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Synthesis of palladium complexes derived from imidazolidin-2-ylidene ligands and used for catalytic amination reactions

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***N*-Aryl amination and the Buchwald–Hartwig reaction are of great synthetic and industrial interest and scientists accept their usefulness and versatility for obtaining arylamines. In this study Ag–N-heterocyclic carbene complexes were used as transmetallation reagents for the synthesis of Pd–N-heterocyclic carbene complexes. The new Pd–N-heterocyclic carbene complexes were characterized using elemental analysis and ^{1}H NMR, ^{13}C NMR and infrared spectroscopies. The crystal structure of one, namely dichlorobis[1,3-bis(2-methylbenzyl)imidazolidin-2-yliden]palladium(II), is presented. The activity of the Pd(II) complexes in the coupling reaction of anilines or amines with bromobenzene was investigated. These complexes exhibited high catalytic activities in the direct synthesis of triarylamines and secondary amines in a single step. Copyright © 2016 John Wiley & Sons, Ltd.**

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Keywords: N-heterocyclic carbene; imidazolidin-2-ylidene; palladium; amination

Introduction

Heterocyclic compounds are of importance because of their abundance in numerous natural products such as vitamins[1] and alkaloids[2] as well as pharmaceuticals of biological activity[3] and electroactive materials.[4] C–N bonds of aromatic compounds supply access to nitrogen-containing molecules of great interest in synthetic, biological, medicinal and materials sciences and that makes it an important transformation.[5,6] The Buchwald–Hartwig amination is a chemical reaction used in organic chemistry for the synthesis of carbon–nitrogen bonds via palladium-catalysed cross-coupling of amines with aryl halides. The numerous applications of Pd–N-heterocyclic carbene systems have been comprehensively reviewed.[7–13]

N-heterocyclic carbenes have been used widely in organometallic chemistry and coordination chemistry for 30 years.[14] Organometallic N-heterocyclic carbene-based complexes have demonstrated their wide scope of application, and thus their usefulness, in the synthesis of complex and valuable molecules. For the preparation of reusable catalysts these important applications transform N-heterocyclic carbene ligands into suitable candidates. The potential offered by N-heterocyclic carbenes as supporting ligands in palladium-mediated catalysis is evident from the continuously growing number of reactions mediated by such complexes.[15] In spite of the certain utility of (hetero)bidentate phosphine-based ligands (*vide supra*), with a detailed survey of the literature it can be seen that the application of conceptually related heterobidentate N-heterocyclic carbenes has received relatively little attention in Buchwald–Hartwig amination chemistry. Palladium–N-heterocyclic carbene systems have been successfully employed in various reactions such as C–C and C–N coupling reactions and oxidation reactions, and more recently a heterogeneous palladium–N-heterocyclic carbene system has been explored for hydrogenation reactions.[16,17]

Within this context we have recently reported implementation of imidazolidin-2-ylidene and benzimidazolidin-2-ylidine complexes in C–N cross-coupling and their catalytic activity for aryl amination using bromobenzene and various anilines or amines.[18,19] Considering the growing interest in catalytic activity of palladium complexes to act as dominant and efficient catalysts in amination reactions, in this article we report six new N-heterocyclic carbene palladium complexes from transmetallation of related Ag–N-heterocyclic carbene complexes. All synthesized compounds were characterized using ^{1}H NMR, ^{13}C NMR and infrared (IR) spectroscopies and elemental analysis, the results of which support the proposed structures. The molecular and crystal structure of the dichlorobis[1,3-bis(2-methylbenzyl)imidazolidin-2-yliden]palladium(II) (**1a**) complex was determined using the single-crystal X-ray diffraction technique. In addition, we examined the activity of the synthesized palladium complexes in the Buchwald–Hartwig amination reaction.

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Experimental

Materials

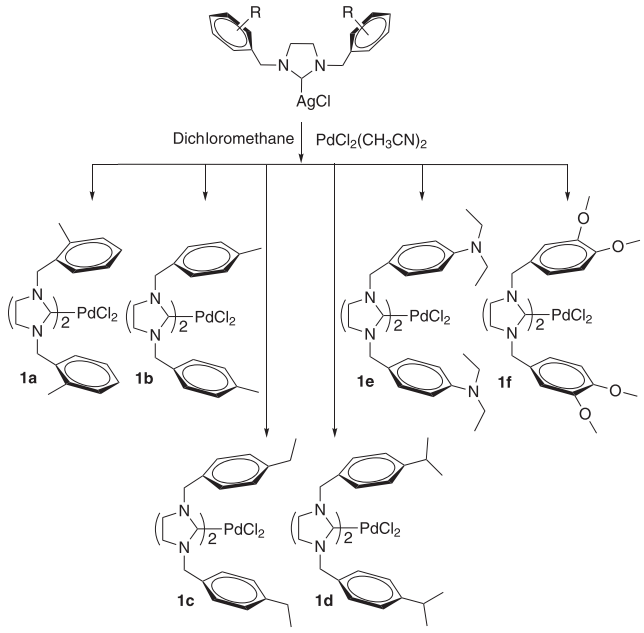
All reactions for the preparation imidazolinium salts and palladium–N-heterocyclic carbene complexes (**1**) were carried out under argon in flame-dried glassware using standard Schlenk techniques. The solvents used were purified by distillation over the drying agents indicated and were transferred under argon: tetrahydrofuran, Et_2O (Na/K alloy), CH_2Cl_2 (P_4O_{10}), hexane, toluene (Na). Glassware was heat-dried in vacuum. Elemental analyses were performed by the Turkish Research Council (Ankara, Turkey) Microlab.

General procedure for preparation of palladium–N-heterocyclic carbene complexes (1a–f)

Imidazolinium salts were prepared according to the literature.[20] The palladium complexes were prepared by means of the Ag–carbene transfer method developed by Wang and Lin.[21] The silver monocarbene complexes, which subsequently served as a carbene transfer agents, were synthesized by the reaction of Ag_2O with 2 equiv. of salts in CH_2Cl_2 at ambient temperature.[22] We conveniently reacted *in situ* generated Ag–N-heterocyclic carbene with $PdCl_2(CH_3CN)_2$ in dark conditions and the mixture was allowed to stir for 24 h at room temperature. When this reaction was carried out using a Ag:Pd ratio of 2:1, dichloro-bis(carbene) complexes **1a**–**f** were observed (Scheme 1). After filtration of AgCl, the solvent was removed in vacuum to yield a pale yellow powder. The crude product was recrystallized from dichloromethane–diethyl ether (1:2) at room temperature.

Typical procedure for catalytic C–N bond formation

Under argon, 1.5 mmol of $KOBu^t$, 1 mol% of catalyst, 1 mmol of amine, 1.2 mmol of bromobenzene and 2 ml of dimethoxyethane were added into an oven-dried Schlenk tube. The mixture was stirred at 80 °C for 15 h. The reaction mixture was allowed to cool to room temperature and was quenched by filtering through a short silica column (ethyl acetate as eluent) and was then concentrated under reduced pressure. After purification by flash chromatography (ethyl acetate–hexane as eluent), the yield was calculated based on anilines.



Scheme 1. Synthesis of Pd–N-heterocyclic carbene complexes.

Characterization

Melting point determination

Melting points were measured in open capillary tubes with an Electrothermal-9200 melting point apparatus and are uncorrected.

IR spectroscopy

Fourier transform IR spectra were recorded as KBr pellets in the range 400–4000 cm^{-1} using a ATI UNICAM 1000 spectrometer.

NMR spectroscopy

^1H NMR and ^{13}C NMR spectra were recorded using a Varian As 400 Merkur spectrometer operating at 400 MHz (^1H) or 100 MHz (^{13}C) in $CDCl_3$ with tetramethylsilane as an internal reference. The NMR studies were carried out using high-quality 5 mm NMR tubes. Signals are quoted in parts per million downfield from tetramethylsilane (0.00 ppm) as an internal standard. Coupling constants (*J* values) are given in hertz. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, m = multiplet signal.

Gas chromatography

All reactions were monitored using an Agilent 6890 N GC system by GC-FID with an HP-5 column of 30 m length, 0.32 mm diameter and 0.25 μm film thickness.

Column chromatography

Column chromatography was performed using silica gel 60 (70–230 mesh). Solvent ratios are given as v/v.

X-ray diffraction

A suitable crystal of **1a** was selected for data collection which was performed using a STOE IPDS II diffractometer with graphite-monochromatic Mo K_α radiation at 296 K. The structures were solved by direct methods using SHELXS-97[23] and refined by full-matrix least-squares methods on F^2 using SHELXL-97[23] from within the WINGX[24] suite of software. All non-hydrogen atoms were refined with anisotropic parameters. The hydrogen atoms were located from different maps and then treated as riding atoms with C–H distances of 0.93–0.97 Å. Molecular diagrams were created using MERCURY.[25] Details of data collection and crystal structure determinations are given in Table 1. The molecular structure of **1a** with the atom labelling is shown in Fig. 1.

*Dichlorobis[1,3-bis(2-methylbenzyl)imidazolidin-2-yliden]palladium(II) (**1a**)*

^1H NMR ($CDCl_3$, δ, ppm): 2.34 (s, 6H, $CH_2C_6H_4(CH_3)$-2), 3.32 (s, 4H, NCH_2CH_2N), 5.25 (s, 4H, $CH_2C_6H_4(CH_3)$-2), 7.08–7.56 (m, 8H, $CH_2C_6H_4(CH_3)$-2). $^{13}C\{H\}$NMR ($CDCl_3$, δ, ppm): 19.6 ($CH_2C_6H_2(CH_3)$-2), 48.1 (NCH_2CH_2N), 51.5 ($CH_2C_6H_4(CH_3)$-2), 126.3 (CH, C_5), 127.7 (CH, C_4), 129.3 (CH, C_6), 130.3 (CH, C_3), 133.9 (C_{ipso}, C_2), 136.7 (C_{ipso}, C_1), 198.8 (Pd–C_{carb}). Anal. Calcd for $C_{38}H_{70}Cl_2N_4Pd$: C, 60.03; H, 9.28; N, 7.37. Found (%): C, 60.08; H, 9.21; N, 7.33.

*Dichlorobis[1,3-bis(4-methylbenzyl)imidazolidin-2-yliden]palladium(II) (**1b**)*

^1H NMR ($CDCl_3$, δ, ppm): 2.33 (s, 6H, $CH_2C_6H_4(CH_3)$-4), 3.49 (s, 4H, NCH_2CH_2N), 5.24 (s, 4H, $CH_2C_6H_4(CH_3)$-4), 7.11–7.25 (m, 8H, $CH_2C_6H_4(CH_3)$-4). $^{13}C\{H\}$NMR ($CDCl_3$, δ, ppm): 21.2 ($CH_2C_6H_2(CH_3)$-

Table 1. Crystal data and structure refinement parameters for **1a**

Empirical formula	$C_{38}H_{44}Cl_2N_4Pd$
Formula weight	734.07
Crystal system	Monoclinic
Space group	P21/c
a (Å)	7.8688(2)
b (Å)	14.5408(4)
c (Å)	16.0025(4)
β (°)	90.536(2)
V (Å^3)	1830.90(8)
Z	2
D_c (g cm^{-3})	1.332
μ (mm^{-1})	0.68
θ range (°)	1.9–28.1
Measured reflections	27 322
Independent reflections	3792
R_{int}	0.025
S	1.05
R_1/wR_2	0.025/0.064
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	0.39/−0.25

4), 47.8 (NCH_2CH_2N), 54.8 ($CH_2C_6H_4(CH_3)$-4), 128.8 (CH, $C_{3,5}$), 129.0 (CH, $C_{2,6}$), 132.9 (C_{ipso}, C_1), 134.7 (C_{ipso}, C_4), 197.9 (Pd–C_{carb}). Anal. Calcd for $C_{38}H_{70}Cl_2N_4Pd$ (%): C, 60.03; H, 9.28; N, 7.37. Found (%): C, 60.09; H, 9.22; N, 7.33.

Dichlorobis[1,3-bis(4-ethylbenzyl)imidazolidin-2-yliden]palladium(II) (***1c***)

^{1}H NMR ($CDCl_3$, δ, ppm): 1.24 (t, *J* = 7.8 Hz, 6H, $CH_2C_6H_4(CH_2CH_3)$-4), 2.66 (q, *J* = 7.8 Hz, 4H, $CH_2C_6H_4(CH_2CH_3)$-4), 3.39 (s, 4H, NCH_2CH_2N), 5.42 (s, 4H, $CH_2C_6H_4(CH_2CH_3)$-4), 7.18 and 7.43 (d, *J* = 7.8 Hz, 8H, $CH_2C_6H_4(CH_2CH_3)$-4). ^{13}C{H}NMR ($CDCl_3$, δ, ppm): 15.4 ($CH_2C_6H_2(CH_2CH_3)$-4), 28.6 ($CH_2C_6H_2(CH_2CH_3)$-4), 47.5 (NCH_2CH_2N), 54.1 ($CH_2C_6H_4(CH_2CH_3)$-4), 128.0 (CH, $C_{3,5}$), 128.9 (CH, $C_{2,6}$), 132.5 (C_{ipso}, C_1), 144.0 (C_{ipso}, C_4), 174.3 (Pd–C_{carb}). Anal. Calcd for $C_{42}H_{53}Cl_2N_4Pd$ (%): C, 63.76; H, 6.75; N, 7.08; Found (%): C, 63.70; H, 6.71; N, 7.01.

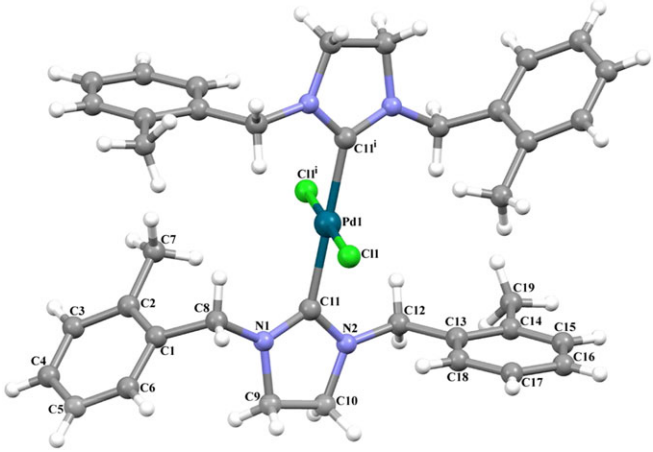


Figure 1. Molecular structure of **1a** showing the atom numbering scheme ((i) −*x* + 1, −*y* + 1, −*z* + 1). Selected bond lengths (Å) and angles (°): Pd1–C11 = 2.0247(17), C11–N1 = 1.322(2), C11–N2 = 1.329(2), Cl1–Pd1 = 2.2997 (5), C11–Pd1–Cl1 = 88.04(5), C11–Pd1–Cl1 = 91.96(5), N2–C11–Pd1 = 124.29(13), N1–C11–Pd1 = 127.00(13).

Dichlorobis[1,3-bis(4-i-propylbenzyl)imidazolidin-2-yliden]palladium(II) (***1d***)

^{1}H NMR ($CDCl_3$, δ, ppm): 1.26 (d, *J* = 6.9 Hz, 12H, $CH_2C_6H_4(CH(CH_3)_2)$-4), 2.90 (h, *J* = 6.9 Hz, 2H, $CH_2C_6H_4(CH(CH_3)_2)$-4), 3.41 (s, 4H, NCH_2CH_2N), 5.25 (s, 4H, $CH_2C_6H_4(CH(CH_3)_2)$-4), 7.17–7.49 (m, 8H, $CH_2C_6H_4(CH(CH_3)_2)$-4). ^{13}C{H}NMR ($CDCl_3$, δ, ppm): 24.0 ($CH_2C_6H_2(CH(CH_3)_2)$-4), 33.8 ($CH_2C_6H_2(CH(CH_3)_2)$-4), 47.6 (NCH_2CH_2N), 54.0 ($CH_2C_6H_4(CH(CH_3)_2)$-4), 126.8 (CH, $C_{3,5}$), 128.8 (CH, $C_{2,6}$), 129.8 (C_{ipso}, C_1), 148.9 (C_{ipso}, C_4), 197.9 (Pd–C_{carb}). Anal. Calcd for $C_{46}H_{86}Cl_2N_4Pd$ (%): C, 63.32; H, 9.93; N, 6.42. Found (%): C, 63.38; H, 9.99; N, 6.47.

Dichlorobis[1,3-bis(4-diethylaminobenzyl)imidazolidin-2-yliden]palladium(II) (***1e***)

^{1}H NMR ($CDCl_3$, δ, ppm): 1.23 (t, *J* = 6.9 Hz, 12H, $CH_2C_6H_4N(CH_2CH_3)_2$–4), 3.50 (q, *J* = 7.2 Hz, 8H, $CH_2C_6H_4N(CH_2CH_3)_2$–4), 5.14 (s, 4H, NCH_2CH_2N), 5.30 (s, 4H, $CH_2C_6H_4N(CH_2CH_3)_2$–4), 6.64 and 7.44 (d, *J* = 8.4 Hz, 8H, $CH_2C_6H_4N(CH_2CH_3)_2$–4). ^{13}C{H}NMR ($CDCl_3$, δ, ppm): 15.3 ($CH_2C_6H_2N(CH_2CH_3)_2$–4), 44.4 ($CH_2C_6H_2N(CH_2CH_3)_2$–4), 47.5 (NCH_2CH_2N), 53.8 ($CH_2C_6H_4N(CH_2CH_3)_2$–4), 111.8 (CH, $C_{3,5}$), 122.8 (CH, $C_{2,6}$), 130.3 (C_{ipso}, C_1), 147.3 (C_{ipso}, C_4), 197.1 (Pd–C_{carb}). Anal. Calcd for $C_{50}H_{74}Cl_2N_8Pd$ (%): C, 62.26; H, 7.73; N, 11.62. Found (%): C, 62.22; H, 7.78; N, 11.66.

Dichlorobis[1,3-bis(3,4-dimethoxybenzyl)imidazolidin-2-yliden]palladium(II) (***1f***)

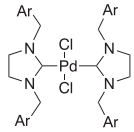
^{1}H NMR ($CDCl_3$, δ, ppm): 3.40 (s, 4H, NCH_2CH_2N), 3.49 (s, 6H, $CH_2C_6H_3(OCH_3)_2$–3), 3.85 (s, 6H, $CH_2C_6H_3(OCH_3)_2$–4), 5.31 (s, 4H, $CH_2C_6H_3(OCH_3)_2$–3,4), 6.75–7.41 (m, 6H, $CH_2C_6H_3(OCH_3)_2$–3,4). ^{13}C{H}NMR ($CDCl_3$, δ, ppm): 47.4 (NCH_2CH_2N), 53.6 ($CH_2C_6H_3(OCH_3)_2$–3), 55.9 ($CH_2C_6H_3(OCH_3)_2$–4), 56.3 ($CH_2C_6H_3(OCH_3)_2$–3,4), 110.7 (CH, C_5), 111.8 (CH, C_2), 121.0 (CH, C_6), 128.5 (C_{ipso}, C_1), 148.7 (C_{ipso}, C_4), 149.4 (C_{ipso}, C_3), 197.0 (Pd–C_{carb}). Anal. Calcd for $C_{42}H_{54}Cl_2N_4O_8Pd$ (%): C, 49.00; H, 5.29; N, 5.44. Found (%): C, 49.05; H, 5.34; N, 5.40.

Results and discussion

The procedure involving Ag–N-heterocyclic carbene, generated by treatment of imidazolium salt with Ag_2O, is probably one of the most general methods, because it generates an air-stable intermediate under mild reaction conditions. It is often used successfully when other methods fail.[26] The use of Ag–N-heterocyclic carbene complexes as carbene transfer reagents provides in many cases a convenient way to overcome the difficulties arising from using strong bases, inert atmospheres and complicated workups. This method was used for the preparation of complexes **1a**–**f**. Firstly, we examined the formation of variously substituted Ag–N-heterocyclic carbene complexes having two aryls on the N-heterocyclic carbene moiety. All these Ag–N-heterocyclic carbene compounds were obtained in high yields.[22] The isolated Ag–N-heterocyclic carbene complexes were converted into yellow Pd–N-heterocyclic carbene complexes (**1a**–**f**) in high yields (Scheme 1).

The air- and moisture-stable palladium carbene complexes **1a**–**f** are soluble in solvents such as dichloromethane and chloroform, and insoluble in nonpolar solvents. The complexes **1a**–**f**, which are very stable in the solid state, were characterized using analytical and spectroscopic techniques. Palladium complexes exhibit a characteristic $\nu_{(NCN)}$ band typically at 1515–1542 cm^{-1} for **1a**–**f**. ^{13}C NMR chemical shifts provide a useful diagnostic tool for this type of metal carbene complex. The chemical shifts for the carbon atom fall in the range 174.3–198.8 ppm and are similar to those found for other palladium–carbene complexes. These complexes show typical spectroscopic signatures, which are in line with those recently reported for other [$PdCl_2$(N-heterocyclic

Table 2. Analytical data for Pd–N-heterocyclic carbene complexes



Complex	Yield (%)	M.p. (°C)	$\nu_{(NCN)}$ (cm^{-1})	^{1}H NMR δ (ppm) $NCH_2CH_2NCH_2Ar$		^{13}C NMR δ C_{carb} (ppm)
1a	90	226–227	1526	3.32	5.25	198.8
1b	95	269–270	1527	3.49	5.24	197.9
1c	92	272–273	1540	3.39	5.42	174.3
1d	94	242–243	1542	3.41	5.25	197.9
1e	91	234–235	1518	3.40	5.30	197.1
1f	93	200–201	1515	3.40	5.31	197.0

carbene)$_2$] complexes.[18,19,27] The analytical data are in good agreement with the compositions proposed for all the complexes and are summarized in Table 2.

Molecular Structure

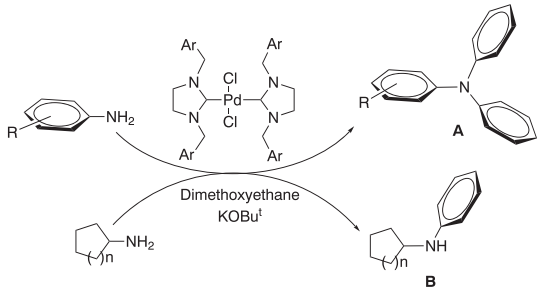
A single crystal of **1a** suitable for X-ray analysis was obtained by slow diffusion of diethyl ether into dichloromethane at room temperature. The crystal and molecular structure of complex **1a** was confirmed using single-crystal X-ray diffractometry. Its molecular structure is depicted in Fig. 1 with selected bond lengths and angles. The X-ray structure shows a square planar geometry around the palladium and the palladium centre in the complex is coordinated by two chloro ligands and two N-heterocyclic carbene ligands in a *trans* position. The bond length between C and Pd is 2.0247 Å.

Catalytic C–N bond formation

Amines are important building blocks possessing wide application in agrochemicals, fine chemical industries, pharmaceuticals, materials science and biotechnology.[28–32] As a consequence, a number of research groups have devoted efforts towards their synthesis.[33–38] The Buchwald–Hartwig amine arylation reaction is a useful and versatile method to obtain aryl amines and so it has great interest in modern synthetic chemistry. These protocols provide access to a range of hindered and functionalized drug-like arylamines in high yield with both electron-deficient and electron-rich aryl and heteroaryl chlorides and bromides.

From the outset our aim was to develop an effective, user-friendly and easily implemented process requiring only general laboratory techniques to carry out the amination protocol. Therefore, we initiated a study focusing on the catalytic activity of new Pd–N-heterocyclic carbene complexes for aryl amination using

Table 3. Coupling reaction of anilines or amines with aryl bromide



Entry	Product	R	Yield (%)					
			1a	**1b**	**1c**	**1d**	**1e**	**1f**
1[a]	A	H	71	80	83	68	77	78
2[a]	A	Me	76	86	87	75	78	89
3[a]	A	OMe	81	91	88	89	90	87
4[b]	B (n = 0)	H	84	92	81	83	86	87
5[b]	B (n = 1)	H	87	92	85	84	89	81
6[b]	B (n = 2)	H	90	86	80	83	85	82

Reaction conditions: catalyst **1a–f** (0.01 mmol), KOBu^t (1.5 mmol), amine (1 mmol), aryl bromide ([a]2.4 mmol; [b]1.2 mmol), dimethoxyethane (2 ml), 80 °C, 15 h. Yields are based on anilines. All reactions were monitored by GC and GC–MS.

bromobenzene and various anilines or amines. As a starting point, the coupling of aniline with bromobenzene was selected as a model reaction. In a typical experiment the preformed, isolated catalyst (0.01 mmol) was dissolved in solvent (2 ml). After the catalyst had completely dissolved, amine (1.00 mmol), aryl bromide (2.4 mmol) and a base (1.5 mmol) were added and the reaction was performed at 80 °C. The reactions were conducted using an amine/catalyst/base molar ratio of 1:0.01:1.5.

The choice of base has often been found to be critical. Alkoxide base acts as an initiator in the present system, leading to the formation of a palladium alkoxide species that is subsequently transformed via a mechanism proposed by Alcazar-Roman and Hartwig.[39] The most successful and widely utilized bases are sodium and potassium *tert*-butoxide, though weaker bases (e.g. Cs_2CO_3)[40] have also been employed. We preferred to use $KOBu^t$ because of observed higher conversions. The amination product was obtained in not more than 20% yield when K_2CO_3 and Cs_2CO_3 were used as bases.

The effect of various solvents on the reaction system was examined. Dimethoxyethane is effective in providing higher conversions, whereas solvents like dioxane, *N*-methyl-2-pyrrolidone, toluene and dimethylformamide show lower conversions. Reaction temperature is another factor critical for these reactions. In studied reactions, when temperature is lower than 80 °C the reaction is very slow. No further increase in the yield of product is observed even when the reaction time is increased. Considering the conditions, we preferred to work with $KOBu^t$ in dimethoxyethane at 80 °C. With these optimized conditions in hand, we continued our investigation of the amination reactions of various substituted anilines.

We have found higher yields for Pd–N-heterocyclic carbene-catalysed amination of primary amines to triarylamines (Table 3, entries 1–3). Also, results of the amination reaction using aniline, *p*-anisidine and *p*-toluidine with bromobenzene are listed in Table 3. With *p*-methoxyaniline and *p*-methylaniline, containing electron-donating groups at the *para* position of aniline, the reaction proceeds with a considerable increase in yield, up to 76–91% (Table 3, entries 2 and 3). The maximum conversion of 4-methoxyaniline to corresponding diarylation product is achieved (Table 3, entry 3). When aryl chlorides are used, the formation of amination product is not appreciable. When no catalyst is added, the blank reaction with dimethoxyethane as solvent and $KOBu^t$ as base exhibits extremely low reactivity, giving low yield of triarylamine, with many by-products formed from the aryl halide substrate.

We also examined the amination of bromobenzene with cyclopentylamine, cyclohexylamine and cycloheptylamine under the same reaction conditions. As evident from Table 3, good yields are obtained (entries 4–6). The aromatic primary amines give diarylated products while primary aliphatic amines lead to monoarylation. These results are similar to those reported previously.[18,19] We observed that the influence of the alkyl on the N atom of the palladium complex is not important. Among the tested complexes, complex **1b** is highly efficient in the amination reaction.

Conclusions

Preparation and characterization of six new Pd–N-heterocyclic carbene complexes and development of Pd-catalysed Buchwald–Hartwig amination protocols utilizing the Pd–N-heterocyclic carbene precatalysts **1a**–**f** have been reported. These protocols allow the preparation of a range of structurally intriguing, drug-like aromatic amines. The catalyst system was applied to the reactions of various anilines and amines with bromobenzene. The present system was found to lead to efficient amination. Our continuing studies in this area will examine the utility of N-heterocyclic carbene ligands in other challenging metal-catalysed reactions.

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