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Palladium-Catalyzed Direct Arylation of Electron-Deficient Polyfluoroarenes with Arylboronic Acids

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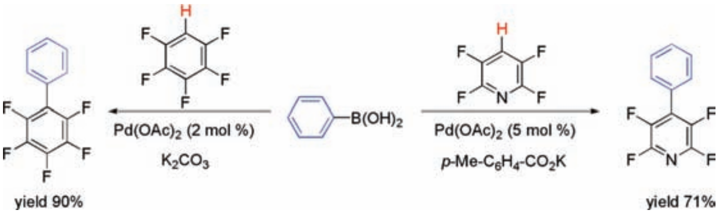
ABSTRACT



The palladium-catalyzed direct arylation of electron-deficient arenes that contain two or more fluorine groups with arylboronic acids was realized. The key to achieving a broad substrate scope with respect to both polyfluorobenzenes and arylboronic acids is the choice of bases depending on acidities of polyfluorobenzenes.

The prevalence of the biaryl substructure in biologically active molecules and functional materials has prompted synthetic chemists to seek efficient methods for the construction of this class of molecules.[1] Consequently, the transition metal-catalyzed cross-coupling reactions between aryl halides and organometallics have evolved into the most powerful synthetic tools for generation of biaryl compounds.[2] The recent advances in metal-catalyzed C−H bond functionalization suggest that it is possible to achieve similar transformations without the need for the preactivation of coupling partners (e.g., preparations of aryl halides and organometallic reagents).[3,4] Strategies for functionalization of C−H bonds not only offer the most efficient synthetic route to the target compounds,[5] but also in some cases provide a solution to the problem arising from the use of unstable or hard to prepare organometallic reagents in traditional cross-coupling

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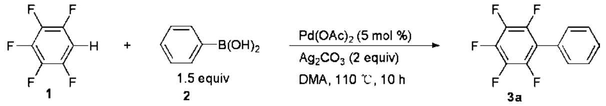
reactions.[6−8] In this regard, Fagnou[6] and Daugulis[7] have successfully developed the direct arylation of electron-deficient polyfluoroarenes or heterocycles for synthesis of fluorobiaryl or heterocycle-containing biaryl compounds.

Recently, efforts made by Yu,[9] Shi,[10] and others[11] have led to the development of palladium-catalyzed C−H bond arylation with organoboron reagents, and Murai and Kakiuchi disclosed a ruthenium-catalyzed ortho C−H arylation of acetophenones with boronic esters.[12] Copper-[13] and iron-based catalysts[14] have successfully been exploited as a cost-efficient replacement for palladium-based catalysts for the direct arylation of arenes with arylboronic acids. These reported reactions are limited to directing group-containing or electron-rich arenes. However, to date, no example has been reported that involves the direct arylation of electron-deficient arenes with organoboron reagents, except for a few substrates bearing directing groups.[9b] In view of the importance of electron-deficient fluorobiaryls in medicinal[15] and materials chemistry,[16] the discovery of new reactions for the synthesis of these valuable compounds remains highly desirable. Herein, we report a palladium-catalyzed method for the direct arylation of electron-deficient polyfluoroarenes with organoboron reagents and also present the result of the preliminary mechanistic study on this reaction.

To achieve the direct arylation of fluoroarenes with arylboronic acids, we need to address the following issue: the cleavage of the C−H bond of electron-deficient fluoroarene generally requires basic conditions that also accelerate the transmetalation between the arylboronic acid and the Pd(II) species, whereas the fast transmetalation would readily lead to the undesired homocoupling of arylboronic acid if the C−H bond cleavage is relatively slow,[17] thus hampering the generation of the desired cross-coupling product. Our strategy to solve this problem is to simultaneously add a weak base, which we believe promotes the C−H bond cleavage, and a weak acid, which we believe reduces the transmetalation rate of arylboronic acid, and therefore suppresses the undesired homocoupling.[10b]

A variety of reaction parameters were screened with the reaction of pentafluorobenzene (**1**) with 1.5 equiv of phenylboronic acid (**2**) as a model reaction system. Selected results that illustrate the effect of acid and base on this reaction are listed in Table 1. In the presence of 5 mol % of $Pd(OAc)_2$ as a catalyst and 2 equiv of Ag_2CO_3 as an oxidant, the reaction carried out in dimethylacetamide (DMA) at 110 °C in the absence of any additive did not afford the desired product in appreciable quantities. Instead, it produced the undesired biphenyl from homocoupling of phenylboronic acid (entry 1, Table 1). The addition of 2 equiv of K_2CO_3 led to the formation of the desired arylation product in 75% yield (entry 2, Table 1). Both Na_2CO_3 and KOAc gave a slightly lower yield (entries 3 and 6, Table 1), but Cs_2CO_3 was almost ineffective for this reaction (entry 4, Table 1). K_3PO_4 was found to be superior to K_2CO_3 (entry 5, Table 1). As expected, the addition of carboxylic acids efficiently

Table 1. Selected Screening Results for Pd-Catalyzed Direct Arylation of Pentafluorobenzene with Phenylboronic Acid[a]



entry	base (equiv)	acid (0.3 equiv)	yield (%)[b]
1			trace
2	K_2CO_3 (2)		75
3	Na_2CO_3 (2)		70
4	Cs_2CO_3 (2)		7
5	K_3PO_4 (2)		80
6	KOAc (2)		69
7	K_2HPO_4 (2)		71
8	p-Me-C_6H_4-CO_2K (2)		55
9	K_2CO_3 (2)	$^tBuCO_2H$	72
10	K_2CO_3 (2)	p-Me-C_6H_4-CO_2H	84
11	K_2CO_3 (2)	o-MeO-C_6H_4-CO_2H	80
12	K_2CO_3 (2)	o-O_2N−C_6H_4-CO_2H	79
13	KF (2.5)	p-Me-C_6H_4-CO_2H	77
14	K_3PO_4 (2)	p-Me-C_6H_4-CO_2H	88
15	K_2CO_3 (0.5)	p-Me-C_6H_4-CO_2H	89
16	K_3PO_4 (0.5)	p-Me-C_6H_4-CO_2H	85
17	K_2CO_3 (0.5)	p-Me-C_6H_4-CO_2H	90[c]

[a] 0.2 mmol scale, 2 mL of DMA (0.1 M). [b] Isolated yields. [c] $Pd(OAc)_2$ (2 mol %) and phenylboronic acid (1.2 equiv).

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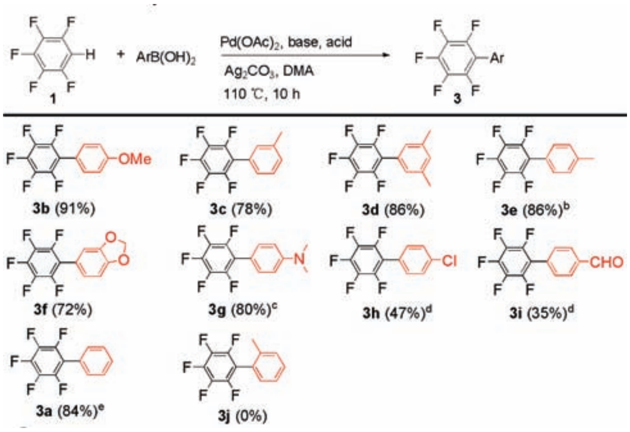
inhibited the homocoupling of phenylboronic acid in the presence of 2.0 equiv of bases. Screening several carboxylic acids and their loadings revealed that 0.3 equiv of *p*-toluic acid in combination with 2.0 equiv of K_3PO_4 or K_2CO_3 provided excellent yields (entries 9−14). We can rule out the possibility that the beneficial effect of *p*-toluic acid arises from potassium *p*-toluate or K_2HPO_4 formed in situ from the reaction of *p*-toluic acid with K_3PO_4 since neither K_2HPO_4 nor potassium *p*-toluate gave a comparable yield in the absence of acid (entries 7 and 8, Table 1). Reducing the amount of K_2CO_3 to 0.5 equiv further improved the reaction in the presence of 0.3 equiv of *p*-toluic acid (entry 15, Table 1). Gratifyingly, 2 mol % of $Pd(OAc)_2$ in conjunction with 0.5 equiv of K_2CO_3 and 0.3 equiv of *p*-toluic acid effected the reaction of pentafluorobenzene with 1.2 equiv of phenylboronic acid with 90% yield (entry 17, Table 1). This reaction also occurred in other polar solvents such as DMSO to give somewhat lower yields than that in DMA, but did not occur in nonpolar or less polar solvents such as toluene and dioxane. The other common oxidants for the Pd(0)/Pd(II) system such as a variety of Cu(II) salts and oxygen were ineffective for this reaction, and other silver sources such as Ag_2O and AgOAc were less efficient than Ag_2CO_3.

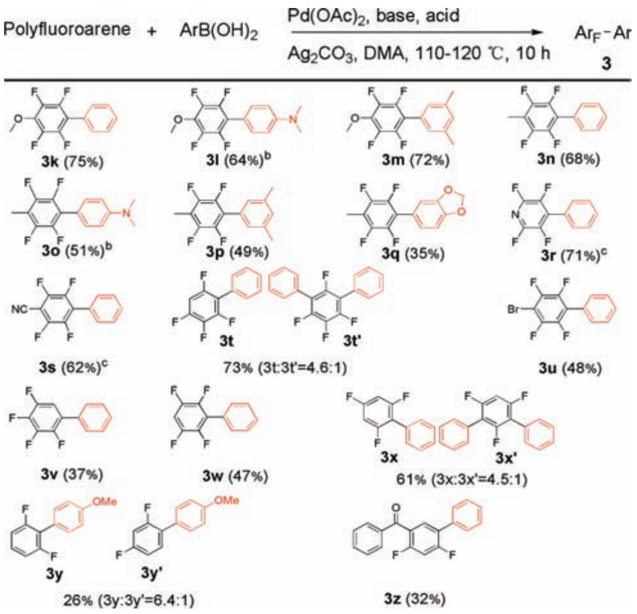
The scope of this reaction with respect to organoboron reagents was further explored by employing the conditions of entry 17 in Table 1. As shown in Scheme 1, a range of organoboron reagents can serve as arylating reagents for the direct arylation of pentafluorobenzene, affording the desired products in moderate to excellent yields. The reactivity of organoboron reagents was observed to rely on the electronic nature of substituents on the aromatic rings. Electron-donating substituents were generally beneficial for this transformation (**3b−d**,**f**) except for the case involving the dimethylamino group, in which 5 mol % of $Pd(OAc)_2$, 1.5 equiv of arylboronic acid, and 2 equiv of K_2CO_3 were required to obtain a good yield (**3g**). Although electron-deficient arylboronic acids suffered from their relatively poor reactivities, using 2.5 equiv of KF in place of 0.5 equiv of K_2CO_3 gave rise to synthetically useful yields (**3h** and **3i**). This transformation can be scaled up, as illustrated by the reaction on 5 mmol scale that offered a yield comparable to that on 0.2 mmol scale (**3a**, Scheme 1). When the arylboronic acid bearing the ortho-substituent on the aromatic ring was used as a coupling partner, neither the cross-coupling product nor the homocoupling product was formed, indicative of the sensitivity of this transformation to steric hindrance (**3j**).

Scheme 1. Pd-Catalyzed Direct Arylation of Pentafluorobenzene with Various Arylboronic Acids[a]



[a] Reaction conditions: pentafluorobenzene **1** (0.2 mmol), arylboronic acid (1.2 equiv), $Pd(OAc)_2$ (2 mol %), K_2CO_3 (0.5 equiv), Ag_2CO_3 (2 equiv), *p*-Me-C_6H_4-CO_2H (0.3 equiv), DMA (2 mL, 0.1 M), 110 °C, 10 h. [b] $Pd(OAc)_2$ (5 mol %) and 4-methylbenzeneboronic acid neopentyl ester (1.5 equiv). [c] $Pd(OAc)_2$ (5 mol %), arylboronic acid (1.5 equiv), and K_2CO_3 (2 equiv). [d] KF (2.5 equiv) as base instead of K_2CO_3. [e] 5 mmol scale.

Scheme 2. Pd-Catalyzed Direct Arylation of Various Polyfluoroarenes with Arylboronic Acids[a]

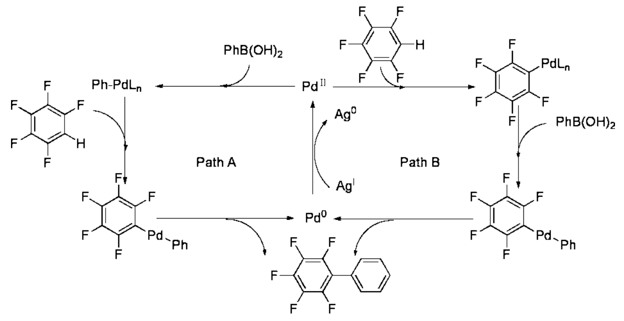


[a] Reaction conditions: **3k−q**: polyfluoroarene (0.2 mmol), arylboronic acid (1.2 equiv), $Pd(OAc)_2$ (2 mol %), K_2CO_3 (0.5 equiv), Ag_2CO_3 (2 equiv), *p*-Me-C_6H_4-CO_2H (0.3 equiv), DMA (2 mL, 0.1 M), 110 °C, 10 h. **3r−z**: polyfluoroarene (3 equiv), arylboronic acid (0.2 mmol), $Pd(OAc)_2$ (5 mol %), K_3PO_4 (0.5 equiv), Ag_2CO_3 (2 equiv), $^tBuCO_2H$ (0.6 equiv), DMA (2 mL, 0.1 M), 120 °C, 10 h. [b] $Pd(OAc)_2$ (5 mol %), arylboronic acid (1.5 equiv) and K_2CO_3 (2 equiv). [c] *p*-Me-C_6H_4-CO_2K (0.5 equiv) as base instead of K_3PO_4.

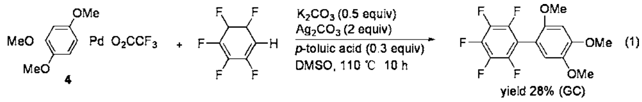
The substrate scope with respect to polyfluorobenzenes was also investigated and is presented in Scheme 2. Under the standard conditions, both 2,3,5,6-tetrafluoroanisole and 2,3,5,6-tetrafluorotoluene smoothly underwent direct arylation with moderate to good yields obtained (**3k−q**). However, these reaction conditions are not suitable for other polyfluorobenzenes such as 1,3,5-trifluorobenzene. It has been established that the reactivity of the C−H bond in electron-deficient arenes depends directly on its acidity. In light of this, we speculated that the identification of the proper base for a specific polyfluorobenzene might be crucial for obtaining efficient transformation. Moreover, the acid required by this reaction system to suppress the homocoupling must match the base used for deprotonation of the polyfluorobenzene. We were pleased to achieve the direct arylation of more C−H acidic polyfluorobenzenes such as 2,3,5,6-tetrafluoropyridine and 2,3,5,6-tetrafluorobenzonitrile by using 0.5 equiv of potassium *p*-toluate as a base in conjunction with 0.6 equiv of pivalic acid and increasing the amount of polyfluorobenzene (3:1 ratio of polyfluorobenzene to arylboronic acid) (**3r** and **3s**), and to realize the direct arylation of less C−H acidic polyfluorobenzenes by using 0.5 equiv of K_3PO_4 combined with 0.6 equiv of pivalic acid (**3t**−**z**). As a result, a wide range of polyfluorobenzenes, some of which contain bromo, cyano, keto, and methoxy groups, can be arylated with arylboronic acids. Although more than one potential site for reaction is available in some of the polyfluorobenzenes, the reactions of these polyfluorobenzenes mainly generated monoarylated product, as exemplified by the reaction of 1,3,5-trifluorobenzene (**3x**). The direct arylation of 1,3-difluorobenzene occurred preferentially at the most acidic C−H bond, which is flanked by two C−F bonds (**3y**). In contrast, the reaction of 2,4-difluorobenzophenone occurred exclusively at the position that is meta to the benzoyl group and para to a fluoride group (**3z**). The palladium-catalyzed meta-selective C−H bond olefination directed by the benzoyl group has been observed by Yu recently.[18]

Two different mechanisms are possible for the direct arylation of polyfluorobenzenes with arylboronic acids (Scheme 3). Path A involves the initial formation of arylpalladium species via the transmetalation from boron to palladium, followed by the palladation of fluorobenzene via concerted metalation−deprotonation[6c,19,20] and reductive elimination. Path B begins with the formation of fluoroarylpalladium species via the cleavage of the C−H bond of fluorobenzene, followed by the transmetalation from boron to the fluoroarylpalladium intermediate and reductive elimination.

Scheme 3. Two Possible Mechanisms of This Reaction



To distinguish between path A and path B, we carried out preliminary mechanistic studies. Stoichiometric reaction of 2,4,5-trimethoxyphenylpalladium trifluoroacetate complex **4**[21] with pentafluorobenzene in DMSO gave the arylated product in 28% yield as well as a lot of the homocoupling product from the palladium complex **4** [eq 1], indicating that an arylpalladium complex is able to arylate electron-deficient polyfluorobenzene via C−H bond cleavage. Further experimentation showed that 5 mol % of palladium complex **4** as a catalyst efficiently catalyzed the direct arylation of pentafluorobenzene with phenylboronic acid in 84% yield, suggesting that the direct arylation of polyfluorobenzene most likely involves the formation of an arylpalldium intermediate and subsequent reaction of the palladium species with fluorobenzene. As shown in Scheme 1, when sterically demanding *o*-tolylboronic acid was used, neither cross-coupling nor homocoupling took place. No homocoupling product from *o*-tolylboronic acid reveals that the transmetalation that generates arylpalladium species was inhibited owing to steric factors.[17] If the transmetalation precedes the palladation of fluorobenzene in a catalytic cycle, the inhibition of transmetalation could be the reason why *o*-tolylboronic acid did not react with **1**. Although path B cannot be ruled out, these observations favor path A. The intermolecular kinetic isotope effect ($k_{H/D}$ = 1.7) in the direct arylation of 2,3,5,6-tetrafluoroanisole with **2** indicated that the C−H bond cleavage was involved in the rate-limiting step.



In conclusion, we have demonstrated a palladium-catalyzed method for the direct arylation of electron-deficient polyfluorobenzenes with arylboronic acids. This method exhibits a broad substrate scope with respect to both polyfluorobenzenes and arylboronic acids, which is attributed to the choice of bases depending on the acidities of the polyfluorobenzenes. The preliminary mechanistic studies suggested that this reaction may involve initial transmetalation from boron to palladium, followed by palladation of fluorobenzene and reductive elimination. Further efforts are underway to expand the substrate scope of this method to other electron-deficient arenes.

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Supporting Information Available: Detailed experimental procedures and characterization for products. This material is available free of charge via the Internet at http://pubs.acs.org.

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