficient indoles, which is consistent with the electrophilic substitution mechanism. On the basis of these results, we proposed a plausible mechanism for the arylation of indoles as shown in Scheme 1. First, the aryl is transferred from the metal boron to metal palladium,[16] which undergoes the electrophilic palladation at the preferential C3-position of indole. The subsequent 1,2-migration gives intermediate **2**, and the deprotonation leads to the production of intermediate **3**, which liberates the biaryl product after the reductive elimination with the generation of Pd(0). The pivotal step in this process involves the oxidation of Pd(0) to Pd(II). We found that $Cu(OAc)_2$ has a poor effect on the reaction as an oxidant, but it played some role for the activation of oxygen. For example, the yields of biaryl increased from 62% to 81% in air after the addition of 10% $Cu(OAc)_2$, and the reaction was sluggish in the absence of oxygen even in the presence of 100 mol % $Cu(OAc)_2$ (Table 1, entries 9−10 and 15).

In conclusion, we have developed a palladium-catalyzed direct arylation of indoles with potassium aryltrifluoroborates combined with copper as a cocatalyst using air as the oxidant. The addition of 10 mol % $Cu(OAc)_2$ significantly improved the reaction and the direct arylation could be performed under surprisingly mild conditions.

Experimental Section

General Procedure. A mixture of indole (0.5 mmol), $Pd(OAc)_2$ (6 mg, 5 mol %), $Cu(OAc)_2$ (9 mg, 10 mol %; in Table 2, entries 8, 9, 18, and 19, and in Table 3, entries 7, 8, 15, and 16, 91 mg, 100 mol %), potassium aryltrifluoroborate (0.75 mmol), and acetic acid (5 mL) was stirred at room temperature under air for 12 h. Afterward, the reaction mixture was filtered through a plug of Celite and the filtrate was evaporated. The resulting oil was dissolved in ether (25 mL) and washed with aqueous $NaHCO_3$ (2 × 15 mL). The organic layer was dried with Na_2SO_4 and concentrated. The residue was purified by flash column chromatography to afford the corresponding products.

2-Phenyl-1*H*-indole [Table 2, entry 1]. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 8.32 (br s, 1 H), 7.62−7.66 (m, 3 H), 7.38−7.45 (m, 3 H), 7.32 (t, 1 H, $J = 7.2$ Hz), 7.19 (t, 1 H, $J = 7.2$ Hz), 7.12 (t, 1 H, $J = 7.2$ Hz), 6.82 (s, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 137.9, 136.38, 132.3, 129.2, 129.0, 127.7, 125.2, 122.4, 120.7, 120.3, 110.9, 100.0; MS (EI) *m/z* (%) 194 (16) [$M^+ + 1$], 193 (100) [M^+], 192 (13) [$M^+ - 1$], 165 (20).[7]

5-Methoxy-2-phenyl-1*H*-indole [Table 3, entry 5]. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 8.23 (br s, 1 H), 7.65 (d, 2 H, $J = 7.6$ Hz), 7.43 (t, 2 H, $J = 7.6$ Hz), 7.31 (q, 1 H, $J = 7.6$ Hz), 7.26 (s, 1 H), 7.09 (d, 1 H, $J = 2.0$ Hz), 6.86 (dd, 1 H, $J = 8.8, 2.4$ Hz), 6.75 (s, 1 H), 3.87 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.5, 138.6, 132.4, 132.0, 129.7, 129.0, 127.6, 125.0, 112.6, 111.6, 102.2, 99.8, 55.8; MS (EI) *m/z* (%) 224 (18) [$M^+ + 1$], 223 (100) [M^+], 208 (72), 180 (21).[8]

Acknowledgment. Funding from Zhejiang Provincial Natural Science Foundation of China (R407106) and the Natural Science Foundation of China (No. 205710631) is acknowledged

Supporting Information Available: General experimental procedures and spectroscopic data for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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[16] (a) Hassan, J.; Sevignon, M.; Gozzi, C.; Lemaire, M. *Chem. Rev* **2002**, *102*, 1359–1469. (b) Moreno-Manas, M.; Pe'rez, M.; Pleixats, R. *J. Org. Chem.* **1996**, *61*, 2346–2351. (c) Aramendia, M. A.; Lafont, F.; Moreno-Manas, M.; Pleixats, R.; Roglans, A. *J. Org. Chem.* **1999**, *64*, 3592–3594.