Synthetic Methods

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

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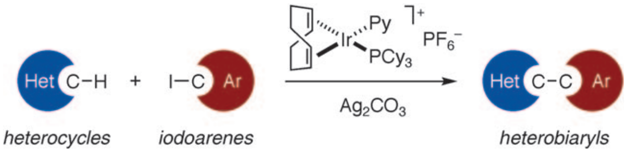
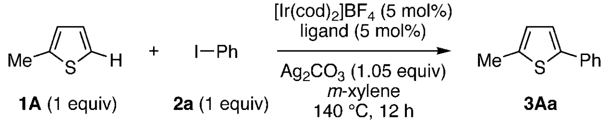


Arylated heteroarenes (heterobiaryls) are ubiquitous in natural products and pharmaceuticals, and are frequently used in organic materials or as ligands for metals.[1] Consequently, the development of efficient methods for making heterobiaryl motifs has been a topic of immense importance in chemical 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 $[(Cp^*IrHCl)_2]$/KO*t*Bu (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 $[RhCl(CO)(P\{OCH(CF_3)_2\}_3)_2]/Ag_2CO_3$ 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/Ag_2CO_3 system as a platform for C−H bond arylation. We report herein our finding that an $Ir^+/PCy_3/Ag_2CO_3$ (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 Ag_2CO_3 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 $P[OCH(CF_3)_2]_3$[12a] proved ineffective (Table 1, entry 1). Thus, the effect of the ligand was investigated, by using $[Ir(cod)_2]BF_4$ (cod = 1,5-cyclooctadiene) as the source of Ir^I. Screening of ligands indicated that PCy_3 was by far the most effective ligand, producing the heterobiaryl **3Aa** in 88 % yield (Table 1, entry 6).[14] A dramatic difference between PCy_3 and other closely related alkylphosphanes, such as $PCyp_3$ (Cyp = cyclopentyl), is notable and intriguing. In developing a stable Ir^+/PCy_3 precatalyst, we identified $[Ir(cod)(py)PCy_3]PF_6$ (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 $[Rh(cod)(py)PCy_3]PF_6$ was totally ineffective under otherwise identical conditions (Table 1, entry 13). The importance of Ag_2CO_3 was also recognized, as other additives, such as AgOTf, AgOAc, $AgSbF_6$, Na_2CO_3, K_2CO_3,

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	$P(C_6H_4OMe\text{-}p)_3$	2
4	$PCy_2(o\text{-biphenyl})$	4
5	PCy_2Ph	29
6	PCy_3	88
7	$PCyp_3$	16
8	$PAd_2(n\text{Bu})$	9
9	$P(n\text{Bu})_3$	5
10	$P(t\text{Bu})_3$	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), $[Ir(cod)_2]BF_4$ (0.02 mmol), ligand (0.02 mmol), Ag_2CO_3 (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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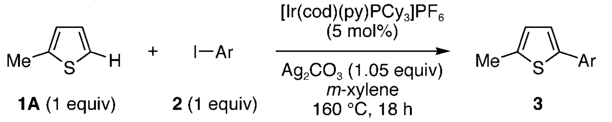
Cs_2CO_3, and KO*t*Bu, did not promote the reaction with the Ir^+/PCy_3 catalyst.

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). 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.

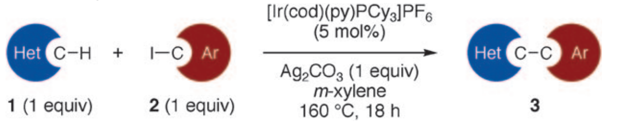
Table 2: Scope of iodoarenes.[a]



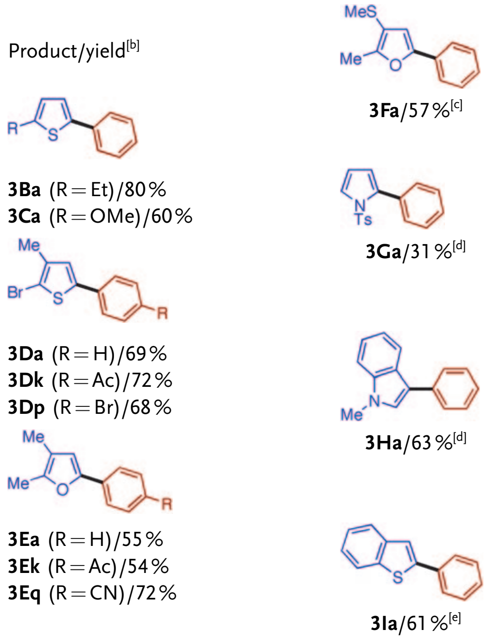
Entry	Ar (**2**)	Product (**3**)	Yield [%][b,c]
1	C_6H_5 (**2a**)	**3Aa**	87
2	*o*-$CH_3C_6H_4$ (**2b**)	**3Ab**	10
3	*m*-$CH_3C_6H_4$ (**2c**)	**3Ac**	69
4	*p*-$CH_3C_6H_4$ (**2d**)	**3Ad**	58
5	*o*-$CH_3OC_6H_4$ (**2e**)	**3Ae**	62
6	*m*-$CH_3OC_6H_4$ (**2f**)	**3Af**	70
7	*p*-$CH_3OC_6H_4$ (**2g**)	**3Ag**	76
8	*m*-$CF_3C_6H_4$ (**2h**)	**3Ah**	72
9	*p*-$CF_3C_6H_4$ (**2i**)	**3Ai**	74
10	*m*-$CH_3C(O)C_6H_4$ (**2j**)	**3Aj**	71
11	*p*-$CH_3C(O)C_6H_4$ (**2k**)	**3Ak**	79
12	*p*-$C_2H_5OC(O)C_6H_4$ (**2l**)	**3Al**	66
13	*m*-$NO_2C_6H_4$ (**2m**)	**3Am**	60
14	*p*-$NO_2C_6H_4$ (**2n**)	**3An**	78
15	*m*-BrC_6H_4 (**2o**)	**3Ao**	70
16	*p*-BrC_6H_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 3: Scope of heteroarenes.[a]



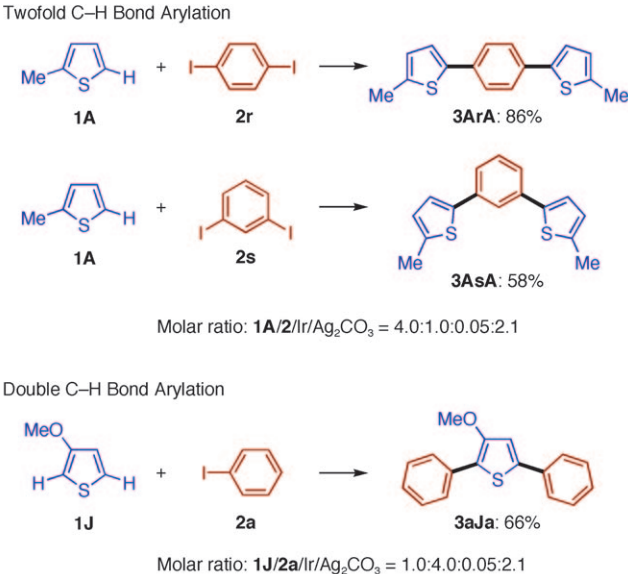
Product/yield[b]



3Ba (R = Et)/80 %
3Ca (R = OMe)/60 %
3Da (R = H)/69 %
3Dk (R = Ac)/72 %
3Dp (R = Br)/68 %
3Ea (R = H)/55 %
3Ek (R = Ac)/54 %
3Eq (R = CN)/72 %
3Fa/57 %[c]
3Ga/31 %[d]
3Ha/63 %[d]
3Ia/61 %[e]

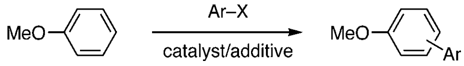
[a] Conditions: **1** (0.40 mmol), **2** (0.40 mmol), Ir catalyst (0.02 mmol), Ag_2CO_3 (0.40 mmol), *m*-xylene (2 mL), 160 °C, 18 h. [b] Yield of isolated product. [c] Reaction for 24 h. [d] 1 mL of *m*-xylene was employed. [e] Reaction for 36 h.

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



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

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$_3$	*p*-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$_3$)$_2$}$_3$)$_2$]/Ag$_2$CO$_3$	*p*-NO$_2$C$_6$H$_4$I	29:0:71[12a]
4	[(Cp*IrHCl)$_2$]/KO*t*Bu	C$_6$H$_5$I	72:16:12[10]
5	Pd(OAc)$_2$/PR$_3$/*t*BuCO$_2$H/K$_2$CO$_3$	*p*-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 Ag$_2$CO$_3$ 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(CF$_3$)$_2$]$_3$/Ag$_2$CO$_3$ system. The site-selectivities reported by Fujita, for [(Cp*IrHCl)$_2$]/KO*t*Bu[10] (Table 4, entry 3), and Fagnou, for Pd(OAc)$_2$/DavePhos/*t*BuCO$_2$H/K$_2$CO$_3$[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)PCy$_3$]PF$_6$ (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 (twofold 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.

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