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Research paper

Synthesis of novel palladium(II) N-heterocyclic carbene complexes and their catalytic activities in the direct C5 arylation reactions

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ABSTRACT

New palladium(II) N-heterocyclic carbene complexes have been easily obtained in good yields from the carbene transfer reaction of silver-NHC complexes with $PdCl_2(PhCN)_2$ and characterized by elemental analysis, ^1H NMR and ^{13}C NMR spectroscopy. These complexes were used as catalysts in the direct C5 arylation of 2-*n*-butylfuran, 2-*n*-butylthiophene and 2-*n*-propylthiazole with various aryl bromides at 130 °C in N,N-dimethylacetamide (DMAc) for 1 h. The arylation reactions were regioselective, and in all cases, only the C5-arylated products were formed. The corresponding arylation products were obtained in moderate to good yields by using 0.5 mol% of palladium-NHC complexes.

1. Introduction

N-heterocyclic carbenes (NHCs) have become popular ligands for metal-catalyzed reactions due to their ease of synthesis, thermal and oxidative stability, functional group tolerance and excellent catalytic activities [1–4]. In 1991, Arduengo and co-workers successfully isolated and characterized the first stable free N-heterocyclic carbene [5]. Since then, many N-heterocyclic carbene-metal complexes have been synthesized and used as catalysts of various transformations such as C–C and C–N arylation [6–10], olefin metathesis [11,12], transfer hydrogenation [13–16], hydrosilylation [17–19] and CO-ethylene co-polymerization reactions [20,21]. Imidazole, benzimidazole, imidazoline and triazole derived NHCs have been reported during the last decade [22–26]. In general, NHC chemistry is dominated by imidazole and imidazoline based carbene ligands [27,28]. On the other hand, benzimidazol-2-ylidenes have received considerably less interest, though in recent years this area has been developed by Hahn and others [29–36]. However, catalytic activity of benzimidazol-2-ylidene metal complexes in C–C coupling reactions [37–40] and transfer hydrogenations [41–43] has been reported. In recent years, the synthesis of arylated heterocycles have received considerable attention because of their biological and physical properties [44]. Bi(hetero)aryl compounds can be prepared via palladium-catalyzed reactions such as Stille, Suzuki, Kumada or Negishi couplings [45–48]. However, these reactions require the organometallic nucleophilic reagents and provide a stoichiometric amount of side products. But, extraordinary reactivities of these reagents as nucleophiles and bases sometimes give rise to the limitations in the synthesis of multifunctional compounds.

In 1990, Ohta and co-workers have reported direct access to arylated heterocycles from heteroaromatics (such as thiophenes, furans or thiazoles) and aryl halides in moderate to good yields by using $[Pd(PPh_3)_4]$ as the catalyst [49]. Since then, the palladium-catalyzed direct arylation of heteroaryl derivatives with aryl halides has become a valuable method for the synthesis of arylated heterocycles [50–67]. So far, there are only a few report on (NHC) Pd-catalyzed direct arylation of heterocycles [68–76]. Therefore, we now report the synthesis and characterization of new palladium(II) complexes with N-heterocyclic carbene ligand from silver complexes and their application as catalysts for the direct 5-arylation of heteroaromatics with various aryl halides.

2. Experimental

2.1. Materials and methods

All reactions for the preparation of the palladium(II)-NHC complexes (**2a-d**) were carried out under argon in flame-dried glassware using standard Schlenk techniques. The solvents used were purified by distillation over the drying agents indicated and were transferred under Ar: THF, Et_2O (Na/K alloy), CH_2Cl_2 (P_4H_{10}), hexane, toluene (Na). All reagents were purchased from Sigma-Aldrich,

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Merck and Fluka. All ^{1}H and ^{13}C NMR were recorded in $CDCl_3$ using a Bruker AC300P FT spectrometer operating at 300.13 MHz (^{1}H) or 75.47 MHz (^{13}C). Chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in hertz. FT-IR spectra were recorded as KBr pellets in the range 400–4000 cm^{-1} on a Mattson 1000 spectrophotometer (wavenumbers, cm^{-1}). GC were measured by GC-FID on a Agilent 6890N gas chromatograph equipped with an HP-5 column of 30 m length, 0.32 mm diameter and 0.25 μm film thickness. Melting points were measured in open capillary tubes with an Electrothermal-9200 melting point apparatus and uncorrected. Elemental analyses were performed at Inönü University research center.

2.2. General procedure for the preparation of Ag(I)-N-heterocyclic carbene complexes, **1**

A solution of benzimidazolium salt (1.0 mmol), Ag_2O (0.5 mmol) and activated molecular sieves Å in dichloromethane (20 mL) was stirred for 24 h under exclusion of light at room temperature. The reaction mixture was filtered through celite and solvent removed under reduced pressure. The crude product was recrystallized from dichloromethane: hexane (1:2) at room temperature. The resulting white solid was isolated by filtration and dried in vacuum.

2.2.1. Bis[1-(1-methyl-2-dimethylaminoethyl)-3-benzylbenzimidazol-2-ylidene]-dichloropalladium(II), **2a**

A solution of chloro-[1-(1-methyl-2-dimethylaminoethyl)-3-benzylbenzimidazol-2-ylidene]silver(I) complex (0.27 g, 0.62 mmol) and $PdCl_2(PhCN)_2$ (0.12 g, 0.32 mmol) in dichloromethane (20 mL) was stirred for 24 h under exclusion of light at room temperature. Then, the solution was filtered through celite, and crystallized from dichloromethane: diethyl ether (1:2) at room temperature. The crystals were filtered, washed with diethyl ether (3 × 10 mL) and dried under vacuum. Yield: 83%; m.p. 248–249 °C; IR $\nu_{(NCN)}$: 1477 cm^{-1}. ^{1}H NMR (300.13 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.91 (d, 6H, J: 6.6 Hz, $CH(CH_3)CH_2N(CH_3)_2$); 2.16 (s, 12H, $N(CH_3)_2$); 3.69–3.74 (m, 2H, $CH(CH_3)CH_2N(CH_3)_2$); 4.60–4.68 (m, 4H, $CH(CH_3)CH_2N(CH_3)_2$); 5.90 and 5.98 (d, 4H, J: 12.9 Hz, CH_2Ar); 7.12–7.38 (m, 18H, Ar-H). ^{13}C NMR (75.47 MHz, $CDCl_3$, 25 °C, TMS): δ = 11.0 ($CH(CH_3)CH_2N(CH_3)_2$); 40.4 ($N(CH_3)_2$); 51.0 and 52.7 ($CH(CH_3)CH_2N(CH_3)_2$); 59.0 (CH_2Ar); 110.8, 110.9, 111.4, 122.8, 122.9, 127.4, 127.5, 128.8, 128.9, 133.7, 135.4 and 135.7 (Ar-C); 181.6 (C-Pd). Anal. Calcd. For $C_{38}H_{46}N_6PdCl_2$: C, 59.73; H, 6.03; N, 11.00. Found: C, 59.78; H, 6.09; N, 11.12%.

2.2.2. Bis[1-(1-methyl-2-dimethylaminoethyl)-3-(2,4,6-trimethylbenzyl)benzimidazol-2-ylidene]-dichloropalladium(II), **2b**

This compound was prepared in same way as **2a** from chloro-[1-(1-methyl-2-dimethylaminoethyl)-3-(2,4,6-trimethylbenzyl-benzimidazol-2-ylidene]silver(I) complex (0.30 g, 0.62 mmol) and $PdCl_2(PhCN)_2$ (0.12 g, 0.32 mmol) in dichloromethane (10 mL). Yield: 85%; m.p. 241–242 °C; IR $\nu_{(NCN)}$: 1475 cm^{-1}. ^{1}H NMR (300.13 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.11 (d, 6H, J: 6.6 Hz, $CH(CH_3)CH_2N(CH_3)_2$); 2.31 (s, 12H, $N(CH_3)_2$); 4.00–4.06 (m, 2H, $CH(CH_3)CH_2N(CH_3)_2$); 2.31 and 2.38 (s, 18H, $CH_2C_6H_2(CH_3)_3$-2,4,6); 4.85–4.98 (m, 4H, $CH(CH_3)CH_2N(CH_3)_2$); 6.42 and 6.45 (s, 4H, CH_2Ar); 6.94 (s, 4H, Ar-H); 7.14–7.43 (m, 8H, Ar-H). ^{13}C NMR (75.47 MHz, $CDCl_3$, 25 °C, TMS): δ = 11.2 ($CH(CH_3)CH_2N(CH_3)_2$); 40.6 ($N(CH_3)_2$); 50.2 and 51.2 ($CH(CH_3)CH_2N(CH_3)_2$); 20.9 and 21.0 ($CH_2C_6H_2(CH_3)_3$-2,4,6); 59.4 (CH_2Ar); 110.6, 111.1, 111.7, 122.4, 122.7, 127.9, 129.6, 134.0, 135.4, 138.1 and 138.4 (Ar-C); 181.9 (C-Pd). Anal. Calcd. For $C_{44}H_{58}N_6PdCl_2$: C, 62.31; H, 6.85; N, 9.91. Found: C, 62.40; H, 6.81; N, 9.98%.

2.2.3. Bis[1-(1-methyl-2-dimethylaminoethyl)-3-(2,3,5,6-tetramethylbenzyl)benzimidazol-2-ylidene]-dichloropalladium(II), **2c**

This compound was prepared in same way as **2a** from chloro-[1-(1-methyl-2-dimethylaminoethyl)-3-(2,3,5,6-tetramethylbenzylbenzimidazol-2-ylidene]silver(I) complex (0.31 g, 0.62 mmol) and $PdCl_2(PhCN)_2$ (0.12 g, 0.32 mmol) in dichloromethane (10 mL). Yield: 80%; m.p. 228–229 °C; IR $\nu_{(NCN)}$: 1474 cm^{-1}. ^{1}H NMR (300.13 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.02 (d, 6H, J: 6.6 Hz, $CH(CH_3)CH_2N(CH_3)_2$); 2.29 (s, 12H, $N(CH_3)_2$); 4.10–4.12 (m, 2H, $CH(CH_3)CH_2N(CH_3)_2$); 2.33 and 2.36 (s, 24H, $CH_2C_6H(CH_3)_4$-2, 3,5,6); 4.98–5.06 (m, 4H, $CH(CH_3)CH_2N(CH_3)_2$); 5.85 and 5.88 (s, 4H, CH_2Ar); 6.31–7.28 (m, 10H, Ar-H). ^{13}C NMR (75.47 MHz, $CDCl_3$, 25 °C, TMS): δ = 11.6 ($CH(CH_3)CH_2N(CH_3)_2$); 40.6 ($N(CH_3)_2$); 50.0 and 51.1 ($CH(CH_3)CH_2N(CH_3)_2$); 16.5 and 20.6 ($CH_2C_6H_2(CH_3)_3$-2, 3,5,6); 59.5 (CH_2Ar); 110.7, 111.9, 122.5, 122.8, 130.7, 132.3, 134.2, 134.3, 134.4, 134.7, 134.8 and 135.3 (Ar-C); 181.8 (C-Pd). Anal. Calcd. For $C_{46}H_{62}N_6PdCl_2$: C, 63.06; H, 7.08; N, 9.60. Found: C, 63.15; H, 7.15; N, 9.68%.

2.2.4. Bis[1-(1-methyl-2-dimethylaminoethyl)-3-(2,3,4,5,6-pentamethylbenzyl)benzimidazol-2-ylidene]-dichloropalladium(II), **2d**

This compound was prepared in same way as **2a** from chloro-[1-(1-methyl-2-dimethylaminoethyl)-3-(2,3,4,5,6-pentamethyl-benzylbenzimidazol-2-ylidene]silver(I) complex (0.32 g, 0.62 mmol) and $PdCl_2(PhCN)_2$ (0.12 g, 0.32 mmol) in dichloromethane (10 mL). Yield: 81%; m.p. 254–255 °C; IR $\nu_{(NCN)}$: 1476 cm^{-1}. ^{1}H NMR (300.13 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.13 (d, 6H, J: 6.6 Hz, $CH(CH_3)CH_2N(CH_3)_2$); 2.27 (s, 12H, $N(CH_3)_2$); 4.09–4.14 (m, 2H, $CH(CH_3)CH_2N(CH_3)_2$); 2.22, 2.29 and 2.34 (s, 30H, $CH_2C_6(CH_3)_5$-2, 3,4,5,6); 5.09–5.14 (m, 4H, $CH(CH_3)CH_2N(CH_3)_2$); 5.83 and 5.86 (s, 4H, CH_2Ar); 6.41–7.79 (m, 8H, Ar-H). ^{13}C NMR (75.47 MHz, $CDCl_3$, 25 °C, TMS): δ = 11.5 ($CH(CH_3)CH_2N(CH_3)_2$); 40.6 ($N(CH_3)_2$); 50.4 and 51.7 ($CH(CH_3)CH_2N(CH_3)_2$); 16.8, 16.9, 17.0, 17.3 and 17.5 ($CH_2C_6(CH_3)_5$-2,3,4,5,6); 59.8 (CH_2Ar); 110.8, 111.1, 112.1, 122.8, 123.0, 127.7, 133.1, 133.8, 134.1, 134.2, 135.1 and 135.9 (Ar-C); 181.6 (C-Pd). Anal. Calcd. For $C_{48}H_{66}N_6PdCl_2$: C, 63.76; H, 7.31; N, 9.30. Found: C, 63.82; H, 7.37; N, 9.38%.

2.3. General procedure for the direct C5 arylations

The heteroaryl derivative (2 mmol), aryl halide (1 mmol), Pd complexes **2a**-**d** (0.005 mmol), KOAc (1 mmol) and DMAc (2 mL) were added into a Schlenk tube equipped with a magnetic stirring bar. The Schlenk tube was purged several times with argon and was placed in a preheated oil bath at 130 °C. The reactants were stirred for 1 h with aryl bromides. The solvent was removed by heating the reaction vessel under vacuum. The products were eluted by using an appropriate ratio of diethyl ether/pentane (1:3). The reaction mixture was purified by flash chromatography on silica gel. The purity of compounds was checked by GC and NMR. Conversions were based on aryl bromides.

3. Results and discussion

3.1. Synthesis of Pd(II)-NHC complexes

Various synthetic methods have been described in the literature for the synthesis of Pd(II)-NHC complexes. One of these methods is the generation of a silver(I)-NHC complex, followed by transfer of the carbene unit to palladium metal. This reaction has successfully been applied to a variety of metals, including ruthenium, rhodium, iridium, gold and nickel [77]. Our previously reported [78] silver (I)-NHC complexes, **1** were prepared by reacting the benzimidazolium salts with Ag_2O in dichloromethane under exclusion of light

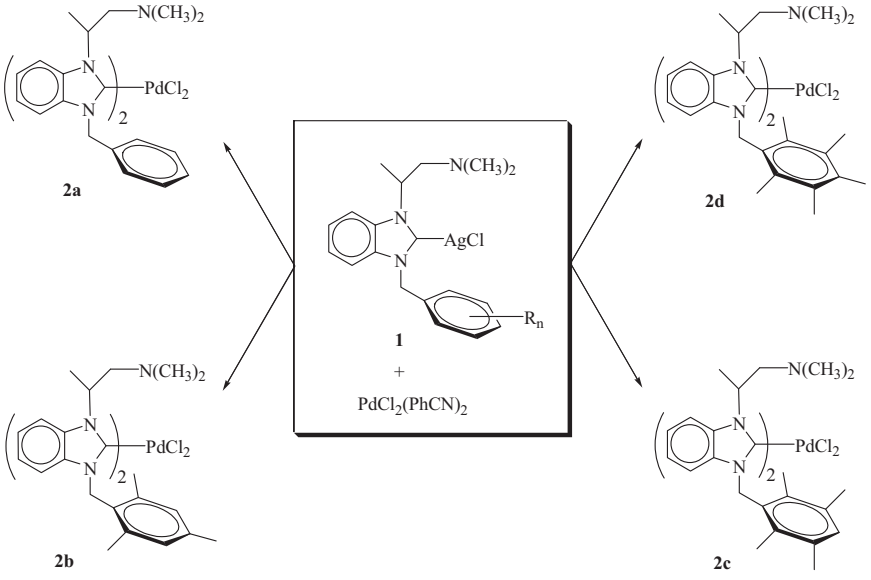
at room temperature. The palladium(II)-NHC complexes **2a**-**d** were prepared by treatment of silver(I)-NHC complexes as a carbene transfer reagent with $PdCl_2(PhCN)_2$ in dichloromethane at room temperature in good yields (Scheme 1). These complexes are stable both in solution and in solid states against air, light and moisture, and are soluble in chlorinated solvents. The new complexes were characterized by ^1H NMR, ^{13}C NMR, IR spectroscopy and elemental analysis techniques, which support the proposed structures. They show a characteristic $\upsilon_{(NCN)}$ band at 1477, 1475, 1474 and 1476 cm^{-1} for **2a**, **2b**, **2c** and **2d**, respectively. NMR analyses of the complexes showed that the N-heterocyclic carbene ligands transferred from silver complexes to palladium center. The ^{13}C NMR spectra of the Pd-NHC complexes exhibit the NCN resonances between 181.6 and 181.9 ppm, which are consistent with reported values for $[PdCl_2(NHC)_2]$ complexes. The geometry of palladium(II) di-NHC complexes may be trans or cis. Generally, The trans geometry was obtained but palladium(II) complexes with cis oriented NHC ligands have been described [79–81]. The geometry of these complexes was not defined, as an appropriate single crystal from these complexes for X-ray diffraction could not be obtained.

*3.2. Catalytic studies: direct arylation of various heteroaromatic compounds with ary bromides using **2a**-**d** as catalyst*

The catalytic activities of palladium complexes as catalysts in the direct arylation reactions to prepare arylated heterocycles, which are important chemicals for many applications were extensively investigated. However, only a few examples of Pd-carbene complexes bearing benzimidazol-2-ylidene ligand for direct arylation of heteroaromatic compounds have been reported so far [69,72,76]. Based on our previous results [76], in this study, N,N-dimethylacetamide (DMAc) was chosen as the solvent and potassium acetate (KOAc) as the base. The reactions were performed at 130 °C for 1 h in presence of palladium(II)-NHC complexes (**2a**-**d**). Under this reaction conditions, three heterocycles substrates (2-*n*-butylfuran, 2-*n*-butylthiophene and 2-*n*-propylthiazole) were reacted with aryl bromides bearing electron-donating or electron-withdrawing groups at the *para* position to furnish the arylated products in moderate to good yields (Tables 1–3). The reactions between the 4-bromoacetophenone with 2-*n*-butylfuran, 2-*n*-butylthiophene or 2-*n*-propylthiazole without palladium(II)-NHC complexes resulted in only 1% yields under this reaction conditions. The coupling reactions proceed selectively at C5 position of heteroaromatic compounds, and in all cases, only the C5-arylated products were formed. Initially, we investigated the reactions of 2-*n*-propylthiazole with bromobenzene for the direct C5 arylation reactions using these new palladium(II)-NHC (**2a**-**d**) complexes as catalyst. The coupling products were obtained with high yields by Pd-NHC complexes (**2b**, **2c** and **2d**) (Table 1, entries 14–16). Then, activated and deactivated aryl bromides were reacted with 2-*n*-propylthiazole in the presence of these complexes (Table 1, entries 1–13). 2-*n*-Propylthiazole has been arylated in good to excellent yields using aryl bromides (Table 1, entries 1–16). Of the five different aryl bromides, those bearing electron-donating groups react with 2-*n*-propylthiazole to give the coupled products in excellent yields (Table 1, entries 5–12). For all aryl bromides, the best conversions were achieved with complexes (**2b**, **2c** and **2d**) in 96–100% conversions.

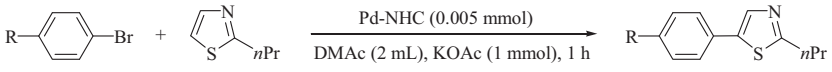
Next, we examined the reactivity of 2-*n*-butylthiophene using the same aryl bromides in the presence of palladium(II)-NHC (**2a**-**d**) complexes as catalyst under similar reaction conditions (Table 2). The coupling products were obtained with high yields. As seen in the reactions of 2-*n*-propylthiazole with aryl bromides, substituents on aryl bromides display a minor effect on the reaction of 2-*n*-butylthiophene with aryl bromides. 4-Bromoacetophenone was successfully coupled with 2-*n*-butylthiophene in presence of palladium(II)-NHC complexes (**2a**-**d**) to give 5-(4-acetylphenyl)-2-*n*-butylthiophene in 65–77% yields. High conversions for 2-*n*-butylthiophene were obtained using the electron-rich 4-bromoanisole in the presence of palladium(II)-NHC (**2a**-**d**) (Table 2, entries 5–8). The catalytic activity of palladium(II)-NHC complexes (**2a**-**d**) in these reactions were similar to the direct C5 arylation of 2-*n*-propylthiazole. The complex **2a** catalyses the reaction of 2-*n*-butylthiophene with aryl bromides in good yields (Table 2, entries 1, 5, 9 and 13), whereas the use of complexes (**2b**, **2c** and **2d**) gave higher yields for these reactions.

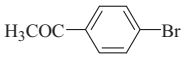
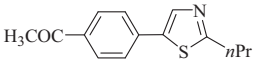
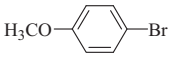
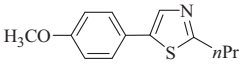
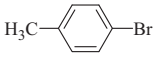
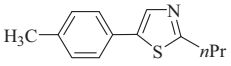
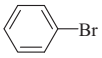
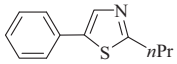
Finally, we studied the reaction of 2-*n*-butylfuran with aryl bromides by using palladium(II)-NHC (**2a**-**d**) catalysts in order to obtain 5-aryl-2-*n*-butylfurans. The reactions were performed with 4-substituted aryl bromides at 130 °C for 1 h in N,N-dimethylacetamide (DMAc) and the results of these reactions are summarized in Table 3. All of the aryl bromides gave moderate to high yields of



Scheme 1. The synthesis of palladium(II)-NHC complexes.

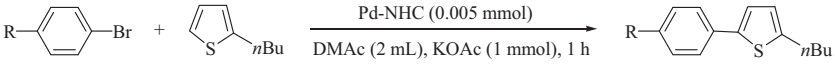
Table 1
Direct C5 arylation of 2-*n*-propylthiazole by using aryl bromides.[abcd]

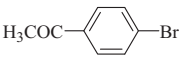
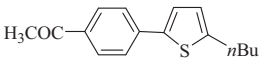
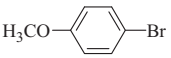
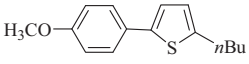
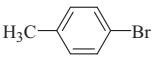
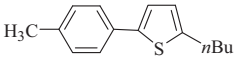
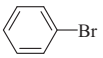
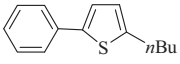


Entry	Aryl bromide	Pd-NHC	Product	Conv. (Yield%)
1		**2a**		90(68)
2		**2b**		99(76)
6		**2c**		98(78)
4		**2d**		96(74)
5		**2a**		96(78)
6		**2b**		100(89)
7		**2c**		100(92)
8		**2d**		99(87)
9		**2a**		98(75)
10		**2b**		98(86)
11		**2c**		99(85)
12		**2d**		99(89)
13		**2a**		94(71)
14		**2b**		98(76)
15		**2c**		99(81)
16		**2d**		97(79)

[a] Reaction condition:2-*n*-propylthiazole (2 mmol), aryl bromide (1 mmol), Pd-NHC (**2a**-**d**) (0.005 mmol), KOAc (1 mmol), N,N-dimethylacetamide (2 mL), 130 °C, 1 h.
[b] Product purity was checked by GC and NMR.
[c] Conversions were calculated according to aryl bromide.
[d] Isolated yields.

Table 2
Direct C5 arylation of 2-*n*-butylthiophene by using aryl bromides.[abcd]

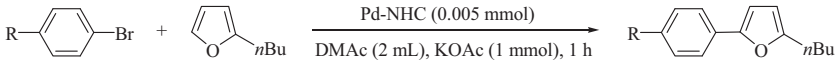


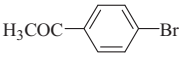
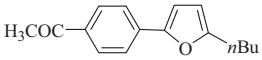
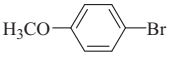
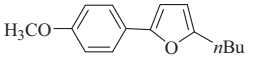
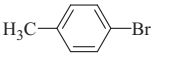
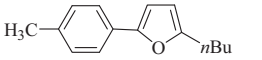
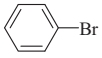
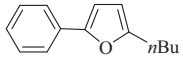
Entry	Aryl bromide	Pd-NHC	Product	Conv. (Yield%)
1		**2a**		88(65)
2		**2b**		94(74)
6		**2c**		96(77)
4		**2d**		95(76)
5		**2a**		93(76)
6		**2b**		99(88)
7		**2c**		100(90)
8		**2d**		97(86)
9		**2a**		94(74)
10		**2b**		98(87)
11		**2c**		97(83)
12		**2d**		96(81)
13		**2a**		90(71))
14		**2b**		95(79)
15		**2c**		97(83)
16		**2d**		96(81)

[a] Reaction condition: 2-*n*-butylthiophene (2 mmol), aryl bromide (1 mmol), Pd-NHC (**2a**-**d**) (0.005 mmol), KOAc (1 mmol), N,N-dimethylacetamide (2 mL), 130 °C, 1 h.
[b] Product purity was checked by GC and NMR.
[c] Conversions were calculated according to aryl bromide.
[d] Isolated yields.

C5 arylation products in the presence of 0.5 mol% catalysts. The reaction of 2-*n*-butylfuran with bromobenzene generated the corresponding product (2-*n*-butyl-5-phenylfuran) in 69–83% yields using palladium(II)-NHC complexes (**2a**-**d**) (Table 3, entries 13–16). High conversions for 2-*n*-butylfuran were obtained using 4-bromoacetophenone in the presence of palladium(II)-NHC (**2a**-**d**) (Table 3, entries 1–4). The catalytic activities of complexes with NHC ligands bearing methyl substituents on benzyl group were quite close to each other. On the other hand, the palladium (II)-NHC complex (**2a**) exhibited low catalytic activity compared

Table 3
Direct C5 arylation of 2-*n*-butylfuran by using aryl bromides.[abcd]



Entry	Aryl bromide	Pd-NHC	Product	Conv. (Yield%)
1		**2a**		95(77)
2		**2b**		98(88)
6		**2c**		99(90)
4		**2d**		96(86)
5		**2a**		87(73)
6		**2b**		94(84)
7		**2c**		97(87)
8		**2d**		95(85)
9		**2a**		85(67)
10		**2b**		97(87)
11		**2c**		93(82)
12		**2d**		95(84)
13		**2a**		88(69)
14		**2b**		90(76)
15		**2c**		94(79)
16		**2d**		97(83)

[a] Reaction condition: 2-*n*-butylfuran (2 mmol), aryl bromide (1 mmol), Pd-NHC (**2a-d**) (0.005 mmol), KOAc (1 mmol), N,N-dimethylacetamide (2 mL), 130 °C, 1 h.
[b] Product purity was checked by GC and NMR.
[c] Conversions were calculated according to aryl bromide.
[d] Isolated yields.

to the other three complexes (**2b-d**) for direct C5 arylation reactions of 2-*n*-butylfuran with using aryl bromides.

4. Conclusion

In summary, The palladium(II)-NHC complexes **2a-d** have been easily prepared by reaction of silver(I)-NHC complexes as a carbene transfer reagent with $PdCl_2(PhCN)_2$ in dichloromethane at room temperature in good yields. The catalytic activity of these complexes was investigated in direct C5 arylation of thiazole, thiophene and furan derivatives in the presence of potassium acetate. Although 3-, 4- and 5-positions of heteroaromatics are open, the coupling reactions proceed selectively at C5 position of heteroaromatic compounds, and in all cases, only the C5-arylated products were formed. In this study, all palladium(II)-NHC complexes demonstrated excellent catalytic activity in direct C5 arylation of thiazole, thiophene and furan derivatives. Among the tested complexes, the palladium complexes (**2b-d)** containing NHC ligands with methyl groups exhibited better catalytic activity.

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