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Efficient palladium catalysts for the amination of aryl chlorides: a comparative study on the use of phosphium salts as precursors to bulky, electron-rich phosphines

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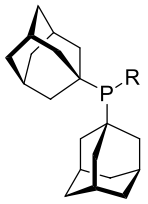
Abstract—Alkyl-di-(1-adamantyl)phosphonium salts are practical ligand precursors for the palladium-catalyzed amination of aryl chlorides. In the presence of typically 0.5 mol% $Pd(OAc)_2$ and 1 mol% of ligand precursor a variety of activated and deactivated aryl chlorides can be aminated in good to excellent yield (73–99%). Applying optimized conditions catalyst turnover numbers up to 10,000 have been achieved.

1. Introduction

The palladium-catalyzed C–N bond formation of aryl halides (Buchwald–Hartwig reaction) is a rapidly developing field of interest due to the importance of anilines and amino-substituted heteroarenes as natural products, drugs, agrochemicals, and fine chemicals.[1] In order to apply such reactions in the fine chemical industry significant cost reduction of a typical lab-scale synthesis is an important requirement. Efforts to substitute costly starting materials such as aryl iodides or triflates by economically more attractive chloro- and bromoarenes, reduction of catalyst concentration, etc. are to be seen in this respect. Despite numerous advances in C–N cross coupling processes,[2] an important factor for industrial applications of palladium-catalyzed amination reactions is the development of more efficient and economically attractive catalysts. Important criteria for such improved catalysts include (1) no special handling of metal complexes and ligands, (2) broad substrate scope, as well as (3) ability to operate under mild reaction conditions and at low catalyst concentration. In this respect there exists still a need for easy-to-use ligands, which lead to highly active catalyst systems, are easily tunable and allow for scale-up.

Herein, we report a novel catalytic system based on phosphonium salts, that meets the above mentioned criteria. Noteworthy are the high catalyst productivity, and the air stability of the ligand precursors, which makes them easy to operate.

Previously we demonstrated, that basic, sterically demanding phosphines with 1-adamantyl substituents[3] (Fig. 1) are suitable ligands for palladium-catalyzed C–C, C–N, and C–O bond forming reactions. Among the various aryl-[4] and alkyl-di-(1-adamantyl)phosphines[5] (cata*CX*ium® A ligands)[6] prepared especially di-(1-adamantyl)-*n*-butylphosphine (**1**) and di-(1-adamantyl)benzylphosphine (**7**) showed good to excellent catalyst performance for different functionalization reactions of aryl chlorides.[7] Very recently, we also reported on the preparation of the respective phosphonium salts via alkylation of di-(1-adamantyl)-phosphine with alkyl or benzyl halides.[8] In this regard it is noteworthy that phosphonium salts of sterically hindered alkylphosphines became interesting as ligand precursors for palladium-catalyzed coupling reactions due to their



1: R = *n*-butyl
2: R = *i*-butyl
3: R = *i*-propyl
4: R = methyl
5: R = allyl
6: R = 2-methoxyethyl
7: R = benzyl

Figure 1. Selected examples of alkyl-di-(1-adamantyl)phosphines (cata*CX*ium® A ligands).

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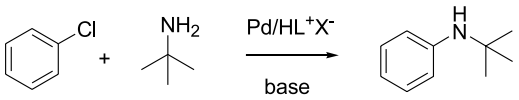


Scheme 1. Coupling reaction of chlorobenzene and *tert*-butylamine.

Table 1. Variation of ligands for the coupling reaction of chlorobenzene and *tert*-butylamine

Entry	Ligand precursor	Conv. (%)[a]	Yield (%)[a]
1	**1**	100	89
2	**H1**$^+$**I**$^-$	100	94
3	**H2**$^+$**I**$^-$	88	69
4	**H3**$^+$**I**$^-$	100	90
5	**H4**$^+$**I**$^-$	26	26
6	**H5**$^+$**Br**$^-$	100	84
7	**H6**$^+$**Br**$^-$	100	88
8	**H7**$^+$**Br**$^-$	63	59

[a] Average of two runs, determined by GC using hexadecane as internal standard.

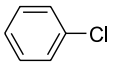
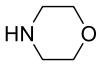
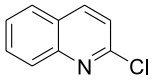
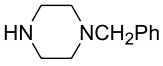
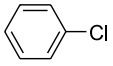
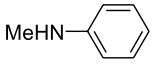
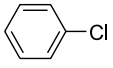
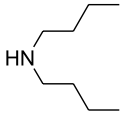
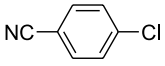
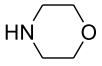
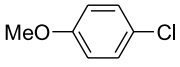
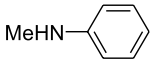
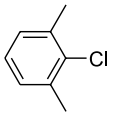
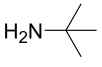
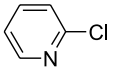
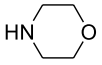
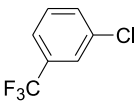
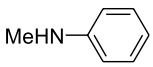
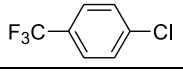
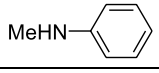
increased stability against air and moisture.[9] However, to the best of our knowledge phosphonium salts have not been tested as ligands in the amination of aryl chlorides.

2. Results and discussion

As a starting point of our investigations we examined the amination of chlorobenzene as an example of a non-activated aryl chloride, with a slight excess of the sterically hindered *tert*-butylamine (Scheme 1, Table 1).

At first the influence of the ligand structure was studied in the presence of 0.5 mol% $Pd(OAc)_2$ and 1 mol% of phosphonium salt with 1.2 equiv NaO*t*Bu as the base in toluene at 120 °C in a sealed tube. These are typical reaction conditions, which have been often used for C–N coupling reactions. Selected results are summarized in Table 1. Interestingly, the variation of the alkyl group has a significant effect on the coupling reaction. Thus, the modular synthesis of cata*CX*ium® A ligands should allow for an easy fine tuning of the ligand properties for other substrates, too.

Table 2. Palladium-catalyzed coupling of aryl chlorides and amines in the presence of **H1**$^+$**I**$^-$ and **H5**$^+$**Br**$^-$[a]

Entry	Aryl chloride	Amine	**H1**$^+$**I**$^-$		**H5**$^+$**Br**$^-$	
			Conv. (%)[b]	Yield (%)[b]	Conv. (%)[b]	Yield (%)[b]
1			100	95	100	99
2[c]			100	99	100	90
3			100	93	100	93
4			100	73	100	87
5			100	75	100	62
6			100	93	100	93
7			100	99	100	79
8			100	95	100	97
9			100	99	100	99
10			100	99	100	99

[a] Conditions: 5 mmol aryl chloride, 6 mmol amine, 6 mmol NaO*t*Bu, 0.5 mol% $Pd(OAc)_2$, 1 mol% ligand, 5 mL toluene, 120 °C, 20 h.
[b] Average of two runs, determined by GC using hexadecane or diethyleneglycol di-*n*-butyl ether as internal standard.
[c] Reaction was carried out on 2 mmol scale.

Control experiments with the free *n*-BuPAd$_2$ ligand (**1**, Table 1, entry 1) indicated that the corresponding phosphonium salt **H1**$^+$**I**$^-$ can be used without any problem (Table 1, entry 2). Good conversion for our model reaction is also observed for di-(1-adamantyl)-*iso*-propyl- (**H3**$^+$**I**$^-$), di-(1-adamantyl)-allyl- (**H5**$^+$**Br**$^-$), and di-(1-adamantyl)-(2-methoxyethyl)phosphonium salts (**H6**$^+$**Br**$^-$, Table 1, entries 4, 6, 7).

Next, the general usefulness of our ligands was examined and is shown in Table 2. Due to the ease of synthesis and the catalytic performance in the model reaction we selected di-(1-adamantyl)-*n*-butyl- and di-(1-adamantyl)-allyl-phosphonium salts (**H1**$^+$**I**$^-$, **H5**$^+$**Br**$^-$) for more detailed studies.

Various secondary amines and *tert*-butylamine can be coupled with different aryl chlorides to give the desired products in high yields. Reactions of chlorobenzene with secondary amines (acyclic, cyclic and aromatic amines) occurred in yields of more than 87% (Table 2, entries 1, 3, 4). In general, the amination of acyclic secondary amines with aryl halides is more challenging than similar reactions with cyclic secondary amines. Nevertheless the di-(1-adamantyl)-allylphosphonium salt is quite effective in the coupling of di-*n*-butylamine and chlorobenzene (Table 2, entry 4). In most of our examples we could not observe a strong dependence of the product yield from donor or acceptor substitution of the chloroarene. For example, electron-rich chloroanisole as well as the electron-poor trifluoromethyl-substituted chlorobenzenes react cleanly with *N*-methylaniline (Table 2, entries 6, 9 and 10). On the other hand, despite favourable electronic conditions, reaction of 4-chlorobenzonitrile with morpholine gave a lower yield of 75% due to side reactions of the nitrile group (Table 2, entry 5).

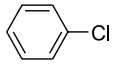
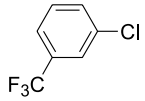
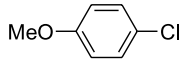
In addition to simple aryl chlorides, also heterocyclic chloroarenes such as 2-chloropyridine and 2-chloroquinoline react well with different amines and demonstrate the scope of our catalyst system (Table 2, entries 2, 8). Furthermore, sterically hindered 2,2′-dimethyl substituted anilines can be obtained in quantitative yield (99%) in the presence of 0.5 mol% palladium catalyst (Table 2, entry 7).

By comparing the performance of the *n*-butyl-substituted phosphonium salt **H1**$^+$**I**$^-$ with the allyl-substituted derivative **H5**$^+$**Br**$^-$ it is obvious that the former one is the (slightly) better ligand precursor in most reactions. However, in case of the arylation of di-*n*-butylamine **H5**$^+$**Br**$^-$ gave reproducibly better results. The reasons for this behaviour are so far unclear, but it suggests that optimized yields can be obtained by further variation of the alkyl group.

Normally, we carried out our catalytic experiments using a standard procedure (see Section 3) with 0.5 mol% Pd(OAc)$_2$ and 1 mol% of phosphonium salt. Clearly, this is a sufficient small amount for lab-scale syntheses of substituted anilines. However, it is well-known that catalyst turnover numbers (TONs) of around 1000–10,000 are required to consider larger scale applications.[10] Therefore, it is surprising that only little attention has been paid to the efficiency (productivity) of the respective palladium catalyst in amination reactions.[11] In general, TONs in the range of 100 are obtained. However, Hartwig et al. have demonstrated very recently that bidentate electron-rich phosphines with a ferrocene backbone lead to highly active and productive catalysts for the amination of aryl chlorides with primary amines.[12]

The results of our study with lower catalyst concentrations are summarized in Table 3. Reactions of *N*-methylaniline with chlorobenzene, 3-chlorobenzotrifluoride and 4-chloroanisole proceed with very good yield (89–94%; TONs 8900–9400) in the presence of only 0.01 mol% Pd(OAc)$_2$ and 0.02 mol% of di-(1-adamantyl)-*n*-butyl-phosphonium iodide at 120 °C.

Table 3. Reaction of aryl chlorides with *N*-methylaniline at low catalyst concentration[a]

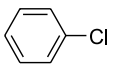
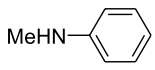
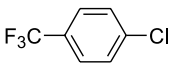
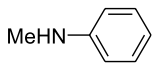
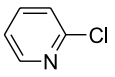
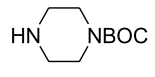
Entry	Aryl chloride	Conv. (%)[b]	Yield (%)[b]
1		100	94
2		100	89
3		100	93

[a] Reaction conditions: 5 mmol aryl chloride, 6 mmol *N*-methylaniline, 6 mmol NaO*t*Bu, 0.01 mol% Pd(OAc)$_2$, 0.02 mol% **H1**$^+$**I**$^-$, 5 mL toluene, 120 °C, 20 h.
[b] Average two runs, determined by GC using diethyleneglycol di-*n*-butyl ether as internal standard.

On the other hand only low conversion and yield is detected under these conditions for the reaction of morpholine with 2-chloropyridine (5–10% yield; TON 500–1000).

Finally, we investigated aminations of various aryl chlorides at lower temperatures (60–80 °C). In order to achieve faster conversion a catalyst concentration of 1 mol% Pd(OAc)$_2$ has been used. As shown in Table 4 reactions of chlorobenzene and 4-chlorobenzotrifluoride with *N*-methylaniline gave 71 and 73% yield, respectively, (Table 4, entries 1–2), which indicates that the amination proceeds

Table 4. Amination of aryl chlorides at lower temperature[a]

Entry	Aryl chloride	Amine	Temp. (°C)	Yield (%)[b]
1			60	71
2			60	73
3			80	98

[a] Reaction conditions: 5 mmol aryl chloride, 6 mmol amine, 6 mmol NaO*t*Bu, 1 mol% Pd(OAc)$_2$, 2 mol% **H1**$^+$**I**$^-$, 5 mL toluene, 120 °C, 20 h.
[b] Average two runs, determined by GC using hexadecane or diethyleneglycol di-*n*-butyl ether as internal standard.

significantly slower at this temperature. Nevertheless, in some cases the use of lower reaction temperatures can be reasonable if one or both of the substrates contain sensitive groups. As an example the amination of 2-chloropyridine with *N*-(*tert*-butoxycarbonyl)piperazine is presented, which gave an excellent yield (98%) at 80 °C (Table 4, entry 3).

In summary, we have shown that phosphonium salts of alkyl-di-(1-adamantyl)phosphines allow for an efficient synthesis of a variety of substituted anilines from aryl or heteroaryl chlorides and amines. Good to excellent yields (75–99%) are obtained at comparatively low catalyst concentration (0.5 mol% $Pd(OAc)_2$; 120 °C). By simply reducing the metal and ligand amount optimized catalyst turnover numbers up to ca. 10,000 have been observed. In addition, the coupling reactions proceed under milder conditions (60–80 °C), albeit with higher catalyst loading.

An important advantage of the presented method is the easy handling of catalyst and ligand precursors. Hence, it is not necessary to exclude strictly air or moisture. Due to the modular synthesis of cata*CX*ium® A ligands a fine tuning of the ligand properties for other substrates is easily possible and should lead to further improved catalyst performance.

3. Experimental

Chemicals were obtained from Aldrich, Fluka and Merck KGaA and used without further purification. Solvents were dried according to standard procedures. ^1H and ^{13}C NMR chemical shifts refer to tetramethylsilane (0 ppm) and $CDCl_3$ (77.0 ppm), respectively. Column chromatography was carried out using silica gel 60 (0.063–0.2 mm Fluka).

3.1. General procedure (Buchwald–Hartwig amination)

A 30 mL pressure tube was loaded with $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), the ligand precursor (0.050 mmol), and NaO*t*Bu (577 mg, 6.0 mmol) and was purged with argon. Then, toluene (5 mL), the aryl chloride (5.0 mmol), and the amine (6.0 mmol) were added successively. The mixture was stirred for 20 h at 120 °C. After cooling to room temperature the mixture was diluted with diethyl ether (5 mL) and washed with water (10 mL). The organic phase was dried over $MgSO_4$, concentrated under vacuum and the product was isolated by column chromatography (ethyl acetate/*n*-hexane or acetone/*n*-hexane). Alternatively, diethyleneglycol di-*n*-butyl ether or hexadecane was added as internal standard and quantitative analysis was done by gas chromatography. The commercially available products were identified by comparison of their GC/MS data with the data of authentic samples, known products were characterized by NMR and mass spectroscopy (for more data see Ref. 4c and cited literature there).

3.1.1. *N*-Phenylmorpholine. MS (EI, 70 eV): *m*/*z* (%): 163 [M^+], 105, 77.

3.1.2. Methyldiphenylamine. MS (EI, 70 eV): *m*/*z* (%): 183 [M^+], 167, 104, 77.

3.1.3. *N*,*N*-Di-*n*-butylaniline. MS (EI, 70 eV): *m*/*z* (%): 205 [M^+], 162, 120, 105, 77.

3.1.4. *N*-*tert*-Butyl-2,6-dimethylaniline. MS (EI, 70 eV): *m*/*z* (%): 177, 162, 121.

3.1.5. *N*-(4-Cyanophenyl)morpholine. MS (EI, 70 eV): *m*/*z* (%): 188 [M^+], 130, 102.

3.1.6. *N*-(4-Methoxyphenyl)-*N*-methylaniline. MS (EI, 70 eV): *m*/*z* (%): 213 [M^+], 198, 77.

3.1.7. *N*-Methyl-*N*-[4-(trifluoromethyl)phenyl]aniline. MS (EI, 70 eV): *m*/*z* (%): 251 [M^+], 77.

3.1.8. *N*-Methyl-*N*-[3-(trifluoromethyl)phenyl]aniline. MS (EI, 70 eV): *m*/*z* (%): 251 [M^+], 145, 77.

3.1.9. *N*-(2-Pyridyl)morpholine. MS (EI, 70 eV): *m*/*z* (%): 164 [M^+], 133, 107, 79.

3.1.10. *N*-Benzyl-*N*′-(2-quinolyl)piperazine. Yellow solid; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.78$ (d, $^3J(H,H) = 9.1$ Hz, 1H), 7.61 (d, $^3J(H,H) = 8.5$ Hz, 1H), 7.50 (d, $^3J(H,H) = 8.3$ Hz, 1H), 7.45 (m, 1H), 7.21 (m, 6H), 6.87 (d, $^3J(H,H) = 9.3$ Hz, 1H), 3.68 (t, $^3J(H,H) = 5.1$ Hz, 4H), 3.49 (s, 2H), 2.51 (t, $^3J(H,H) = 5.1$ Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 157.9$, 148.3, 137.8, 129.9, 129.7, 128.7, 127.6, 127.0, 123.5, 122.7, 109.9, 63.6, 53.5, 44.5; MS (EI, 70 eV): *m*/*z* (%): 303 [M^+], 157, 128, 91.

3.1.11. *N*-*tert*-Butoxycarbonyl-*N*′-(2-pyridyl)piperazine. Yellow solid; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 8.18$ (m, 1H), 7.48 (m, 1H), 6.63 (m, 2H), 3.52 (s (br), 8H), 1.47 (s, 9H); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 159.3$, 154.8, 148.0, 137.6, 113.6, 107.2, 79.9, 45.1, 43.3 (br), 28.4; MS (EI, 70 eV): *m*/*z* (%): 263 [M^+], 190, 120, 107, 78.

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