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Palladium *N*-heterocyclic carbene complexes: Synthesis, characterization and catalytic properties in amination

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ABSTRACT

Transmetalation has proved to be a promising procedure to obtain NHC–metal complexes, which typically involves treatment of the imidazolium salt with Ag_2O to form the Ag–NHC complex, followed by transmetalation to a species such as $[PdCl_2(CH_3CN)_2]$ gave the palladium complex in which the *N*-heterocyclic carbene was bound to the metal center. New *bis*(NHC)–Pd complexes were synthesized and characterized by elemental analysis, ^1H NMR, ^{13}C NMR, and IR spectroscopy. The crystal and molecular structure of the *trans-dichlorobis{1-(2,3,5,6-tetramethylbenzyl)-3-(2,3,4,5,6-pentamethylbenzyl)imidazolidin-2-yliden}palladium(II)* complex was determined by single-crystal X-ray diffraction. The activity of the Pd(II) complexes in the coupling reaction of anilines or amines with bromobenzene was investigated. A preliminary catalytic study showed that these *bis*(NHC)–Pd complexes were highly active in the direct synthesis of triarylamines and secondary amines in a single step.

1. Introduction

The *N*-aryl amination (Buchwald–Hartwig reaction) has attracted enormous interest over the last 20 years and belongs nowadays to an indispensable set of cross-coupling reactions, which finds its application in all areas of organic chemistry, ranging from the laboratory bench, the synthesis of pharmaceutical fine chemicals and the production of bulk chemicals [1,2]. The most research groups are focused on the development of palladium complexes with newly designed ligand systems in order to improve their efficiency, scope, and applicability as catalyst [2]. Up to now, there have been several categories of ligands listed as the most frequently used: phosphine, palladacycle, metalcontaining bidentate phosphine, *N*-heterocyclic carbenes (NHCs) [3]. Nucleophilic *N*-heterocyclic carbenes(NHC) have emerged as a class of highly useful ligands in organometallic chemistry during the last 15 years [4]. Two main scientific achievements may have comprised the initial spur to this development: (i) the first use by Herrmann and coworkers of NHC complexes in catalysis [5] and (ii) the preparation of the Grubbs' second generation catalyst and related catalysts [6]. Among numerous successful applications of NHC ligands are highly efficient Pd catalyzed amination, Heck olefin arylation, and coupling reactions of arenes [7]. To perform a coupling reaction, two approaches are available to generate a catalytically active species. One approach employs a Pd(0) source combined with an ancillary ligand to generate the catalyst in situ [8] and the second uses a precatalyst, mostly Pd(II) complexes [9], which will be activated in the reaction mixture. We have been strongly interested in the efficiency of Pd–NHC complexes in the catalytic C–N coupling reaction. Here we decided to examine their efficiency in the *N*-arylation of anilines and amines to form triarylamines and secondary amines, respectively.

2. Results and discussion

2.1. Synthesis and characterization of Pd–NHC complexes

Transmetalation has proved to be a promising procedure to obtain NHC–metal complexes [10], which typically involves treatment of the imidazolium salt with Ag_2O to form the Ag–NHC complex, followed by transmetalation to a species such as $[PdCl_2(CH_3CN)_2]$ to give the Pd–NHC complex (Scheme 1). They were isolated as a pale yellow solid. 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 afforded the corresponding crystals. The six new complexes were characterized by ^1H NMR, ^{13} C NMR, IR and elemental analysis techniques which support the proposed structures. The products 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. Correspondingly, the ^{13}C

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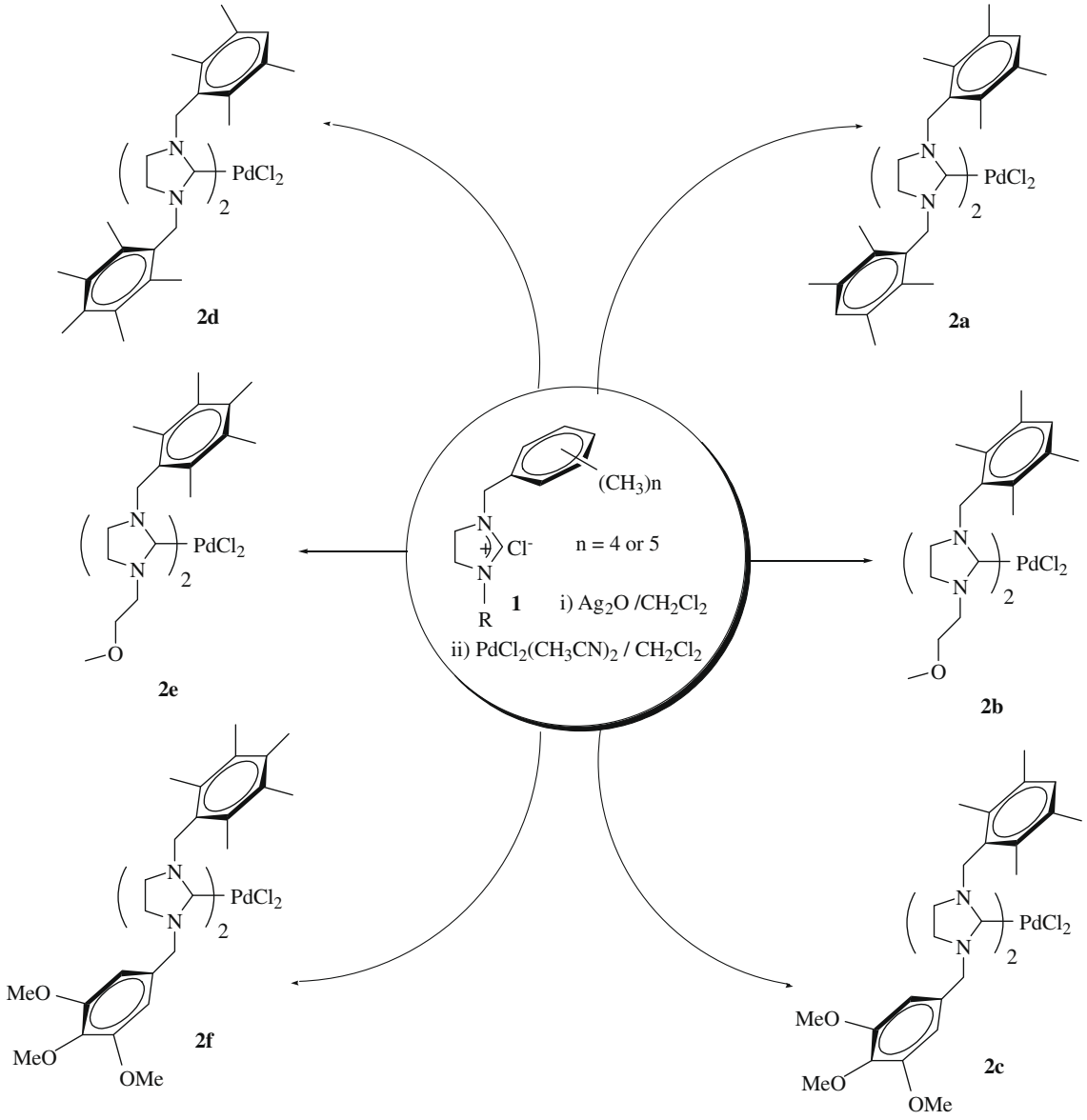


Scheme 1. Synthesis of NHC–Pd(II) complexes.

NMR spectrums show the characteristic coordinated carbene signals at δ ca. 198.2, 198.7, 197.9, 198.1, 198.6 and 197.8 ppm, respectively **2a–f**.

Crystal of **2d** suitable for X-ray analysis were obtained from a chloroform solution layered with diethyl ether. The molecular structure of complex (**2d)** has been confirmed by X-ray diffractometry. Its molecular structure is depicted in Fig. 1. The palladium center in complex is coordinated by two chloro ligands and two NHC ligands in a trans fashion. Molecular structure (30% probability level for the thermal ellipsoids) of **2d**.

Selected bond distances (Å) and angles (°): C1–N1 1.326 (7); C1–N2 1.334 (7); C1–Pd1 2.017 (6); Cl1–Pd1 2.3122 (17); Pd1–$Cl1^{i}$ 2.3122 (17); Pd1–$C1^{i}$ 2.017 (6); N1–C1–N2 108.7 (5); N2–C1–Pd1 124.0 (4); N1–C1–Pd1 127.4 (4); C1–Pd1–$C1^{i}$ 180.000 (2); C1–Pd1–$Cl1^{i}$ 88.66 (17); $C1^{i}$–Pd1–Cl1 88.66 (17); $Cl1^{i}$–Pd1–Cl1 180.000 (1).

2.2. Applications of Pd(NHC) complexes (*2a–f*) in amination reactions

As known, an efficient metal-catalyzed cross-coupling reaction is regulated by a number of factors such as base, solvent, temperature and reaction time [11]. The coupling of aniline with bromobenzene was selected as a model reaction.

The effect of various bases on the reaction system was studied. It was observed that inorganic bases like potassium carbonate and potassium phosphate were also effective, but gave lower conversions while the organic 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.

The effect of various solvents on the reaction system was studied. It was observed that dimethoxyethane (DME) was effective providing higher conversions whereas solvents like NMP, toluene, DMF, dioxane showed lower conversions.

Temperature effect on 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 improves the conversion. No further increase in the yield of the amination product was observed even when the reaction time was increased for a longer time.

Under the optimized conditions we set out to check the generality of the method by running test reactions with differently

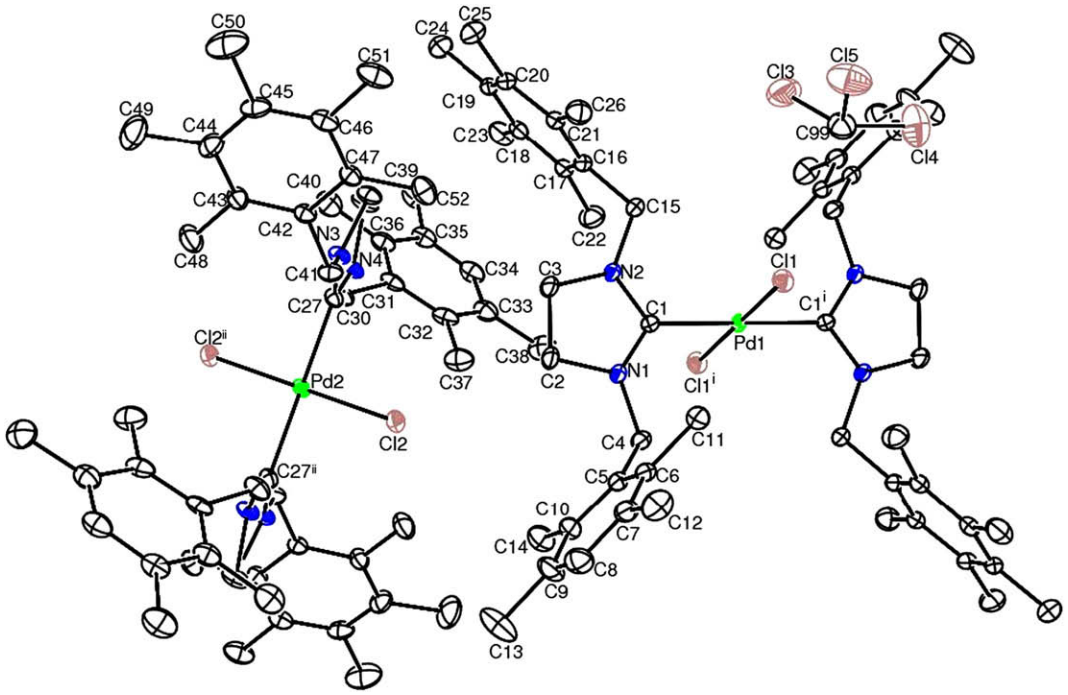
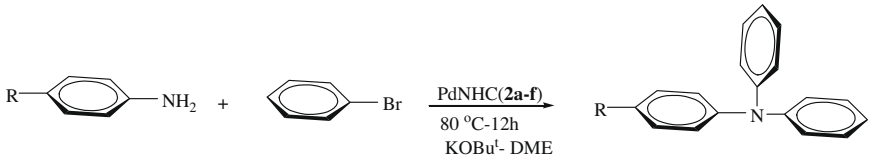


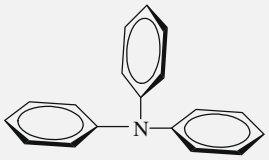
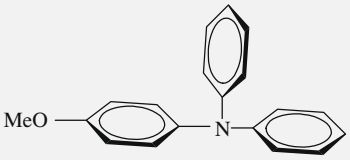
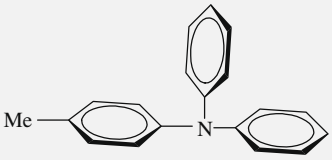
Fig. 1. ORTEP drawing of complex **2d**.

substituted anilines. The results are reported in Table 1. We have demonstrated for the higher yields Pd–NHC catalyzed amination of primary amines to triarylamines (Table 1 entry 5, 8 and 17). With *p*-anisidine containing electron donating group at *para* position, the amination reaction proceeds with considerable increase in the yield up to 72–95% (Table 1, entries 7–12).

We also examined the amination of bromobenzene (1.2 mmol) with aliphatic amines (1 mmol) under the same reaction conditions. As shown in Table 2, moderate to good yields were obtained (entry, 5, 8, and 17). 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

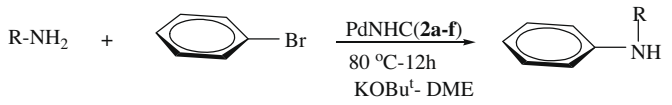
Table 1
NHC–Pd(II) catalyzed amination of bromobenzene with anilines.

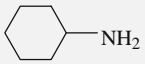
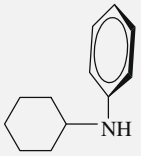
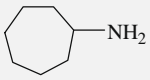
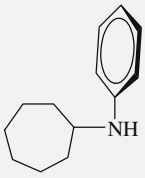
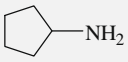
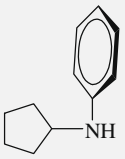


Entry	Pd(NHC)	R	Product	Yield (%)[a]
1	**2a**	H		83
2	**2b**	H		82
3	**2c**	H		82
4	**2d**	H		79
5	**2e**	H		85
6	**2f**	H		65
7	**2a**	OMe		89
8	**2b**	OMe		95
9	**2c**	OMe		81
10	**2d**	OMe		72
11	**2e**	OMe		86
12	**2f**	OMe		80
13	**2a**	Me		80
14	**2b**	Me		74
15	**2c**	Me		71
16	**2d**	Me		73
17	**2e**	Me		83
18	**2f**	Me		77

[a] Reaction conditions: catalyst (**2a–f**) (0.01 mmol), KOBu^t (1.5 mmol), aniline (1 mmol), bromobenzene (2.4 mmol), DME (2 mL), 80 °C-12 h. Yields are based on anilines. All reactions were monitored by TLC and GC.

Table 2
NHC–Pd(II) catalyzed amination of bromobenzene with aliphatic amines.



Entry	Pd(NHC)	Amine	Product	Yield (%)[a]
1	**2a**			87
2	**2b**			80
3	**2c**			75
4	**2d**			83
5	**2e**			90
6	**2f**			77
7	**2a**			95
8	**2b**			97
9	**2c**			72
10	**2d**			69
11	**2e**			93
12	**2f**			75
13	**2a**			82
14	**2b**			90
15	**2c**			86
16	**2d**			93
17	**2e**			97
18	**2f**			74

[a] Reaction conditions: catalyst (**2a–f**) (0.01 mmol), $KOBu^t$ (1.5 mmol), aliphatic amine (1 mmol), bromobenzene (1.2 mmol), DME (2 mL), 80 °C-12 h. Yields are based on amines. All reactions were monitored by TLC and GC.

only to *N*-monoarylation and gave secondary amines in a high yield but we did not observe *N*-diarylation.

2.3. X-ray diffraction studies

A single-crystal of **2d** suitable for data collection was mounted on glass fibres and data collection was performed on a STOE IPDS II diffractometer with graphite monochromated Mo Kα (λ = 0.71073 Å) radiation at 296 K. The structure was solved by direct-methods using SHELXS-97 and refined by full-matrix least-squares methods on F^2 using SHELXL-97 [12] from within the WINGX [13] suite of software. All non-hydrogen atoms were refined with anisotropic parameters. Hydrogen atoms bonded to carbon were placed in calculated positions (C–H = 0.93–0.98 Å) and treated using a riding model with U = 1.2 times the U value of the parent atom for CH, CH_2 and CH_3. Complete structure data have been deposited. Molecular diagrams were created using ORTEP-III [14]. Geometric calculations were performed with PLATON [15]. Salient crystal data are: $C_{53}H_{73}Cl_5N_4Pd$: Mf = 1049.80, triclinic, space group $P\bar{1}$, a = 12.4625(8) Å, b = 13.4165(10) Å, c = 18.6253(14) Å, α = 105.451 (6)°, β = 109.405(5)°, γ = 97.869(6)°, V = 2742.7(4) $Å^3$, Z = 2, D_{calc} = 1.271 g cm^{-3}, μ = 0.62 mm^{-1} and θ_{max} = 26.5°. Of 38711 reflections collected, 11373 were independent, R_{int} = 0.109, and 5763 were observed ($I > 2\sigma(I)$); final R indices: GOF = 0.98, R_1 = 0.070 ($I > 2\sigma(I)$) and wR_2 = 0.174.

3. Experimental

3.1. General considerations

All preparations were carried out in an atmosphere of purified argon using standard Schlenk techniques. Solvents were dried with standard methods and freshly distilled prior to use. Starting materials and reagents used in reactions were obtained commercially from Aldrich Chemical Co. Elemental analyses were performed by Turkish Resarch Council (Ankara, Turkey) Microlab. Melting points were measured in open capillary tubes with an Electrothermal-9200 melting point apparatus. FT-IR spectra were recorded as KBr pellets in the range 400–4000 cm^{-1} on a ATI UNICAM 1000 spectrometer.

^1H NMR and ^{13}C NMR spectra were recorded using a Varian As 400 Merkur spectrometer operating at 400 MHz (^1H), 100 MHz (^{13}C) in $CDCl_3$ with tetramethylsilane as an internal reference. All catalytic reactions were monitored on a 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 the palladium(NHC) complexes (*2a–f*)

Imidazolinium salts (**1**) prepared according to the literature [16]. The palladium complexes were prepared by means of Ag–carbene-transfer method developed by Wang and Lin [17]. The silver monocarbene complexes, which should subsequently serve as a carbene-transfer agent, were synthesized by the reaction of Ag_2O with 2 equiv. of salts (**1**) in CH_2Cl_2 at ambient temperature. We conveniently reacted in situ generated Ag–NHC with $PdCl_2(CH_3CN)_2$ in dark condition and the mixture was allowed to stir for 24 h at room temperature. When this reaction was carried out in a salt:Pd ratio of 2:1, formation of the dichloro-bis(carbene)complex (**2**) was expected (Scheme 1). After filtration of the 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.

3.2.1. Dichlorobis{1,3bis(2,3,5,6-tetramethylbenzyl)imidazolidin-2-yliden}palladium(II), ***2a***

Yield: 0.74 g (82%). M.p.: 299–300 °C. FT-IR (KBr pellet, cm^{-1}): ν_{CN} 1506 cm^{-1}. *Anal.* Calc. for $C_{50}H_{68}N_4PdCl_2$: C, 66.55; H, 7.60; N, 6.21. Found: C, 66.59; H, 7.63; N: 6.18%. ^1H NMR (δ, 399.9 MHz, $CDCl_3$): 2.24 and 2.42 [s, 24H, $CH_2C_6H(CH_3)_4$]; 3.08 [s, 8H, NCH_2CH_2N]; 5.52 [s, 8H, $CH_2C_6H(CH_3)_4$]; 6.95 [s, 4H, $CH_2C_6H(CH_3)_4$]. ^{13}C {H} NMR (δ, 100.5 MHz, $CDCl_3$): 16.5 and 20.5 [$CH_2C_6H(CH_3)_4$]; 47.1 [NCH_2CH_2N]; 48.9 [$CH_2C_6H(CH_3)_4$]; 131.5, 131.7, 133,9 and 134.5 [$CH_2C_6H(CH_3)_4$]; 198.2 [$C_{carbene}$].

3.2.2. Dichlorobis{1-(2,3,5,6-tetramethylbenzyl)-3-(2-methoxyethyl)imidazolidin-2-yliden}palladium(II), ***2b***

Yield: 0.51 g (70%). M.p.: 296–297 °C. FT-IR (KBr pellet, cm^{-1}): ν_{CN} 1520 cm^{-1}. *Anal.* Calc. for $C_{34}H_{52}N_4O_2PdCl_2$: C, 56.24; H, 7.22; N, 7.72. Found: C, 56.21; H, 7.25; N: 7.77%. ^1H NMR (δ, 399.9 MHz, $CDCl_3$): 2.23, 2.28, 2.38 and 2.41 [s, 24H, $CH_2C_6H(CH_3)_4$]; 3.19 and 3.62 [t, 8H, J = 10.8 Hz, NCH_2CH_2N]; 3.43 [s, 6H, $CH_2CH_2OCH_3$]; 3.88–3.94 [m, 4H, $CH_2CH_2OCH_3$]; 4.23–4.30 [m, 4H, $CH_2CH_2OCH_3$]; 5.38 and 5.42 [s, 4H, $CH_2C_6H(CH_3)_4$]; 6.95 [s, 2H, $CH_2C_6H(CH_3)_4$]. ^{13}C {H} NMR (δ, 100.5 MHz, $CDCl_3$): 16.5 and 20.5 [$CH_2C_6H(CH_3)_4$]; 47.7 and 48.5 [NCH_2CH_2N]; 49.8 [$CH_2C_6H(CH_3)_4$]; 50.3 [$CH_2CH_2OCH_3$]; 58.9 [$CH_2CH_2OCH_3$]; 73.1 [$CH_2CH_2OCH_3$]; 131.6, 134.0, 134.4 and 134.6 [$CH_2C_6H(CH_3)_4$]; 198.7 [$C_{carbene}$].

3.2.3. Dichlorobis{1-(2,3,5,6-tetramethylbenzyl)-3-(3,4,5-trimethoxybenzyl)imidazolidin-2-yliden}palladium(II), ***2c***

Yield: 0.83 g (86%). M.p.: 309–310 °C. FT-IR (KBr pellet, cm^{-1}): ν_{CN} 1591 cm^{-1}. *Anal.* Calc. for $C_{48}H_{64}N_4O_6PdCl_2$: C, 59.41; H, 6.65; N, 5.77. Found: C, 59.48; H, 6.60; N: 5.82%. ^1H NMR (δ, 399.9 MHz, $CDCl_3$): 2.22, 2.23, 2.34 and 2.41 [s, 24H, $CH_2C_6H(CH_3)_4$]; 3.16–3.23 and 3.27–3.34 [m, 8H, NCH_2CH_2N]; 3.83, 3.86 and 3.91 [s, 18H, $CH_2C_6H_2(OCH_3)_3$-3,4,5]; 5.21 and 5.28 [s, 4H, $CH_2C_6H(CH_3)_4$]; 5.42 and 5.51 [s, 4H, $CH_2C_6H_2(OCH_3)_3$-

3,4,5]; 6.86 and 6.92 [s, 4H, $CH_2C_6H_2(OCH_3)_3$-3,4,5]; 6.94 [s, 2H, $CH_2C_6H(CH_3)_4$]. ^{13}C {H} NMR (δ, 100.5 MHz, $CDCl_3$): 16.1, 16.4, 16.5 and 20.5 [$CH_2C_6H(CH_3)_4$]; 47.7 and 48.6 [NCH_2CH_2N]; 54.4 [$CH_2C_6H(CH_3)_4$]; 54.5 [$CH_2C_6H_2(OCH_3)_3$-3,4,5]; 56.4, 56.5 and 60.8 [$CH_2C_6H_2(OCH_3)_3$-3,4,5]; 131.5, 134.0, 134.4 and 134.7 [$CH_2C_6H(CH_3)_4$]; 105.6, 132.1, 137.4 and 153.4 [$CH_2C_6H_2(OCH_3)_3$-3,4,5], 197.9 [$C_{carbene}$].

3.2.4. Dichlorobis{1-(2,3,5,6-tetramethylbenzyl)-3-(2,3,4,5,6-pentamethylbenzyl)imidazolidin-2-yliden}palladium(II), **2d**

Yield: 0.75 g (81%). M.p.: 231–232 °C. FT-IR (KBr pellet, cm^{-1}): ν_{CN} 1508 cm^{-1}. *Anal.* Calc. for $C_{52}H_{72}N_4PdCl_2$: C, 67.12; H, 7.80; N, 6.02. Found: C, 67.10; H, 7.85; N: 5.97%. ^{1}H NMR (δ, 399.9 MHz, $CDCl_3$): 2.24, 2.43 and 2.48 [s, 54H, $CH_2C_6H(CH_3)_4$ and $CH_2C_6(CH_3)_5$]; 3.10 [s, 8H, NCH_2CH_2N]; 5.52 [s, 4H, $CH_2C_6H(CH_3)_4$]; 5.55 [s, 4H, $CH_2C_6(CH_3)_5$]; 6.95 [s, 2H, $CH_2C_6H(CH_3)_4$]. ^{13}C {H} NMR (δ, 100.5 MHz, $CDCl_3$): 16.6, 16.8, 17.1, 17.5 and 20.6 [$CH_2C_6H(CH_3)_4$ and $CH_2C_6(CH_3)_5$]; 47.1 [NCH_2CH_2N]; 48.9 and 49.3 [$CH_2C_6H(CH_3)_4$ and $CH_2C_6(CH_3)_5$]; 131.5, 131.8, 134.1 and 134.5 [$CH_2C_6H(CH_3)_4$]; 129.2, 132.7, 133.9 and 134.9 [$CH_2C_6(CH_3)_5$]; 198.1 [$C_{carbene}$].

3.2.5. Dichlorobis{1-(2,3,4,5,6-pentamethylbenzyl)-3-(2-methoxyethyl)imidazolidin-2-yliden}palladium(II), **2e**

Yield: 0.57 g (76%). M.p.: 294–295 °C. FT-IR (KBr pellet, cm^{-1}): ν_{CN} 1518 cm^{-1}. *Anal.* Calc. for $C_{36}H_{56}N_4O_2PdCl_2$: C, 57.33; H, 7.48; N, 7.43. Found: C, 57.38; H, 7.51; N: 7.48%. ^{1}H NMR (δ, 399.9 MHz, $CDCl_3$): 2.22, 2.24, 2.27, 2.43 and 2.46 [s, 30H, $CH_2C_6(CH_3)_5$]; 3.25 and 3.621 [t, 8H, J = 10.8 Hz, NCH_2CH_2N]; 3.43 [s, 6H, $CH_2CH_2OCH_3$]; 3.88–3.94 [m, 4H, $CH_2CH_2OCH_3$]; 4.23–4.29 [m, 4H, $CH_2CH_2OCH_3$]; 5.40 and 5.44 [s, 4H, $CH_2C_6(CH_3)_5$]. ^{13}C {H} NMR (δ, 100.5 MHz, $CDCl_3$): 16.8, 16.9, 17.0, 17.1 and 17.5 [$CH_2C_6(CH_3)_5$]; 47.7 and 48.8 [NCH_2CH_2N]; 49.8 [$CH_2C_6(CH_3)_5$]; 50.2 [$CH_2CH_2OCH_3$]; 58.9 [$CH_2CH_2OCH_3$]; 73.2 [$CH_2CH_2OCH_3$]; 128.9, 132.7, 134.0 and 134.9 [$CH_2C_6(CH_3)_5$]; 198.6 [$C_{carbene}$].

3.2.6. Dichlorobis{1-(2,3,4,5,6-pentamethylbenzyl)-3-(3,4,5-trimethoxybenzyl)imidazolidin-2-yliden}palladium(II), **2f**

Yield: 0.89 g (89%). M.p.: 305–306 °C. FT-IR (KBr pellet, cm^{-1}): ν_{CN} 1593 cm^{-1}. *Anal.* Calc. for $C_{50}H_{68}N_4O_6PdCl_2$: C, 60.15; H, 6.86; N, 5.61. Found: C, 60.10; H, 6.92; N: 5.57%. ^{1}H NMR (δ, 399.9 MHz, $CDCl_3$): 2.21, 2.22, 2.24, 2.39 and 2.45 [s, 30H, $CH_2C_6(CH_3)_5$]; 3.18–3.35 [m, 8H, NCH_2CH_2N]; 3.83, 3.86 and 3.91 [s, 18H, $CH_2C_6H_2(OCH_3)_3$-3,4,5]; 5.21 and 5.27 [s, 4H, $CH_2C_6(CH_3)_5$]; 5.44 and 5.52 [s, 4H, $CH_2C_6H_2(OCH_3)_3$-3,4,5]; 6.86 and 6.91 [s, 4H, $CH_2C_6H_2(OCH_3)_3$-3,4,5]. ^{13}C {H} NMR (δ, 100.5 MHz, $CDCl_3$): 16.7, 16.8, 17.0, 17.4 and 17.5 [$CH_2C_6(CH_3)_5$]; 47.7 and 49.0 [NCH_2CH_2N]; 54.4 [$CH_2C_6(CH_3)_5$]; 54.5 [$CH_2C_6H_2(OCH_3)_3$-3,4,5]; 56.4, 56.5 and 60.8 [$CH_2C_6H_2(OCH_3)_3$-3,4,5]; 128.4, 132.8, 133.9, and 135.0 [$CH_2C_6(CH_3)_5$]; 105.6, 132.2, 137.4 and 153.4 [$CH_2C_6H_2(OCH_3)_3$-3,4,5], 197.8 [$C_{carbene}$].

3.3. General procedure for the catalytic N-diarylation of anilines

Under the argon, 1.5 mmol of KO^tBu, 1 mol% of catalyst, 1 mmol aniline, 2.4 mmol bromobenzene and 2 mL dimethoxyethane (DME) were added into oven-dried Schlenk tube. The mixture was stirred at 80 °C for 12 h. The reaction mixture was allowed to cool to room temperature and was 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 anilines.

3.4. General procedure for the catalytic N-arylation of amines

Under the argon, 1.5 mmol of $KOBu^t$, 1 mol% of catalyst, 1 mmol amine, 1.2 mmol bromobenzene and 2 mL dimethoxyethane (DME) were added into oven-dried Schlenk tube. The mixture was stirred at 80 °C for 12 h. The reaction mixture was allowed to cool to room temperature and was 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 amines.

4. Conclusion

We have prepared six new palladium–NHC complexes (**2a–f**) whose structures were confirmed by ^{1}H NMR, ^{13} C NMR, IR, elemental analysis and complex **2d** has been characterized by single-crystal X-ray diffraction studies. This work represents an integral part of the application of Pd–NHC complexes in the catalytic C–N coupling reactions. The current catalyst system was successfully applied to various anilines or amines with bromobenzene. Research in our laboratory is currently on-going to extend the coordination chemistry of functionalized NHCs to other transition metals and to explore their potential applications in catalysis. In addition our further research will focus on the development of more efficient catalytic systems for this reaction.

5. Supplementary material

CCDC 742819 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

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