Direct Arylation of Heteroarenes Catalyzed by a Palladium–1,10-Phenanthroline Complex

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This paper is dedicated to Professors Xiyan Lu and Li Xin Dai for their life-long contributions to the development of organic chemistry.

Abstract: A new entry in direct arylation of heteroarenes using $Pd(OAc)_2$ and 1,10-phenanthroline as a nitrogen-based ligand is reported. The long induction period observed at the initial stage of the reaction was effectively reduced by modification of the catalyst preparation, leading to improved chemical yields (69–92%) and shortening of reaction times (3–10 h).

Key words: direct arylation, palladium, 1,10-phenanthroline, heteroarenes, biaryls

Efficient transformation of versatile building blocks in medicinal or material chemistry has been pursued to achieve easy access to functional molecules in a cost-effective and environmentally benign manner. Direct functionalization of non-activated arenes via the disconnection of the arene C–H bond serves as one such effective transformation.[1–3] Compared to preparation methods using activated arenes (e.g. organometallic reagents in cross-coupling reactions), such direct reactions have the great advantages of reduced waste, lower cost, and shorter processes.

Heteroarenes are a significant class of arenes due to their wide range of applications. For instance, thiophene derivatives are used extensively in organic electronic materials, and indole derivatives are ubiquitous in biologically active compounds. Thus, efficient transformations of these heteroarenes are of great interest. In this context, direct arylation of heteroarenes[4] with haloarenes or pseudohaloarenes as coupling partners has been intensively investigated, and many kinds of transition metal species have been found to facilitate the reaction.[5–10] Among them, palladium-based catalysts have been most widely utilized.[5,6,10] Despite rapid progress in this field, direct arylation still encounters notable limitations, especially in terms of substrate generality.

Under those reaction conditions, two mechanisms have been mostly considered. It has been traditionally accepted that direct arylation of electron-rich heteroarenes would proceed via electrophilic aromatic substitution, namely, an S_EAr-type mechanism.[1,5o,z,11] Recently, some groups has proposed 'concerted metalation mechanism,' in which carboxylato ligands act as an internal base to achieve deprotonation of heteroarenes and concurrent metalation.[6e,k,12] Given that Pd^{II} species, which could be generated by oxidative addition of haloarenes to Pd^0 species, are involved in both mechanisms, the thermodynamic stability of Pd^{II} species in the higher oxidation state should be crucial to obtain a sufficient concentration of active species. The Pd-catalyzed reactions thus far reported were exclusively performed by the use of phosphine ligands or under ligand-free conditions.[5,6] On the other hand, nitrogen-based ligands, which should stabilize Pd^{II} species rather than Pd^0 species and are advantageous in the metalation step, have been scarcely utilized in this area.[13–15] Herein, we report the results of our investigations leading to a $Pd(OAc)_2$–1,10-phenanthroline catalyst, which enables direct arylation of thiophene, furan, and indole derivatives with various iodoarenes in good yields and short reaction times.

First, the reaction conditions were optimized for direct arylation of 2-methylthiophene (**2a**) with iodobenzene (**1a**), using a variety of nitrogen-based ligands (Table 1). The combination of 2,2′-bipyridyl with a catalytic amount of $Pd(OAc)_2$ and one equivalent of Cs_2CO_3 in DMF at 100 °C afforded only a trace amount of the desired product **3aa** after 24 hours (entry 1). On the other hand, the use of 1,10-phenanthroline (**A**) was found to have a dramatic impact on the reactivity, and the chemical yield of **3aa** was improved to 79% as confirmed by GLC analysis (entry 2). Other 1,10-phenanthroline derivatives with electron-donating substituents provided less satisfactory results (entries 3–5). Related aromatic nitrogen-based bidentate ligands with a planar structure and TMEDA as an aliphatic diamine ligand were also ineffective (entries 6–9). Thus, rigid bidentate coordination of a less basic ligand would be of importance.[16] Compounds with pyridine and phosphine moieties showed slight catalytic activities, and Ph_3P was also unsuitable for these reaction conditions (entries 10–12). Bromobenzene formed **3aa** in low yield (12%), and chlorobenzene was unreactive under the reaction conditions of entry 2.

Next, we examined the effects of palladium sources. The reactions were carried out at a controlled reaction time (4

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h). The combination of $Pd(OAc)_2$ and 1,10-phenanthroline provided a 77% yield of the arylated product in this time period (entry 13). The use of $Pd(O_2CCF_3)_2$ decreased the catalytic activity (entry 14), and dichloro complexes were less effective (entries 15 and 16). In addition, $Pd_2(dba)_3·CHCl_3$ and CpPd(η^3-allyl) exhibited very poor catalytic activity under the reaction conditions (entries 17 and 18). Consequently, $Pd(OAc)_2$ and 1,10-phenanthroline were proven to be the catalyst combination of choice.

Table 1 Optimization of Pd-Catalyzed Direct Arylation of 2-Methylthiophene (**2a**) with Iodobenzene (**1a**)

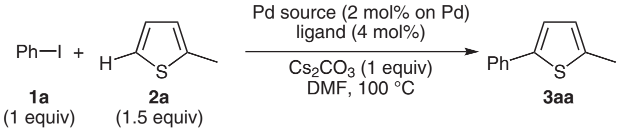
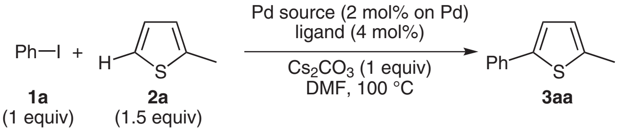
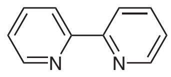
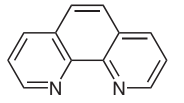
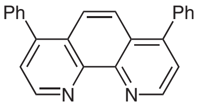
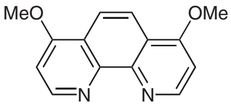
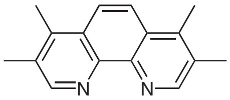
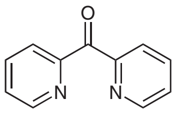
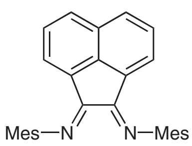
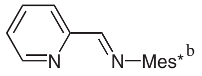
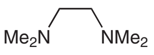
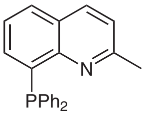
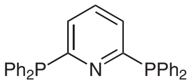


Table 1 Optimization of Pd-Catalyzed Direct Arylation of 2-Methylthiophene (**2a**) with Iodobenzene (**1a**) (continued)



Entry	Ligand	Pd source	Time (h)	Yield (%)[a]
1		$Pd(OAc)_2$	24	1
2	 **A**	$Pd(OAc)_2$	24	79
3		$Pd(OAc)_2$	24	27
4		$Pd(OAc)_2$	24	0
5		$Pd(OAc)_2$	24	3
6		$Pd(OAc)_2$	24	5
7		$Pd(OAc)_2$	24	0
8		$Pd(OAc)_2$	24	trace
9		$Pd(OAc)_2$	24	trace
10		$Pd(OAc)_2$	24	5
11		$Pd(OAc)_2$	24	9
12	PPh_3[c]	$Pd(OAc)_2$	24	8
13	**A**	$Pd(OAc)_2$	4	77
14	**A**	$Pd(O_2CCF_3)_2$	4	56
15	**A**	$PdCl_2(tmeda)$	4	2
16	**A**	$PdCl_2(PhCN)_2$	4	21
17	**A**	$Pd_2(dba)_3·CHCl_3$	4	trace
18	**A**	CpPd(η^3-allyl)	4	trace

[a] GLC yields based on tridecane as an internal standard.

[b] Mes* = 2,4,6-tri-*tert*-butylphenyl.

[c] The use of 8 mol% of Ph_3P gave the same chemical yield (8%).

Even after the optimal catalyst combination was determined, the chemical yield remained moderate even with prolonged reaction time (entries 2 and 13, Table 1). Therefore, the reaction profile was investigated by GLC using tridecane as an internal standard. The blue curves in Figures 1a and 1b are the time-course of conversion of **1a** and yield of **3aa**, respectively, under the reaction conditions of entry 13 in Table 1 (condition A), where the substrates (**1a** and **2a**), base (Cs_2CO_3), and catalyst precursors [$Pd(OAc)_2$ and 1,10-phenanthroline] were mixed together in DMF, and then heated at 100 °C. It is seen that, following the 60 minutes induction period, **1a** starts to be converted to **3aa** in ca. 80% selectivity.[17]

On the other hand, preheating the catalyst precursors in DMF in the presence of iodobenzene (**1a**) and Cs_2CO_3 at 100 °C for 30 minutes reduces the induction period nearly in half (condition B). The red reaction curves in Figures 1a and 1b show the time-course of the amounts of **1a** and **3aa** after the addition of 2-methylthiophene (**2a**) to the system. The reaction is accelerated and the product selectivity is improved to ca. 90%. As a result, **3aa** was obtained in 89% yield after four hours as confirmed by GLC. It was noted that the treatment of $Pd(OAc)_2$ and 1,10-phenanthroline with **1a** and base prior to the catalytic reaction is essential for gaining improved catalytic activity. No acceleration effect was observed when the catalyst precursors were heated only with Cs_2CO_3 or with **2a** and Cs_2CO_3 (see Supporting Information).

The reaction procedure of condition B was effective for direct arylation of 2-methylthiophene (**2a**), 2-pentylfuran (**2b**), and *N*-methylindole (**2c**), as summarized in Table 2.

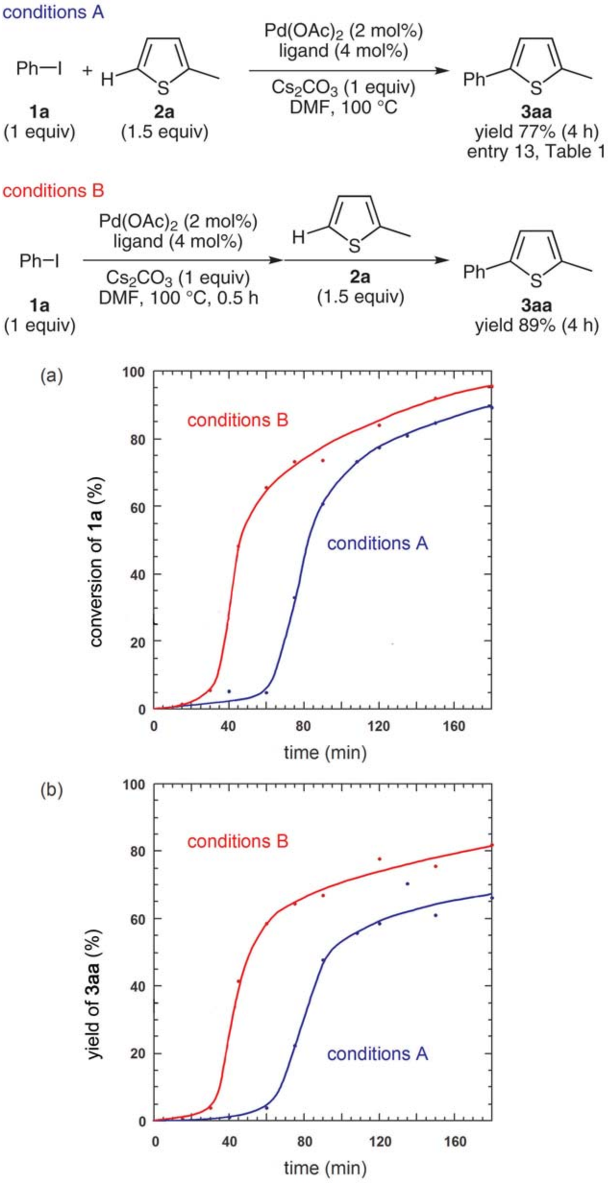
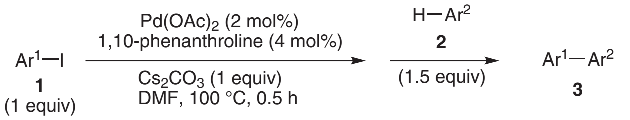
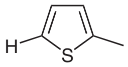
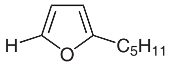
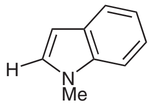


Figure 1 Comparison of the reaction profiles of direct arylation catalyzed by $Pd(OAc)_2$ and 1,10-phenanthroline under conditions A and B: (a) conversion of iodobenzene (**1a**); (b) GLC yield of the corresponding product (**3aa**)

Table 2 Direct Arylation of Heteroarenes Catalyzed by a Palladium–1,10-Phenanthroline Complex



Entry	Ar^1 (Ar^1I)	HAr^2	Time (h)	Yield (%)[a]
1	Ph (**1a**)	 **2a**	4	84
2	4-MeC_6H_4 (**1b**)	**2a**	4	79
3	1-naphthyl (**1c**)	**2a**	9	82
4	4-$MeOC_6H_4$ (**1d**)	**2a**	6	68
5	4-$EtO_2CC_6H_4$ (**1e**)	**2a**	3	80
6	Ph (**1a**)	 **2b**	4	85
7	1-naphthyl (**1c**)	**2b**	5	92
8	4-$MeOC_6H_4$ (**1d**)	**2b**	10	76
9	4-$EtO_2CC_6H_4$ (**1e**)	**2b**	4	86
10	4-$EtO_2CC_6H_4$ (**1e**)	 (**2c**)	6.5	69

[a] Isolated yield.

2-Methylthiophene (**2a**) reacted with various iodoarenes (entries 1–5), including sterically hindered (**1c**), electron-rich (**1d**), and electron-deficient (**1e**) substrates, to afford the desired products in 68–84% yields. The reactions were completed in 3–9 hours. 2-Pentylfuran (**2b**) was also smoothly coupled with iodoarenes in 76–92% yields (entries 7–9). *N*-Methylindole (**2c**) reacted with ethyl iodobenzoate (**1e**) exclusively at the 2-position (entry 10).

In conclusion, we have developed a new catalyst system for direct arylation of heteroarenes using $Pd(OAc)_2$ and 1,10-phenanthroline as catalyst precursors. It was found that preheating the catalyst precursors with PhI and Cs_2CO_3 reduces the induction period to a considerable extent and affords highly efficient catalysis with good chemical yields and short reaction times. A plausible process during the catalyst preparation is the formation of a phenylpalladium intermediate via reduction of $Pd(OAc)_2$, followed by oxidative addition of PhI to a Pd(0) species. If the reduction of $Pd(OAc)_2$ is a significantly slow process in the present catalytic system using 1,10-phenanthroline as a nitrogen-based ligand, the notably long induction period may be rationalized.[18] Investigations on the mechanistic details and further applications of this novel catalyst system are ongoing in our laboratory.

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synlett.

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(4) In this manuscript, the term 'direct arylation of heteroarenes' denotes the reaction of heteroarenes with (pseudo)haloarenes. For other types of reactions (e.g., directing-group-controlled reactions or the reaction of arenes with organometallic reagents), see ref. 1.

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