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# Synthesis and characterization of bidentate NHC–Pd complexes and their role in amination reactions

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#### ABSTRACT

The new well-defined and air-stable *ortho*-xylyl-linked *N*-heterocyclic carbene (NHC) Pd complexes (**2a-d**) have been synthesized and characterized by elemental analysis, <sup>1</sup>H NMR, <sup>13</sup>C NMR, IR spectroscopy, and single crystal X-ray diffraction studies. The palladium atom in the complex **2a** lies on a crystallographic mirror plane and can be described as having a square-planar coordination environment with the carbene atoms of the benzimidazole rings of the ligand occupying two coordination sites in *cis* positions. Two further coordination sites are occupied by chloride ligands. The benzimidazole rings are connected to each other by an *ortho*-xylyl bridge. The catalytic activity of these palladium complexes has been tested in the coupling reactions of various *N*-containing substrates with bromobenzene. A preliminary catalytic study shows that the *bis*(NHC)–Pd complexes are highly active in the Buchwald– Hartwig amination reaction.

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#### 1. Introduction

Since Arduengo's report on stable imidazol-2-ylidenes [1], the first use by Herrmann and co-workers of N-heterocyclic carbene complexes in catalysis [2] and the preparation of the Grubbs' second generation catalyst and related catalysts [3], there has been a growing interest in the use of these NHC ligands as supporting ligands in both organometallic chemistry and homogeneous catalysis [4]. The NHCs have gained great popularity as they are, in most cases, better  $\sigma$ -donors than phosphines and in general possess higher thermal stability, and the use of NHC as a supporting ligand usually leads to better complex stability [5]. This is especially true in the area of palladium-mediated cross-coupling reactions. NHC-containing Pd-catalysts [6] have proven to be an excellent alternative to catalytic systems involving tertiary phosphines [7]. Cross-coupling reactions catalyzed by palladium species are increasingly important for the formation of C-Y bonds (Y = C, O and N) [8]. During the last decade, efficient catalytic C-N bond forming methods have been developed, for example palladium catalyzed amination of aryl halides [9], hydroamination [10] and hydroaminomethylation of olefins or alkynes [11]. Bidentate ligands containing NHCs have found widespread applications [12]. It is expected that when the NHC orientation is perturbed in space, the catalytic activity of the linked metal site should be greatly modified. This influence leads to the design of new chelating NHC complexes. Examples of *bis*-NHC carbenes [13], mixed pyridine-carbene [14] and oxazoline-carbene [15] complexes have already been reported. Theoretical calculations indicated that certain bidentate chelating ligands could favor the oxidative-addition process [16] and improve the stability of the catalyst, which may exclude the side pathway of  $\beta$ -H elimination.

We are interested in bidentate NHC ligands based on *ortho*xylyl-linked azolium systems [17]. In this article, some of the benzimidazolium salts that are precursors to these NHC ligands are readily synthesized [17d] and the subsequent formation of mononuclear complexes of Pd(II) has proved facile. The reaction of the NHC precursors with Pd(OAc)<sub>2</sub> in DMSO afforded the *bis*(NHC)-Pd complexes. All the synthesized compounds were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, IR and elemental analysis techniques, which support the proposed structures. The molecular and crystal structure of the *cis*-dichloro{1,1'-di[2,3,4,5,6-pentamethylbenzyl]-3,3'-o-xylyldibenzimidazol-2,2'-diylidene} palladium(II) complex was determined by the single crystal X-ray diffraction technique. In addition, we examined the activity of the synthesized palladium complexes in the Buchwald–Hartwig amination of various *N*-containing substrates with bromobenzene in this study.



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#### 2. Results and discussion

#### 2.1. Synthesis and characterization of bis(NHC)-Pd complexes

The NHC precursors were prepared by established procedures [17d]. The reaction of *ortho*-xylyl-linked *bis*(benzimidazolium) chloride with  $Pd(OAc)_2$  in DMSO, according to Scheme 1, led to the formation of the desired mononuclear complexes of Pd(II) in 68–82% yield. The crude product was recrystallized from a dichloromethane:diethyl ether mixture (1:2) at room temperature, which afforded the corresponding crystals. The new complexes were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, IR and elemental analysis techniques, which support the proposed structures.

The air and moisture-stable palladium–carbene complexes (**2a–d**) were soluble in halogenated solvents and insoluble in non-polar solvents. The palladium complexes exhibit a characteristic  $v_{(NCN)}$  band, typically at 1394–1413 cm<sup>-1</sup>. The formation of the Pd–NHC complexes was confirmed by the absence of the <sup>1</sup>H NMR resonance signal of the acidic benzimidazolium C2–H. The <sup>13</sup>C NMR spectra of the *bis*(NHC)–Pd complexes exhibit a resonance signal in the 173.5–175.7 ppm range ascribed to the carbenic carbon atom, which is consistent with reported values for Pd–NHC complexes. The <sup>13</sup>C chemical shifts of known Pd–NHC complexes appear in the range 182.4–149.5 ppm, depending upon the ancillary ligands [18].

#### 2.2. X-ray diffraction studies

A crystal of **2a** suitable for X-ray single crystal diffraction analysis was obtained from a chloroform solution layered with diethyl ether. The crystal and molecular structure of complex **2a** has been confirmed by X-ray single crystal diffractometry. The molecular structure of complex **2a**, with the atom-numbering scheme, is shown in Fig. 1 [19].

The complex crystallizes in the *orthorhombic*, space group *Cmca* (Z = 8). The palladium atom in the title compound lies on a crystallographic mirror plane and is coordinated by the two carbene atoms of the benzimidazole rings and two chlorine atoms. The structure of **2a** shows a minor distortion from an ideal square planar geometry (Fig. 1). The palladium atom is displaced slightly at a distance of 0.040(1) Å from the coordination plane defined by the atoms Cl1, Cl1A, C1, and C1A.

In the compound, the two benzimidazole units are linked by an *ortho*-xylyl bridge. So, the formation of a 9-membered chelate ring imposes distortion around the palladium atom. Both carbene atoms and chlorine atoms are *cis* to each other, with C1–Pd1–C1A and Cl1–Pd1–C1A angles of 94.7(4) and 91.46(9)°, respectively. The Cl1–Pd1–Cl1A and  $C_{carben}$ –Pd– $C_{carben}$  angles are larger than the expected value of 90°. This distorted square planar geometry is typical of this class of compounds with a *cis* substitution pattern around the central palladium atom [20].



Scheme 1. Synthesis of o-xylyl linked palladium(II) N-heterocyclic carbene complexes.



**Fig. 1.** ORTEP drawing of complex **2a**. Displacement ellipsoids are drawn at the 50% probability level.

 Table 1

 Selected bond lengths (Å) and angles (°) of the Pd complex.

Bond lengths (Å)			
Pd(1)-C(1)	1.979(7)	N(2)-C(7)	1.418(10)
Pd(1)-Cl(1)	2.3390(19)	N(2)-C(8)	1.488(9)
N(1)-C(1)	1.331(9)	C(2)-C(7)	1.343(11)
N(1)-C(2)	1.380(10)	C(8)-C(9)	1.463(11)
N(1)-C(20)	1.500(10)	C(20)-C(21)	1.496(11)
N(2)-C(1)	1.379(10)		
Bond angles (°)			
C(1)A-Pd(1)-C(1)	94.7(4)	C(1)-N(2)-C(8)	122.5(6)
C(1)A-Pd(1)-Cl(1)	86.9(2)	C(7)-N(2)-C(8)	129.8(6)
C(1) - Pd(1) - Cl(1)	177.3(2)	N(1)-C(1)-N(2)	106.5(6)
Cl(1)A-Pd(1)-Cl(1)	91.46(9)	N(1)-C(1)-Pd(1)	127.5(6)
C(1)-N(1)-C(2)	111.2(7)	N(2)-C(1)-Pd(1)	125.8(5)
C(1)-N(1)-C(20)	122.9(6)	C(9)-C(8)-N(2)	114.3(6)
C(2)-N(1)-C(20)	124.7(6)	C(21)-C(20)-N(1)	114.0(6)
C(1)-N(2)-C(7)	107.7(6)		

In a series of related palladium carbene complexes, the corresponding Pd–C<sub>carben</sub> bond length values are 1.983(5) and 1.971(5) Å in [21], 1.990(3) and 1.978(4) Å in [20], and 1.993(2) and 1.971(2) Å in [22], following a similar trend to those in complex **2a**. However, the Pd–C<sub>carben</sub> distances are slightly shorter than other Pd–C<sub>carben</sub> single bond distances (2.036(5) Å in [23], 2.037(1) Å in [24], 2.067(10) Å in [25], 2.016(5) Å in [26], and 2.035(2) Å in [27]). The molecular structure and selected geometrical parameters of the palladium complex are presented in Fig. 1 and Table 1, respectively.

The benzimidazole ring is almost planar and the maximum deviations from planarity are 0.039(6) Å for the atom N1 and, 0.038(8) Å for the atom C1. The dihedral angle of the two benzimidazole moieties is  $71.54(6)^{\circ}$ . In addition, the benzimidazole moiety forms dihedral angles of  $87.5(3)^{\circ}$  and  $55.8(4)^{\circ}$  with the mean planes through the 2,3,4,5,6-pentamethylbenzyl and 1,2-phenylene rings, respectively.

The crystal structure of **2a** is stabilized by intermolecular C–H···Cl hydrogen bonds which link the molecules into a threedimensional molecular network (C4–H4···Cl1<sup>*i*</sup>: C4–H4 0.96 Å, H4–Cl1 2.76 Å, C4···Cl1 3.691(10) Å, C4–H4···Cl1 164°; Symmetry code (i): 1/2 + x, 3/2 - y, 1 - z).

### 2.3. Catalytic applications of Pd(NHC) complexes (**2a–2d**) in amination reactions

Among cross-coupling reactions, N-aryl amination has emerged as a practical and popular method for the formation of C-N bonds [28]. Since pioneering work, notably by Buchwald and Hartwig [29], palladium catalyzed N-aryl amination has gathered increasing interest, especially because this reaction has filled the deficiencies of classic organic methodology in this area [30]. Therefore, having new bis-NHC containing palladium complexes on hand, we initiated a study focusing on their catalytic activity for aryl amination using bromobenzene and various anilines or amines. The target product was obtained in not more than 20% yield when K<sub>2</sub>CO<sub>3</sub> and Cs<sub>2</sub>CO<sub>3</sub> were used as bases. However, the reactions could be dramatically improved in the presence of KOBu<sup>t</sup> as a base under the same conditions. It was observed that dimethoxyethane (DME) was effective in providing higher conversions, whereas solvents like NMP, toluene, DMF, dioxane showed lower conversions. The effect of temperature on the coupling of aniline with bromobenzene was studied. It was observed that the reaction was very slow at 50 °C but an increase in the temperature to 80 °C significantly improved the conversion. No further increase in the yield of the amination product was observed even when the reaction time was increased. With these optimized conditions in hand, we continued our investigation of the amination reactions of other substrates. The results are summarized in Table 2. We have demonstrated conditions for higher yields of the Pd-NHC catalyzed amination of aniline, p-methoxyaniline and p-methylaniline to triarylamines (Table 2, entries 3, 8, and 12). With p-methoxyaniline and *p*-methylaniline, containing electron donating groups at the *para* position, the amination reaction proceeds with a considerable increase in the yield, up to 77-95% (Table 2, entries 5-12). When no catalyst was added, the blank reaction with the solvent DME and KO<sup>t</sup>Bu as a base exhibited extremely low reactivity towards the yield of the triarylamine, with many byproducts from the aryl halide substrate. We also examined the amination of bromobenzene (1.2 mmol) with cycloheptyl amine, cyclohexylamine, cyclopentylamine, morpholine and 2-aminopyridine (1 mmol) under the same reaction conditions. As shown in Table 2, moderate to good yields were obtained (entries 13, 15, 18, 22, 25, 26, 27, and 32). With piperazine (1 mmol) and bromobenzene (2.4 mmol), the amination reaction proceeds with a considerable increase in the yield, up to 61-79% (Table 2, entries 33-36). We observed that the influence of the alkyl on the N atom of the palladium complex is not important.

#### 3. Experimental

#### 3.1. General considerations

The syntheses were carried out by using standard Schlenk techniques under an inert argon atmosphere with previously dried solvents. <sup>1</sup>H and <sup>13</sup>C NMR were performed in CDCl<sub>3</sub> or DMSO-d<sub>6</sub>. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded using a Varian As 400 Merkur spectrometer operating at 400 MHz (<sup>1</sup>H), 100 MHz (<sup>13</sup>C). Chemical shifts ( $\delta$ ) are given in ppm relative to TMS, coupling constants (*J*) in Hz. Infrared spectra were recorded as KBr pellets in the range 400–4000 cm<sup>-1</sup> on an ATI UNICAM 1000 spectrometer. Melting points were measured in open capillary tubes with an Electrothermal-9200 melting point apparatus and are uncorrected. Elemental analyses were performed by the Turkish Research Council (Ankara, Turkey) Microlab. Single crystal X-ray data were collected on a Rigaku AFC8S Mercury CCD diffractometer [31] using monochromated Mo K $\alpha$  radiation. The structure was solved by direct and conventional Fourier methods [32]. Full-matrix

#### Table 2

Buchwald-Hartwig amination reaction using o-xylyl-linked NHC-Pd complexes.



Reaction conditions: catalyst (**2a-d**) (0.01 mmol), KOBu<sup>t</sup> (1.5 mmol), aniline (1 mmol), bromobenzene (2.4 mmol) (entries 1–12 and 33–36); 1.2 mmol (entries 13–32), DME (2 mL), 80 °C-15 h. Yields are based on anilines. All reactions were monitored by TLC and GC.

#### Table 3

Crystal data and structure refinement for complex **2a**.

Empirical formula	$C_{46}H_{50}Cl_2N_4Pd$	
Formula weight	836.20	
Temperature (K)	158(2)	
Wavelength (Å)	0.71073	
Crystal system, space group	orthorhombic, Cmca	
Unit cell dimensions		
a (Å)	18.741(4)	
b (Å)	18.476(4)	
<i>c</i> (Å)	29.049(6)	
α (°)	90	
β (°)	90	
γ (°)	90	
Volume (Å <sup>3</sup> )	10058(3)	
Z, $D_{\text{calc}}$ (mg/m <sup>3</sup> )	8, 1.104	
Absorption coefficient $(mm^{-1})$	0.505	
F(0 0 0)	3472	
Crystal size (mm)	$0.26\times0.05\times0.05$	
$\theta$ Range for data collection (°)	2.59-25.60	
Limiting indices	$-20 \le h \le 22$	
	$-12 \le k \le 22$	
	$-35 \le l \le 33$	
Reflections collected/unique	$22953/4873 [R_{int} = 0.1152]$	
Completeness to $\theta$ = 25.60	99.7%	
Absorption correction	REQAB (multi-scan)	
Maximum and minimum transmission	0.9752 and 0.8798	
Refinement method	Full-matrix least-squares on $F^2$	
Data/restraints/parameters	4873/0/246	
Goodness-of-fit on F <sup>2</sup>	0.983	
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0896, wR_2 = 0.2275$	
R indices (all data)	$R_1 = 0.1340, wR_2 = 0.2562$	
Largest difference in peak and hole, (e $Å^{-3}$ )	1.713 and -0.758	

least-squares refinement was based on  $F^2$  [32]. Apart from hydrogen, all atoms were refined anisotropically; hydrogen atom coordinates were calculated at idealized positions and refined using a riding model. Further details concerning data collection and refinement are given in Table 3. All catalytic reactions were monitored on an Agilent 6890 N 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).

# 3.2. General procedure for the preparation of palladium complexes (**2a-2d**)

About 1.0 mmol of bisbenzimidazolium salt (1) and  $Pd(OAc)_2$  (0.22 g, 1.0 mmol) were dissolved in 5 mL DMSO and stirred at room temperature for 5 h. Afterwards the mixture was heated for 5 h at 50 °C, then for 2 h at 90 °C and then for 1 h 120 °C. The volatile compounds were removed *in vacuo* and the precipitate was washed twice with 5 mL THF. The complexes were recrystallized from dichloromethane:diethylether (1:2 ratio) at room temperature (Scheme 1).

# 3.2.1. Dichloro{1,1'-[di-2,3,4,5,6-pentamethylbenzyl]-3,3'-o-xylyldibenzimidazolidin-2,2'-diylidene}palladium (II), **2a**

Yield: 0.57 g (68%). M.p.: 282–283 °C,  $\nu_{(CN)}$ : 1394 cm<sup>-1</sup>. <sup>1</sup>H NMR (399.9 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 8.09–8.14, 7.36–7.48, 7.17–7.22, 8.82–6.90, and 6.55–6.62 [m, 12H, NC<sub>6</sub>H<sub>4</sub>N and –CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>–], 5.96–6.15, 5.69–5.82, and 5.45–5.60 [m, 8H, CH<sub>2</sub>C<sub>6</sub>(CH<sub>3</sub>)<sub>5</sub>–2,3,4,5,6 and –CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>–], 2.25, 2.24, 2.17, 2.14, and 1.99 [s, 30H, CH<sub>2</sub>C<sub>6</sub>(CH<sub>3</sub>)<sub>5</sub>–2,3,4,5,6]. <sup>13</sup>C NMR (100.5 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 175.0 (C<sub>carbene</sub>), 136.1, 135.1, 134.3, and 132.9 [CH<sub>2</sub>C<sub>6</sub>(CH<sub>3</sub>)<sub>5</sub>–2,3,4,5,6], 134.8, 134.1, and 123.4 [–CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>–], 134.2, 133.9, 129.4, 127.5, 112.2, and 111.9 [NC<sub>6</sub>H<sub>4</sub>N], 54.7 [–CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>–], 52.4 [CH<sub>2</sub>C<sub>6</sub>(CH<sub>3</sub>)<sub>5</sub>–2,3,4,5,6], 17.8, 17.4, and 17.0 [CH<sub>2</sub>C<sub>6</sub>(CH<sub>3</sub>)<sub>5</sub>–2,3,4,5,6], Anal. Calc. for C<sub>46</sub>H<sub>50</sub>N<sub>4</sub>PdCl<sub>2</sub>: C, 66.07; H, 6.03; N, 6.70. Found: C, 66.11; H, 6.09; N, 6.74%.

### 3.2.2. Dichloro{1,1'-[di-2,3,5,6-tetramethylbenzyl]-3,3'-o-xylyldibenzimidazolidin-2,2'-diylidene}palladium (II), **2b**

Yield: 0.59 g (73%). M.p.: 287–288 °C,  $\nu_{(CN)}$ : 1400 cm<sup>-1</sup>. <sup>1</sup>H NMR (399.9 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.97–8.01 [m, 2H, –CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>–], 7.45–7.48 [m, 2H, –CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>–], 7.89 [d, 2H, *J* = 8.1 Hz, NC<sub>6</sub>H<sub>4</sub>N], 7.49–7.61 and 7.21–7.28 [m, 4H, NC<sub>6</sub>H<sub>4</sub>N], 7.08 [s, 2H, CH<sub>2</sub>C<sub>6</sub>H(CH<sub>3</sub>)<sub>4</sub>–2.3,5,6], 6.87 [t, 2H, *J* = 8.1 Hz, NC<sub>6</sub>H<sub>4</sub>N], 6.78, 6.73, 6.10, 6.07, 6.05, 5.61, and 5.56 [s, 8H, CH<sub>2</sub>C<sub>6</sub>H(CH<sub>3</sub>)<sub>4</sub>–2.3,5,6] and –CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>–], 2.23 and 2.10 [s, 24H, CH<sub>2</sub>C<sub>6</sub>H(CH<sub>3</sub>)<sub>4</sub>–2.3,5,6]. <sup>13</sup>C NMR (100.5 MHz, CDCl<sub>3</sub>)  $\delta$ : 175.7 (*C*<sub>carbene</sub>), 134.8, 134.6, 133.6, 132.9, 129.6, 129.4, 123.5, 123.1, 112.0, and 111.2 [CH<sub>2</sub>C<sub>6</sub>H(CH<sub>3</sub>)<sub>4</sub>–2.3,5,6], -CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>–, and CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>], 52.0 and 51.1 [–CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>– and CH<sub>2</sub>C<sub>6</sub>H(CH<sub>3</sub>)<sub>4</sub>–2.3,5,6], 20.6 and 16.5 [CH<sub>2</sub>C<sub>6</sub>H(CH<sub>3</sub>)<sub>4</sub>–2.3,5,6]. *Anal.* Calc. for C<sub>44</sub>H<sub>46</sub>N<sub>4</sub>PdCl<sub>2</sub>: C, 65.39; H, 5.74; N, 6.93. Found: C, 65.41; H, 5.70; N, 6.96%.

#### 3.2.3. Dichloro{1,1'-[dicyclohexylbenzyl]-3,3'-o-

xylyldibenzimidazolidin-2,2'-diylidene}palladium (II), 2c

Yield: 0.58 g (82%). M.p.: 286–287 °C,  $v_{(CN)}$ : 1407 cm<sup>-1</sup>. <sup>1</sup>H NMR (399.9 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 8.23 [d, 2H, J = 8.1 Hz, NC<sub>6</sub>H<sub>4</sub>N], 8.13–8.16 [m, 2H, –CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>–], 7.45–7.42 [m, 2H, –CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>–], 7.73 [d, 2H, J = 7.8 Hz, NC<sub>6</sub>H<sub>4</sub>N], 7.39–7.28 [m, 4H, NC<sub>6</sub>H<sub>4</sub>N], 7.25, 7.21, 5.81, and 5.76 [s, 4H, –CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>–], 4.64–4.71 and 4.33–4.41 [m, 4H, CH<sub>2</sub>C<sub>6</sub>H<sub>11</sub>], 2.73–2.79 and 1.03–1.73 [m, 22H, CH<sub>2</sub>C<sub>6</sub>H<sub>11</sub>]. <sup>13</sup>C NMR (100.5 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 173.5 ( $C_{carbene}$ ), 135.3, 134.3, and 123.7 [–CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>–], 133.5, 129.6, and 112.5 [NC<sub>6</sub>H<sub>4</sub>N], 54.5 [–CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>–], 50.6 [CH<sub>2</sub>C<sub>6</sub>H<sub>11</sub>], 37.6, 30.9, 30.9, 26.2, 25.8, and 25.5 [CH<sub>2</sub>C<sub>6</sub>H<sub>11</sub>]. Anal. Calc. for C<sub>36</sub>H<sub>4</sub>2N<sub>4</sub>PdCl<sub>2</sub>: C, 61.07; H, 5.98; N, 7.91. Found: C, 61.11; H, 5.93; N, 7.85%.

## 3.2.4. Dichloro{1,1'-[di-(2-diizopropylaminoethyl)]-3,3'-o-xylyldibenzimidazolidin-2,2'-diylidene}palladium (II), **2d**

Yield: 0.60 g (78%). M.p.: 258–259 °C,  $v_{(CN)}$ : 1413 cm<sup>-1</sup>. <sup>1</sup>H NMR (399.9 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.97–8.01 [m, 2H,  $-CH_2C_6H_4CH_2$ –], 7.83–7.86 [m, 2H,  $NC_6H_4N$ ], 7.51–5.54 [m, 2H,  $-CH_2C_6H_4CH_2$ –], 7.28–7.48 [m, 6H,  $NC_6H_4N$ ], 5.41, 5.36, 5.27, and 4.32 [s, 4H,  $-CH_2C_6H_4CH_2$ –], 2.72–3.42 [m, 8H,  $CH_2CH_2NCH(CH_3)_2$ ], 0.76–1.45 [m, 28H,  $CH_2CH_2NCH(CH_3)_2$ ]. <sup>13</sup>C NMR (100.5 MHz, CDCl<sub>3</sub>)  $\delta$ : 174.6 ( $C_{carbene}$ ), 134.7, 134.3, and 123.6 [ $-CH_2C_6H_4CH_2$ –], 134.1, 129.7, and 111.8 [ $NC_6H_4N$ ], 52.0 [ $-CH_2C_6H_4CH_2$ –], 50.7 [ $CH_2CH_2NCH(CH_3)_2$ ], 49.3 [ $CH_2CH_2NCH(CH_3)_2$ ], 44.2 [ $CH_2CH_2NCH(CH_3)_2$ ], 21.0 [ $CH_2CH_2N-CH(CH_3)_2$ ], 40.3 [ $CH_2CH_2NCH(CH_3)_2$ ], 44.2 [ $CH_2CH_2NCH(CH_3)_2$ ], 21.0 [ $CH_2CH_2N-CH(CH_3)_2$ ]. Anal. Calc. for  $C_{38}H_{52}N_6PdCl_2$ : C, 59.26; H, 6.81; N, 10.91. Found: C, 59.30; H, 6.77; N, 10.95%.

#### 3.3. General procedure for the catalytic C–N bond formation

Under argon, 1.5 mmol of KO<sup>t</sup>Bu, 1 mol% of catalyst, 1 mmol aniline, 2.4 mmol bromobenzene (for diarylation) or 1.2 mmol bromobenzene (for monoarylation), and 2 mL dimethoxyethane (DME) 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, quenched by filtering through a short silica column (eluent: ethyl acetate) and then concentrated under reduced pressure. After purification by flash chromatography (eluent: ethyl acetate/hexane), the yield was calculated based on the aniline.

#### 4. Conclusion

We have prepared o-xylyl-linked palladium–NHC complexes (**2a–d**), whose structures were confirmed by <sup>1</sup>H NMR, <sup>13</sup>C NMR, IR and elemental analysis, and complex **2a** has been characterized by single crystal X-ray diffraction studies. These complexes are effective catalysts for palladium catalyzed C–N coupling reactions. The catalyst–KOBu<sup>t</sup>–DME system was found to be very efficient for

amination of bromobenzene with a variety of primary and secondary amines. Research in our lab is currently on-going to extend the coordination chemistry of functionalized NHCs to other transition metals, such as Ru, Rh, Ag, and Au, and to explore their potential applications in catalysis. In addition our further research will focus on the development of more efficient catalytic systems for aryl chlorides and various aryl bromides in this reaction.

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#### Appendix A. Supplementary data

CCDC 771186 contains the supplementary crystallographic data for complex **2a**. These data can be obtained free of charge via http:// www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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