C–H Activation

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A Versatile Palladium/Triphosphane System for Direct Arylation of Heteroarenes with Chloroarenes at Low Catalyst Loading**

David Roy, Sophal Mom, Matthieu Beaupérin, Henri Doucet, and Jean-Cyrille Hierso**

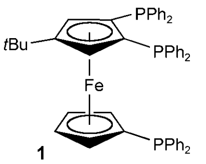
In memory of Keith Fagnou and Pascal Le Floch

Palladium-catalyzed cross-coupling reactions between organometallic nucleophilic reagents and electrophilic organic halides or pseudohalides emerged as powerful synthetic tools for the construction of C–C bonds.[1–2] Such catalytic coupling processes are applied to a wide array of fields, which range from biological sciences to materials chemistry.[3–4] Their applications to heteroaromatic substrates set the stage for convergent synthetic routes to valuable substituted heterocyclic structures.[5] Because of the necessity of limiting costly and contaminant metallic reagents, the research focus has shifted to the direct arylation of heteroaromatic substrates by the combined C–H/C–X activation (X = halide or pseudohalide).[6] This type of methodology presents the advantage of circumventing the preparation of organometallic nucleophilic reagents. It also avoids stoichiometric formation of metallic side products, from which undesired contamination could be appalling for pharmaceutical, agrochemical, and related biological applications.

Reports of palladium-catalyzed direct arylations of heteroaromatics have described the use of organic bromides,[7] iodides,[8] triflates,[9] mesylates and tosylates,[10] sulfamates and phosphates,[11] iodonium salts,[12] and potassium trifluoroborates[13] as useful reagents. Organic chlorides remained noticeably uncommon partners,[14] despite the fact that among halides and pseudohalides, chlorides are arguably the most useful single class of substrates because of their straightforward access, their lower cost, and the wider diversity of available compounds. However, chloroarenes are most often unreactive under the conditions employed to couple other more reactive starting materials. Few monodentate electron-rich catalysts,[15] and a catalytic system based on a chelating diphosphane[16] have achieved a limited number of intermolecular couplings[17] between mostly unsubstituted or electron-deficient aryl chlorides and heteroaromatic compounds. Despite this remarkable progress, more sustainable catalytic systems, employing significantly less palladium/ligand catalyst, for the coupling of a wide array of diversely substituted aryl chlorides to heteroaromatic compounds have not yet been reported. Herein, we disclose a new air-stable, moisture and temperature tolerant palladium/triphosphane system that is highly efficient for the direct arylation of substituted furan, pyrrole, thiophene, and thiazole substrates. Notably, these findings represent an economically attractive direct arylation of hetero- and diheteroaromatic substrates with chloroarenes by using less than 1 mol% of the palladium/ligand catalyst. This versatile system highlights also the potential of tridentate ferrocenyl polyphosphane ligands as air-stable, easy to handle auxiliaries in demanding intermolecular C–H/C–Cl activations.

As a part of our program directed towards the development of robust polydentate auxiliaries for various cross-coupling reactions,[18] we probed various ferrocenyl polyphosphane ligands for direct arylation of different classes of hetero- and diheteroaromatic compounds using demanding bromoarenes.[19] In the course of these studies we observed the apparent superior efficiency of ferrocenyl triphosphane ligands over related mono-, di-, and tetraphosphanes. We therefore focused our efforts on providing a sustainable and efficient palladium-catalyzed method for the challenging intermolecular direct arylation of functionalized chloroarenes by using systems that incorporated the modified ferrocenyl triphosphanes **1**–**4**, and the diphosphane **5**.

In earlier work, we determined that triphosphane **1** was useful for demanding C–H/C–Br activation, but inefficient



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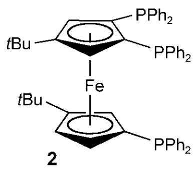

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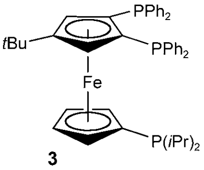

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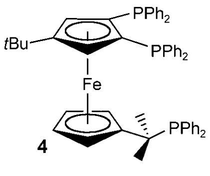

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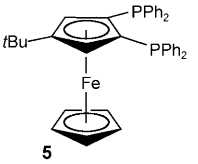

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[*] S. Mom, M. Beaupérin, Prof. Dr. J.-C. Hierso
Université de Bourgogne, Institut de Chimie Moléculaire de
l'Université de Bourgogne (ICMUB) UMR-CNRS 5260
9, avenue Alain Savary 21078 Dijon (France)
Fax: (+33) 3-8039-3682
E-mail: jean-cyrille.hierso@u-bourgogne.fr

D. Roy, Dr. H. Doucet
Université de Rennes I, Institut Sciences Chimiques de Rennes
(ISCR) UMR-CNRS 6226
Campus de Beaulieu 35042 Rennes (France)
Fax: (+33) 2-2323-6939
E-mail: henri.doucet@univ-rennes1.fr

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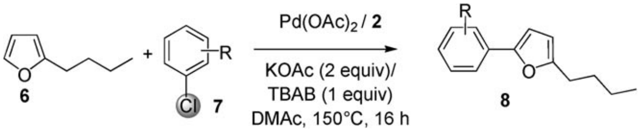
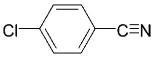
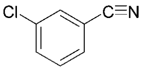
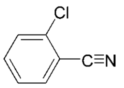
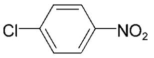
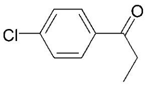
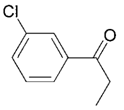
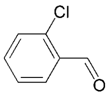
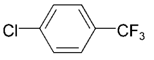
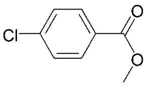
with electron-poor 4-chloroacetophenone.[19] Thus, as illustrated in Tables S1–S3 in the Supporting Information, neither ligand **1** nor its related congeners **3**–**5** are as effective as triphosphane **2** for the palladium-catalyzed direct arylation of heteroaromatic compounds with functionalized chloroarenes. Under the practical reaction conditions pioneered by Otha ($[Pd(PPh_3)_4]$),[14a] McClure ($PdCl_2/PCy_3$),[20] and Fagnou ($Pd(OH)_2/C^*$),[21] deficient coupling reactions were obtained. A catalytic system comprising $Pd(OAc)_2$ and the constrained ferrocenyl triphosphane ligand **2**, as well as KOAc as a cheap base and DMAc as the solvent, was optimized for in depth studies of the coupling for a variety of heteroaromatic compounds. Notably, the addition of tetra-*n*-butylammonium bromide was found to be beneficial for the arylation of chloroarenes; and we observed that ligand-free conditions were totally inefficient. The scope of this procedure was studied using various heteroaryl derivatives and chloroarenes (Tables 1–4). The reactivity of 2-, 3-, or 4-chlorobenzonitrile was found to be very similar for their coupling with 2-*n*-butylfuran (Table 1, entries 1–3), high yields of the coupling products **8a**–**8c** were obtained. Excellent results were also obtained in the presence of diversely functionalized chloroarenes such as 4-chloronitrobenzene, 3- or 4-chloropropiophenone, 4-trifluoromethylchlorobenzene, and 2-chlorobenzaldehyde (Table 1, entries 4–10); very good yields were obtained when only using 0.5 mol% catalyst. In some cases 0.1 mol% of catalyst allowed a fairly good conversion in 16 hours (Table 1, entries 6 and 10). Conversely, the coupling of 4-chlorobenzoic acid methyl ester was unsatisfactory (Table 1, entry 11).

With regards to the more challenging functionalization of electron-poor furans, the reactivity of methyl 2-methylfuran-3-carboxylate was examined (Table 2). With this furan derivative, satisfactory to moderate yields of the desired compounds **10a**–**10g** were obtained, however, side products, *n*-butyl 5-aryl-2-methylfuran-3-carboxylate derivatives, were obtained in low yield. The highly oxygenated products **10a**–**10g** were isolated in 40 to 60% yield.

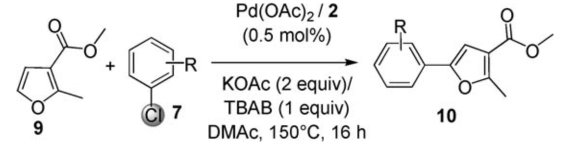
Table 1: Direct arylation of the electron-rich furan **6** with chloroarenes **7**.[a]

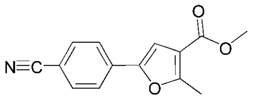
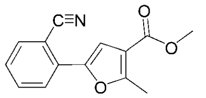
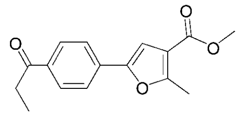
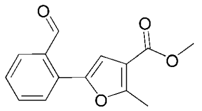


Entry	7		Cat. [mol%]	Product	Yield [%]
1		**7a**	0.5	**8a**	83
2		**7b**	0.5	**8b**	85
3		**7c**	0.5	**8c**	87
4		**7d**	0.5	**8d**	74
5		**7e**	0.5	**8e**	84
6		**7e**	0.1	**8e**	41
7		**7f**	0.5	**8f**	72
8		**7g**	0.5	**8g**	82
9		**7h**	0.5	**8h**	73
10		**7h**	0.1	**8h**	43
11		**7i**	0.5	**8i**	15

[a] Reaction conditions: $Pd(OAc)_2$/ligand **2** (1:1), aryl chloride (1 mmol), 2-*n*-butylfuran (2 mmol), KOAc (2 mmol), DMAc 3 mL, TBAB (1 mmol), 150°C, 16 h under argon. Yields of isolated products reported (average of two experiments). DMAc = *N*,*N*-dimethylacetamide , TBAB = tetra-*n*-butylammonium bromide.

Table 2: Direct arylation of electron-poor furan **9** with chloroarenes **7**.[a]

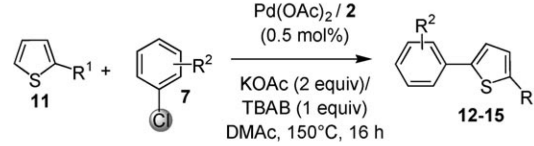


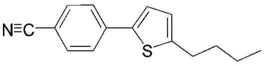
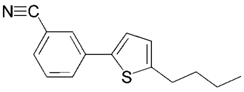
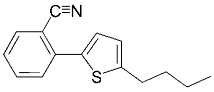
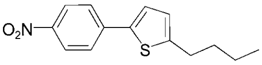
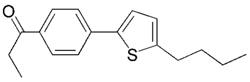
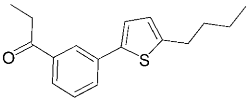
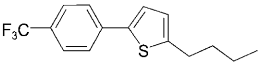
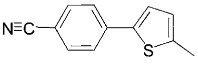
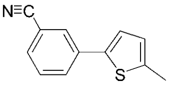
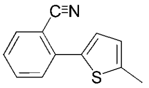
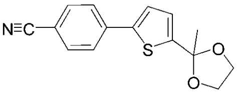
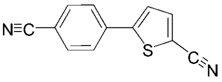
Entry	7	Product		Yield [%]
1	**7a**		**10a**	58
2	**7c**		**10c**	55
3	**7e**		**10e**	38
4	**7g**		**10g**	42

[a] Same reaction conditions as described in the Table 1, with 0.5 mol% $Pd(OAc)_2$/**2** as the catalyst.

Under the same optimized reactions, 2-*n*-alkylthiophenes were found viable substrates for palladium-catalyzed direct arylations.[7e,i] High yields of 5-arylation products were obtained for the coupling of 4-chlorobenzonitrile, 4-chloronitrobenzene, 4-trifluoromethylchlorobenzene, and 3- or 4-chloropropiophenone with 2-*n*-butylthiophene (Table 3, entries 1, 4, 5, 7, and 8). Conversely, compounds **12b** and **12c** were obtained in only low to moderate yields because of the partial conversion of 2- or 3-chlorobenzonitrile (Table 2, entries 2 and 3). The presence of sulfur-containing substrates did not appear to poison the catalyst system, even at 0.5 mol% loading.

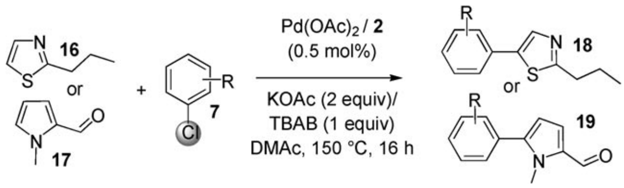
Table 3: Direct arylation of thiophenes **11** with chloroarenes **7**.[a]

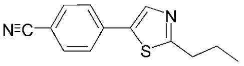
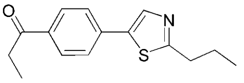
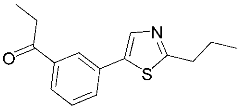
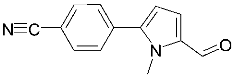
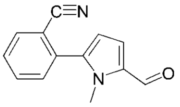
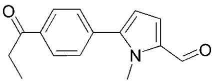
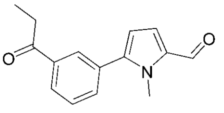
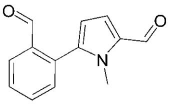


Entry	11	7	Product		Yield [%]
1	**11a**	**7a**		**12a**	90
2	**11a**	**7b**		**12b**	17
3	**11a**	**7c**		**12c**	52
4	**11a**	**7d**		**12d**	80
5	**11a**	**7e**		**12e**	63
6	**11a**	**7e**		**12e**	90[b]
7	**11a**	**7f**		**12f**	73
8	**11a**	**7h**		**12h**	81
9	**11b**	**7a**		**13a**	69
10	**11b**	**7b**		**13b**	25
11	**11b**	**7c**		**13c**	62
12	**11c**	**7a**		**14a**	79
13	**11d**	**7a**		**15a**	52

[a] Same reaction conditions as described in the Table 1, with 0.5 mol% $Pd(OAc)_2$/**2** as the catalyst. [b] 1 mol% $Pd(OAc)_2$/**2** as the catalyst.

Table 4: Direct arylation of heteroarenes thiazole **16** and pyrrole **17** using chloroarenes **7**.[a]



Entry	Heteroarene	7	Product		Yield [%]
1	**16**	**7a**		**18a**	92
2	**16**	**7e**		**18e**	83
3	**16**	**7f**		**18f**	62
4	**17**	**7a**		**19a**	89
5	**17**	**7c**		**19c**	63
6	**17**	**7e**		**19e**	77
7	**17**	**7f**		**19f**	50
8	**17**	**7g**		**19g**	63

[a] Same reaction conditions as described in the Table 1, with 0.5 mol% $Pd(OAc)_2$/**2** as the catalyst.

We had observed that the direct 5-arylation of thiazoles can be performed using 1 to 5 mol% of $[PdCl(dppb)(C_3H_5)]$ (dppb = bis(diphenylphosphanyl)butane) as the catalyst.[16] The arylation of thiazoles with chloroarenes appears to be generally easier than the direct arylation of furans or thiophenes. As expected, the $Pd(OAc)_2$/**2** system used at 0.5 mol% loading efficiently catalyzes the coupling of 4-chlorobenzonitrile, or 3- or 4-chloropropiophenone with 2-*n*-propylthiazole to give **18a**, **18e**, and **18f**, respectively, in yields within the range of 62–92% (Table 4, entries 1–3). The intermolecular palladium-catalyzed direct arylation of pyrroles using chloroarenes is of interest,[17c] and mostly intramolecular cyclizations[17a] or reactions using heteroaryl chlorides[14a] have been reported. We observed that the coupling of 1-methyl-2-formylpyrrole with several chloroarenes selectively gives the desired coupling products **19a**–**19g** in excellent to fairly good yields (Table 4, entries 4–8). Electron-deficient *para*-, *meta*-, or *ortho*-substituted chloroarenes displaying important functional groups can be employed.

In summary, we have reported the use of an air-stable, easy to handle catalytic system that is efficient for the coupling of functionalized chloroarenes to a variety of heteroaromatic compounds at low palladium loadings. Electron-rich, electron-poor, and polysubstituted furans, thiophenes, pyrroles, and thiazoles were arylated by using catalyst loadings ranging between 0.1 and 0.5 mol%. This catalytic system tolerates important and useful functional groups, which can be manipulated for accessing more sophisticated heterocyclic molecules, such as formyl, nitriles, nitro, keto, and ester groups in *para*, *meta*, or *ortho* positions. This scope demonstrates the synthetic utility of this catalyst. Besides the well-known interest of classical electron-rich monodentate ligands, the present study highlights the usefulness of robust tridentate ferrocenylphosphane catalytic auxiliaries in direct C–H/C–Cl activation reactions.

Experimental Section

In a typical experiment, the aryl chloride (1 mmol), heteroaromatic derivative (2 mmol), KOAc (2 mmol), and Bu_4NBr (1 mmol) were introduced into a Schlenk tube equipped with a magnetic stirring bar. The $Pd(OAc)_2$/ligand **2** (ratio 1:1) catalyst and DMAc (3 mL) were added, and the Schlenk tube purged several times with argon. The Schlenk tube was placed in an oil bath preheated to 150°C, and the mixture was stirred for 16 h. The reaction mixture was then analyzed by gas chromatography to determine the conversion of the aryl chloride. The solvent was removed by heating of the reaction vessel under vacuum and the residue was charged directly onto a silica gel column. The products were eluted using an appropriate ratio (depending on the polarity of the coupling products) of diethyl ether and pentanes.

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