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Recyclable Catalysts for Palladium-Catalyzed Aminations of Aryl Halides

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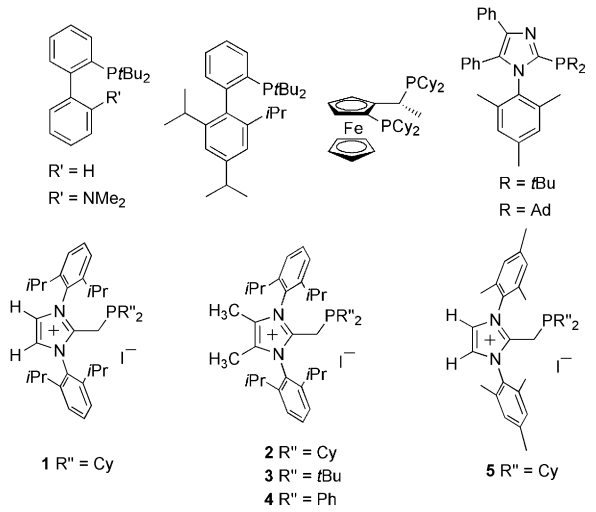
Aromatic amines and their derivatives are of significant importance in organic chemistry and play an important role as intermediates for agrochemicals, pharmaceuticals, conducting polymers, and dyes in the chemical industry.[1] In 1985, the first palladium-catalyzed aminations of simple amines were reported by Yagu-pol'skii and co-workers.[2] Later on, Buchwald[3] and Hartwig[4] independently developed this methodology further. Based on their elegant work in the last two decades, transition-metal-catalyzed aminations of aryl halides as well as related substrates have become the most popular tool for their preparation on a laboratory scale.[5–7]

Whereas easily activated substrates such as aryl iodides and activated bromides can be coupled with primary and secondary amines in the presence of a plethora of palladium and copper catalysts, more challenging substrates including heterocyclic arenes, aryl mesylates, and chlorides do require specifically designed ligands for successful coupling processes. It is generally accepted that sterically hindered and electron-rich mono- and bidentate phosphanes represent state-of-the-art ligands for the latter processes. Typical examples include the Buchwald-biaryl ligands,[8] Josiphos-type ferrocenylphosphanes,[9] aryl-heteroaryl ligands[10,11] and trialkylphosphanes[12] (Scheme 1).

Regarding the amine, selective coupling reactions using ammonia towards primary anilines have only recently been realized compared with the well-established synthesis of secondary and tertiary amines.[13] The difficulties in synthesizing primary amines have been attributed to the formation of catalytically inactive Pd–ammonia complexes[14] during the oxidative addition, and the tendency of the complexes to form stable bridging dimers.[15] Furthermore, the increased reactivity of the initially resulting anilines might lead to diaryl amines. Hence, a variety of ammonia equivalents were employed in the synthesis of anilines. Nevertheless, direct amination with ammonia is the method of choice due to its atom efficiency, availability, and low cost.[16]

In 2006, the first selective direct amination of aryl halides with ammonia was published by Hartwig and Shen[17] employing a bulky Josiphos-type phosphane. Recently, Buchwald et al. showed the possibility of palladium-catalyzed aminations in flow with a fully automated microfluidic system instead of using a batch reaction,[18] whereas Stradiotto and co-workers developed a flexible catalyst system for the cross-coupling of aryl chlorides.[19] Notably, also copper-catalyzed aminations using ammonia were realized elegantly by Taillefer and co-workers.[20] Despite of all these achievements still further advancements are desired to improve the efficiency of the corresponding catalysts. In this respect, especially the recycling of sophisticated homogenous catalysts in coupling reactions is still challenging.[21,22] Recently, we demonstrated that cationic imidazolium-based ligands could be used for this purpose. Indeed, improved catalytic turnover numbers were achieved for palladium-catalyzed hydroxylations.[23]

Herein, we report a full account of our work using 2-phosphanylmethyl-*N*,*N*′-biarylimidazolium ligands in the palladium-catalyzed aminations of aryl halides. The required ligands are prepared in a straightforward two-step methylation–phosphorylation sequence from the corresponding heterocycles. Notably, our strategy allows the synthesis of imidazolium salts with different substituents in the 1-, 3-, 4-, and 5-position. This modular preparation is important for the fine-tuning of the respective ligands.



Scheme 1. Selected examples of phosphane ligands for Pd-catalyzed amination (second row: novel cationic imidazolium-based posphane ligands).

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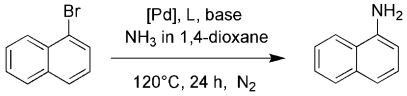
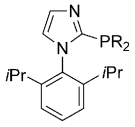
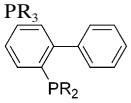
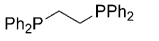
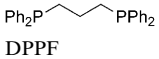
Exploratory experiments using the amination of 1-bromonaphthalene as a model system showed that a combination of $Pd(OAc)_2$ and ligand **2** proved to be the optimal catalyst system using an ammonia solution in 1,4-dioxane (0.5 M) and NaO*t*Bu as base. To our delight, 97% of 1-aminonaphthalene was obtained under these conditions (Table 1, entry 2). Comparable results were also achieved in the presence of $[Pd(CH_3CN)_2Cl_2]$ as a precursor.

Table 1. Pd-catalyzed amination of 1-bromonaphthalene with ammonia: Variation of different ligands.



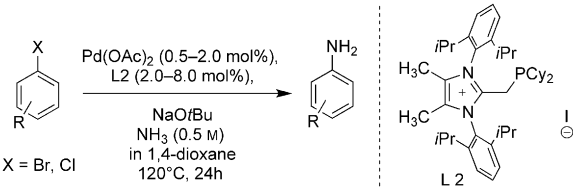
Entry	Ligand	R	Yield[b] [%]
1	**1**		20
2	**2**		97
3	**3**		34
4	**4**		0
5	**5**		17
6		Ad	27
7		*t*Bu	49
8		Cy	58
9	PR_3	Cy	13
10	PR_3	Ph	0
11	PR_3	*o*-Tolyl	0
12		*t*Bu	7
13			0
14			0
15	DPPF		15

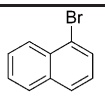
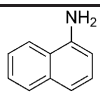
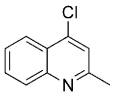
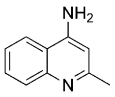
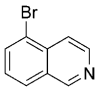
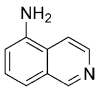
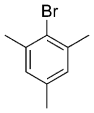
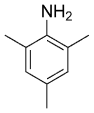
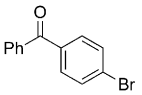
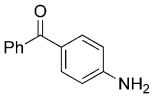
[a] Reaction conditions: 1-Bromonaphthalene (0.2 mmol), $Pd(OAc)_2$ (2.0 mol%), L (8.0 mol%), NaO*t*Bu (1.2 equiv), NH_3 in 1,4 dioxane (0.5 M, 2.0 mL), N_2 (10 bar). [b] Determined twice by gas chromatography with internal standard hexadecane. DPPF = diphenylphosphanylferrocene.

Interestingly, cyclohexyl-substituted ligands **1** and **5** without methyl substituents in 4- and 5-position of the ligand backbone revealed much less activity compared with **2**, yielding the product only in 20 and 17% yields, respectively (Table 1, entries 1 and 5). It should be noted that ligand **1**, which was the best ligand for our recently published catalytic hydroxylations,[23] offered only low yields in the respective amination reaction. Using ligand **4**, in which the cyclohexyl groups are exchanged by phenyl substituents, no product at all was obtained. On the other hand, in the presence of the cyclohexyl-substituted imidazol-based ligand, 58% of the desired aniline was obtained demonstrating the advantage of the imidazolium backbone (Table 1, entry 8).[24] Using other commercial available ligands such as PCy_3 and DPPE gave no or very low yield in this direct amination (Table 1, entries 9–15).

Next, we applied the optimized catalyst system $Pd(OAc)_2$/L2 to the amination of various aryl bromides and chlorides with ammonia (Table 2). Heterocycles such as 4-chloroquinaldine and 5-bromoisoquinoline were aminated in excellent yield (Table 2, entries 4, 9). Also, sterically hindered as well as unhindered aryl halides reacted very well (Table 2, en-

Table 2. Palladium-catalyzed amination of aryl halides with ammonia.



Entry	Substrate	Product	Yield[b] [%]
1			98
2			97[c]
3			77[d]
4			99
5			99[c]
6			99[d]
7			98[c]
8			79[d]
9			99
10			99[c]
11			86[d]
12			97
13			90[c]
14			50[d]
15			99[c]
16			99[d]
17			96
18			75
19			62

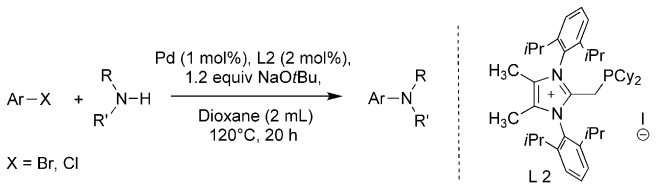
[a] Reaction conditions: Aryl halide (0.2 mmol), $Pd(OAc)_2$ (2.0 mol%), L2 (8.0 mol%), NaO*t*Bu (2.0 equiv), NH_3 (0.5 M, 2.0 mL), 120 °C, 24 h, N_2 (10 bar). [b] Determined twice by gas chromatography with internal standard hexadecane. [c] $Pd(OAc)_2$ (1.0 mol%), L2 (4.0 mol%). [d] $Pd(OAc)_2$ (0.5 mol%), L2 (2.0 mol%).

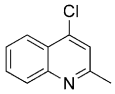
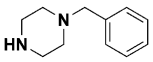
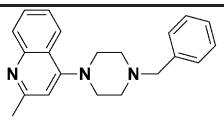
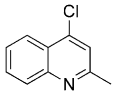
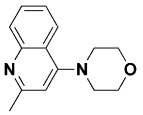
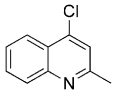
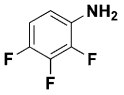
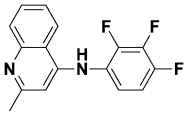
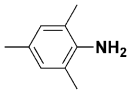
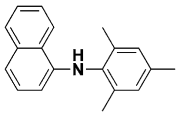
tries 7, 10, and 1). However, the highly activated 4-bromobenzophenone yielded the corresponding primary amine in moderate yield (62%; Table 2, entry 19). Notably, the amination of 1,2-dihaloarenes selectively proceeded to the monoaminated products in 99 and 75% yield, respectively (Table 2, entries 15 and 18). In the case of bromo-chloroarenes, the substitution of the bromide is fully chemoselective, which resulted in 96% of the corresponding 2-chloroaniline (Table 2, entry 17). It should be noted, that for all substrates no diarylated byproducts were found and, in many cases, the palladium loading could be decreased to 0.5 mol% giving also excellent yields (Table 2, entries 3, 6, 8, 11, 14, and 16).

To further demonstrate the general applicability of our catalyst system, we studied the palladium-catalyzed Buchwald–Hartwig aminations with primary and secondary amines (Table 3). Again, we adopted the optimized reaction conditions from the direct amination with ammonia to various aryl bromides and aryl chlorides in the presence of 13 different amines. Both cyclic and noncyclic aliphatic primary amines reacted smoothly in the amination (Table 3, entries 16 and 17). In addition, sterically hindered as well as unhindered anilines were fully converted to the corresponding amines with excellent yields (Table 3, entries 8 and 11, 10 and 13).

N-aromatic-*N*-aliphatic amines are efficiently transformed to tertiary amines (Table, entry 15) and the activated 2,3,4-trifluoraniline led to the desired aminated product in 95% yield (Table 3, entry 7). Also, morpholine and 1-benzylpiperazine were fully converted showing that hetero-

Table 3. Palladium-catalyzed aminations of aryl halides with different amines.



Entry	Aryl halide	Amine	Product	Yield[b] [%]
1				99
2				99
3				99[c]
4				70[d]
5				78[e]
6				0[f]
7				95
8				98
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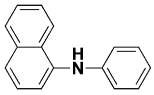
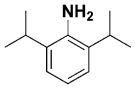
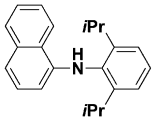
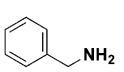
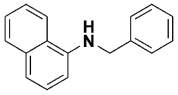
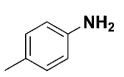
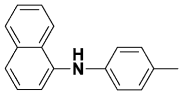
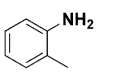
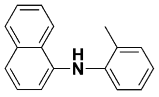
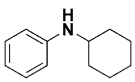
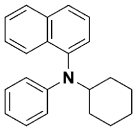
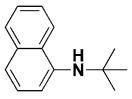
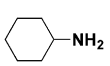
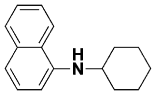
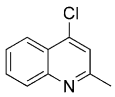
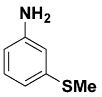
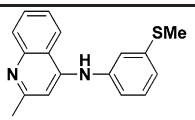
10				97
11				98
12				92
13				95
14				93
15				89
16				81
17				99
18				98[g]

Table 3. (Continued)

Entry	Aryl halide	Amine	Product	Yield[b] [%]
19				47

[a] Reaction conditions: Aryl halide (1.0 mmol), $Pd(OAc)_2$ (1.0 mol%), L2 (2.0 mol%), NaO*t*Bu (2.0 equiv), amine (1.2 mmol), 120°C, 20 h. [b] Determined twice by gas chromatography with internal standard hexadecane. [c] 50°C. [d] Room temp. [e] $Pd(OAc)_2$ (0.25 mol%), L2 (0.5 mol%). [f] without $Pd(OAc)_2$ and ligand. [g] Yield of isolated product.

cyclic amines are easily tolerated in this reaction (Table 3, entries 1 and 2). Similar to the aminations with ammonia, no diarylation was observed and only mono-arylated amines were obtained showing the high chemoselectivity of the catalyst system. In addition, no palladium black was formed during the reaction. Investigating the reaction of 4-chloroquinaldine with morpholine more closely, we observed that our catalyst system also allows for aminations at room temperature giving the corresponding amine in 70% yield (Table 3, entry 4). Furthermore, the catalyst loading is successfully decreased to 0.25 mol% Pd without a significant loss in productivity (Table 3, entry 5). Notably, product was not observed without the addition of palladium and ligand.

Finally, we investigated the recycling of the cationic catalyst system, similar to our previously reported procedure for the palladium-catalyzed hydroxylation of aryl bromides.[22] In these reactions we used the possibility of precipitating the resulting amines just by adding hydrogen chloride, whereas the catalyst remains in solution. After successful conversion, the reaction solution was separated from the precipitated product and just refilled in a new Schlenk flask, in which only the substrates morpholine and 4-chloroquinaldine as well as the base were added. In this regard we were able to run three consecutive aminations in yields in between 89–99% (Figure 1). This recycling strategy allows reuse of the catalyst in a multiple batch reactor.

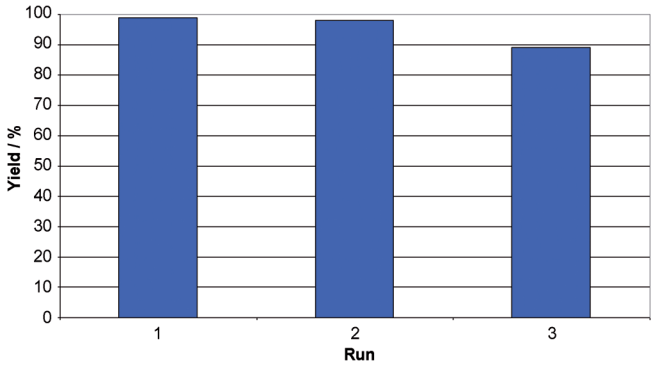


Figure 1. Recycling experiment: amination of 4-chloroquinaldine with morpholine. Reaction conditions: Aryl halide (1.0 mmol), $Pd(OAc)_2$ (1.0 mol%), L2 (2.0 mol%), NaO*t*Bu (1.2 equiv), amine (1.2 mmol), 120°C, 20 h. Determined by gas chromatography.

In summary, a stable and versatile palladium/imidazolium–phosphane system has been established for the catalytic direct amination of aryl halides with ammonia and several primary as well as secondary amines. A simple recycling of this catalyst system has been demonstrated. The active catalyst is easily generated in situ from the air- and water-stable cationic imidazolium phosphanes and $Pd(OAc)_2$. In general, the catalytic aminations of most substrates proceed without special precautions in the presence of comparably low palladium loadings. Also, room temperature amination are possible with this system.

Experimental Section

General: All reactions were performed under an inert nitrogen atmosphere (1–10 bar) by using an eightfold parallel autoclave. All starting materials as well as reactants were applied in the way as they were received from commercial suppliers. Phosphane ligands were stored in Schlenk flasks but scaled under air. Mass spectra were recorded on an AMD 402 double focusing, magnetic sector spectrometer (AMD Intectra). GCMS spectra were recorded on a HP 5989 A (Hewlett Packard) chromatograph equipped with a quadropole analyzer. Gas chromatography analyses were performed on a HP 6890 (Hewlett Packard) chromatograph using a HP 5 column. All yields were determined by calibration of the corresponding products (anilines, amines) with hexadecane as an internal standard and analysis by using gas chromatography.

General procedure for the direct amination of aryl halides with ammonia: A 3.0 mL autoclave was charged with ligand **2** (3.0 mg, 2.0 mol%) and NaO*t*Bu (38.4 mg, 2 equiv). The (hetero)aryl halide was also added at this point, if it is a solid. In case of a liquid it was added at a later point (see 4 lines below). The filled autoclave was placed into the autoclave device, evacuated, backfilled with argon, and then 0.2 mL of a $Pd(OAc)_2$-stock solution (5.0 mM $Pd(OAc)_2$ 1,4-dioxane, 0.5 mol%) was added and the mixture was stirred at room temperature for 10 min. Then, (if liquid) the corresponding aryl halide (0.2 mmol) and a 0.5 M NH_3 solution (2.0 mL) in 1,4-dioxane (5.0 equiv NH_3) were added successively under an argon atmosphere. The reaction mixture was pressurized with 10 bar N_2 and heated up to 120°C for 24 h. After the mixture had been cooled to room temperature, it was laced with hexadecane (20 mL) as an internal standard. The mixture was filtered and the yield was determined by gas chromatography.

General procedure for the Buchwald–Hartwig amination of aryl halides: A 15.0 mL ace pressure tube was charged with $Pd(OAc)_2$ (2.2 mg, 1.0 mol%), ligand **2** (15.1 mg, 2.0 mol%) and NaO*t*Bu (115.3 mg, 1.2 mmol). The filled ace pressure tube was evacuated and backfilled with argon three times. Then the corresponding (hetero)aryl halide (1.0 mmol), the amine (1.2 mmol), and 1,4-dioxane (2.0 mL) were added successively under an argon atmosphere. The pressure tube was closed and heated up to 120°C for 20 h. After the mixture had been cooled to room temperature, it was laced with hexadecane (20 μL) as an internal standard. The mixture was filtered and the yield was determined by gas chromatography.

General procedure for the re-use of the catalyst in Buchwald–Hartwig-aminations: The reaction was carried out to run in 25 mL Schlenk tubes, added with $Pd(OAc)_2$ (2.2 mg, 1.0 mol%), ligand **2** (15.1 mg, 2.0 mol%) and NaO*t*Bu (115.3 mg, 1.2 mmol). The filled Schlenk tube was evacuated and backfilled with argon three times. Then 4-chloroquinaldine

(202 μL, 1.0 mmol), morpholine (105 μL, 1.2 mmol) and 1,4-dioxane (2.0 mL) was added successively under an argon atmosphere. The Schlenk tube was closed and heated up to 70 °C for 16 h. After finishing the reaction, the mixture was cooled down to room temperature and subsequently mixed with dry hydrogen chloride solution (4N in dried 1,4-dioxane). The immediately formed bright yellow precipitate was separated by filtration and washed carefully with dried 1,4-dioxane, whereas the intensive red-orange-colored supernatant was just refilled in a new Schlenk-tube for the next run. In this tube only 4-chloroquinaldine, morpholine and the base NaO*t*Bu were added. The procedure had been done three times and all reactions were performed under an argon atmosphere.

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Keywords: amination · anilines · imidazolium ligands · palladium · phosphane ligands

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