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ARYLATION OF ANILINE AND AMINES BY Pd-(N-HETEROCYCLIC CARBENE) COMPLEXES

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Abstract – Aminoarenes constitute valuable building blocks in organic synthesis and an essential skeleton ubiquitously found in ligands, agrochemicals, and pharmaceuticals. This synopsis presents recent amination methods using nitrogen-heteroatom bonds as a powerful and versatile platform to rapidly synthesize diverse aminoarenes, with transition-metal catalyzed arene C-H amination. The Buchwald-Hartwig amination has been investigated theoretically and experimentally to examine the scope of possible bases under different reaction conditions. We report examples of the palladium NHC (N-heterocyclic carbene) catalyzed amination of aryl halides with anilines and amines in the presence of dimethoxyethane solvent and potassium tertiary-butoxide as a base.

INTRODUCTION

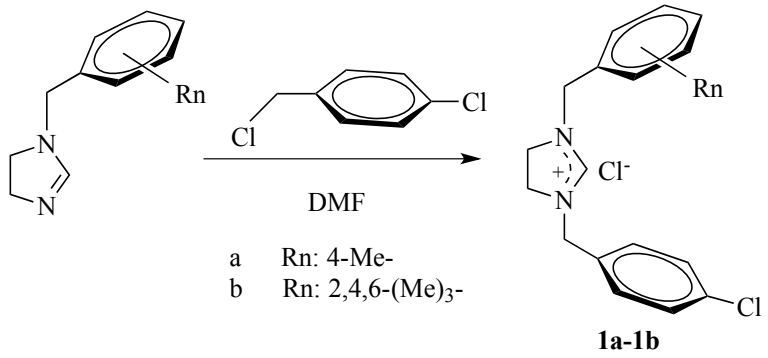
Cross-coupling reaction is a very powerful strategy to generate aryl-carbon and aryl-heteroatom covalent bonds and may occur following different routes.[1-5] Among these, the formation of the C–N bonds elicited a large interest in the synthesis of compounds with pharmaceutical, cosmetic, agrochemical and optical devices applications. Because of this it received a great industrial and academic importance in the past two decades.[6-13] To ensure the efficiency of the reaction, the nature of the active palladium species involved in the reaction is of crucial importance. Indeed, in order to circumvent the various limitations of the cross-coupling type reaction, strong σ-donor ligands are usually employed. The high σ-donor and low π-acceptor ability of NHCs augment their potential to tether to many metal ions. Although NHCs were thought to be pure NHC-to-metal σ→d donors, it has been realized that they are also involved in

metal-to-NHC d→π* and NHC-to-metal π→d donations when bonded to a metal.[14] NHC Complexes have wide range of applications, mainly in catalysis. The strong σ-donating but weak π--accepting abilities of NHCs make their metal complexes fascinating catalysts in a plethora of reactions, including hydroacylation,[15,16] the Suzuki–Miyaura reaction,[17,18] hydrogenation,[19,20] and ruthenium based olefin metathesis.[21-25]

Recently, we reported the synthesis of a novel type of NHC-palladium complexes bearing imidazolidin-2-ylidene and benzimidazol-2-ylidene ligands. In addition, we found that these complexes showed efficient catalytic activity toward amination reactions, C-C cross coupling (Suzuki and Heck coupling reactions) and arylation of benzothiazole.[26-30] In this paper, we reported the series of imidazolinium salts as NHC precursor and their silver complexes as carbene transfer agent, and Pd–NHC complexes as catalyst for amination reaction.

RESULTS AND DISCUSSION

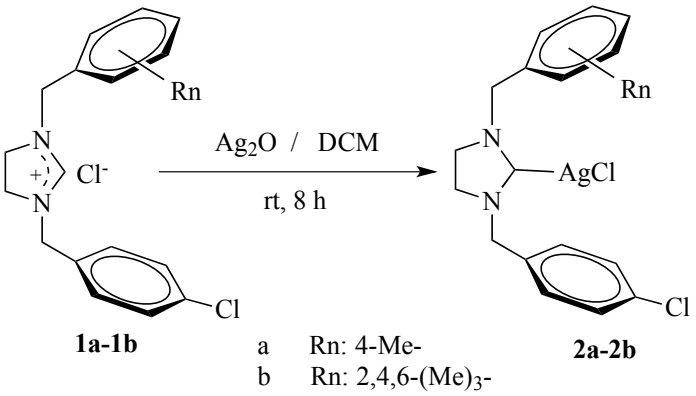
NHCs are a very important class of ligands because of their strong σ-donor and poor π-acceptor abilities.[31-34] They are neutral, two-electron donor ligands with a heterocyclic core, which can consist of imidazole, pyrazole, triazole, tetrazole, and benzimidazole, among others. The imidazolinium salts that serve as the ligand precursors of NHCs are readily synthesized in high yields. We are interested in the possibility of using imidazolinium salts as NHC precursors because they are structurally simple, readily available, and inexpensive, and they allow for simplistic introduction of various substituents into their structure. Heating of 4-chlorobenzyl chloride with 1-alkylimidazoline in DMF at 80 ºC finally afforded desired functionalized imidazolinium chloride as an white powder in 83-92% yield (Scheme 1).



Scheme 1. The synthesis of imidazolinium salts

The ^{1}H NMR spectra of the imidazolinium salts (**1a**, **1b**) in $CDCl_3$ exhibits as a singlet in the range δ 10.67 and 10.50 ppm characteristic of the NC*H*N proton, respectively. Correspondingly, the ^{13}C NMR spectrums show the characteristic chemical shift of C2 carbon at 159.1 and 158.9 ppm respectively **1a**, **1b**.

Silver(I)–NHC complexes have been observed to be very stable to air and moisture. In 1993, Arduengo et reported the first example of an Ag(I)–NHC complex by the reaction of a free carbene derived from 1,3-dimesitylimidazole with silver triflate in THF.[35] Further, pyridyl/benzene-bridged bis-carbene helical complexes of Ag(I) are reported. However, to conquer the difficulties with the free carbene method, in Wang and Lin reported a convenient in situ deprotonation reaction, by the reaction of basic silver oxide with NHC precursors.[36] This method is more advantageous than the free carbene method and has become more common in the preparation Ag(I)–NHC complexes. Another method utilizes the reaction of azolium salts with silver bases such as Ag_2CO_3 and AgOAc at ambient temperature to yield Ag-carbene Among these methods the use of Ag_2O has made the synthesis of silver(I)-NHC complexes much easier more convenient. We chose this method preparation pathway that we obtained excellent yields by in situ deprotonation with Ag_2O in this work (Scheme 2).

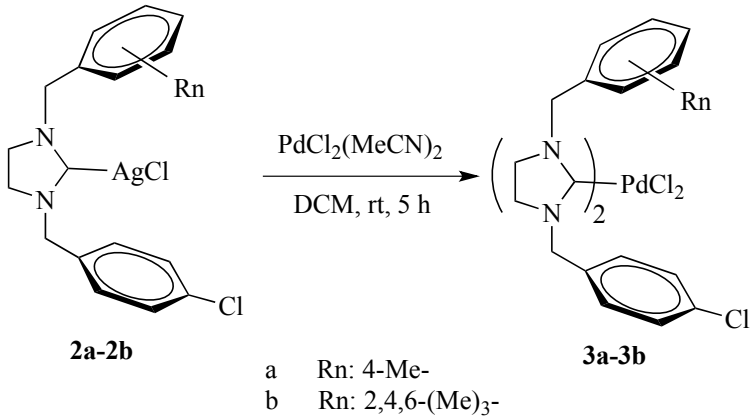


Scheme 2. The synthesis of new silver-NHC complexes

As shown in Scheme 2, the silver complexes (**2a**, **2b**) are synthesized by the treatment of the salts (**1a**, **1b**) with Ag_2O as an white powder in 75-82% yield. The successful formation of Ag(I)–carbene complexes is indicated by the disappearance of the acidic C2 proton characteristic of NHC precursors in ^{1}H NMR spectra of complexes. The absence of the resonances for the acidic proton (NC*H*N) around ppm showed the formation of expected Ag-NHC complexes. The ^{13}C NMR spectrum, the resonances for carbene carbons were not detected, which was also mentioned in the literature and given a reason of the fluxional behavior of the NHCs complexes.[37,38]

Three main pathways may be envisioned for the synthesis of palladium-NHC complexes: One is widely followed in the synthesis of these complexes, involves the in situ reaction of an azolium salt in the of a base to generate free NHC and then free NHC is trapped palladium.[39] The other approach is more economical synthetic pathways to synthesize Pd–NHC complexes even in the absence of a base. Basic metal salt such as palladium acetate [$Pd(OAc)_2$] play a role as both a Pd source and a base.[40] Another for the preparation of Pd-NHC complexes is the transmetallation reaction from Ag(I)-NHC complexes to

Pd precursors; this approach has currently been attracting numerous researchers.[41] We used the last procedure to obtain Pd-NHC complexes, which typically involves treatment of the imidazolinium salt Ag_2O to form the Ag-NHC complex, followed by transmetalation to a species such as $[PdCl_2(MeCN)_2]$ to give the Pd-NHC complex (Scheme 3).



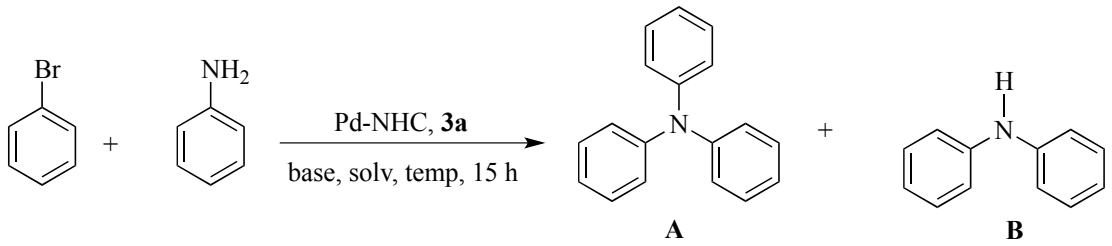
Scheme 3. The synthesis of new Pd-NHC complexes with transmetallation reaction

Palladium-NHC complexes are stable to air and moisture and very soluble in dichloromethane and chloroform, but insoluble in diethyl ether and hexane. The crude products recrystallized from dichloromethane:diethyl ether (1:2) at room temperature. The Pd-NHC complexes (**3a**, **3b**) appear to be spectroscopically pure, and exhibit signals slightly upfield in comparison with the parent carbene precursors (**1**); as expected, the C_2-H signal is absent. The characteristic coordinated carbene signals at δ. 198.3 and 197.4 ppm are in agreement with reported data for other imidazolidin-2-ylidene palladium complexes.[26,42]

As known, an efficient metal catalyzed cross coupling reaction is regulated by a number of factors such as base, solvent, temperature and reaction time. Initially, standard reactions were carried out using bromobenzene and aniline as the substrates in the presence of NHC-Pd(II) complex, **3a**, at 50 ^oC for 15 h to find out the best solvent and base. Some representative results are shown in Table 1.

It was found that the solvents and bases drastically affected the reactions. For example, in the first round, using $KOBu^t$ as the base, dimethoxyethane (DME) appeared to be the best solvent to give the desired product A in 84% yield (Table 1, entry 6). In other solvents, such as tetrahydrofuran (THF), *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), dioxane, and toluene, low yield or no reaction was observed (Table 1, entries 1-5). The reaction proceeded well when $KOBu^t$ was used as the base (Table 1, entry 6), whereas other bases, such as, $NaOBu^t$, and NaOH were ineffective (Table 1, entries 7-8). In addition, the effect of various bases on the reaction system was studied. It was observed

Table 1. Representative results for the optimization of complex **3a** catalyzed reaction between bromobenzene and aniline.



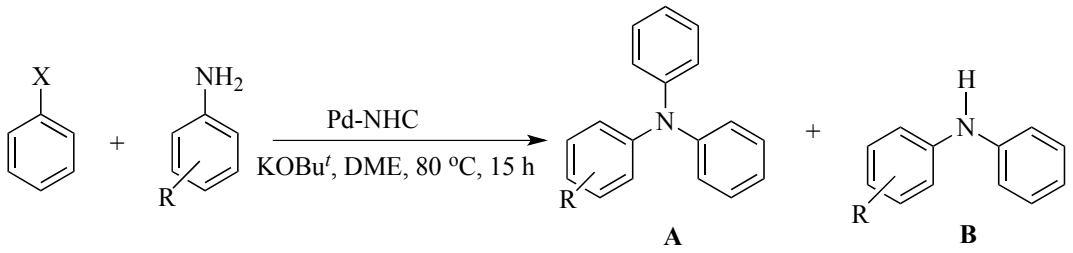
A **B**

Entry	Solvent	Base	Conversion (%)	Yield (%)	
				A	B
1	THF	KOBu^t	10	65	35
2	DMF	KOBu^t	25	trace	-
3	DMSO	KOBu^t	20	trace	-
4	dioxane	KOBu^t	15	70	30
5	toluene	KOBu^t	55	75	25
6	DME	KOBu^t	80	84	16
7	DME	NaOBu^t	25	56	44
8	DME	NaOH	15	trace	-
9[b]	DME	KOBu^t	90	92	8

[a] Reaction conditions: catalyst (**3a)** (0.01 mmol), base (1.5 mmol), aniline (1 mmol), bromobenzene (2.4 mmol), solvent (2 mL), 50 ^{o}C, 15 h. Yields are based on anilines. All reactions were monitered by TLC and GC. [b] The reaction was carried out at 80 ^{o}C.

that bases like potassium carbonate and potassium phosphate were also effective, but gave lower conversions while the base like KOBu^t provided higher conversions. The probable reason for the difference in the results obtained was due to the use of organic and inorganic bases and may be due to the higher solubility of alkoxide base in organic solvents. Temperature effect on coupling of aniline with bromobenzene was studied. Better result was obtained when the temperature was elevated to 80 ^{o}C (Table 1, entry 9). Under the optimized conditions we set out to check the generality of the method by running test reactions with differently substituted anilines. The results are reported in Table 2.

Table 2. NHC-Pd(II) Catalyzed amination of bromobenzene and chlorobenzene with aniline derivatives



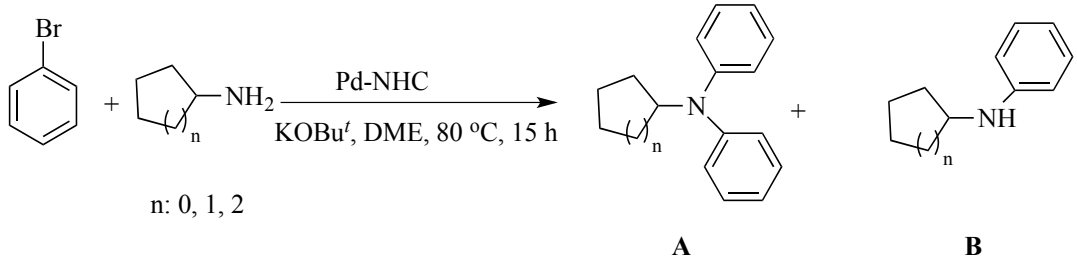
Entry	Pd-NHC	R	X	Conversion (%)	Yield (%)	
					A	B
1	**3a**	H	Br	90	92	8
2	**3b**	H	Br	82	79	21
3	**3a**	Me	Br	92	90	10
4	**3b**	Me	Br	87	91	9
5	**3a**	OMe	Br	94	93	7
6	**3b**	OMe	Br	85	74	26
7	**3a**	H	Cl	25	73	27
8	**3b**	H	Cl	13	78	22
9	**3a**	Me	Cl	32	68	32
10	**3b**	Me	Cl	21	57	43
11	**3a**	OMe	Cl	41	63	37
12	**3b**	OMe	Cl	35	51	49

[a] Reaction conditions: catalyst (**3a-3b)** (0.01 mmol), $KOBu^t$ (1.5 mmol), aniline (1 mmol), bromobenzene or chlorobenzene (2.4 mmol), DME (2 mL), 80 °C, 15 h. Yields are based on anilines. All reactions were monitered by TLC and GC.

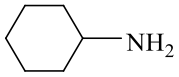
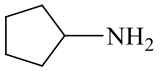
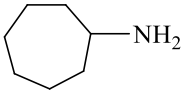
We have demonstrated for the good yields Pd-NHC catalyzed amination of primary amines to triarylamines. With *p*-toluidine and *p*-anisidine containing electron donating group at *para* position, the amination reaction proceeds with considerable increase in the yield up to 74-93% (Table 2, entries 1-6). Use of chlorobenzene with aniline derivatives gave less conversion than bromobenzene (Table 2, entries 7-12).

We also examined the amination of bromobenzene with aliphatic amines under the same reaction conditions (Table 3).

Table 3. NHC-Pd(II) catalyzed amination of bromobenzene with amine derivatives.



A **B**

Entry	Pd-NHC	Amine	Conversion (%)	Yield (%) A	Yield (%) B
1	**3a**		94	15	85
2	**3b**		88	22	78
3	**3a**		85	8	92
4	**3b**		87	6	94
5	**3a**		91	5	95
6	**3b**		86	13	87

[a] Reaction conditions: catalyst (**3a-3b)** (0.01 mmol), KOBu^t (1.5 mmol), amine (1 mmol), bromobenzene (1.2 mmol), DME (2 mL), 80 ^{o}C, 15 h. Yields are based on amine. All reactions were monitered by TLC and GC.

The coupling reaction was performed under the standard conditions where amine (1 mmol) coupled bromobenzene (2.4 mmol), but it was found that the reaction proceeded *N*-monoarylation and gave secondary amines in a high yield and we observed *N*-diarylation extremely low yield. 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 1, 4, 5). The aromatic primary amines give diarylated products while primary aliphatic amines lead to monoarylation. We examined the role of chlorobenzyl group substituted NHC ligands but these type ligand is not so efficient than other ligand. These results are similar to those reported previously.[26,42,43] The best catalyst performance is observed in the presence of the 2,4,6-trimethylbenzyl based NHC complex in amination reaction.

In summary, new imidazolidinium salts and their silver and palladium complexes have been synthesized and characterized by analytical and spectral methods. The utility of the palladium complexes as catalysts for the Buchwald–Hartwig amination reaction has been highlighted. Further studies on the potential application of Pd-NHC complexes in other related cross-coupling reactions are under investigation in our laboratory.

EXPERIMENTAL

All reactions for the preparation of imidazolidinium salts as ligand and their metal complexes were carried out under argon in flame-dried glassware using standard Schlenk techniques. Chemicals were obtained from Sigma Aldrich and Fluka. Melting points were determined in glass capillaries under air with an Electrothermal-9200 melting point apparatus. FT-IR spectra were recorded as KBr pellets in the range 400-4000 cm^{-1} on a Perkin Elmer Spectrum 100. ^{1}H- and ^{13}C-NMR spectra were recorded with a Varian AS 400 Merkur spectrometer operating at 400 MHz (^{1}H), 100 MHz (^{13}C) in $CDCl_3$ with tetramethylsilane as an internal reference. Coupling constants (*J* values) are given in hertz. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, hept = heptet, and m = multiplet signal. All catalytic reactions were monitored on an Agilent 6890N GC system by GC-FID with a HP-5 column of 30 m length, 0.32 mm diameter and 0.25 μm film thickness. Column chromatography was performed using silica gel 60 (70-230 mesh). Solvent ratios are given as v/v.

Synthesis and characterization of imidazolidinium salts (1a-1b)

To a solution of 1-alkylimidazole (5 mmol) in DMF (10 mL) was added slowly 4-chlorobenzyl chloride (5 mmol) at 25 °C and the resulting mixture was stirred at 80 °C for 10 h. Et_2O (15 mL) was added to obtain a white crystalline solid which was filtered off. The solid was washed with Et_2O (3x15 mL), dried under vacuum. The crude product was recrystallized from EtOH/Et_2O. Melting points were measured in open capillary tubes.

[1-(4-Methylbenzyl)-3-(4-chlorobenzyl)]imidazolidinium chloride 1a

Yield: 0.28 g (83%), mp 182-183 °C, $\nu_{(CN)}$= 1648 cm^{-1}. ^{1}H NMR (399.9 MHz, $CDCl_3$) δ (ppm) = 10.67 (s, 1H, NC*H*N), 7.42, (d, 2H, *J* = 8.4 Hz, $CH_2C_6H_4(CH_3)$-4), 7.34 (d, 2H, *J* = 8.4 Hz, $CH_2C_6H_4(CH_3)$-4), 7.27 (d, 2H, *J* = 7.8 Hz, $CH_2C_6H_4(Cl)$-4), 7.18 (d, 2H, *J* = 7.8 Hz, $CH_2C_6H_4(Cl)$-4), 4.93 (s, 2H, $CH_2C_6H_4(CH_3)$-4), 4.81 (s, 2H, $CH_2C_6H_4(Cl)$-4), 3.74 (s, 4H, NCH_2CH_2N), 2.35 (s, 3H, $CH_2C_6H_4(CH_3)$-4). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ (ppm) = 159.1 (N*C*HN), 139.1, 135.1, 131.2, 130.4, 129.9, 129.5, 129.4, 128.8 ($CH_2C_6H_4(CH_3)$-4) and $CH_2C_6H_4(Cl)$-4), 52.2, 51.5 ($CH_2C_6H_4(CH_3)$-4 and $CH_2C_6H_4(Cl)$-4), 47.5 (NCH_2CH_2N), 21.2 ($CH_2C_6H_4(CH_3)$-4). Anal. Calcd for $C_{18}H_{20}N_2Cl_2$: C: 64.48; H: 6.01; N: 8.36. Found: C: 64.41; H: 6.06; N: 8.31.

[1-(2,4,6-Trimethylbenzyl)-3-(4-chlorobenzyl)]imidazolidinium chloride 1b

Yield: 0.32 g (89%), mp 153-154 °C, $\nu_{(CN)}$= 1652 cm^{-1}. ^{1}H NMR (399.9 MHz, $CDCl_3$) δ (ppm) = 10.50 (s, 1H, NC*H*N), 7.41 (d, 2H, *J* = 8.4 Hz, $CH_2C_6H_4(Cl)$-4), 7.34 (d, 2H, *J* = 8.4 Hz, $CH_2C_6H_4(Cl)$-4), 6.88 (s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 4.94 (s, 2H, $CH_2C_6H_4(Cl)$-4), 4.89 (s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6,), 3.84-3.62 (m, 4H, NCH_2CH_2N), 2.35 (s, 6H, $CH_2C_6H_4(CH_3)$-2,4,6), 2.30 (s, 3H, $CH_2C_6H_4(CH_3)$-2,4,6). ^{13}C NMR

(100.5 MHz, $CDCl_3$) δ (ppm) = 158.9 (N*C*HN), 139.1, 137.8, 135.1, 131.4, 130.4, 129.9, 129.4, 125.2 ($CH_2C_6H_2(CH_3)_3$-2,4,6) and $CH_2C_6H_4$(Cl)-4), 51.4 ($CH_2C_6H_2(CH_3)_3$-2,4,6 and $CH_2C_6H_4$(Cl)-4), 47.4, 46.3 (NCH_2CH_2N), 20.9, 20.2 ($CH_2C_6H_2(CH_3)_3$-2,4,6). Anal. Calcd for $C_{20}H_{24}N_2Cl_2$: C: 66.12; H: 6.66; N: 7.71. Found: C: 66.17; H: 6.60; N: 7.65.

Synthesis and characterization of silver complexes (2a-2b)

A solution of imidazolidinium salt (1.0 mmol), Ag_2O (0.5 mmol) and activated 4Å molecular sieves in CH_2Cl_2 (30 mL) was stirred room temperature for 8 h in dark condition. The reaction mixture was filtered through celite and the solvent removed under reduced pressure. The crude product was recrystallized from CH_2Cl_2/hexane at room temperature.

Chloro[1-(4-methylbenzyl)-3-(4-chlorobenzyl)imidozolidin-2-ylidene]silver(I) 2a

Yield: 0.23 g (53%), mp 198-199 ºC, $\nu_{(CN)}$= 1512 cm^{-1}. ^1H NMR (399.9 MHz, $CDCl_3$) δ (ppm) = 7.38-7.14 (m, 8H, $CH_2C_6H_4(CH_3)$-4 and $CH_2C_6H_4$(Cl)-4), 4.72 (s, 2H, $CH_2C_6H_4(CH_3)$-4), 4.71 (s, 2H, $CH_2C_6H_4$(Cl)-4), 3.49 (s, 4H, NCH_2CH_2N), 2.37 (s, 3H, $CH_2C_6H_4(CH_3)$-4). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ (ppm) = 138.4, 134.4, 133.4, 131.6, 129.7, 129.3, 129.2, 127.9 ($CH_2C_6H_4(CH_3)$-4) and $CH_2C_6H_4$(Cl)-4), 55.3, 54.8 ($CH_2C_6H_4(CH_3)$-4 and $CH_2C_6H_4$(Cl)-4), 48.6, 48.5 (NCH_2CH_2N), 21.2 ($CH_2C_6H_4(CH_3)$-4). Anal. Calcd for $C_{18}H_{19}N_2AgCl_2$: C: 48.90; H: 4.33; N: 6.34. Found: C: 48.95; H: 4.28; N: 6.40.

Chloro[1-(2,4,6-trimethylbenzyl)-3-(4-chlorobenzyl)imidazolidin-2-ylidene]silver(I) 2b

Yield: 0.28 g (61%), mp 185-186 ºC, $\nu_{(CN)}$= 1508 cm^{-1}. ^1H NMR (399.9 MHz, $CDCl_3$) δ (ppm) = 7.34 (d, 2H, *J* = 8.4 Hz, $CH_2C_6H_4$(Cl)-4), 7.21 (d, 2H, *J* = 8.4 Hz, $CH_2C_6H_4$(Cl)-4), 6.91 (s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 4.78 (s, 2H, $CH_2C_6H_4$(Cl)-4), 4.71 (s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6,), 3.41 (s, 4H, NCH_2CH_2N), 2.35 (s, 6H, $CH_2C_6H_4(CH_3)$-2,4,6), 2.29 (s, 3H, $CH_2C_6H_4(CH_3)$-2,4,6). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ (ppm) = 138.5, 137.6, 134.4, 133.5, 129.7, 129.4, 129.2, 127.3 ($CH_2C_6H_2(CH_3)_3$-2,4,6) and $CH_2C_6H_4$(Cl)-4), 55.0, 49.1 ($CH_2C_6H_2(CH_3)_3$-2,4,6 and $CH_2C_6H_4$(Cl)-4), 48.4, 47.9 (NCH_2CH_2N), 20.9, 20.5 ($CH_2C_6H_2(CH_3)_3$-2,4,6). Anal. Calcd for $C_{20}H_{23}N_2AgCl_2$: C: 51.09; H: 4.93; N: 5.96. Found: C: 51.02; H: 4.85; N: 5.92.

Synthesis and characterization of palladium complexes (3a-3b)

Silver complex (**2a-2b**) (0.20 mmol) was dissolved in CH_2Cl_2 (30 mL) to which [$PdCl_2(MeCN)_2$] (0.10 mmol) was added. The mixture was allowed to stir for 5 h at room temperature. The suspension was filtered using G3 sintered funnel through celite and the filtrate was evaporated. The crude product was recrystallized from CH_2Cl_2/hexane at room temperature to obtain a pale yellow crystal.

Bis[1-(4-methylbenzyl)-3-(4-chlorobenzyl)imidozolidin-2-ylidene]dichloropalladium(II) 3a

Yield: 0.48 g (62%), mp 235-236 ºC, $\nu_{(CN)}$= 1562 cm^{-1}. ^1H NMR (399.9 MHz, $CDCl_3$) δ (ppm) = 7.51-7.11 (m, 16H, $CH_2C_6H_4(CH_3)$-4 and $CH_2C_6H_4(Cl)$-4), 5.22 (s, 4H, $CH_2C_6H_4(CH_3)$-4), 5.19 (s, 4H, $CH_2C_6H_4(Cl)$-4), 3.34 (s, 8H, NCH_2CH_2N), 2.33 (s, 6H, $CH_2C_6H_4(CH_3)$-4). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ (ppm) = 198.3 (Pd-Carbene), 137.5, 134.5, 133.6, 132.8, 130.1, 129.9, 129.3, 128.8 ($CH_2C_6H_4(CH_3)$-4) and $CH_2C_6H_4(Cl)$-4), 53.7, 53.3 ($CH_2C_6H_4(CH_3)$-4 and $CH_2C_6H_4(Cl)$-4), 47.9 (NCH_2CH_2N), 21.1 ($CH_2C_6H_4(CH_3)$-4). Anal. Calcd for $C_{36}H_{38}N_4PdCl_4$: C: 55.80; H: 4.94; N: 7.23. Found: C: 55.73; H: 4.91; N: 7.15.

Bis[1-(2,4,6-trimethylbenzyl)-3-(4-chlorobenzyl)imidazolidin-2-ylidene]dichloropalladium(II) 3b

Yield: 0.46 g (56%), mp 228-229 ºC, $\nu_{(CN)}$= 1560 cm^{-1}. ^1H NMR (399.9 MHz, $CDCl_3$) δ (ppm) = 7.47 (d, 4H, *J* = 8.4 Hz, $CH_2C_6H_4(Cl)$-4), 7.23 (d, 4H, *J* = 8.4 Hz, $CH_2C_6H_4(Cl)$-4), 6.77 (s, 4H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 5.29 (s, 4H, $CH_2C_6H_4(Cl)$-4), 5.17 (s, 4H, $CH_2C_6H_2(CH_3)_3$-2,4,6,), 3.18-3.11 (m, 8H, NCH_2CH_2N), 2.38 (s, 12H, $CH_2C_6H_4(CH_3)$-2,4,6), 2.17 (s, 6H, $CH_2C_6H_4(CH_3)$-2,4,6). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ (ppm) = 197.2 (Pd-Carbene), 137.3, 136.7, 133.7, 132.7, 128.9, 128.2, 127.8, 127.5 ($CH_2C_6H_2(CH_3)_3$-2,4,6) and $CH_2C_6H_4(Cl)$-4), 52.5, 52.3 ($CH_2C_6H_2(CH_3)_3$-2,4,6 and $CH_2C_6H_4(Cl)$-4), 47.2, 46.6 (NCH_2CH_2N), 19.9, 19.8 ($CH_2C_6H_2(CH_3)_3$-2,4,6). Anal. Calcd for $C_{40}H_{46}N_4PdCl_4$: C: 57.81; H: 5.58; N: 6.74. Found: C: 57.75; H: 5.55; N: 6.81.

General procedure for the NHC-Pd catalyzed amination reactions

Under an inert atmosphere, $KOBu^t$ (1.5 mmol), NHC-Pd complex (0.01 mmol), DME (2 mL), aniline or amine (1 mmol), and bromobenzene/chlorobenzene (2.4 mmol) were successively added into a Schlenk reaction tube. The mixture was stirred at 80 ºC for 15 h. The solvent was removed under reduced pressure and the residue was purified by a flash chromatograph on silica gel to give the pure products.

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