

Short communication

# Synthesis of novel palladium–carbene complexes as efficient catalysts for amination of aryl chlorides in ionic liquid

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## Abstract

The synthesis and characterization of  $[\text{PdCl}_2(\text{N-heterocyclic carbene})_2]$  (**2**, **3**), an air and moisture-stable complexes are reported. Amination of aryl halides in 1-methyl-3-butyl-imidazolium tetrafluoroborate in the presence of palladium–carbene complexes as catalysts are described. Aryl chlorides undergo smooth nucleophilic substitution reactions with primary amines in ionic liquid to afford the corresponding arylamines in excellent yields under mild conditions.

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**Keywords:** Amination; *N*-heterocyclic carbene; Palladium complexes; Imidazolinylidene; Ionic liquid

## 1. Introduction

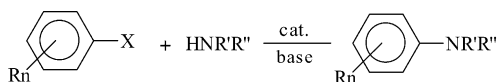
The advancement of modern organic synthesis necessitates the wide use of catalytic reactions, which make it possible to simplify the synthesis of different target molecules, avoiding the use of toxic reagents and considerably lowering the number of steps and thus minimizing the operation costs. One of the biggest challenges for modern organic chemists is the employment of the most efficient catalytic method for a specific part in a synthesis strategy.

Significant improvements of catalyst performance have recently been brought benefits to fine chemistry via simple substitution of a phosphine ligand by a nucleophilic heterocyclic diaminecarbene, such as an imidazol-2-ylidene ligand. Interested in *N*-heterocyclic carbene (NHC) ligands has continued to grow given the beneficial effects they often have on homogeneous catalysis. Nucleophilic carbenes have been shown to behave as phosphine mimics [1] and *N*-heterocyclic carbenes of type 1,3-imidazolinylidene are now currently used in transition metal chemistry as ancillary ligands [2]. This is

largely due to their recently revealed ability to create specific catalytic activity [3,4] and attempts are currently made to modify the coordination sphere of the metal with the hope to find an even better application profile. Illustrative examples are found in various catalytic reactions with palladium catalysts in cross-coupling or Heck and Suzuki reactions [5,6] and ruthenium catalysts for the formation of furans, cyclopropanation [7,8] alkene metathesis [9,10] and cycloisomerisation [11].

Nucleophilic aromatic substitution has become a very useful and diverse synthetic route for introducing amine functionality onto a benzene ring [12]. Classical methods for the synthesis of arylamines typically require a large excess of base, highly polar solvents such as DMF, DMSO at high temperatures with highly activated aryl halides [13] and under high pressure conditions [14]. The Buchwald–Hartwig amination of aryl halides has emerged as a powerful technique for the formation of *N*-substituted anilines (Scheme 1) [15]. A major recent focus in coupling chemistry has been on the development of catalysts that are able to activate aryl chloride substrates since these tend to be cheaper and more readily available than their bromide and iodide counterparts, factors that make them particularly relevant to the industrial sector.

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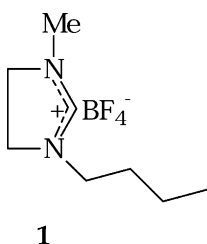
Scheme 1.

Unfortunately the comparatively high C–Cl bond strength makes their activation by oxidative-addition comparatively difficult [16]. While there are now many reports on the use of aryl chlorides in amination [17] in most cases the catalysts employed need to be used in relatively high loading. Therefore the advantages associated with the use of aryl chlorides may be negated by the high cost of the catalyst systems and the need to remove palladium residues from the products down to the ppm level for use in fine chemicals.

In recent years, ionic liquids have emerged as a set of green solvents with unique properties such as tunable polarity, high thermal stability, and immiscibility with a number of organic solvents, negligible vapor pressure and recyclability [18]. Their high polarity and the ability to solubilise both inorganic and organic compounds can result in enhanced rates of chemical processes and can provide higher selectivities compared to conventional solvents. Accordingly they are emerging as novel replacements for volatile organic solvents in organic synthesis. They are particularly promising, as solvents for various reactions [19,20]. Moreover, ionic liquids are simple and inexpensive to prepare and easy to recycle and their properties can be fine-tuned by changing the anion or alkyl group attached to cation.

The ionic liquids could be an alternative to organic solvents for catalyzed synthesis in environmentally-friendly reaction media because of their negligible vapour pressure and excellent solubility properties and chemical and thermal stabilities [18]. But, their intriguing aspect is the possibility to alter their physical and chemical properties by varying their structure, with respect to the choice of organic cations (e.g. tetraalkylammonium, 1-alkyl-3-methylimidazolium cations) and anions (e.g.  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ,  $\text{Tf}_2\text{N}^-$  anions), and the alkyl substituents in the cation. Thus, ionic liquid have been described as ‘designer solvents’ [21].

In view of the emerging importance of imidazolidinium based ionic liquid, **1**, as novel reaction media, we wish to explore the use of ionic liquids as promoters and recyclable solvents systems for the synthesis of arylamines under mild conditions.

**1**

The catalyst system was chosen owing to (i) the high activity of molecular catalyst in the homogeneously catalyzed conversion of deactivated aryl chlorides, (ii) its stability under the reaction conditions commonly employed for the amination of aryl chlorides.

## 2. Experimental

Manipulations were prepared with standard Schlenk techniques under an inert atmosphere of nitrogen with previously dried solvents. The 1,3-bis(alkyl)imidazolidinium and benzimidazolium chlorides was prepared according to known methods [22]. Infrared spectra were recorded as KBr pellets in the range  $400\text{--}4000\text{ cm}^{-1}$  on a ATI UNICAM 2000 spectrometer.  $^1\text{H}$  NMR (300 MHz) and  $^{13}\text{C}$  NMR (75.5 MHz) were recorded on a Bruker AM 300 WB FT spectrometer with chemical shifts referenced to residual solvent  $\text{CDCl}_3$ . Microanalyses were performed by the TÜBITAK analyses center.

### 2.1. Preparations 1-butyl-3-methyl-4,5-dihydroimidazolium iodide

The 1-butyl-3-methyl-4,5-dihydroimidazolium iodide was prepared from 1-butylimidazolidine (22.30 g, 176.90 mmol) and methyl iodide (25.54 g, 179.90 mmol) at ambient temperature in toluene (120 mL). The ionic liquid layer was separated by the toluene in a separatory funnel, washed twice with diethylether and dried under vacuum. Yield 47.2 g (99%). The product is liquid at room temperature.

$^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ): 0.80 [t,  $J$  6.9, 3H,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ]; 1.38 [m, 2H,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ]; 1.92 [quin.,  $J$  7.6 Hz, 2H,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ]; 3.50 [t,  $J$  7.5 Hz, 2H,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ]; 3.32 [s, 3H,  $\text{NCH}_3$ ]; 3.01 and 3.19 [t,  $J$  5.1 Hz, 4H,  $\text{NCH}_2\text{CH}_2\text{N}$ ]; 9.07 [s, 1H,  $\text{NCHN}$ ].

The ionic liquid **1** were synthesized according to literature [23]. The novel 1-butyl-3-methyl-4,5-dihydroimidazolium tetrafluoroborate was obtained from 1-butyl-3-methyl-4,5-dihydroimidazolium iodide (45 g, 167.82 mmol) with  $\text{NH}_4\text{BF}_4$  (17.60 g, 167.87 mmol) in anhydrous methylene chloride. Yield 36.35 g (95%),  $d = 1.315\text{ g/mL}$ . This ionic liquid soluble in methanol, water, chloroform, dimethylformamide.

$^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ): 0.82 [t,  $J$  6.9 Hz, 3H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ]; 1.39 [m, 2H,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ]; 1.93 [quin.,  $J$  7.6 Hz, 2H,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ]; 3.63 [t,  $J$  7.5 Hz, 2H,  $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ]; 3.38 [s, 3H,  $\text{NCH}_3$ ]; 3.03 and 3.21 [t,  $J$  5.1 Hz, 4H,  $\text{NCH}_2\text{CH}_2\text{N}$ ]; 9.61 [s, 1H, 2-CH].  $^{13}\text{C}$  {H} NMR ( $\delta$ ,  $\text{CDCl}_3$ ): 156.8 [NCHN]; 45.8, 46.5 [ $\text{NCH}_2\text{CH}_2\text{N}$ ]; 47.7 [ $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ]; 31.4 [ $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ]; 19.9 [ $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ]; 13.7 [ $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ]; 33.2 [ $\text{NCH}_3$ ]. Anal. cal. for  $\text{C}_8\text{H}_{17}\text{N}_2\text{BF}_4$ ; C: 42.14, H: 7.51, N: 12.28; found C: 42.22, H: 7.69, N: 12.45.  $\nu_{(\text{NCN})} = 1648\text{ cm}^{-1}$ .

## 2.2. General procedure for the preparation of the palladium–carbene complex, **2, 3**

A stirred DMSO solution (10 mL) of 1,3-bis(alkyl)imidazolidinium and benzimidazolinium chloride (2 mmol) and Pd(OAc)<sub>2</sub> (1 mmol) was heated 60 °C for 3 h and then at 110 °C for a further 2 h, during which time the reaction solution from being initially orange. The remaining DMSO was then removed in vacuo to give a pale yellow solids, **2, 3**. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O. The crystals were filtered, washed with diethyl ether (3 × 10 mL) and dried under vacuum.

### 2.3. PdCl<sub>2</sub>[CN{CH<sub>2</sub>C<sub>6</sub>H<sub>2</sub>(OMe)<sub>3</sub>-3,4,5}CH<sub>2</sub>CH<sub>2</sub>N}{CH<sub>2</sub>C<sub>6</sub>H<sub>2</sub>(OMe)<sub>3</sub>-3,4,5}]} (**2a**)

Yield 0.92 g (89%) <sup>1</sup>H NMR (δ, CDCl<sub>3</sub>): 3.32 [s, 8H, NCH<sub>2</sub>CH<sub>2</sub>N]; 6.76 [s, 8H, CH<sub>2</sub>C<sub>6</sub>H<sub>2</sub>(OMe)<sub>3</sub>-3,4,5]; 5.11 [s, 8H, CH<sub>2</sub>C<sub>6</sub>H<sub>2</sub>(OMe)<sub>3</sub>-3,4,5]; 3.74 and 3.76 [s, 36H, CH<sub>2</sub>C<sub>6</sub>H<sub>2</sub>(OMe)<sub>3</sub>-3,4,5]. <sup>13</sup>C {H} NMR (δ, CDCl<sub>3</sub>): 199.1 [C<sub>carb.</sub>]; 48.5 [NCH<sub>2</sub>CH<sub>2</sub>N]; 106.7, 132.8, 138.7 and 154.7 [CH<sub>2</sub>C<sub>6</sub>H<sub>2</sub>(OMe)<sub>3</sub>-3,4,5]; 54.9 [CH<sub>2</sub>C<sub>6</sub>H<sub>2</sub>(OMe)<sub>3</sub>-3,4,5]; 57.1 and 61.5 [CH<sub>2</sub>C<sub>6</sub>H<sub>2</sub>(OMe)<sub>3</sub>-3,4,5]. Anal. cal. for C<sub>46</sub>H<sub>60</sub>N<sub>4</sub>O<sub>12</sub>PdCl<sub>2</sub>; C: 53.21, H: 5.82, N: 5.39; found C: 53.27, H: 5.79, N: 5.44. ν(NCN) = 1463 cm<sup>-1</sup>.

### 2.4. PdCl<sub>2</sub>[CN{CH<sub>2</sub>C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>-2,4,6}CH<sub>2</sub>CH<sub>2</sub>N}{CH<sub>2</sub>C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>-2,4,6}]} (**2b**)

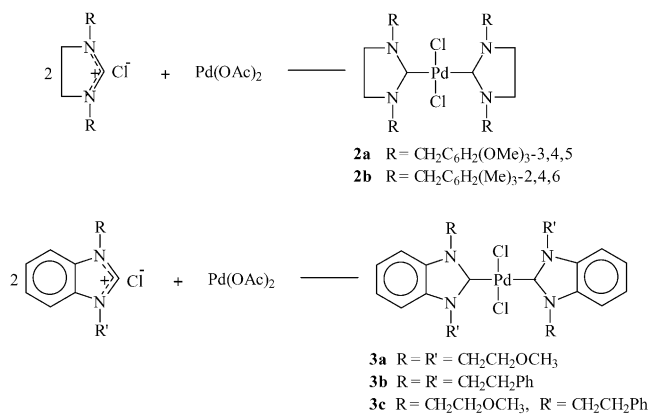
Yield 0.70 g (83%) <sup>1</sup>H NMR (δ, CDCl<sub>3</sub>): 2.99 [s, 8H, NCH<sub>2</sub>CH<sub>2</sub>N]; 6.76 [s, 8H, CH<sub>2</sub>C<sub>6</sub>H<sub>2</sub>(Me)<sub>3</sub>-2,4,6]; 5.33 [s, 8H, CH<sub>2</sub>C<sub>6</sub>H<sub>2</sub>(Me)<sub>3</sub>-2,4,6]; 2.16 and 2.38 [s, 36H, CH<sub>2</sub>C<sub>6</sub>H<sub>2</sub>(Me)<sub>3</sub>-2,4,6]. <sup>13</sup>C {H} NMR (δ, CDCl<sub>3</sub>): 198.9 [C<sub>carb.</sub>]; 47.5 [NCH<sub>2</sub>CH<sub>2</sub>N]; 129.3, 129.6, 137.9 and 138.8 [CH<sub>2</sub>C<sub>6</sub>H<sub>2</sub>(Me)<sub>3</sub>-2,4,6]; 48.8 [CH<sub>2</sub>C<sub>6</sub>H<sub>2</sub>(Me)<sub>3</sub>-2,4,6]; 21.2 and 21.3 [CH<sub>2</sub>C<sub>6</sub>H<sub>2</sub>(Me)<sub>3</sub>-2,4,6]. Anal. cal. for C<sub>46</sub>H<sub>60</sub>N<sub>4</sub>PdCl<sub>2</sub>; C: 65.28, H: 7.14, N: 6.62; found C: 65.33, H: 7.16, N: 6.67. ν(NCN) = 1448 cm<sup>-1</sup>.

### 2.5. PdCl<sub>2</sub>[CN{CH<sub>2</sub>CH<sub>2</sub>OMe}C<sub>6</sub>H<sub>4</sub>N}{CH<sub>2</sub>CH<sub>2</sub>OMe}]} (**3a**)

Yield 0.49 g (76%) <sup>1</sup>H NMR (δ, CDCl<sub>3</sub>): 7.30 and 7.56 [m, 8H, NC<sub>6</sub>H<sub>4</sub>N]; 4.22 [t, J 5.9 Hz, 8H, NCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>]; 5.06 [t, J 5.9 Hz, 8H, NCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>]; 3.41 [s, 12H, NCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>]. <sup>13</sup>C {H} NMR (δ, CDCl<sub>3</sub>): 183.4 [C<sub>carb.</sub>]; 112.1, 124.1 and 136.2 [NC<sub>6</sub>H<sub>4</sub>N]; 48.8 [NCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>]; 72.8 [NCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>]; 59.9 [NCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>]. Anal. cal. for C<sub>26</sub>H<sub>36</sub>N<sub>4</sub>O<sub>4</sub>PdCl<sub>2</sub>; C: 48.35, H: 5.62, N: 8.67; found C: 48.37, H: 5.65, N: 8.70. ν(NCN) = 1477 cm<sup>-1</sup>.

### 2.6. PdCl<sub>2</sub>[CN{CH<sub>2</sub>CH<sub>2</sub>Ph}C<sub>6</sub>H<sub>4</sub>N}{CH<sub>2</sub>CH<sub>2</sub>Ph}]} (**3b**)

Yield 0.70 g (85%) <sup>1</sup>H NMR (δ, CDCl<sub>3</sub>): 7.08 and 7.19 [m, 8H, NC<sub>6</sub>H<sub>4</sub>N]; 3.50 [dd, J 6.78 Hz, 8H,



Scheme 2.

NCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]; 5.05 [dd, J 6.78 Hz, 8H, NCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]; 6.94 [m, 20H, NCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]. <sup>13</sup>C {H} NMR (δ, CDCl<sub>3</sub>): 182.7 [C<sub>carb.</sub>]; 111.3, 123.7, 135.4 and 135.5 [NC<sub>6</sub>H<sub>4</sub>N]; 37.01 [NCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]; 50.4 [NCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]; 123.6, 127.8, 129.7, 130.1, 139.7 and 148.0 [NCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]. Anal. cal. for C<sub>46</sub>H<sub>44</sub>N<sub>4</sub>PdCl<sub>2</sub>; C: 66.55, H: 5.34, N: 6.75; found C: 66.53, H: 5.36, N: 6.73. ν(NCN) = 1477 cm<sup>-1</sup>.

### 2.7. PdCl<sub>2</sub>[CN{CH<sub>2</sub>CH<sub>2</sub>OMe}C<sub>6</sub>H<sub>4</sub>N}{CH<sub>2</sub>CH<sub>2</sub>Ph}]} (**3c**)

Yield 0.64 g (87%) <sup>1</sup>H NMR (δ, CDCl<sub>3</sub>): 7.23 and 7.47 [m, 8H, NC<sub>6</sub>H<sub>4</sub>N]; 3.95 [m, 4H, NCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>]; 4.98 [m, 8H, NCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub> and NCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]; 3.18 [s, 6H, NCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>]; 3.44 [m, 4H, NCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]; 7.1 [m, 10H, NCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]. <sup>13</sup>C {H} NMR (δ, CDCl<sub>3</sub>): 187.6 [C<sub>carb.</sub>]; 116.9, 117.3, 128.8, 134.5, 134.6 and 134.8 [NC<sub>6</sub>H<sub>4</sub>N]; 54.8 [NCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>]; 77.31 [NCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>]; 64.6 [NCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>]; 41.5 [NCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]; 67.4 [NCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]; 115.9, 132.6, 134.6, 140.07, 144.2 and 144.4 [NCH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]. Anal. cal. for C<sub>36</sub>H<sub>40</sub>N<sub>4</sub>O<sub>2</sub>PdCl<sub>2</sub>; C: 58.58, H: 5.46, N: 7.59; found C: 58.62, H: 5.40, N: 7.63. ν(NCN) = 1475 cm<sup>-1</sup>.

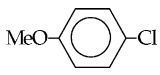
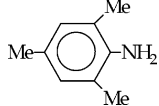
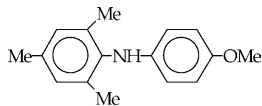
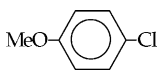
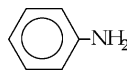
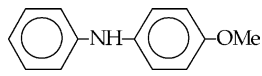
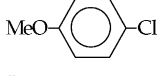
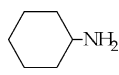
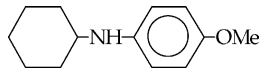
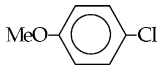
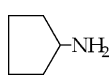
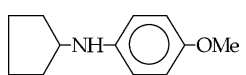
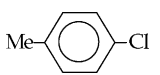
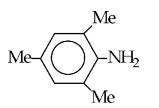
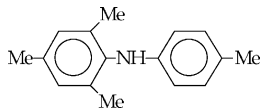
## 2.8. General procedure for amination of aryl chlorides

A mixture of aryl chlorides (1 mmol), KO<sup>t</sup>Bu (1.2 mmol) and primary amines (1.2 mmol), palladium carbene (1 mmol%) in 1-methyl-3-butyl-imidazolidinium tetrafluoroborate (1.5 mL) was stirred at 50 °C for 4 h. After

Table 1  
Selected analytical data for the new palladium–carbene complexes (**2,3**)

Complex	Isolated yield (%)	mp (°C)	ν(NCN) (cm <sup>-1</sup> )	<sup>13</sup> C NMR Pd–C <sub>carb.</sub> δ (ppm)
<b>2a</b>	89	222.0–222.5	1463	199.1
<b>2b</b>	83	299.5–300.0	1448	198.9
<b>3a</b>	76	229.0–229.5	1477	183.4
<b>3b</b>	85	295.0–295.5	1478	182.7
<b>3c</b>	87	250.0–251.0	1475	187.6

Table 2  
Amination of aryl chlorides with palladium–carbene complexes<sup>a</sup>

Entry	Catalyst	Arylchlorides	Amines	Products	Yield (%) <sup>bc</sup>
1	<b>2a</b>				94
2	<b>2b</b>	"	"	"	91
3	<b>3a</b>	"	"	"	95
4	<b>3b</b>	"	"	"	90
5	<b>3c</b>	"	"	"	91
6	<b>2b</b>				83
7	<b>3a</b>	"	"	"	89
8	<b>3b</b>	"	"	"	92
9	<b>3c</b>	"	"	"	79
10	<b>2a</b>				94
11	<b>3a</b>	"	"	"	89
12	<b>3b</b>	"	"	"	87
13	<b>3c</b>	"	"	"	84
14	<b>2a</b>				92
15	<b>2b</b>	"	"	"	94
16	<b>3a</b>	"	"	"	89
17	<b>3b</b>	"	"	"	83
18	<b>3c</b>	"	"	"	86
19	<b>2a</b>				86
20	<b>2b</b>	"	"	"	76
21	<b>3b</b>	"	"	"	74

<sup>a</sup> Reaction conditions: 1.0 mmol of *p*-R-C<sub>6</sub>H<sub>4</sub>Cl, 1.2 mmol of primary amines, 1.2 mmol KO<sup>t</sup>Bu, 1 mol% Pd catalyst, ionic liquid (1.5 mL).

<sup>b</sup> Isolated yield (purity of yield checked by NMR).

<sup>c</sup> All reactions were monitored by TLC.

completion of reaction as indicated by TLC, the reaction mixture was washed with Et<sub>2</sub>O (3 × 15 mL). The combined ether extracts were concentrated in vacuo and resulting product was directly charged onto a small silica gel column and eluted with a mixture of ethyl acetate: *n*-hexane (1:10) to afford pure arylamine. The ionic liquid is extracted with methylene dichloride and dried under vacuum to eliminate traces of the solvent and the rest of viscous ionic liquid was thoroughly washed with ether and reused in subsequent reactions without further purification.

### 3. Results and discussion

The 1,3-bis(alkyl)imidazolidinium and benzimidazolium chlorides was prepared according to known methods. The reaction of azolium salts, with the Pd(OAc)<sub>2</sub> complex proceeded smoothly as shown in Scheme 1, during which time the reaction give the PdCl<sub>2</sub>(1,3-dialkyl-imidazolinyli-dene)<sub>2</sub>, **2**, or PdCl<sub>2</sub>(1,3-

dialkyl-benzimidazolinyli-dene)<sub>2</sub>, complexes **3** as crystalline solids in 76–89% yields (Scheme 2, Table 1).

Complexes **2**, **3**, which are very stable in the solid state have been characterized by analytical and spectroscopic techniques (Table 1). Palladium complexes exhibit a characteristic ν(NCN) band (Table 1) typically at 1448–1477 cm<sup>-1</sup> [7,8,11]. <sup>13</sup>C chemical shifts, which provide a useful diagnostic tool for metal carbene complexes, show that C<sub>carb</sub> is substantially deshielded. Values of δ(<sup>13</sup>C<sub>carb</sub>) are in the range 182–199 ppm and are similar to those found in other carbene complexes. These new complexes show typical spectroscopic signatures which are in line with those recently reported for other PdCl<sub>2</sub>(*N*-heterocyclic carbene)<sub>2</sub> complexes [24].

Recently, we have developed improved procedures Heck and Suzuki reactions of aryl chlorides making use of novel ligands 1,3-bis(2,4,6-trimethylbenzyl)imidazolium chloride [22], 1-alkylimidazoline, α-bis(imine) [25].

There is growing interest in room temperature ionic liquids as potential green solvents for a broad variety of solutes, ranging from weakly polar to polar ones. The melting points

of ionic compounds depend on the nature of the cations and anions involved, with packing inefficiency being conducive to lower melting points. As a result, certain cations, such as the imidazolium and *N,N'*-dialkylimidazolium cations have been extensively studied [18,19].

The 1-butyl-3-methyl-4,5-dihydroimidazolium tetrafluoroborate (**1**) is liquid at room temperature. We report here the amination of chloroarenes reaction performed in ionic liquid, **1**, in the presence of palladium–carbene complexes.

The coupling of activated and deactivated aryl halogenides and primary amines proceeds in high yields and quite rapidly even with a low catalyst loading. The treatment of 2,4,6-trimethylaniline with *p*-chloroanisole in 1-methyl-3-butyl-imidazolium tetrafluoroborate, **1**, ionic liquid resulted in the formation of (*p*-methoxyphenyl)(2,4,6-trimethylphenyl)amine in 94% yield. As shown in Table 2 primary cyclic aliphatic and aromatic amines can be coupled to a variety of aryl chlorides. In general, good to excellent yields are obtained in the presence of 1 mol% of palladium–carbene complexes (**2** or **3**) in ionic liquid at 50 °C. This method is even effective with sterically hindered amine (Table 2, entry 1, 3, and 19). The experimental procedure is very simple and convenient and in addition, this method did not require any aqueous work-up thereby avoiding the generation of toxic waste. Lately, non-aqueous ionic liquids have been attracting attention for the application of many homogeneous reactions to biphasic systems. Therefore the imidazolium cation are largely the most widely investigated [18]. We think that palladium–carbene complexes dissociated in reaction medium giving rise to the reaction with 1-butyl-3-methyl-4,5-dihydroimidazolium tetrafluoroborate with KO<sup>t</sup>Bu and new formed carbene. And thus carbene reacted with the dissociated palladium and could form novel carbene complexes [26]. Since the products were weakly soluble in the ionic liquid, they were easily separated by simple extraction with ether. The rest of the viscous ionic liquid was thoroughly washed with ether and recycled in subsequent reactions. Second and third reactions using recovered ionic liquid afforded similar yields to those obtained in the first run.

#### 4. Conclusion

We report the synthesis and aryl amination reactivity of an air stable *N*-heterocyclic-palladium complexes (**2**, **3**). Non-activated aryl chlorides react with sterically hindered amines in very good yields to give corresponding anilines. Also ionic liquid is proved to be a useful and novel reaction media for aromatic amination, avoiding the use of highly polar organic solvents such as DMSO or DMF and high temperature reaction conditions playing the dual role of solvent and promoter. The use of an easily accessible and recyclable ionic liquid makes this procedure convenient, economic and user friendly. Investigations focusing on the reactivity profile of **2** or **3** and related palladium complexes, their efficacy as catalysts in cross-coupling reactions are ongoing in our laboratories.

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