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Palladium(II)–NHC complexes containing benzimidazole ligand as a catalyst for C–N bond formation

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The reaction of 2-(2-bromoethyl)-1,3-dioxane with 1-alkylbenzimidazole derivatives results in the formation of the new benzimidazolium salts (1). The reaction of $Pd(OAc)_2$ with 1,3-dialkylbenzimidazolium salts (1a–c) yields palladium *N*-heterocyclic carbene (NHC) complexes (2a–c). All synthesized compounds were characterized by ^{1}H NMR, ^{13}C NMR, IR and elemental analysis techniques which support the proposed structures. As catalysts, these new palladium complexes offer a simple and efficient methodology for the synthesis of triarylamines and secondary amines from anilines and amines and in a single step with potassium tertiary butoxide as a base.

Keywords: benzimidazolium salt; palladium catalysis; amination; *N*-heterocyclic carbene

Introduction

N-Heterocyclic carbenes (NHCs) are widely employed as supporting ligands in transition metal-catalyzed reactions,[1–3] including ubiquitous palladium-catalyzed cross-coupling reactions,[4,5] in which their introduction has allowed a dramatic increase in catalytic performance. Furthermore, palladium complexes of the type $Pd(pyridine)Cl_2(NHC)$ and $PdCl_2(NHC)_2$ have been found to exhibit potent anticancer activity.[6,7] Since Arduengo *et al*.[8] introduced the first stable NHCs in the early 1990s, this class of ligands has become increasingly popular in catalysis.[9–14] The nucleophilic NHCs as ancillary ligands find numerous applications in catalyst systems for C–C cross-coupling reactions,[15–17] and C–N coupling processes.[18–21]

Nitrogen-containing heterocycles are one the most important classes of medicinal compounds and are structural components of many bioactive natural products and organic materials.[22] Copper-catalyzed Ullmann-type reactions are traditional methods to assemble these compounds.[23–25] For a long time, these reactions were carried out at high temperatures and many functional groups could not be tolerated, and therefore their use was greatly limited. As an answer to these limitations, Hartwig and Buchwald's palladium-catalyzed aromatic amination has become a powerful tool for the synthesis of a great variety of products, ranging from laboratory to technical scale.[26,27] The palladium metal centers are supported and controlled by strong donor ligands. The most common ligand concepts comprise a wide range of phosphines, including phosphapalladacycles, cyclodiphosphazane and N-heterocyclic carbenes.[18–21,28–30] Pd/imidazolium salt systems[18] and the well-defined Pd–NHCs complexes[19] were found to be highly efficient for N-arylation of a wide range of nitrogen-containing substrates. However, it has not been demonstrated yet that these systems are effective for triarylamines. Hence, in this work, we report the results of our investigations on C–N bond formation using Pd–NHC catalysts. These compounds can be readily synthesized directly from benzimidazolium salts (**1**) and $Pd(OAc)_2$ in DMSO and have proven to be highly efficient in the Buchwald–Hartwig amination of anilines and amines to form triarylamine and secondary amines respectively.

Experimental

Materials

All procedures were carried out under an inert atmosphere using standard Schlenk line techniques. Chemicals and solvents were purchased from Sigma Aldrich Co. (Dorset, UK). 1-Alkylbenzimidazoles were synthesized in our laboratory. Solvents were dried with standard methods and freshly distilled prior to use. Elemental analyses were performed by Turkish Resarch Council (Ankara, Turkey) Microlab.

Melting Point Determination

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

IR Spectroscopy

FT-IR spectra were recorded as KBr pellets in the range 400–4000 cm^{-1} on a ATI Unicam 1000 spectrophotometer.

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NMR Spectroscopy

^{1}H NMR and ^{13}C NMR spectra were recorded using 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. The NMR studies were carried out in high-quality 5 mm NMR tubes. Signals are quoted in parts per million as δ downfield from tetramethylsilane (δ 0.00) as an internal standard. Coupling constants (*J*-values) are given in hertz. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, m = multiplet signal.

Gas Chromatography

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

Column Chromatography

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

General Procedure for the Preparation of the Benzimidazolium Salts (1)

To a solution of 1-alkylbenzimidazole (5 mmol) in DMF (10 ml) was added under argon slowly 2-(2-bromoethyl)-1,3-dioxane (5 mmol) at 25 °C and the resulting mixture was stirred at 80 °C for 10 h. Diethyl ether (15 ml) was added to obtain a white crystalline solid which was filtered off. The solid was washed with diethyl ether (3 × 15 ml), and dried under vacuum. The crude product was recrystallized from EtOH/Et_2O. Melting points were measured in open capillary tubes.

[1-(methoxyethyl)-3-(2-(ethyl)-1,3-dioxane)]benzimidazolium bromide, ***1a***

Yield: 3.14 g (87%); m.p.: 152–153 °C, $\nu_{(CN)}$ = 1567 cm^{-1}. ^{1}H NMR (399.9 MHz, $CDCl_3$) δ (ppm) = 11.0 (s, 1H, NC*H*N), 7.61–7.89 (m, 4H, C_6H_4), 3.36 (s, 3H, $NCH_2CH_2OCH_3$), 4.77 (t, 2H, *J* = 4 Hz, $NCH_2CH_2OCH_3$), 4.91 (t, 2H, *J* = 4 Hz, $NCH_2CH_2OCH_3$), 4.01 (t, 2H, *J* = 4 Hz, $NCH_2CHO_2CH_2CH_2$), 2.32 (m, 2H, *J* = 4 Hz, $NCH_2CH_2CHO_2CH_2CH_2CH_2$), 4.82 (t, 1H, *J* = 4 Hz, $NCH_2CH_2CHO_2CH_2CH_2CH_2$), 3.96 (t, 2H, *J* = 4 Hz, $NCH_2CH_2CHO_2CH_2CH_2CH_2$), 3.78 (t, 2H, *J* = 4 Hz, $NCH_2CH_2CHO_2CH_2CH_2CH_2$), 1.92 (m, 2H, $NCH_2CH_2CHO_2CH_2CH_2CH_2$). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ (ppm) = 143.5 (NCHN), 132.2; 131.3; 127.1; 113.0 (C_6H_4), 59.3 ($NCH_2CH_2OCH_3$), 70.7 ($NCH_2CH_2OCH_3$), 47.9 ($NCH_2CH_2OCH_3$), 42.8 ($NCH_2CH_2CHO_2CH_2CH_2CH_2$), 34.2 ($NCH_2CH_2CHO_2CH_2CH_2CH_2$), 99.2 ($NCH_2CH_2CHO_2CH_2CH_2CH_2$), 66.9 ($NCH_2CH_2CHO_2CH_2CH_2CH_2$), 25.6 ($NCH_2CH_2CHO_2CH_2CH_2CH_2$). Anal. calcd for $C_{16}H_{24}O_3N_2Br$: C: 51.62; H: 6.50; N: 7.52 Found C: 51.68; H: 6.57; N: 7.59.

[1-(2,4,6-trimethylbenzyl)-3-(2-(ethyl)-1,3-dioxane)]benzimidazolium bromide, ***1b***

Yield: 3.87 g (85%); m.p.: 203–204 °C, $\nu_{(CN)}$ = 1571 cm^{-1}. ^{1}H NMR (399.9 MHz, $CDCl_3$) δ (ppm) = 10.68 (s, 1H, NC*H*N), 7.36–7.80 (m, 4H, C_6H_4), 6.94 [s, 2H, 2,4,6-$(CH_3)_3C_6H_2CH_2$], 5.85 [s, 2H, 2,4,6-$(CH_3)_3C_6H_2CH_2$], 2.34 [s, 6H, 2,6-$(CH_3)_3C_6H_2CH_2$], 2.30 [s, 3H, 4-$(CH_3)_3C_6H_2CH_2$], 4.81 (t, 2H, *J* = 8 Hz, $NCH_2CH_2CHO_2CH_2CH_2CH_2$), 2.52 (q, 2H, *J* = 8 Hz, $NCH_2CH_2CHO_2CH_2CH_2CH_2$), 4.79 (t, 1H, *J* = 8 Hz, $NCH_2CH_2CHO_2CH_2CH_2CH_2$), 3.88 (t, 2H, *J* = 8 Hz, $NCH_2CH_2CHO_2CH_2CH_2CH_2$), 3.71 (t, 2H, *J* = 8 Hz, $NCH_2CH_2CHO_2CH_2CH_2CH_2$), 1.81 (m, 2H, $NCH_2CH_2CHO_2CH_2CH_2CH_2$). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ (ppm) = 143.1 (NCHN), 131.8; 131.5; 127.2, 127.1; 113.9; 113.5 (C_6H_4), 139.9; 138.3; 130.3; 125.4 [2,4,6-$(CH_3)_3C_6H_2CH_2$], 20.4 [2,6-$(CH_3)_3C_6H_2CH_2$], 21.3 [4-$(CH_3)_3C_6H_2CH_2$], 47.3 [2,4,6-$(CH_3)_3C_6H_2$-CH_2], 42.8 ($NCH_2CH_2CHO_2CH_2CH_2CH_2$), 34.1 ($NCH_2CH_2CHO_2CH_2CH_2CH_2$), 99.5 ($NCH_2CH_2CHO_2CH_2CH_2CH_2$), 66.9 ($NCH_2CH_2CHO_2CH_2CH_2CH_2$), 25.6 ($NCH_2CH_2CHO_2CH_2CH_2CH_2$). Anal. calcd for $C_{23}H_{30}O_2N_2Br$: C, 61.88; H, 6.77; N, 6.28. Found: C, 61.86; H, 6.67; N, 6.25.

[1-(3,4,5-trimethoxybenzyl)-3-(2-(ethyl)-1,3-dioxane)benzimidazolium bromide, ***1c***

Yield: 4.55 g (90%); m.p.: 218–219 °C. $\nu_{(CN)}$ = 1595 cm^{-1}. ^{1}H NMR (399.9 MHz, $CDCl_3$) δ (ppm) = 11.41 (s, 1H, NC*H*N), 7.56–7.83 (m, 4H, C_6H_4), 6.93 [s, 2H, 3,4,5-$(OCH_3)_3C_6H_2CH_2$], 5.82 [s, 2H, 3,4,5-$(OCH_3)_3C_6H_2CH_2$], 3.84 [s, 6H, 3,5-$(OCH_3)_3C_6H_2$ CH_2], 3.77 [s, 3H, 4-$(OCH_3)_3C_6H_2CH_2$], 4.77 (t, 2H, *J* = 5.6 Hz, NCH_2CH_2CH), 2.89 (q, 2H, *J* = 5.6 Hz, NCH_2CH_2CH), 4.72 (t, 1H, *J* = 8.0 Hz, NCH_2CH_2CH), 3.67 (t, 2H, *J* = 6.8 Hz, $NCH_2CH_2CHO_2CH_2CH_2CH_2$), 3.87 (t, 2H, *J* = 6.8 Hz, $NCH_2CH_2CHO_2CH_2CH_2CH_2$), 1.84 (m, 2H, $NCH_2CH_2O_2CH_2CH_2CH_2$). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ (ppm) = 143.3 (NCHN), 153.7; 138.5; 126.9; 106.3 (3,4,5-$(OCH_3)_3C_6H_2CH_2$), 131.4; 131.1; 128.6;127.0; 113.7; 113.0 (C_6H_4), 56.8 [3,5-$(OCH_3)_3C_6H_2CH_2$], 60.8 [4-$(OCH_3)_3C_6H_2CH_2$], 51.2 [3,4,5-$(OCH_3)_3C_6H_2CH_2$], 42.5 (NCH_2CH_2CH), 33.9 (NCH_2CH_2CH), 99.0 (NCH_2CH_2CH), 66.7 ($NCH_2CH_2CHO_2CH_2CH_2CH_2$), 25.3 ($NCH_2CH_2CHO_2CH_2CH_2CH_2$). Anal. calcd for $C_{23}H_{29}O_5N_2Br$: C, 55.99; H, 5.92; N, 5.68. Found: C, 55.94; H, 5.95; N, 5.61.

General procedure for the preparation of the palladium(NHC) complexes, ***2***

To a solution of benzimidazolium salts (10 mmol) in DMSO (5 ml) was added under argon palladium(II) acetate (5 mmol) and the resulting mixture was stirred at room temperature for 2 h, 60 °C for 4 h, at 80 °C for 2 h and finally at 110 °C for 2 h. Volatiles were removed *in vacuo* and the residue was washed twice with THF (5 ml) and then crude product was recrystallized from CH_2Cl_2–Et_2O.

Bis[1-(methoxyetyl)-3-(2-(ethyl)-1,3-dioxane)]benzimidazol-2-ylidene]dibromo palladium(II), ***2a***

Yield: 0.35 g, (75%); m.p.: 312–313 °C, $\nu_{(CN)}$ = 1472 cm^{-1}. ^{1}H NMR (399.9 MHz, $CDCl_3$) δ (ppm) = 7.27–7.73 (m, 4H, C_6H_4), 3.31 (s, 3H, $NCH_2CH_2OCH_3$), 4.68 (t, 2H, *J* = 6.6 Hz, $NCH_2CH_2OCH_3$), 4.89 (t, 2H, *J* = 6.6 Hz, $NCH_2CH_2OCH_3$), 4.39 (t, 2H, *J* = 4.8 Hz, $NCH_2CHO_2CH_2CH_2$), 2.48 (m, 2H, $NCH_2CH_2CHO_2CH_2CH_2CH_2$), 4.94 (t, 1H, *J* = 4.8 Hz, $NCH_2CH_2CHO_2CH_2CH_2CH_2$), 4.06 (m, 4H, $NCH_2CH_2CHO_2CH_2CH_2CH_2$), 2.06 (m, 2H, $NCH_2CH_2CHO_2CH_2CH_2CH_2$). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ (ppm) = 173.5 ($Pd_{carbene}$), 134.4; 133.8; 123.5; 112.5 (C_6H_4), 58.9 ($NCH_2CH_2OCH_3$), 70.7 ($NCH_2CH_2OCH_3$), 49.3 ($NCH_2CH_2OCH_3$), 43.6 ($NCH_2CH_2CHO_2CH_2CH_2CH_2$), 34.1 ($NCH_2CH_2CHO_2CH_2CH_2CH_2$), 99.3 ($NCH_2CH_2CHO_2CH_2CH_2CH_2$), 66.7 ($NCH_2CH_2CHO_2CH_2CH_2CH_2$), 25.8 ($NCH_2CH_2CHO_2CH_2CH_2CH_2$). Anal. calcd for $C_{16}H_{23}Br_2N_2O_3Pd$: C: 34.46; H: 4.16; N: 5.02 Found: C: 34.41; H: 4.12; N: 4.95.

Bis[1-(2,4,6-trimethylbenzyl)-3-(2-(ethyl)-1,3-dioxane)]benzimidazol-2-ylidene] dibromo palladium(II), ***2b***

Yield: 0.37 g (71%); m.p.: 310–311 °C, $\nu_{(CN)}$ = 1478 cm^{-1}. ^1H NMR (399.9 MHz, $CDCl_3$) δ (ppm) = 7.11–7.50 (m, 4H, C_6H_4), 6.94 [s, 2H, 2,4,6-$(CH_3)_3C_6H_2CH_2$], 6.09 [s, 2H, 2,4,6-$(CH_3)_3C_6H_2CH_2$], 2.43 [s, 6H, 2,6-$(CH_3)_3C_6H_2CH_2$], 2.36 [s, 3H, 4-$(CH_3)_3C_6H_2CH_2$], 5.07 (t, 2H, J = 3.3 Hz, $NCH_2CH_2CHO_2CH_2CH_2CH_2$), 2.63 (q, 2H, J = 3.3 Hz, $NCH_2CH_2CHO_2CH_2CH_2CH_2$), 4.70 (t, 1H, J = 3.3 Hz, $NCH_2CH_2CHO_2CH_2CH_2CH_2$), 3.81 (t, 2H, J = 3.3 Hz, $NCH_2CH_2CHO_2CH_2CH_2CH_2$), 3.72 (t, 2H, J = 3.3 Hz, $NCH_2CH_2CHO_2CH_2CH_2CH_2$), 1.88 (m, 2H, $NCH_2CH_2CHO_2CH_2CH_2CH_2$). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ (ppm) = 182.6 ($Pd_{carbene}$), 134.9; 134.6; 128.5, 122.6; 122.2; 111.7 (C_6H_4), 138.9; 138.3; 129.5; 122.7 [2,4,6-$(CH_3)_3C_6H_2CH_2$], 21.2 [2,6-$(CH_3)_3C_6H_2CH_2$], 20.0 [4-$(CH_3)_3C_6H_2CH_2$], 50.7 [2,4,6-$(CH_3)_3C_6H_2CH_2$], 43.4 ($NCH_2CH_2CHO_2CH_2CH_2CH_2$), 35.2 ($NCH_2CH_2CHO_2CH_2CH_2CH_2$), 99.7 ($NCH_2CH_2CHO_2CH_2CH_2CH_2$), 66.7 ($NCH_2CH_2CHO_2CH_2CH_2CH_2$), 25.9 ($NCH_2CH_2CHO_2CH_2CH_2CH_2$). Anal. calcd for $C_{23}H_{29}Br_2N_2O_2Pd$: C: 43.73; H: 4.63; N: 4.43. Found: C: 43,77; H: 4.58; N: 4.37.

Bis[1-(3,4,5-trimethoxybenzyl)-3-(2-(ethyl)-1,3-dioxane)benzimidazol-2-ylidene] dibromo palladium(II), ***2c***

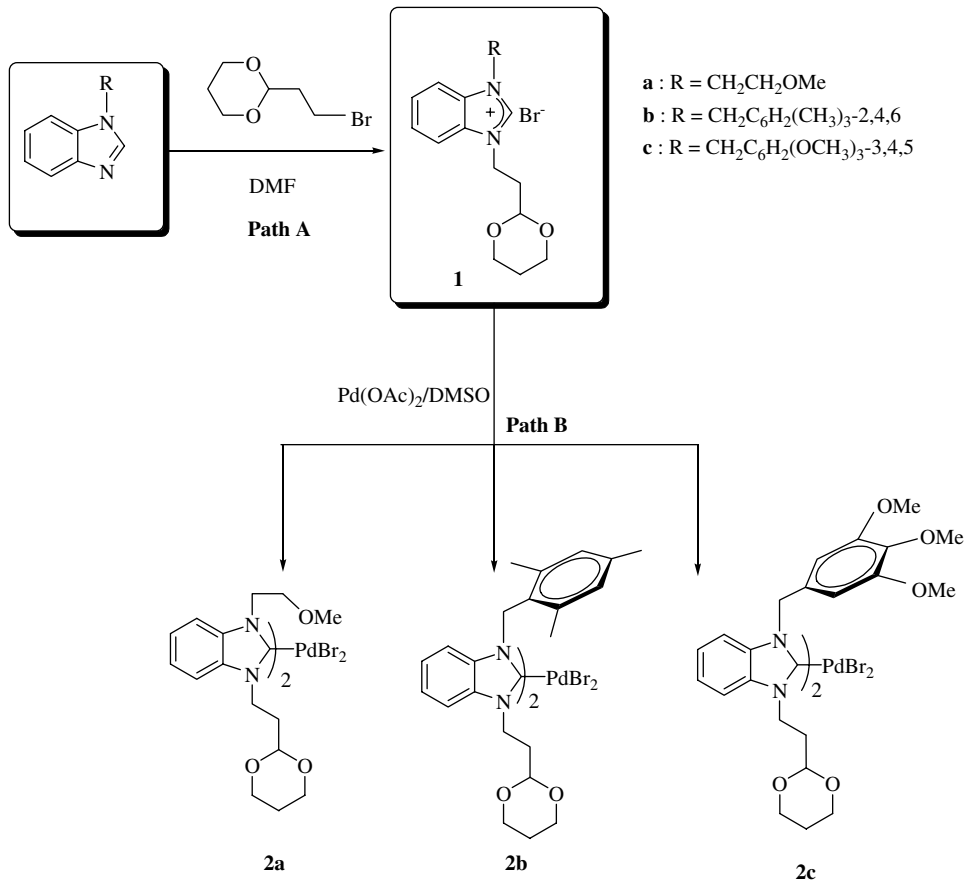
Yield: 0.43 g (74%); m.p.: 330–331 °C, $\nu_{(CN)}$ = 1461 cm^{-1}. ^1H NMR (399.9 MHz, $CDCl_3$) δ (ppm) = 7.15–7.61 (m, 4H, C_6H_4), 6.90 [s, 2H, 3,4,5-$(OCH_3)_3C_6H_2CH_2$], 6.42 [s, 2H, 3,4,5-$(OCH_3)_3C_6H_2CH_2$], 3.72 [s, 6H, 3,5-$(OCH_3)_3C_6H_2CH_2$], 3.63 [s, 3H, 4-$(OCH_3)_3C_6H_2CH_2$], 4.96 (t, 2H, J = 3.6 Hz, NCH_2CH_2CH), 2.67 (q, 2H, J = 3.6 Hz, NCH_2CH_2CH), 4.82 (t, 1H, J = 3.6 Hz NCH_2CH_2CH), 4.13 (m, 4H, $NCH_2CH_2CHO_2CH_2CH_2CH_2$), 2.13 (m, 2H, $NCH_2CH_2O_2CH_2CH_2CH_2$). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ (ppm) = 174.7 ($Pd_{carbene}$), 153.7; 137.7; 130.2; 106.2 [3,4,5-$(OCH_3)_3C_6H_2CH_2$], 134.4; 133.9; 130.0; 123.6; 112.0; 106.0 (C_6H_4), 56.8 [3,5-$(OCH_3)_3C_6H_2CH_2$], 60.9 [4-$(OCH_3)_3C_6H_2CH_2$], 53.7 [3,4,5-$(OCH_3)_3C_6H_2CH_2$], 44.6 (NCH_2CH_2CH), 34.2 (NCH_2CH_2CH), 99.4 (NCH_2CH_2CH), 66.8 (NCH_2CH_2 $CHO_2CH_2CH_2CH_2$), 25.9 ($NCH_2CH_2CHO_2CH_2CH_2CH_2$). Anal. calcd for $C_{23}H_{29}Br_2N_2O_5Pd$: C: 40.64; H: 4.30; N: 4.12. Found: C: 40.59; H: 4.35; N: 4.09.

General Procedure for the Catalytic N-diarylation of Anilines

Under argon, 1.5 mmol of KO^{t}Bu, 1 mol% of catalyst **2a–c**, 1 mmol aniline, 2.4 mmol bromobenzene and 2 ml 1,2-dimethoxyethane (DME) were added into oven-dried Schlenk tube (10 ml). The mixture was stirred at 80 °C for 15 h. The reaction mixture was allowed to cool to room temperature and was quenched by filtering through a short silica column (eluent: ethyl acetate) and then concentrated under reduced pressure. After purification by flash chromatography (eluent, ethyl acetate–hexane; ratio, 1 : 5 ml), the yield was calculated by GC based on anilines.

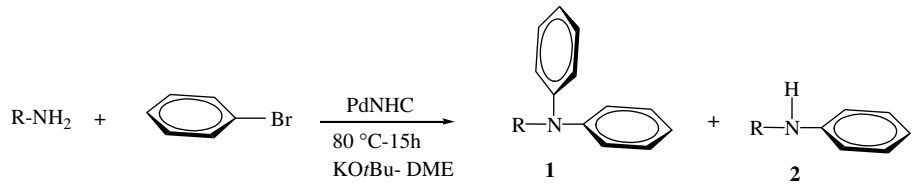
General Procedure for the Catalytic N-arylation of Amines

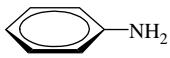
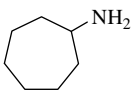
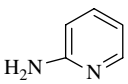
Under argon, 1.5 mmol of KO^{t}Bu, 1 mol% of catalyst **2a–c**, 1 mmol amine, 1.2 mmol bromobenzene and 2 ml 1,2-dimethoxyethane (DME) were added into oven-dried Schlenk tube (10 ml). The



Scheme 1. Synthesis of benzimidazolium salts (path A) and NHC-Pd(II) complexes (path B).

Table 1. Catalytic activation of Pd–NHC for amination reaction



Entry	Aniline/amine	Pd–NHC	Product (%)[a] 1	Product (%)[a] 2
1		**2a**	66	34
2		**2b**	84	16
3		**2c**	62	38
4		**2a**	75	25
5		**2b**	87	13
6		**2c**	89	11
7		**2a**	73	27
8		**2b**	82	18
9		**2c**	86	14
10		**2a**	17	83
11		**2b**	14	86
12		**2c**	9	91
13		**2a**	19	81
14		**2b**	17	83
15		**2c**	10	90

[a] Reaction conditions: catalyst (**2a–c**) (0.01 mmol), KO^{t}Bu (1.5 mmol), aniline/amine (1 mmol), bromobenzene (2.4 mmol, entries 1–9; 1.2 mmol, entries 10–15), DME (2 ml), 80 °C–15 h. Yields are based on aniline or amine. All reactions were monitored by TLC and GC.

mixture was stirred at 80 °C for 15 h. The reaction mixture was allowed to cool to room temperature and was quenched by filtering through a short silica column (eluent, ethyl acetate) and then concentrated under reduced pressure. After purification by flash chromatography (eluent, ethyl acetate–hexane; ratio, 1 : 5 ml), the yield was calculated by GC based on amines.

Results and Discussion

Preparation and Structural Properties of the Benzimidazolium Salts

Heating 2-(2-bromoethyl)-1,3-dioxane with 1-alkylbenzimidazole in DMF at 80 °C affords the desired dioxane-functionalized benzimidazolium bromide as a white powder in 85–90% yield (Scheme 1, path A). The ^{1}H NMR spectra of the benzimidazolium salts (**1a–c**) in $CDCl_3$ exhibit as a singlet in the range δ 10.68–11.41 ppm, characteristic of the NC*H*N benzimidazolium proton. The chemical shift of the C2 carbon at 143.5, 143.1 and 143.3 ppm is in agreement with data reported for other benzimidazolium salts.[13,17,31] The IR spectra of all the salts show strong C–N bands at around 1567, 1571 and 1595 cm^{-1} as expected.

Preparation and Structural Properties of the Palladium(NHC) Complexes

Direct reaction of 2 equiv. of imidazolium salt (**1**) with palladium acetate stirred at different temperatures for different periods of time results in high yields of complex **2** (Scheme 1, path B). If the reaction is strirred directly at high temperature, palladium(II) is reduced to palladium(0) and the resulting palladium black precipitates during the reaction period. All Pd–NHC complexes were fully characterized by elemental analyses, IR, ^{1}H and ^{13}C NMR techniques. The complexes 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 in the ^{1}H-NMR is absent. Correspondingly, the ^{13}C NMR spectra show the characteristic coordinated carbene signals at 173.5, 182.6 and 174.7 ppm, respectively **2a–2c**, which are in the typical range observed for (benzimidazolin-2-ylidene)complexes of Pd(II).[32] The IR data for the Pd–carbene complexes clearly indicate the

presence of the C–N group with a $\upsilon_{(CN)}$ vibration between 1461 and 1478 cm^{-1}.

Applications of Pd(NHC) Complexes in Amination Reaction

As known, the performance of a successful metal-catalyzed cross-coupling reaction is governed by a number of factors.[33] By finding optimized reaction conditions, the effects of various bases, temperatures, solvents and reaction hours on the amination process employing Pd–NHC complexes were surveyed. 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 organic bases like KO^{t}Bu provided higher conversions, which may be due to higher solubility in organic solvents. The solubility of the reactants and catalyst in the solvent is important to the success of the coupling reaction. The effect of various solvents on the reaction system was studied. It was observed that dimethoxyethane (DME) was effective in providing higher conversions whereas solvents like NMP, toluene, DMF and dioxane showed lower conversions, probably due to solvent polarity. Reaction temperature is another factor critical for amination reaction. Pd–NHC complex catalysis for the amination of aryl bromide was explored at 80 °C because poor performance was observed when the reaction temperature was 60 °C or below 60 °C. No further increase in the yield of the amination product was observed, even when the reaction temperature was increased above 80 °C. The scope of Pd–NHC complex catalysts (**2a–c**) for the amination of aryl halide was explored by coupling reaction of bromobenzene with anilines/amines using KO^{t}Bu as base in the solvent DME at 80 °C. The results are reported in Table 1. We have demonstrated high yields Pd–NHC catalyzed amination of primary amines to triarylamines (Table 1 entries 2, 6 and 9). With *p*-anisidine containing electron donating group at the *para* position, the amination reaction proceeds with considerable increase in the yield up to 75–89% (Table 1, entries 4–6).When no catalyst was added, the blank reaction with solvent DME, KO^{t}Bu as base exhibited extremely low reactivity towards the yield of triarylamine with many byproducts from the aryl halide substrate.

We also examined the amination of bromobenzene (1.2 mmol) with cycloheptylamine or 2-aminopyridine (1 mmol) under the same reaction conditions and moderate to good yields were obtained (Table 1, entries 12 and 15). 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 only to N-monoarylation and gave secondary amines in a high yield and we observed N-diarylation in extremely low yield. The best catalyst performance was observed in the presence of the 3,4,5-trimethoxybenzyl-based NHC complex in the amination reaction.

Conclusions

We have prepared dioxane-functionalized benzimidazolium salts (**1a–c**) and palladium–NHC complexes (**2a–c**) whose structures were confirmed by ^{1}H NMR, ^{13} C NMR, IR, elemental analysis. Palladium-catalyzed C–N bond forming reactions of aryl bromide were carried out and it was found that all the complexes worked as active catalysts for the amination of aryl halide. 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.

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