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Copper-Catalyzed Suzuki–Miyaura Coupling of Arylboronate Esters: Transmetalation with (PN)CuF and Identification of Intermediates

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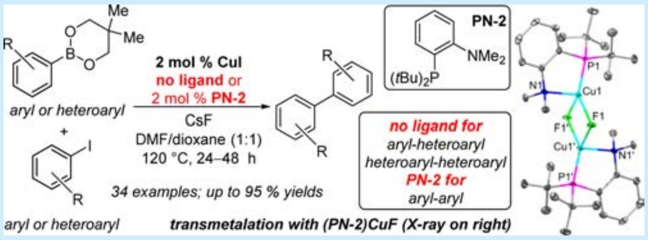
S *Supporting Information*

ABSTRACT: An efficient Cu^I-catalyzed Suzuki–Miyaura reaction was developed for the coupling of aryl- and heteroarylboronate esters with aryl and heteroaryl iodides at low catalyst loadings (2 mol %). The reaction proceeds under ligand-free conditions for aryl–heteroaryl and heteroaryl–heteroaryl couplings. We also conducted the first detailed mechanistic studies by synthesizing $[(\textbf{PN-2})CuI]_2$, $[(\textbf{PN-2})CuF]_2$, and (**PN-2**)CuPh (**PN-2** = *o*-(di-*tert*-butylphosphino)-*N*,*N*-dimethylaniline) and demonstrated that $[(\textbf{PN-2})CuF]_2$ is the species that undergoes transmetalation with arylboronate esters.



Over the last three decades, the Pd-catalyzed Suzuki–Miyaura reaction has developed into a highly useful synthetic tool that is capable of coupling a range of organoboron reagents with organohalides and pseudohalides to construct carbon–carbon (C–C) bonds.[1] As a result, application of this coupling process encompasses a wide array of synthetic targets, ranging from manufacturing of materials and pharmaceuticals to the synthesis of building blocks and natural products.[2] Despite the maturity of the transformation with regard to its substrate scope, catalytic turnover, and application, the current desire to replace palladium with earth-abundant and inexpensive metals[3] has reshaped recent investigations.[4] In this regard, a copper nanocluster was demonstrated in 2002 to have catalytic activity for the Suzuki–Miyaura coupling of phenylboronic acid with iodobenzene.[5]

Despite this inspirational work from more than a decade ago and subsequent reports,[6] the Cu-catalyzed Suzuki–Miyaura reaction is strictly limited to the couplings of nonheteroarylboronic acids with nonheteroaryl iodides.[7] Cu-based catalysts are rarely known to perform aryl–heteroaryl and heteroaryl–heteroaryl couplings[8] to generate heterocyclic biaryl motifs.[9] In addition, the reported Cu-catalyzed aryl–aryl coupling protocols suffer from low catalytic turnovers requiring high loadings of catalysts and ligands, 10–20 mol %[6b–f] in most cases and stoichiometric amounts in some instances.[6b]

As a result, the Cu catalysts' attractive features of being earth-abundant and inexpensive are surpassed by the high performance of the noble metal palladium-based catalysts.[1] Moreover, the fledgling Cu-catalyzed Suzuki–Miyaura coupling lacks mechanistic studies, and the synthesis and characterization of potential reaction intermediates that can lead to detailed insights and possible catalytic scenarios remain unexplored.

In this work, we report a versatile Cu-catalyzed cross-coupling of aryl- and heteroarylboronate esters with aryl- and heteroaryl iodides that affords biaryl products in good to excellent yields using 2 mol % catalyst/ligand loadings. Delightfully, the current protocol allows aryl-heteroaryl and heteroaryl-heteroaryl couplings to proceed under ligand-free conditions. We have also synthesized a rare CuF species ligated to *o*-(di-*tert*-butylphosphino)-*N*,*N*-dimethylaniline (**PN-2**) that generates the active catalyst $[(\textbf{PN-2})CuF]_2$. We further demonstrated that $[(\textbf{PN-2})CuF]_2$ is also generated from the reaction of CsF with $[(\textbf{PN-2})CuI]_2$ under catalytic reaction conditions at room temperature, which then undergoes facile transmetalation with arylboronate esters to generate a (**PN-2**)CuAr intermediate. These three potential reaction intermediates were characterized by NMR spectroscopy, elemental analysis, and single-crystal X-ray diffraction. We also devised a possible catalytic cycle based on our investigations incorporating the discrete reaction intermediates and catalytic and sequential stoichiometric reaction studies.

We recently discovered that *o*-(diphenylphosphino)-*N*,*N*-dimethylaniline (**PN-1**) was capable of executing the Cu-catalyzed Hiyama coupling of $ArSi(OEt)_3$ with ArI in the presence of CsF.[10] In our effort to develop a Cu-catalyzed Suzuki–Miyaura reaction, we applied this condition to the coupling of phenylboronate ester **1** with *p*-iodotoluene. We were pleased to find that *p*-phenyltoluene (**2**) was formed in 61% yield when the reaction was conducted in DMF/dioxane (1:1) (Table 1, entry 1). Gratifyingly, the reaction required only 2 mol % of **PN-1**/CuI. Further screening of PN-ligands **PN-2-PN-4** demonstrated that electron-rich and sterically hindered ligand **PN-2** afforded **2** in 95% yield (entry 2). In the absence of the PN ligand, the reaction generates the product in 21% yields (entry 5). The reaction does not proceed in the absence of either the Cu catalyst or CsF and affords **2** in 5–30% when CsF is replaced with other bases or fluoride

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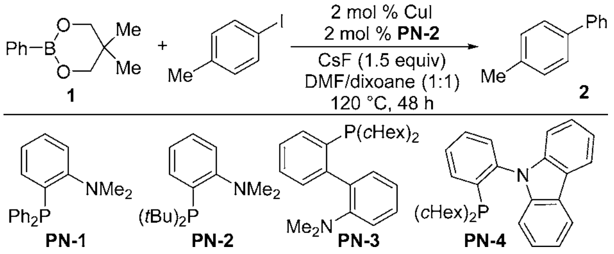
Table 1. Optimization of Reaction Conditions^a

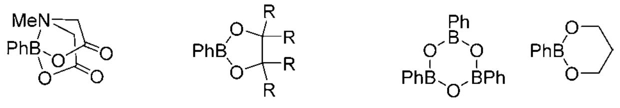


entry	modified conditions	yield^b (%)
1	**PN-1** instead of **PN-2**	61
2	standard conditions	95 (91)^c
3	**PN-3** instead of **PN-2**	73
4	**PN-4** instead of **PN-2**	65
5	without ligand	21
6	without CuI	0
7	without CsF	0
8	KF, KOH, Cs_2CO_3, K_3PO_4, or KO-*t*-Bu instead of CsF	18–30
9	LiF, NaF, RbF, or TBAF instead of CsF	<5
10	BaO, CaO, MgO, $Ca(OH)_2$, or $Mg(OH)_2$ instead of CsF	<5
11	CuOtBu (sublimed) instead of CuI	81

^{a}0.10 mmol scale, 0.5 mL of DMF/dioxane (1:1). CuI (99.999%) and CsF (99.9%) were used. ^{b}Calibrated GC yields using 2-nitrobiphenyl as a standard. ^{c}The number in parentheses is the isolated yield from a 5.0 mmol scale reaction.

sources (entries 6–10). Replacing CuI with CuO-*t*-Bu (purified by sublimation) generated the product in 81% yield (entry 11). With the exception of phenylboronic acid MIDA ester (**3**), phenylboronate ester **1** can also be replaced with other organoboron reagents such as **4–11** (Scheme 1) to obtain the product in good to excellent yields.

Scheme 1. Coupling of *p*-Iodotoluene with Different Phenylboron Reagents^a



3, trace   95% (R = H, **4**); 43% (R = Me, **5**)   **6**, 46%   **7**, 93%

$PhB(OH)_2$ (**8**), 77%; Ph_3B (**9**), 66%; Ph_4BCs (**10**), 66%; $PhBF_3K$ (**11**), 47%

^{a}Key: 0.50 mmol scale, 2.5 mL of DMF/dioxane (1:1). Calibrated GC yields using 2-nitrobiphenyl as a standard.

Table 2. Coupling of Aryl- and Heteroarylboronate Esters with Aryl and Heteroaryl Iodides^a

entry	Ar in $ArB(OR)_2$^{b}	Ar′–I	Ar–Ar′	yield^c (%)
	aryl–aryl (in the presence of PN-2)			
1	Ph	4-MeC_6H_4I	**2**	91
2	Ph	4-MeOC_6H_4I	**12**	95
3	4-MeC_6H_4	PhI	**2**	81
4	4-MeC_6H_4	4-BrC_6H_4I	**13**	71^d
5	4-MeC_6H_4	3-ClC_6H_4I	**14**	64
6	4-MeC_6H_4	$3,5\text{-(CF}_3)_2C_6H_3I$	**15**	84^e
7	4-MeOC_6H_4	4-FC_6H_4I	**16**	83
8	4-MeOC_6H_4	4-ClC_6H_4I	**17**	81
9	4-MeOC_6H_4	3-ClC_6H_4I	**18**	94
10	4-MeOC_6H_4	$4\text{-CF}_3C_6H_4I$	**19**	64
11	4-MeOC_6H_4	$3\text{-CF}_3C_6H_4I$	**20**	85
12	4-MeOC_6H_4	$3,5\text{-(CF}_3)_2C_6H_3I$	**21**	73
13	4-FC_6H_4	4-MeC_6H_4I	**22**	90
14	4-FC_6H_4	$4\text{-CF}_3C_6H_4I$	**23**	87
15	4-FC_6H_4	$3,5\text{-F}_2C_6H_3I$	**24**	77^f
16	4-FC_6H_4	$3,5\text{-(CF}_3)_2C_6H_3I$	**25**	67
17	$3,5\text{-F}_2CeH_3$	4-FC_6H_4I	**24**	83
18	$3,5\text{-F}_2C_6H_3$	4-MeC_6H_4I	**26**	69
19	$3,5\text{-(CF}_3)_2C_6H_3$	4-FC_6H_4I	**25**	88
20	$3,5\text{-(CF}_3)_2C_6H_3$	4-MeC_6H_4I	**15**	86
21	naphthyl	$4\text{-CF}_3C_6H_4I$	**27**	78^e
	aryl–heteroaryl/heteroaryl–heteroaryl (no ligand)			
22	Ph	2-chloro-4-iodopyridine	**28**	80^g
23	4-MeC_6H_4	2-chloro-4-iodopyridine	**29**	71^h
24	4-MeOC_6H_4	2-chloro-4-iodopyridine	**30**	70
25	4-MeOC_6H_4	2-iodopyrazine	**31**	75^i
26	4-MeOC_6H_4	7-chloro-4-iodoquinoline	**32**	93^h
27	4-FC_6H_4	2-chloro-4-iodopyridine	**33**	81^h
28	4-FC_6H_4	2-iodopyrazine	**34**	88
29	4-FC_6H_4	7-chloro-4-iodoquinoline	**35**	71
30	$3,5\text{-(CF}_3)_2C_6H_3$	7-chloro-4-iodoquinoline	**36**	84
31	2-benzofuryl	4-MeC_6H_4I	**37**	73
32	2-benzofuryl	4-FC_6H_4I	**38**	60
33	2-benzofuryl	2-chloro-4-iodopyridine	**39**	82
34	2-benzofuryl	7-chloro-4-iodoquinoline	**40**	95

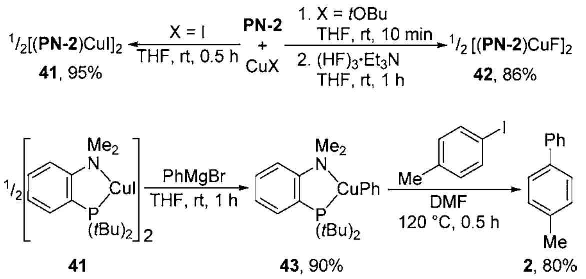
^{a}Standard conditions from Table 1, entry 2, 1.0 mmol scale, 48 h [DMF/dioxane (1:1)] for nonheteroaryl, 24 h (DMF) for heteroaryl substrates. ^{b}Arylboronic acid neopentylglycol ester. ^{c}Isolated yields. ^{d}2 mol % of CuI/**PN-1**, 24 h. ^{e}5 mol % of CuI/**PN-2**. ^{f}60 h. ^{g}Phenylboronic acid 1,3-propanediol ester **7** was used instead of **1**. ^{h}5 mol % of CuI. ^{i}5 mol % CuI, 60 h.

After establishing the optimal conditions (Table 1), we examined the substrate scope of the new coupling protocol. The current conditions allow the reactions to proceed for aryl–aryl, aryl–heteroaryl, and heteroaryl–heteroaryl couplings (Tables 2). Reactions conducted with **PN-2** provided good to excellent yields of products for the couplings of non-heterocyclic arylboronate esters with non-heterocyclic ArI (entries 1–21). Similarly, the coupling tolerates a variety of functional groups and proceeds well with electron-deficient and electron-rich aryl rings on both coupling partners.[11] Halogens, exemplified using Br, Cl, and F, are also tolerated (entries 4, 5, 7–9, and 13–19).

Fortunately, the reactions for aryl–heteroaryl and heteroaryl–heteroaryl couplings proceeded without **PN-2** and afforded the products in good to excellent yields (Table 2, entries 22–34). Similar to aryl–aryl couplings, the aryl–heteroaryl/heteroaryl–heteroaryl couplings also tolerate a variety of functional groups and proceed with electron-deficient and electron-rich aryl rings. Both aryl–heteroaryl and heteroaryl–heteroaryl couplings also tolerate halides such as F and Cl (entries 22–24, 26–30, and 32–34).

To understand the mechanistic intricacies for the present Cu^I-catalyzed Suzuki–Miyaura coupling, we conducted detailed studies via the synthesis of potential reaction intermediates and execution of stoichiometric and catalytic reactions. [(**PN-2**)CuI]$_2$, [(**PN-2**)CuF]$_2$, and (**PN-2**)CuPh complexes **41**, **42**, and **43** were synthesized as outlined in Schemes 2. [(**PN-2**)CuI]$_2$ was formed in 95% yield simply by mixing equimolar quantities of **PN-2** and CuI in THF at room temperature. [(**PN-2**)CuF]$_2$ was synthesized in 86% yield from the reaction of $(HF)_3\cdot Et_3N$ with [(**PN-2**)CuO-*t*-Bu], generated in situ by mixing **PN-2** and CuO*t*Bu[12] in THF at room temperature.[13] Complex **43** was synthesized from the reaction of **42** with

Scheme 2. Synthesis of Cu^{I} Complexes



PhMgBr in 90% yield.[14] These novel Cu complexes were characterized by NMR spectroscopy, elemental analysis, and X-ray crystallography. On the basis of the X-ray structures, both **41** and **42** exist as halide-bridged dimers with each copper atom in a tetrahedral geometry (Figure 1).[15] Complex **43** is a three-coordinate monomeric species with a central planar copper atom ligated to **PN-2** and a phenyl group (Figure 1). Complex **43** also reacts with *p*-iodotoluene in DMF at 120 °C in 0.5 h and affords *p*-phenyltoluene in 80% yield, suggesting that **43** is a chemically competent complex.[16]

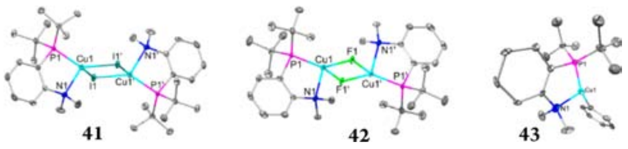
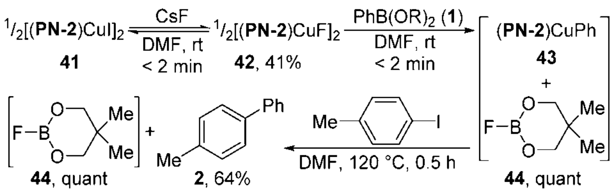


Figure 1. X-ray structures of **41**−**43**. Selected bond lengths (Å) and angles (deg). **41**: Cu1−P1, 2.2171(5), Cu1−N1, 2.2769(15), Cu1−I1, 2.6320(3); P1−Cu1−N1, 86.80(4), P1−Cu1−I1, 126.048(16). **42**: Cu1−F1, 1.971(2), Cu1−P1, 2.1200(12), Cu1−N1, 2.279(3); F1−Cu1−P1, 147.22(8), P1−Cu1−N1, 88.08(9). **43**: Cu1−C17, 1.948(8), Cu1−P1, 2.199(2), Cu1−N1, 2.305(6); C17−Cu1−P1, 163.1(2), C17−Cu1−N1, 113.8(3), P1−Cu1−N1, 83.15(16).

With the potential reaction intermediates in hand, we performed stepwise stoichiometric studies by monitoring with ^{1}H, ^{19}F, ^{11}B, and ^{31}P NMR spectroscopy and comparing the NMR spectra of the reaction mixture with those of the fully characterized standard samples plus quantifying the products by ^{19}F NMR with C_6F_6 as an internal standard (Scheme 3).

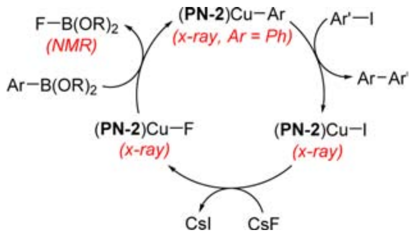
Scheme 3. Stepwise Stoichiometric Reaction Studies by ^{1}H, ^{19}F, ^{11}B, and ^{31}P NMR Spectroscopy



Initially, we mixed equimolar quantities of [(**PN-2**)CuI]$_2$ (**41**) and phenylboronate ester **1** in DMF at room temperature and monitored the reaction by both ^{11}B and ^{31}P NMR. No transmetalation was observed. However, we found that [(**PN-2**)CuI]$_2$ (**41**) reacts with CsF in DMF at room temperature to generate [(**PN-2**)CuF]$_2$ (**42**) in 41% yield in less than 2 min. It is noteworthy that the yield of **42** did not change even after 30 min at room temperature despite the presence of dissolved CsF in DMF. The fluoride complex **42** then underwent transmetalation with phenyboronate ester **1** immediately at room temperature[17] to form the complex **43** and fluoroboronate ester **44** quantitatively. The results that complex **42** is formed only in 41% yield, but **44** is formed quantitatively, implies that the formation of **42** could be reversible. The formation of fluoroboronate ester **44** was confirmed by the observation of fluorine−boron coupling (^{19}F NMR, δ = 150.6 ppm, quartet, $J_{\mathrm{F-B}}$ = 16.9 Hz). The resulting mixture then reacts with *p*-iodotoluene to afford the cross-coupled product **2** in 64% GC yield. Moreover, the fluoroboronate ester **44** was also formed in quantitative yields based on ^{19}F NMR under catalytic conditions before (based on CuI) and after (based on phenylboronate ester **1**) heating the reaction at 120 °C for 24 h.

Based on our mechanistic investigations with the possible reaction intermediates and the stoichiometric studies, we have proposed a catalytic cycle (Scheme 4). In this pathway, CsF converts [(**PN-2**)CuI]$_2$ to [(**PN-2**)CuF]$_2$, a catalytically active species that undergoes transmetalation with arylboronate ester to generate (**PN-2**)CuAr complex.[18] However, a mechanistic scenario reminiscent of the Pd-catalyzed Suzuki−Miyaura coupling,[19] where [(**PN-2**)CuF]$_2$ would undergo transmetalation with the fluoride-activated arylborates, also cannot be ruled out at this time.[3] In either scenario, once the (**PN-2**)CuAr species is generated it is expected to react with aryl halides to form a cross-coupled product and regenerate [(**PN-2**)CuI]$_2$.[20]

Scheme 4. Proposed Catalytic Cycle



In summary, we have developed an efficient Cu^{I}-catalyzed Suzuki−Miyaura coupling of aryl- and heteroarylboronate esters with aryl- and heteroaryl iodides that generates cross-coupled products in good to excellent yields at low catalyst loadings (2 mol %). The reaction for aryl−heteroaryl and heteroaryl−heteroaryl coupling proceeds even without a ligand. We have also conducted detailed mechanistic studies via the synthesis of potential reaction intermediates and execution of catalytic and sequential stoichiometric reactions and proposed a catalytic cycle. We synthesized and fully characterized [(**PN-2**)CuI]$_2$, [(**PN-2**)CuF]$_2$, and (**PN-2**)CuPh as possible reaction intermediates. We discovered that CsF converts [(**PN-2**)CuI]$_2$ to [(**PN-2**)CuF]$_2$, which then undergoes transmetalation with arylboronate esters to form (**PN-2**)CuAr species before cross-coupling with ArI to generate the final product.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, characterization and crystallographic data (CIF), and the ^{1}H and ^{13}C NMR spectra of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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