

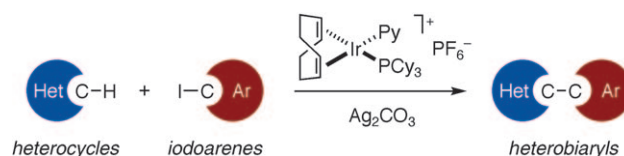
Iridium Catalysis for C–H Bond Arylation of Heteroarenes with Iodoarenes**

Benoît Join, Takuya Yamamoto, and Kenichiro Itami*

Arylated heteroarenes (heterobiaryls) are ubiquitous in natural products and pharmaceuticals, and are frequently used in organic materials or as ligands for metals.^[1] Consequently, the development of efficient methods for making heterobiaryl motifs has been a topic of immense importance in chemical synthesis.^[2] Typically, heterobiaryls have been constructed by means of Pd-catalyzed cross-coupling reactions of metalated (hetero)arenes and halogenated (hetero)arenes.^[2] More recently, the direct C–H bond arylation of heteroarenes with haloarenes (Het–H + Ar–X → Het–Ar) has emerged as an area of extensive research because it can streamline the synthesis by skipping the premetalation step in the cross-coupling strategy.^[3,4] Although a number of useful catalytic systems incorporating Pd,^[5] Rh,^[6] Ru,^[7] and Cu^[8] have been developed for the C–H bond arylation of heteroarenes with haloarenes,^[9] the repertoire of applicable catalysts still remains rather limited. Fujita and Yamaguchi have reported an interesting [(Cp*IrHCl)₂]/KOtBu (Cp* = pentamethylcyclopentadienyl) system that promotes the C–H bond arylation of unactivated arenes (benzene, toluene, and anisole) with iodoarenes.^[10,11] However, this Ir-based catalytic system employs the arene substrate as a solvent (40 equivalents), and cannot be applied to heteroaromatic substrates.^[10]

As an initial foray into this area,^[12] we recently reported that the system [RhCl(CO)(P(OCH(CF₃)₂)₃)₂]/Ag₂CO₃ promoted the C–H bond arylation of arenes with iodoarenes.^[12a] To develop a new metal catalyst based on this lead, we set out to explore the Ir^I/Ag₂CO₃ system as a platform for C–H bond arylation. We report herein our finding that an Ir⁺/PCy₃/Ag₂CO₃ (Cy = cyclohexyl) system catalyzes the C–H bond arylation of electron-rich heteroarenes with iodoarenes.

We began our study by applying various iridium complexes with Ag₂CO₃ to the reaction of 2-methylthiophene (**1A**, one equivalent) and iodobenzene (**2a**, one equivalent) in *m*-xylene (140 °C, 12 h).^[13] In contrast to Rh catalysis, a cationic Ir^I complex with P(OCH(CF₃)₂)₃^[12a] proved ineffective (Table 1, entry 1). Thus, the effect of the ligand was



investigated, by using [Ir(cod)₂]BF₄ (cod = 1,5-cyclooctadiene) as the source of Ir^I. Screening of ligands indicated that PCy₃ was by far the most effective ligand, producing the heterobiaryl **3Aa** in 88% yield (Table 1, entry 6).^[14] A dramatic difference between PCy₃ and other closely related alkylphosphanes, such as PCyp₃ (Cyp = cyclopentyl), is notable and intriguing. In developing a stable Ir⁺/PCy₃ pre-catalyst, we identified [Ir(cod)(py)PCy₃]PF₆ (Crabtree's catalyst;^[15,16] py = pyridine) to be very convenient (Table 1, entry 11). A quantitative coupling using an equimolar quantity of each coupling partner was possible at 160 °C with this catalyst (Table 1, entry 12). Interestingly, the corresponding rhodium complex [Rh(cod)(py)PCy₃]PF₆ was totally ineffective under otherwise identical conditions (Table 1, entry 13). The importance of Ag₂CO₃ was also recognized, as other additives, such as AgOTf, AgOAc, AgSbF₆, Na₂CO₃, K₂CO₃,

Table 1: Effect of ligands in Ir-catalyzed coupling of **1A** and **2a**.^[a]

Entry	Ligand ^[b]	Yield [%] ^[c]
1	P(OCH(CF ₃) ₂) ₃	< 1
2	PPh ₃	2
3	P(C ₆ H ₄ OMe- <i>p</i>) ₃	2
4	PCy ₂ (<i>o</i> -biphenyl)	4
5	PCy ₂ Ph	29
6	PCy ₃	88
7	PCyp ₃	16
8	PAd ₂ (<i>n</i> Bu)	9
9	P(<i>n</i> Bu) ₃	5
10	P(<i>t</i> Bu) ₃	2
11 ^[d]	[Ir(cod)(py)PCy ₃]PF ₆	85
12 ^[d,e]	[Ir(cod)(py)PCy ₃]PF ₆	> 99
13 ^[d]	[Rh(cod)(py)PCy ₃]PF ₆	< 1

[a] Conditions: **1A** (0.40 mmol), **2a** (0.40 mmol), [Ir(cod)₂]BF₄ (0.02 mmol), ligand (0.02 mmol), Ag₂CO₃ (0.42 mmol), *m*-xylene (2 mL), 140 °C, 12 h. [b] Cy = cyclohexyl, Cyp = cyclopentyl, Ad = 1-adamantyl, *n*Bu = *n*-butyl, *t*Bu = *tert*-butyl, cod = 1,5-cyclooctadiene, py = pyridine. [c] Determined by GC analysis using *n*-decane as an internal standard. [d] Isolated complex was employed as a catalyst. [e] Reaction was conducted at 160 °C for 18 h.

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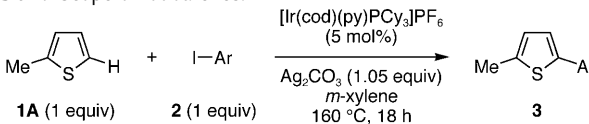
[**] This work was supported by the PRESTO program of JST, and a Grant-in-Aid for Scientific Research from MEXT and JSPS. B.J. is a recipient of a JSPS Postdoctoral Fellowship.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.200806358>.

Cs_2CO_3 , and KOtBu , did not promote the reaction with the Ir^+/PCy_3 catalyst.

Having established a new and efficient Ir-based catalytic system, the scope of iodoarenes **2** (Table 2) and heteroarenes **1** (Table 3) was examined.^[13] Various electronically and structurally diverse iodoarenes **2** were applied to this coupling

Table 2: Scope of iodoarenes.^[a]

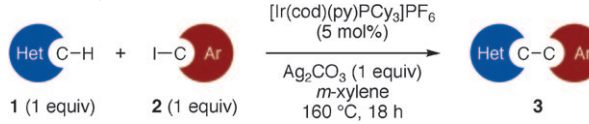
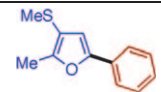
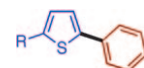
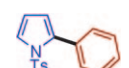
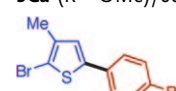
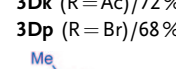
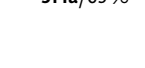
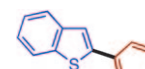
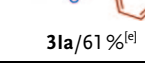
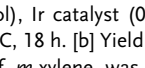
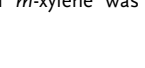
			
Entry	Ar (2)	Product (3)	Yield [%] ^[b,c]
1	C_6H_5 (2a)	3Aa	87
2	$o\text{-CH}_3\text{C}_6\text{H}_4$ (2b)	3Ab	10
3	$m\text{-CH}_3\text{C}_6\text{H}_4$ (2c)	3Ac	69
4	$p\text{-CH}_3\text{C}_6\text{H}_4$ (2d)	3Ad	58
5	$o\text{-CH}_3\text{OC}_6\text{H}_4$ (2e)	3Ae	62
6	$m\text{-CH}_3\text{OC}_6\text{H}_4$ (2f)	3Af	70
7	$p\text{-CH}_3\text{OC}_6\text{H}_4$ (2g)	3Ag	76
8	$m\text{-CF}_3\text{C}_6\text{H}_4$ (2h)	3Ah	72
9	$p\text{-CF}_3\text{C}_6\text{H}_4$ (2i)	3Ai	74
10	$m\text{-CH}_3\text{C}(\text{O})\text{C}_6\text{H}_4$ (2j)	3Aj	71
11	$p\text{-CH}_3\text{C}(\text{O})\text{C}_6\text{H}_4$ (2k)	3Ak	79
12	$p\text{-C}_2\text{H}_5\text{OC}(\text{O})\text{C}_6\text{H}_4$ (2l)	3Al	66
13	$m\text{-NO}_2\text{C}_6\text{H}_4$ (2m)	3Am	60
14	$p\text{-NO}_2\text{C}_6\text{H}_4$ (2n)	3An	78
15	$m\text{-BrC}_6\text{H}_4$ (2o)	3Ao	70
16	$p\text{-BrC}_6\text{H}_4$ (2p)	3Ap	70

[a] Conditions: **1A** (0.40 mmol), **2** (0.40 mmol), Ir catalyst (0.02 mmol), Ag_2CO_3 (0.42 mmol), *m*-xylene (2 mL), 160 °C, 18 h. [b] Yield of isolated product. [c] Average of two runs.

(Table 2). Efficient coupling proceeds even with equimolar quantities of each coupling partner. Moreover, a range of functional groups, such as ketone, ester, and nitro groups, was tolerated in this coupling. Although *ortho*-methyl substitution was detrimental (Table 2, entry 2), *ortho*-methoxy substitution was tolerated (Table 2, entry 5). Thiophenes, furans, pyrroles, indoles, and benzothiophenes were applied as the heteroarene coupling partner (Table 3). In all cases examined, arylation took place in a regioselective fashion; α -positions for thiophenes, furans, and pyrroles; 2-positions for benzothiophenes; 3-positions for indoles. Notably, Br-containing substrates (**1D**, **2o**, **2p**) underwent C–H bond arylation leaving the C–Br bond intact, which is attractive for further synthetic elaboration.

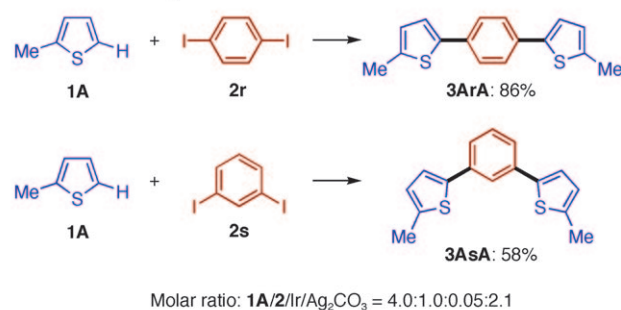
In view of efficient aryl–aryl bond formation, the current Ir catalysis should have broad potential for the construction of a range of extended π -electron systems (Scheme 1).^[13] For example, when 1,4-diiodobenzene (**2r**) was treated with an excess amount of **1A**, a twofold C–H bond arylation took place, which gave the thiophene–benzene–thiophene triad **3ArA**, isolated in 86 % yield. A *meta*-linked isomer **3AsA** was also obtained from the reaction, by using 1,3-diiodobenzene (**2s**) as a coupling partner for **1A**. Double C–H bond arylation of the same heteroarene core was also achieved. For example, when 3-methoxythiophene (**1J**) was treated with an excess amount of **2a**, a double C–H bond arylation of the thiophene

Table 3: Scope of heteroarenes.^[a]

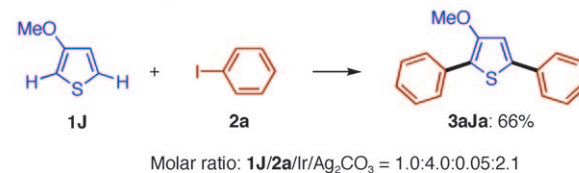
	
Product/yield ^[b]	
	3Fa /57 % ^[c]
	3Ba (R = Et)/80 %
	3Ca (R = OMe)/60 %
	3Da (R = H)/69 %
	3Dk (R = Ac)/72 %
	3Dp (R = Br)/68 %
	3Ha /63 % ^[d]
	3Ea (R = H)/55 %
	3Ek (R = Ac)/54 %
	3Eq (R = CN)/72 %
	3Ia /61 % ^[e]

[a] Conditions: **1** (0.40 mmol), **2** (0.40 mmol), Ir catalyst (0.02 mmol), Ag_2CO_3 (0.40 mmol), *m*-xylene (2 mL), 160 °C, 18 h. [b] Yield of isolated product. [c] Reaction for 24 h. [d] 1 mL of *m*-xylene was employed. [e] Reaction for 36 h.

Twofold C–H Bond Arylation



Double C–H Bond Arylation



Scheme 1. Multiple C–H bond arylation producing extended π -electron systems.

core **1J** took place at the 2- and 5-positions, furnishing the benzene–thiophene–benzene triad **3aJa**, isolated in 66 % yield.

Table 4: Site-selectivity for anisole functionalization.

Entry	Catalyst/additive	Ar-X	Site selectivity ^[a] (o/m/p)
1	[Ir(cod)(py)PCy ₃]PF ₆ /Ag ₂ CO ₃	<i>p</i> -NO ₂ C ₆ H ₄ I	37:17:46
2	[Ir(cod)(py)PCy ₃]PF ₆ /Ag ₂ CO ₃	C ₆ H ₅ I	39:13:48
3	[RhCl(CO)(P{OCH(CF ₃) ₂ }) ₂]/Ag ₂ CO ₃	<i>p</i> -NO ₂ C ₆ H ₄ I	29:0:71 ^[12a]
4	[(Cp*IrHCl) ₂]/KOtBu	C ₆ H ₅ I	72:16:12 ^[10]
5	Pd(OAc) ₂ /PR ₃ /tBuCO ₂ H/K ₂ CO ₃	<i>p</i> -CH ₃ C ₆ H ₄ Br	22:53:25 ^[5m]
6	Ir-catalyzed borylation	n/a	1:74:25 ^[11a]

[a] Selectivity refers to site of borylation.

Although the mechanism of this newly developed Ir-catalyzed reaction remains unknown, one possibility involves Ir^I/Ir^{III} redox catalysis initiated by the oxidative addition of an iodoarene **2** (Ar-I) to a cationic Ir^I complex **4** yielding an [Ar-Ir^{III}-I]⁺ species **5**. Subsequently, abstraction of iodide from **5** by Ag₂CO₃ takes place to generate a highly electrophilic [Ar-Ir^{III}]²⁺ species **6**, and subsequent electrophilic metalation of heteroarene **1** (Het-H). The resulting [Ar-Ir^{III}-Het]⁺ intermediate **7** then undergoes heteroaryl-aryl reductive elimination, furnishing heterobiaryl **3** with concurrent regeneration of **4**. A preliminary kinetic isotope effect study was also performed. From the inter- and intramolecular competitive reactions of deuterium-labeled thiophenes with iodobenzene, the *k*_H/*k*_D value for thiophene arylation was estimated to be 1.9 (See the Supporting Information).

To gain more insight into the C-H bond cleaving process, anisole was utilized as a substrate (Table 4). Although low-yielding (9% yield), the reaction of anisole and **2n** under our standard Ir-catalyzed conditions afforded the *ortho*-, *meta*-, and *para*-arylated anisoles with 37:17:46 molar ratio (Table 4, entry 1). Similar site-selectivity (*o*/*m*/*p* = 39:13:48) was detected when **2a** was used instead of **2n** (Table 4, entry 2). Although a non-negligible amount of *meta*-isomer is produced, the current Ir-based catalytic system manifests a clear *ortho/para* preference, which is consistent with the electrophilic metalation mechanism, as is the case for our previous Rh/P[OCH(CF₃)₂]/Ag₂CO₃ system. The site-selectivities reported by Fujita, for [(Cp*IrHCl)₂]/KOtBu^[10] (Table 4, entry 3), and Fagnou, for Pd(OAc)₂/DavePhos/tBuCO₂H/K₂CO₃^[5m] (Table 4, entry 5), as well as that in the Ir-catalyzed borylation reaction by Ishiyama and Miyaura^[11a] (Table 4, entry 6) are also different from those for this arylation reaction. Further detailed study for the elucidation of the reaction mechanism and development of second-generation catalysts based on these findings are currently underway.

In summary, a new Ir-based catalytic system for the C-H bond arylation of electron-rich heteroarenes with iodoarenes has been established. The dramatic ligand effect on reaction efficiency was uncovered, which led to the discovery that [Ir(cod)(py)PCy₃]PF₆ (commercially available Crabtree's catalyst^[15,16]) is optimal as a catalyst precursor. In many instances, efficient coupling using equimolar quantities of the coupling partners was achieved with this catalyst. Multiple

C-H bond arylation reactions (two-fold C-H arylation and double C-H arylation) are also possible to construct extended π-electron systems very quickly. This newly discovered reactivity of iridium should open an avenue for a range of new catalytic C-H bond transformations by merging it with the unique reactivity of iridium in other organic transformations.

Received: December 29, 2008

Revised: March 5, 2009

Published online: April 7, 2009

Keywords: biaryls · C-C coupling · heterocycles · homogeneous catalysis · iridium

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