Selective Palladium-Catalyzed Aminations on 2-Chloro-3-iodo- and 2-Chloro-5-iodopyridine

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Abstract: Regioselective palladium-catalyzed aminations with anilines on 2-chloro-3-iodo- and 2-chloro-5-iodopyridine have been performed with excellent yields and good selectivity. The use of a large excess of Cs_2CO_3 in combination with Pd–BINAP catalyst was essential to obtain sufficiently fast reactions. The mild conditions permit the presence of base sensitive functional groups. Moreover, the catalytic system developed also allows the arylamination of aryl iodides.

Key words: palladium, aminations, chloro-iodopyridines, iodobenzenes, diarylamines

Tin free palladium-catalyzed amination, independently discovered by Buchwald and Hartwig, has established itself as a very powerful tool for the synthesis of arylamines including diarylamines.[1,2] Diarylamines are of synthetic importance since several applications as pharmaceuticals are known. They are indeed considered as 'privileged structures': single molecular frameworks, able to provide ligands for diverse receptors.[3] As a part of a new synthetic project, our laboratory focuses on the synthesis of arylamino substituted pyridines, quinolines and naphthyridines via palladium-catalyzed amination reactions. Recently, we described a very efficient regioselective palladium-catalyzed amination protocol for the arylamination of dichloropyridines.[4] Compounds 2,3-, 2,5- and 2,6-dichloropyridine could be regioselectively aminated in the 2-position with an arylamine yielding 3-, 5- and 6-chloro substituted 2-arylaminopyridines respectively.

As a continuation of this selective amination study we wanted to prepare the isomeric 3-arylamino-2-chloro- and 5-arylamino-2-chloropyridines. Therefore, we studied regioselective palladium-catalyzed amination on easily accessible 2-chloro-3-iodopyridine and 2-chloro-5-iodopyridine.[5] Palladium-catalyzed C-C bond forming cross-coupling reactions on 2-chloro-3-iodopyridine and 2-chloro-5-iodopyridine with selective substitution of the iodine atom have already been reported, but no report of a similar selective Buchwald–Hartwig C–N bond formation has appeared up to now.[5,6] More generally, to the best of our knowledge no palladium-catalyzed aminations on azaheteroaryl iodides have been described in the literature yet.[7] Moreover, during the development of intermolecular Buchwald–Hartwig aminations, aryl iodides have been pointed out to be less effective substrates than the corresponding aryl bromides (in contrast to the C–C bond forming reactions).[8–10] All these factors make a selective amination study on 2-chloro-3-iodopyridine and 2-chloro-5-iodopyridine an interesting and not self-evident task.

As a model reaction we chose the palladium-catalyzed coupling of *p*-toluidine with 2-chloro-3-iodopyridine. For this substrate we first tried to use our conditions reported for the arylamination of chloropyridazin-3(2*H*)-ones and dichloropyridines.[4,11] Refluxing 2-chloro-3-iodopyridine, *p*-toluidine (1.2 equivalents), 2 mol% Pd–BINAP catalyst and a large excess of K_2CO_3 (5 equivalents) as the base in toluene gave a selective amination in the 3 position. Interestingly, neither 2- nor 2,3-diaminated product was formed. However, only a slow reaction rate was observed. In order to increase the reaction rate, other bases (K_3PO_4 and Cs_2CO_3) were screened. In a comparative study using 5 equivalents of K_2CO_3, K_3PO_4 and Cs_2CO_3, the last one gave the best results.[12] It is important to note that in an initial study to couple amines with aryl iodides Buchwald also used the Pd–BINAP catalyst system but in this case NaO*t*-Bu was utilized as the base.[13] No successful report on intermolecular aminations on aryl iodides using milder bases such as Cs_2CO_3 in combination with Pd–BINAP has been published yet.[8,14] Remarkably, a large excess of mild base was essential to obtain good results. When 5 equivalents of Cs_2CO_3 were used, a yield of 90% of 2-chloro-3-(4-methylphenylamino)pyridine was obtained after refluxing for 8 hours, whereas the use of 2 equivalents of the same base gave only a yield of 68% in the same reaction time. This rate increase in palladium-catalyzed aminations caused by the use of a large excess of base has already been observed by us in palladium-catalyzed aminations of dichloropyridines and chloropyridazin-3(2*H*)-ones.[4,11] Since the excess of base responsible for the accelerating effect does not dissolve in the reaction mixture, an interphase mechanism might be involved. However, the true nature of this effect remains unclear and will be the subject of further investigation.

Next, we probed the optimized conditions for the coupling of 2-chloro-3-iodopyridine with other substituted anilines. Table 1 clearly shows that activated as well as deactivated anilines can be smoothly coupled with 2-

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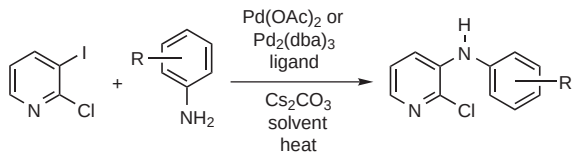
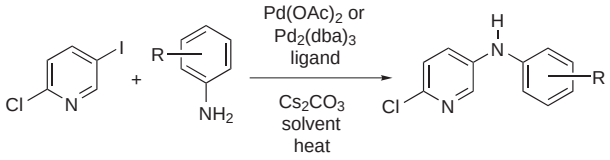
Table 1 Selective Pd-Catalyzed Amination on 2-Chloro-3-iodopyridine[20–22]



Entry	R	Mol% Pd	Mol% ligand	Yield (%)[a]
1	4-CH_3	2	2	92[b]
2	4-CH_3	2	2	97[c]
3	4-CH_3	2	2	97[c,d]
4	3-CH_3	2	2	92[b]
5	4-CH_3O	3	3	92[b]
6	4-F	2	2	97[b]
7	4-EtOOC	2	2	93[b]
8	2-CN	3	3	80[b]
9	2-Cl	2	2	80[b] (16)[e]

[a] All reactions were run overnight (17 hours); reaction times were not minimized.
[b] $Pd(OAc)_2$, BINAP, 2-chloro-3-iodopyridine (1.5 mmol), aniline (1.8 mmol), Cs_2CO_3 (7.5 mmol), toluene (15 mL), oil bath temperature 120 °C.
[c] $Pd_2(dba)_3$, XANTPHOS, 2-chloro-3-iodopyridine (1.5 mmol), aniline (1.8 mmol), Cs_2CO_3 (2.1 mmol), dioxane/ triethylamine (2:1, 4.5 mL), oil bath temperature 100 °C.
[d] 5 equivalents Cs_2CO_3 instead of 1.4 equivalents were used.
[e] Yield of diaminated pyridine based on 2-chloro-3-iodopyridine.

Table 2 Selective Pd-Catalyzed Amination on 2-Chloro-5-iodopyridine[20–22]



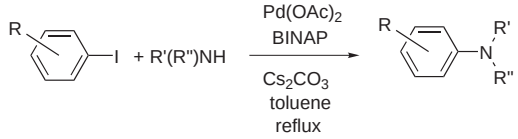
Entry	R	Mol% Pd	Mol% ligand	Yield (%)[a]
1	4-CH_3	2	2	95[b]
2	4-CH_3	2	2	45[c]
3	4-CH_3	2	4	81[c]
4	4-CH_3	2	4	90[c,d]
5	4-CH_3O	2	2	93[b]
6	4-F	2	2	92[b]
7	4-EtOOC	3	3	98[b]

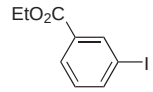
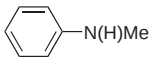
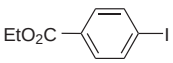
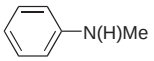
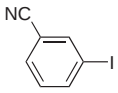
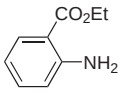
[a] All reactions were run overnight (17 hours); reaction times were not minimized.
[b] $Pd(OAc)_2$, BINAP, 2-chloro-5-iodopyridine (1.5 mmol), aniline (1.8 mmol), Cs_2CO_3 (7.5 mmol), toluene (15 mL), oil bath temperature 120 °C.
[c] $Pd_2(dba)_3$, XANTPHOS, 2-chloro-5-iodopyridine (1.5 mmol), aniline (1.8 mmol), Cs_2CO_3 (2.1 mmol), dioxane/triethylamine (2:1, 4.5 mL), oil bath temperature 100 °C.
[d] 5 equivalents Cs_2CO_3 instead of 1.4 equivalents were used.

chloro-3-iodopyridine in excellent yields (entries 1, 4–9). Also base sensitive anilines such as benzocaine (Table 1, entry 7) and *o*-aminobenzonitrile (Table 1, entry 8) could be efficiently coupled under our reaction conditions. Even the presence of sterical hindrance in the aniline such as in *o*-aminobenzonitrile (Table 1, entry 8) and *o*-chloroaniline (Table 1, entry 9) does not seem to hamper the reaction. Attempts to expand these selective aminations towards the isomeric substrate 2-chloro-5-iodopyridine gave similar results (Table 2, entries 1, 5–7). All reactions were typically run overnight, and a higher loading of catalyst was taken in those cases where overnight reflux still gave an incomplete reaction. In all cases selective substitution of the iodine was observed, and only trace amounts of the diaminated pyridines could be detected in the MS analyses of the crude reaction mixtures. A sole exception was observed, in the coupling reaction of *o*-chloroaniline with 2-chloro-3-iodopyridine: the diaminated product [2,3-bis(2-chlorophenylamino)pyridine] was isolated in 16% yield (Table 1, entry 9).

As already mentioned before, aryl iodides have been shown to be less effective substrates than their bromide counterparts in amination chemistry; reports on intermolecular palladium-catalyzed amination on aryl iodides up to 2001 used strong base (*t*-BuOM) limiting the scope to non-base sensitive functional groups.[13–18] Only recently, Buchwald's group thoroughly reinvestigated palladium-catalyzed aminations on aryl iodides.[10] For the synthesis of diarylamines with base sensitive functionalities Buchwald succesfully used 9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene (XANTPHOS) as ligand for the palladium catalyst in combination with the weak base Cs_2CO_3 in a mixture of dioxane and triethylamine as solvent.[10] In order to compare our catalytic system with Buchwald's we used identical conditions as reported by Buchwald in the coupling of 2-chloro-3-iodo- and 2-chloro-5-iodopyridine with *p*-toluidine [1 mol% $Pd_2(dba)_3$, 2 mol% XANTPHOS, *p*-toluidine (1.2 equivalents), Cs_2CO_3 (1.4 equivalents), mixture of dioxane/NEt_3 (2:1)]. For the synthesis of 2-chloro-3-(4-methylphenylamino)pyridine a similar yield (97% in comparison with 92%) was obtained with XANTPHOS (Table 1, entries 1 and 2), whereas with this catalyst, the synthesis of the isomer 2-chloro-5-(4-methylphenylamino)pyridine gave a very poor result: overnight reflux gave an incomplete reaction and an isolated yield of only 45% (Table 2, entry 2). Doubling the amount of XANTPHOS resulted in a better yield (81%) (Table 2, entry 3).[19] A further slight improvement was obtained by using 5 equivalents of Cs_2CO_3 instead of 1.4 equivalents (90%) (Table 2, entry 4).

Table 3 Synthesis of Diarylamines via Pd-Catalyzed Amination on Aryl Iodides[23]



Entry	Aryl iodide	Aniline	Mol% Pd	Mol% BINAP	Yield (%)[a]	Literature yield[10] (%)[b]
1			1	1	98	84
2			1	1	98	86
3			1	1	95	91

[a] All reactions were run overnight (17 hours); reaction times were not minimized. $Pd(OAc)_2$, BINAP, aryl iodide (1.5 mmol), aniline (1.8 mmol), Cs_2CO_3 (7.5 mmol), toluene (15 mL), oil bath temperature 120 °C.
[b] 0.5 mol% $Pd_2(dba)_3$, 2 mol% XANTPHOS, aniline, Cs_2CO_3 (1.4 equivalents), mixture of dioxane/NEt_3 (2:1) or dioxane/*t*-BuOH (2:1), heat.

In testing the applicability of our catalytic system on other aromatic iodides, we tried to use it for the preparation of diarylamines: *N*-(3-carbethoxyphenyl)-*N*-methylaniline, *N*-(4-carbethoxyphenyl)-*N*-methylaniline and 3-cyano-2′-carbethoxydiphenylamine (Table 3). Recently, these three diarylamines were prepared by Buchwald'a group via the amination of ethyl 3-iodobenzoate and ethyl 4-iodobenzoate with *N*-methylaniline and 3-iodobenzonitrile with ethyl 2-aminobenzoate respectively using the Pd–XANTPHOS catalytic system [0.5 mol% $Pd_2(dba)_3$, 2 mol% XANTPHOS, aniline, Cs_2CO_3 (1.4 equivalents), mixture of dioxane/Et_3N (2:1) or dioxane/*t*-BuOH (2:1)].[10] Gratifyingly, we found that using our reaction procedure an equal loading of catalyst gave similar results. As for aminations on chloro-iodopyridines, a large excess of base was essential to obtain good results. When 5 equivalents of Cs_2CO_3 were used a yield of 79% of *N*-(3-carbethoxyphenyl)-*N*-methylaniline was obtained after refluxing for 3 hours, whereas the use of 2 equivalents of the same base gave only a yield of 51% in the same reaction time.

In conclusion we have clearly shown that a regioselective arylamination on 2-chloro-3-iodo- and 2-chloro-5-iodopyridine can be performed using a Pd–BINAP catalytic system in combination with a large excess of Cs_2CO_3. The mild conditions allow the use of base sensitive functional groups on both coupling partners. The broader use of this procedure for the palladium-catalyzed amination of aryl iodides with anilines in general, is another attractive feature of our methodology.

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(19) Buchwald originally used a double amount of XANTPHOS (Pd/2L instead of Pd/L)

(20) General procedure for the selective Pd-catalyzed aminations on 2-chloro-3-iodopyridine and 2-chloro-5-iodopyridine using $Pd(OAc)_2$–BINAP:
A round bottom flask was charged with $Pd(OAc)_2$ (Acros, 0.03 mmol or 0.045 mmol), (±)-BINAP (Strem Chemicals, 0.03 mmol or 0.045 mmol) and toluene (Acros, 99%, 5 mL). The mixture was flushed with nitrogen for 10 minutes under magnetic stirring. In another round bottom flask chloro-iodopyridine (0.359 g, 1.5 mmol), aniline (1.8 mmol) and Cs_2CO_3 (Acros, 99.5%, 2.444 g, 7.5 mmol) were weighed. Then, the $Pd(OAc)_2$–BINAP solution was added, and the flask was rinsed well with an additional amount of toluene (10 mL). The resulting mixture was flushed with nitrogen for 5 minutes under magnetic stirring and subsequently heated in an oil bath under vigorous magnetic stirring (oil bath temperature 120 °C, N_2 atmosphere). After overnight reflux the mixture was cooled down to room temperature. The solid material was filtered off and washed well with CH_2Cl_2 (200 mL). The filtrate was evaporated and the resulting crude product was purified by flash column chromatography.

(21) General procedure for the selective Pd-catalyzed aminations on 2-chloro-3-iodopyridine and 2-chloro-5-iodopyridine using $Pd_2(dba)_3$–XANTPHOS:
A round bottom flask was charged with $Pd_2(dba)_3$ (Acros, 0.015 mmol), XANTPHOS (Strem Chemicals, 0.03 mmol or 0.06 mmol) and freshly distilled dioxane (Acros, stabilized 99+%; dried over sodium/benzophenone, 3 mL). The mixture was flushed with nitrogen for 10 minutes under magnetic stirring. In another round bottom flask chloro-iodopyridine (0.359 g, 1.5 mmol), aniline (1.8 mmol) and Cs_2CO_3 (Acros, 99.5%, 2.1 mmol or 7.5 mmol) were weighed. Then, the $Pd_2(dba)_3$–XANTPHOS solution was added, and the flask was rinsed well with triethylamine (Aldrich, 99%; stored over K_2CO_3, 1.5 mL). The resulting mixture was flushed with nitrogen for 5 minutes under magnetic stirring and subsequently heated in an oil bath under vigorous magnetic stirring (oil bath temperature 100 °C, N_2 atmosphere). After overnight reflux the mixture was cooled down to room temperature. The solid material was filtered off and washed well with CH_2Cl_2 (200 mL). The filtrate was evaporated and the resulting crude product was purified by flash column chromatography.

(22) Spectroscopic data of selected compounds:
2-Chloro-3-(4-methylphenylamino)pyridine (Table 1, entries 1–3):
δ_H (400 MHz, $CDCl_3$): 7.78 (dd, *J* = 4.6, 1.7 Hz, 1 H, H-6), 7.34 (dd, *J* = 8.1, 1.7 Hz, 1 H, H-4), 7.14 (d, *J* = 8.1 Hz, 2 H, H-3′,5′), 7.03 (d, *J* = 8.1 Hz, 2 H, H-2′,6′), 7.00 (dd, *J* = 8.1 Hz, 4.6 Hz, 1 H, H-5), 6.08 (br s, 1 H, NH), 2.32 (s, 3 H, CH_3); δ_C (400 MHz, $CDCl_3$): 138.5, 138.3, 138.0, 137.6, 133.7, 130.0, 122.9, 121.9, 120.4, 20.6.
2-Chloro-5-(4-methylphenylamino)pyridine (Table 2, entries 1–4):
δ_H (400 MHz, $CDCl_3$): 8.13 (dd, *J* = 3.1 Hz, 0.5 Hz, 1 H, H-6), 7.35 (dd, *J* = 8.5 Hz, 3.1 Hz, 1 H, H-4), 7.20 (dd, *J* = 8.5 Hz, 0.5 Hz, 1 H, H-3), 7.19 (d, *J* = 8.4 Hz, 2 H, H-3′,5′), 7.04 (d, *J* = 8.4 Hz, 2 H, H-2′,6′), 5.74 (br s, 1 H, NH), 2.39 (s, 3 H, CH_3); δ_C (400 MHz, $CDCl_3$): 141.5, 140.1, 138.7, 138.3, 132.8, 130.2, 125.7, 124.2, 119.9, 20.7.

(23) General procedure for the synthesis of diarylamines via Pd-catalyzed aminations on iodobenzenes:
A round bottom flask was charged with $Pd(OAc)_2$ (Acros, 0.0034 g, 0.015 mmol), (±)-BINAP (Strem Chemicals, 0.0094 g, 0.015 mmol) and toluene (Acros, 99%, 5 mL). The mixture was flushed with nitrogen for 10 minutes under magnetic stirring. In another round bottom flask aryl iodide (1.5 mmol), aniline (1.8 mmol) and Cs_2CO_3 (Acros, 99.5%, 2.444 g, 7.5 mmol) were weighed. Then, the $Pd(OAc)_2$–BINAP solution was added, and the flask was rinsed well with an additional amount of toluene (10 mL). The resulting mixture was flushed with nitrogen for 5 minutes under magnetic stirring and subsequently heated in an oil bath under vigorous magnetic stirring (oil bath temperature 120 °C, N_2 atmosphere). After overnight reflux the mixture was cooled down to room temperature. The solid material was filtered off and washed well with CH_2Cl_2 (200 mL). The filtrate was evaporated and the resulting crude product was purified by flash column chromatography. The characterization data of *N*-(3-carbethoxyphenyl)-*N*-methylaniline, *N*-(4-carbethoxyphenyl)-*N*-methylaniline and 3-cyano-2′-carbethoxydiphenylamine were identical with those reported in the literature.[10]