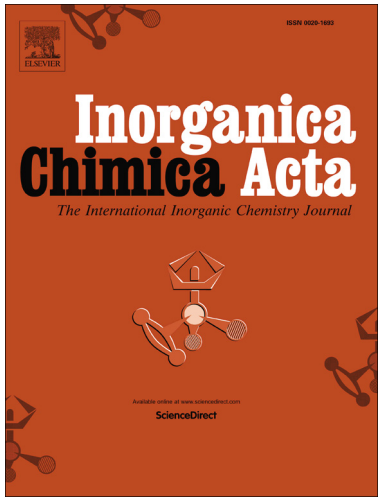


Dichlorido(3-chloropyridine-*N*)[1,3-dialkylbenzimidazol-2-ylidene]palladium(II) complexes: Synthesis, characterization and catalytic activity in the arylation reaction

Senem Akkoç, Yetkin Gök

PII: S0020-1693(15)00021-3
DOI: http://dx.doi.org/10.1016/j.ica.2015.01.019
Reference: ICA 16368

To appear in: *Inorganica Chimica Acta*

Received Date: 15 November 2014
Revised Date: 9 January 2015
Accepted Date: 11 January 2015

Please cite this article as: S. Akkoç, Y. Gök, Dichlorido(3-chloropyridine-*N*)[1,3-dialkylbenzimidazol-2-ylidene]palladium(II) complexes: Synthesis, characterization and catalytic activity in the arylation reaction, *Inorganica Chimica Acta* (2015), doi: http://dx.doi.org/10.1016/j.ica.2015.01.019

Dichlorido(3-chloropyridine-*N*)[1,3-dialkylbenzimidazol-2-ylidene]palladium(II) complexes: Synthesis, characterization and catalytic activity in the arylation reaction

Senem Akkoç[a*] and Yetkin Gök[b]

[a]Erciyes University, Faculty of Science, Department of Chemistry, 38039, Kayseri, Turkey

[b]Inönü University, Faculty of Science and Arts, Department of Chemistry, 44280, Malatya, Turkey

ABSTRACT

Six novel **P**yridine **E**nhanced **P**recatalyst **P**reparation, **S**tabilization and **I**nitiation (PEPPSI) themed palladium *N*-heterocyclic carbene (Pd-NHC) complexes (**2a-f**) were synthesized in good yields from the reaction of 1,3-dialkylbenzimidazolium salts with $PdCl_2$ in the presence of K_2CO_3 as base in 3-chloropyridine. These synthesized complexes were characterized by means of elemental analysis, FT-IR, ^1H and ^{13}C NMR spectroscopic methods. The fully characterized novel complexes (**2a-f**) were tested as catalysts in the direct arylation of 2-*n*-propylthiazole, 2-*n*-butylthiophene and 2-*n*-butylfuran with different aryl bromides at 130 ºC for 1 h. The complexes exhibited fairly high catalytic activities under the given conditions. The highest conversions were achieved when complexes **2a**, **2e** and **2f** were used as catalysts in direct arylation.

Keywords: PEPPSI palladium complexes; *N*-heterocyclic carbene; Benzimidazole; Catalyst; Direct arylation.

Corresponding author. Tel: +90 352 437 52 62 **Fax:** +90 352 437 49 33

E-mail address: senemakkoc@erciyes.edu.tr

1. Introduction

After the independent discovery of *N*-heterocyclic carbenes (NHCs) by Wanzlick [1] and Öfele [2], the interest in NHCs has increased with the studies of Arduengo in 1991 [3]. NHCs have several interesting properties such as high stability, low toxicity, strong σ-donating, weak π-accepting abilities, and steric and electronic effects in generating strong bonds to a metal [4-8]. Because of these characteristic properties of metal NHC complexes, various benzimidazole and imidazole based Pd-NHC and PEPPSI Pd-NHC complexes have been used to carry out Sonogashira [9, 10], Suzuki-Miyaura [11-13], Kumada-Tamao-Corriu [12, 14], Negishi [12, 15-17], Hiyama [18] and Mizoroki-Heck [4, 19] cross-coupling reactions. The use of these complexes has also been reported for arylation [20-22], amination [23], allylation [24], Buchwald-Hartwig amination [25] and hydroarylation reactions [26].

Our interest was aroused by a study which describes synthesized Pd-PEPPSI complexes using an imidazole nucleus by Organ et al. in 2006 [15]. A lot of work has been done by many groups since 2006 on these types of complexes, which are extremely stable in air and moisture. In general, an imidazole nucleus has been used in these kinds of studies [27-31]. Therefore, we used a benzimidazole nucleus for this study. We present the synthesis of six novel PEPPSI themed [1,3-dialkylbenzimidazol-2-ylidene]$PdCl_2$(3-chloropyridine) complexes (**2a-f**) which were prepared from 1,3-dialkylbenzimidazolium salts with $PdCl_2$ in the presence of K_2CO_3 as a base in 3-chloropyridine. The structures of these compounds were identified with spectroscopic and elemental analysis techniques. The novel generated PEPPSI complexes were tested for catalytic activity in the direct arylation reaction. As a catalyst, these complexes gave very good results at short reaction time and low catalyst loading (**2a-f**) when they were used in this reaction for the formation of aryl-aryl bonds.

2. Experimental

2.1 Materials and methods

All reactions for the synthesis of the PEPPSI Pd-NHC complexes (**2a-f**) were done using standard Schlenk type flasks and standard high vacuum line techniques. The solvents used were of analytical grade. All reagents and solvents were purchased from Sigma-Aldrich, Merck and Fluka. All ^{1}H NMR and ^{13}C NMR analyses were performed in $CDCl_3$. The ^{1}H NMR and ^{13}C NMR spectra were recorded by using a Bruker AC300P FT spectrometer operating at 300.13 MHz (^{1}H) and 75.47 MHz (^{13}C). Chemical shifts (δ) were given in ppm according to relative tetramethylsilane (TMS). The coupling constants (*J*) were given in Hz. The FT-IR spectra of the synthesized novel complexes were recorded in the 450–4000 cm^{-1} region with a Shimadzu FT-IR 8400 spectrophotometer. Melting points were determined in open capillary tubes with an Electrothermal-9200 melting point device. Gas chromatographic analysis was conducted with an Agilent 6890N Network GC System using an HP-5 column with a length of 30 m, column diameter of 0.32 mm, a column filler size of 0.25 µm and temperature range from -60 °C to 325 °C. Elemental analyses were performed by using CHNS-932 LECO apparatus.

Synthesis of 1,3-dibenzylbenzimidazol-2-ylidene-N-(3-chloropyridine)dichloropalladium(II) complex, 2a

1,3-dibenzylbenzimidazolium salt (0.2 g, 0.6 mmol), $PdCl_2$ (0.1 g, 0.6 mmol) and K_2CO_3 (0.4 g) in 3-chloropyridine (3 mL) were heated at 80 ºC for 16 h. After completion of the reaction, the reaction mixture was cooled to room temperature and was added to dichloromethane (20 mL). The obtained mixture was filtered into a silica gel column and then the solvent was removed under reduced pressure. The product was washed with diethyl ether (3×8 mL) and dried under vacuum. Very light yellow colored crystals were

obtained; yield: 70 %; m.p.: 215-216 ºC; FT-IR$_{\nu(CN)}$: 1409.9 cm^{-1}. ^{1}H NMR (300.13 MHz, $CDCl_3$, 298 K, TMS), δ; 6.28 (s, 4 H, NC*H*$_2$C$_6$H$_5$); 7.12-8.87 (m, 18 H, Ar-*H*). ^{13}C NMR (75.47 MHz, $CDCl_3$), δ; 53.2 (NC*H*$_2$C$_6$H$_5$); 111.5, 123.4, 124.9, 125.3, 127.7, 128.0, 128.2, 128.3, 129.1, 132.7, 134.9, 138.2, 149.3 and 150.3 (Ar-*C*); 163.4 (N-*C*$_{NHC}$-N). Elemental analysis calcd. (%) for $C_{26}H_{22}Cl_3N_3Pd$ (589.25 g/mol): C 53.00, H 3.76, N 7.13; found: C 52.96, H 3.80, N 7.11.

Synthesis of 1-naphthalenomethyl-3-benzylbenzimidazol-2-ylidene-N-(3-chloropyridine)dichloropalladium(II) complex, 2b

According to the same conditions and procedure for the **2a** complex, the **2b** complex was prepared from 1-naphthalenomethyl-3-benzylbenzimidazolium salt (0.2 g, 0.5 mmol) and $PdCl_2$ (0.09 g, 0.5 mmol) in 3-chloropyridine (3 mL) at 80 ºC for 16 h. A cream colored powder was obtained; yield: 68 %; m.p.: 120-121 ºC; FT-IR$_{\nu(CN)}$: 1413.7 cm^{-1}. ^{1}H NMR (300.13 MHz, $CDCl_3$, 298 K, TMS), δ; 6.31 (s, 2 H, NC*H*$_2$C$_6$H$_5$); 6.72 (s, 2 H, NC*H*$_2$C$_{10}$H$_7$); 7.08-7.92 (m, 20 H, Ar-*H*). ^{13}C NMR (75.47 MHz, $CDCl_3$), δ; 50.4 (NC*H*$_2$C$_6$H$_5$); 53.4 (NC*H*$_2$C$_{10}$H$_7$); 111.4, 111.5, 122.6, 123.5, 124.8, 125.6, 126.0, 126.8, 128.3, 128.9, 129.1, 130.1, 130.9, 132.6, 133.7, 135.0, 138.1, 147.5, 148.2 and 150.3 (Ar-*C*); 164.2 (N-*C*$_{NHC}$-N). Elemental analysis calcd. (%) for $C_{30}H_{24}Cl_3N_3Pd$ (639.31 g/mol): C 56.36, H 3.78, N 6.57; found: C 56.30, H 3.82, N 6.55.

Synthesis of 1-phenyl-3-naphthalenomethylbenzimidazol-2-ylidene-N-(3-chloropyridine)dichloropalladium(II) complex, 2c

According to the same conditions and procedure for the **2a** complex, the **2c** complex was prepared from 1-phenyl-3-naphthalenomethylbenzimidazolium salt (0.2 g,

0.5 mmol) and $PdCl_2$ (0.09 g, 0.5 mmol) in 3-chloropyridine (3 mL). A cream colored powder was obtained; yield: 69 %; m.p.: 149-150 ºC; FT-$IR_{v(CN)}$: 1503.8 cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$, 298 K, TMS), δ; 6.78 (s, 2 H, $NCH_2C_{10}H_7$); 6.99-8.89 (m, 20 H, Ar-*H*). ^{13}C NMR (75.47 MHz, $CDCl_3$), δ; 50.4 ($NCH_2C_{10}H_7$); 111.2, 111.5, 122.8, 123.9, 124.7, 125.7, 126.1, 126.9, 128.0, 128.8, 129.1, 129.7, 130.9, 132.5, 133.8, 134.1, 135.9, 137.0, 138.0, 149.1 and 150.2 (Ar-*C*); 164.1 (N-C_{NHC}-N). Elemental analysis calcd. (%) for $C_{29}H_{22}Cl_3N_3Pd$ (625.28 g/mol): C 55.70, H 3.55, N 6.72; found: C 55.75, H 3.57, N 6.72.

Synthesis of 1-naphthalenomethyl-3-(4-methylbenzyl)benzimidazol-2-ylidene-N-(3-chloropyridine)dichloropalladium(II) complex, 2d

According to the same conditions and procedure for the **2a** complex, the **2d** complex was prepared from 1-naphthalenomethyl-3-(4-methylbenzyl)benzimidazolium salt (0.2 g, 0.5 mmol) and $PdCl_2$ (0.09 g, 0.5 mmol) in 3-chloropyridine (3 mL). A cream colored powder was obtained; yield: 71 %; m.p.: 107-108 ºC; FT-$IR_{v(CN)}$: 1507.2 cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$, 298 K, TMS), δ; 2.36 (s, 3 H, $NCH_2C_6H_4CH_3$); 6.27 and 6.71 (s, 4 H, $NCH_2C_6H_4CH_3$; $NCH_2C_{10}H_7$); 6.98-8.98 (m, 22 H, Ar-*H*). ^{13}C NMR (75.47 MHz, $CDCl_3$), δ; 21.1 ($NCH_2C_6H_4CH_3$); 50.5 and 53.2 ($NCH_2C_{10}H_7$; $NCH_2C_6H_4CH_3$); 111.4, 111.5, 122.6, 123.5, 124.8, 125.6, 126.0, 126.8, 128.3, 128.9, 129.1, 130.1, 130.9, 132.6, 133.7, 135.0, 138.0, 148.9, 149.2 and 150.3 (Ar-*C*); 163.9 (N-C_{NHC}-N). Elemental analysis calcd. (%) for $C_{31}H_{26}Cl_3N_3Pd$ (653.34 g/mol): C 56.99, H 4.01, N 6.43; found: C 56.93, H 4.07, N 6.43.

Synthesis of 1-phenyl-3-(2,3,5,6-tetramethylbenzyl)benzimidazol-2-ylidene-N-(3-chloropyridine)dichloropalladium(II) complex, 2e

According to the same conditions and procedure for the **2a** complex, the **2e** complex was prepared from 1-phenyl-3-(2,3,5,6-tetramethylbenzyl)benzimidazolium salt (0.2 g, 0.5 mmol) and $PdCl_2$ (0.09 g, 0.5 mmol) in 3-chloropyridine (3 mL). A very light cream colored powder was obtained; yield: 65 %; m.p.: 212-213 ºC; FT-$IR_{\nu(CN)}$: 1500.5 cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$, 298 K, TMS), δ; 2.31 and 2.34 (s, 12 H, C*H*$_3$); 6.36 [s, 2 H, NC*H*$_2$CH(CH$_3$)$_4$]; 6.99-8.86 (m, 20 H, Ar-*H*). ^{13}C NMR (75.47 MHz, $CDCl_3$), δ; 16.5 and 20.6 (*C*H$_3$); 51.0 [N*C*H$_2$CH(CH$_3$)$_4$]; 110.9, 111.6, 123.2, 123.7, 124.8, 128.2, 129.5, 130.1, 132.7, 134.4, 135.3, 135.9, 137.0, 137.9, 147.6, 149.1 and 150.2 (Ar-*C*); 162.9 (N-*C*$_{NHC}$-N). Elemental analysis calcd. (%) for $C_{29}H_{28}Cl_3N_3Pd$ (631.33 g/mol): C 55.17, H 4.47, N 6.66; found: C 55.11, H 4.49, N 6.65.

Synthesis of 1-phenyl-3-(2,3,4,5,6-pentamethylbenzyl)benzimidazol-2-ylidene-N-(3-chloropyridine)dichloropalladium(II) complex, 2f

According to the same conditions and procedure for the **2a** complex, the **2f** complex was prepared from 1-phenyl-3-(2,3,4,5,6-pentamethylbenzyl)benzimidazolium salt (0.2 g, 0.5 mmol) and $PdCl_2$ (0.09 g, 0.5 mmol) in 3-chloropyridine (3 mL). A cream colored powder was obtained; yield: 63 %; m.p.: 241-242 ºC; FT-$IR_{\nu(CN)}$: 1508.2 cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$, 298 K, TMS), δ; 2.09 and 2.45 (s, 15 H, C*H*$_3$); 6.38 [s, 2 H, NC*H*$_2$C(CH$_3$)$_5$]; 6.75-8.87 (m, 20 H, Ar-*H*). ^{13}C NMR (75.47 MHz, $CDCl_3$), δ; 16.9, 17.4 and 17.5 (*C*H$_3$); 51.7 [N*C*H$_2$C(CH$_3$)$_5$]; 110.9, 111.7, 123.1, 123.6, 124.8, 127.4, 128.2, 129.5, 132.5, 133.2, 134.6, 134.8, 135.9, 136.2, 137.0, 137.9, 149.1 and 150.2 (Ar-*C*);

162.8 (N-C_{NHC}-N). Elemental analysis calcd. (%) for $C_{30}H_{30}Cl_3N_3Pd$ (645.36 g/mol): C 55.83, H 4.69, N 6.51; found: C 55.88, H 4.75, N 6.53.

2.2 General method for direct arylation

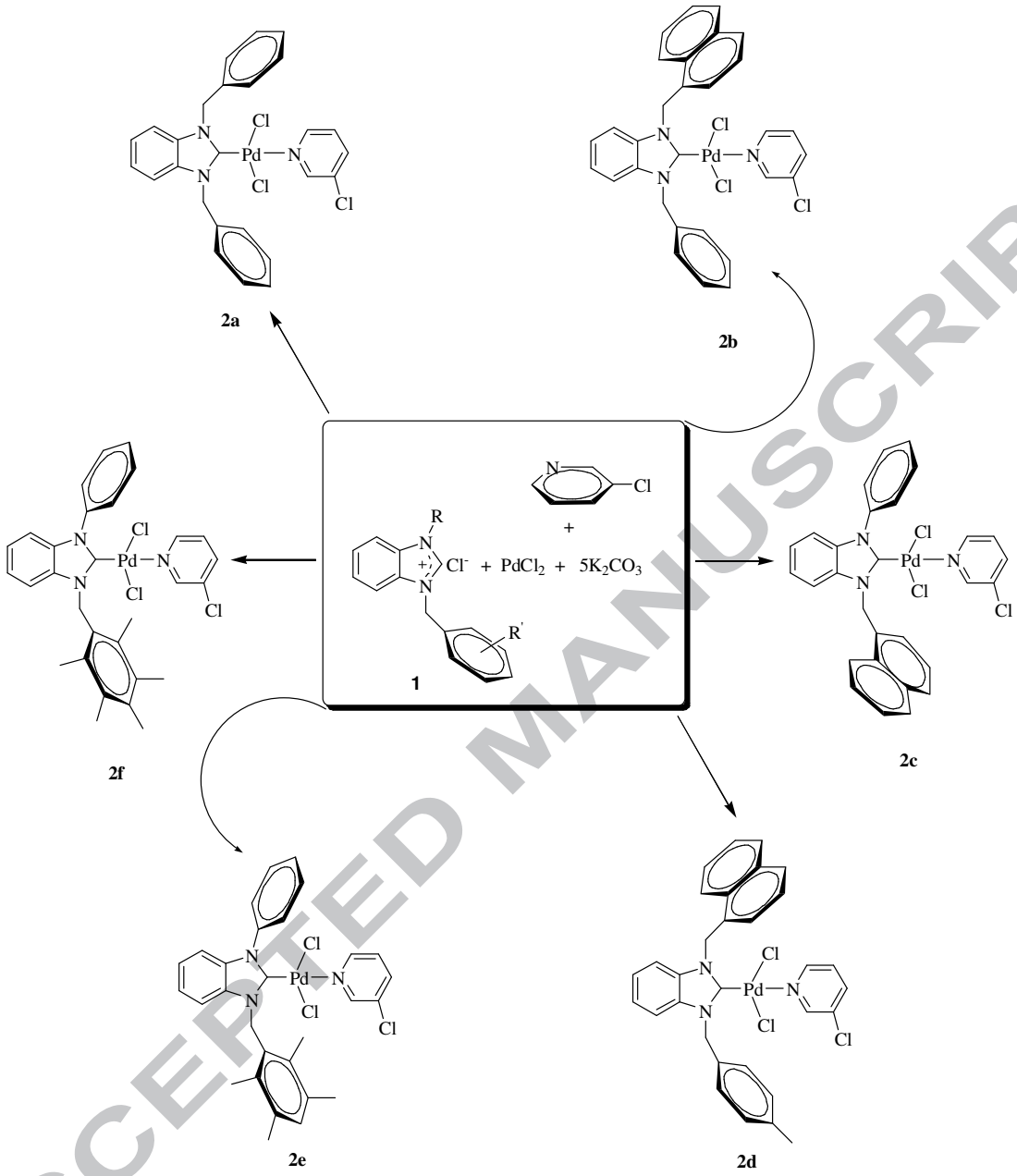
Heteroaryl derivative (2-*n*-butylfuran, 2-*n*-butylthiophene and 2-*n*-propylthiazole) (2 mmol), aryl bromide (*p*-bromoacetophenone, *p*-bromoanisole, *p*-bromotoluene and bromobenzene) (1 mmol), PEPPSI Pd-NHC complexes **2a-f** (0.003 mmol), KOAc (1 mmol) and N,N-dimethylacetamide (DMAc) (2 mL) were added to a small Schlenk tube equipped with a magnetic stirring bar as described in the literature [20-22]. The Schlenk tube was heated in an oil bath at 130 ºC for 1 h. When the reaction was completed, the solvent in the reaction media was removed by heating the reaction vessel under vacuum. Then, the pentane and diethyl ether mixture (3:1) was added to the reaction ambient. As a result of this process, the obtained product was purified by using flash chromatography on silica gel. The purity of the compound was checked by GC and NMR. Conversions were based on aryl bromides.

3. Results and Discussion

3.1 Synthesis of PEPPSI palladium N-heterocyclic carbene complexes

1,3-dialkylbenzimidazolium salts as carbene precursors, which were synthesized in our previous studies [32, 33], were obtained by the reaction of *N*-alkylbenzimidazole with alkyl halides in DMF at 80 ºC for 24 hrs. The PEPPSI Pd-NHC complexes were obtained by the treatment of 1,3-dialkylbenzimidazolium salts with $PdCl_2$ in the presence of K_2CO_3 in 3-chloropyridine at 80 ^oC for 16 h in 70 %, 68 %, 69 %, 71 %, 65 % and 63 % yields for **2a-f**, respectively (Scheme 1). These compounds were soluble in different solvents such as dimethyl sulfoxide, chloroform and dichloromethane. The formation of the six novel

symmetrical and nonsymmetrical substituted complexes was confirmed by FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopic methods and elemental analysis techniques. These spectroscopic methods, which are seen to be spectroscopically pure, are consistent with the recommended formulae. In the ^{1}H NMR spectra, the benzimidazolium salts as compared to the PEPPSI Pd-NHC complexes were identified by a characteristic proton peak at the 2-position (NC*H*N) of the benzimidazole ring which appeared highly downfield shifted as sharp singlets at 11.70, 9.59 and 11.38 ppm for **1c**, **1e** and **1f**, respectively [31]. It was known that the PEPPSI Pd-NHC complexes had successfully synthesized because the signal of the acidic benzimidazolium C2-H proton between 9 and 12 ppm in the ^{1}H NMR spectra was not observed. The Pd-$C_{carbene}$ resonances of these novel PEPPSI Pd-NHC complexes in the ^{13}C NMR spectra appeared highly downfield shifted at δ ca. 163.4, 164.2, 164.1, 163.9, 162.9 and 162.8 ppm for **2a-f**, respectively. When the results of the elemental analysis, which is one of the analytical techniques used to prove the synthesis of compounds, were evaluated, it was observed that the calculated values were very close to the found values. The FT-IR data clearly indicated the presence of $\nu_{(CN)}$ at 1409.9, 1413.7, 1503.8, 1507.2, 1500.5 and 1508.2 cm^{-1} for the PEPPSI Pd-NHC complexes (**2a-f**), respectively. Unfortunately, we were unable to obtain an appropriate single crystal from these new complexes for X-ray diffraction.



Scheme 1. Synthesis of dichlorido(3-chloropyridine-*N*)[1,3-dialkylbenzimidazol-2-ylidene]palladium(II) complexes (**2a-f**).

3.2 Catalytic practice of PEPPSI Pd-NHC complexes (2a-f) in direct arylation reactions

The catalytic activities in the direct arylation reactions of the six novel PEPPSI Pd-NHC complexes (**2a-f**) as catalysts for forming aryl-aryl bonds, which are highly crucial in

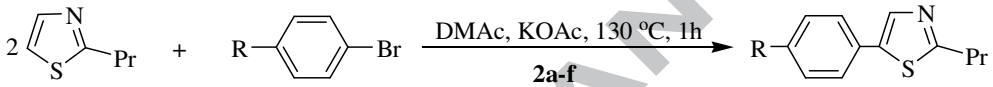
organic chemistry, were investigated. Conversions of intended products changed depending on the conditions of the reaction. When the catalytic activity results of the PEPPSI Pd-NHC complexes were analyzed, it was found that the catalytic activity values of these compounds were very similar to each other and they resulted in very high conversions. Small differences can be attributed to the substituents present on the ligands. Electron factors determined the reactivity of the substrates. Aryl bromides as substrates can tolerate different functional groups like OCH_3 and CH_3. The best conversions were acquired when aryl bromides containing a moderate level of both electron-donating and electron-withdrawing groups were employed. However when aryl bromide containing the electron-neutral group was used, lower conversions were obtained according to other groups. The obtained results were given in Table 1-3.

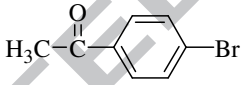
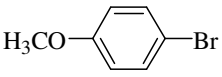
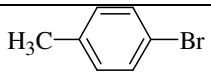
3.2.1 Using PEPPSI Pd-NHC catalysts, the direct arylation of various heteroaromatic groups with arylbromides

In our previous study, we saw that Pd-NHC complexes were very effective in the direct arylation of different heteroaromatic groups with various aryl halides [21]. Thus, we began by applying these reaction conditions in the direct arylation of novel PEPPSI Pd-NHC complexes with different aryl bromides (Table 1-3). Initially, we commenced our works by attempting to make the direct arylation at the 5-position of 2-*n*-propylthiazole using PEPPSI Pd-NHC complexes as catalyst. In this screening process, the reaction of 2-*n*-propylthiazole and p-bromoacetophenone was used as a model reaction. The following reaction may be given as an example: treatment of 2-*n*-propylthiazole (2 mmol) with p-bromoacetophenone (1 mmol) in the presence of PEPPSI Pd-NHC complex **2c** (0.003 mmol) and potassium acetate (KOAc) (1 mmol) as a base in *N*,*N*-dimethylacetamide (DMAc) (2 mL) by heating in an oil bath at 130 ^{o}C for 1 h afforded product in 78 %

conversion. After that, we investigated the PEPPSI Pd-NHC catalyzed direct arylation at the 5-position of 2-*n*-propyl thiazole with p-bromoanisole and p-bromotoluene in excellent conversions; such as 99.9 % and 100 % (Table 1; entries: 4-8). Then, we conducted research on the catalytic activities in the direct arylation of 2-*n*-butylthiophene and 2-*n*-butyl furan rings with identical aryl bromides as used in the 2-*n*-propylthiazole in the presence of PEPPSI Pd-NHC complexes (**2a-f**) as catalysts (Table 2, 3).

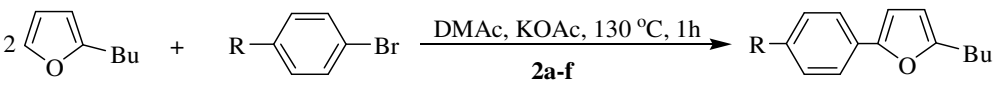
Table 1. Pd-NHC catalysed direct arylation of 2-*n*-propylthiazole by using aryl bromides.[a]

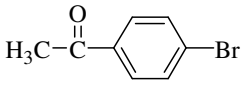
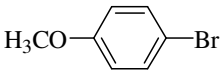
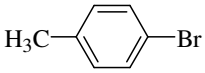
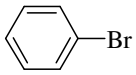


Entry	Ar-Br	PEPPSI Pd-NHC	Conv. (%)
1		**2c**	78
2		**2e**	97
3		**2f**	98
4		**2a**	100
5		**2c**	100
6		**2e**	100
7		**2a**	100
8		**2e**	99.9

[a]Reaction conditions: 2-*n*-propylthiazole (2 mmol), aryl bromide (1 mmol), PEPPSI Pd-NHC (0.003 mmol), KOAc (1 mmol), DMAc (2 mL), 130 °C, 1 h. Product purity was checked by GC and NMR, conversions were calculated according to aryl bromide.

Table 2. Pd-NHC catalysed direct arylation of 2-*n*-butylfuran by using aryl bromides.[a]



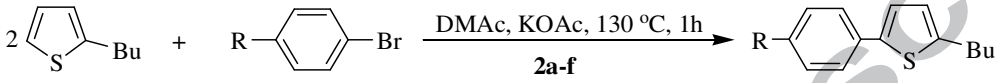
Entry	Ar-Br	PEPPSI Pd-NHC	% Conv.
1		**2a**	99
2		**2b**	99.9
3		**2e**	99.6
4		**2f**	99
5		**2a**	84
6		**2d**	90
7		**2e**	88
8		**2a**	94
9		**2b**	99
10		**2c**	76
11		**2d**	90
12		**2a**	87
13		**2b**	75
14		**2c**	70
15		**2d**	83
16		**2e**	95

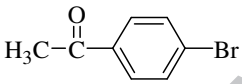
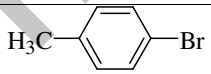
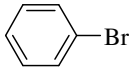
[a]Reaction conditions: 2-*n*-butylfuran (2 mmol), aryl bromide (1 mmol), PEPPSI Pd-NHC (0.003 mmol), KOAc (1 mmol), DMAc (2 mL), 130 ^{o}C, 1 h. Product purity was checked by GC and NMR, conversions were calculated according to aryl bromide.

Use of *p*-bromoanisole with 2-*n*-propylthiazole gave product in 100 % conversion (Table 1, entries: 4-6), but when *p*-bromoanisole was used with 2-*n*-butylfuran it resulted in a lower conversion, such as 84 %, 88 % and 90 % (Table 2, entries: 5-7). When *p*-bromoanisole was put into the reaction ambient instead of *p*-bromoacetophenone as a coupling partner with 2-*n*-propylthiazole, the conversion of product increased (Table 1, entries: 4-6). The use of *p*-bromoanisole with 2-*n*-butylthiophene gave the desired coupling product for different complexes (**2a**, **2c** and **2f**) as catalysts in good conversion, such as 96 %, 100 % and 98 %, respectively (Table 3, entries: 5-7). Aryl bromide bearing

an electron-donating group like p-bromotoluene smoothly coupled with 2-*n*-propylthiazole, 2-*n*-butylfuran and 2-*n*-butylthiophene and provided the corresponding products in moderate conversions (Table 1-3).

Table 3. Pd-NHC catalysed direct arylation of 2-*n*-butylthiophene by using aryl bromides.[a]



Entry	Ar-Br	PEPPSI Pd-NHC	% Conv.
1		**2a**	100
2		**2c**	100
3		**2e**	98
4		**2f**	99
5		**2a**	96
6		**2c**	100
7		**2f**	98
8		**2c**	100
9		**2f**	99
10		**2f**	89

[a]Reaction conditions: 2-*n*-butylthiophene (2 mmol), aryl bromide (1 mmol), PEPPSI Pd-NHC (0.003 mmol), KOAc (1 mmol), DMAc (2 mL), 130 °C, 1 h. Product purity was checked by GC and NMR, conversions were calculated according to aryl bromide.

In this study, as previously stated, we investigated the catalytic activities of six novel PEPPSI Pd-NHC complexes in the direct arylation reaction using electron-withdrawing, electron-donating and electron-neutral groups by applying short time periods such as 1 h. The best results for p-bromoacetophenone and p-bromotoluene were obtained

with catalysts **2a**, **2e** and **2f**. The best conversions for p-bromoanisole were gained with catalysts **2c** and **2f**. Generally, the synthesized novel complexes were found to be effective catalysts in the direct arylation reaction.

4. Conclusions

In summary, six novel Pd-PEPPSI-type NHC complexes (**2a-f**), which were confirmed by FT-IR, ^{1}H NMR, ^{13}C NMR and elemental analysis, were synthesized from different 1,3-dialkylbenzimidazolium salts with $PdCl_2$ in the presence of K_2CO_3 as base in 3-chloropyridine in good yields. These novel PEPPSI Pd-NHC complexes, which were obtained from the successful deprotonation of benzimidazolium salts, are practical catalysts for the direct regioselective C5 arylation of heteroaromatic groups using both electron-deficient and electron-rich aryl bromides as coupling partners. The best results in terms of conversions were obtained with low catalysts loading.

Acknowledgments

We would like to thank to Erciyes University in Kayseri and İnönü University in Malatya for their financial support.

References

[1] H.-W. Wanzlick, H.-J. Schönherr, Angew. Chem. 80 (1968) 154.

[2] K. Öfele, J. Organomet. Chem. 1968, 12, P42.

[3] A.J. Arduengo III, R.L. Harlow, M. Kline, J. Am. Chem. Soc. 113 (1991) 361.

[4] L. Faraji, K. Jadidi, B. Notash, Tetrahedron Lett. 55 (2014) 346.

[5] A.C. Hillier, G.A. Grasa, M.S. Viciu, H.M. Lee, C. Yang, S.P. Nolan, J. Organomet. Chem. 653 (2002) 69.

[6] T. Weskamp, V.P.W. Böhm, W.A. Herrmann, J. Organomet. Chem. 600 (2000) 12.

[7] N.M. Scott, S.P. Nolan, Eur. J. Inorg. Chem. (2005) 1815.

[8] R. Dorta, E.D. Stevens, N.M. Scott, C. Costabile, L. Cavallo, C.D. Hoff, S.P. Nolan, J. Am. Chem. Soc. 127 (2005) 2485.

[9] A. John, S. Modak, M. Madasu, M. Katari, P. Ghosh, Polyhedron 64 (2013) 20.

[10] M.K. Samantaray, M.M. Shaikh, P. Ghosh, J. Organomet. Chem. 694 (2009) 3477.

[11] H. Ren, Y. Xu, E. Jeanneau, I. Bonnamour, T. Tu, U. Darbost, Tetrahedron 70 (2014) 2829.

[12] J. Nasielski, N. Hadei, G. Achonduh, E.A.B. Kantchev, C.J. O'Brien, A. Lough, M.G. Organ, Chem. Eur. J. 16 (2010) 10844.

[13] J.J. Dunsford, K.J. Cavell, Organometallics 33 (2014) 2902.

[14] C.E. Hartmann, S.P. Nolan, C.S.J. Cazin, Organometallics 28 (2009) 2915.

[15] M.G. Organ, S. Avola, I. Dubovyk, N. Hadei, E.A.B. Kantchev, C.J.O. Brien, C. Valente, Chem. Eur. J. 12 (2006) 4749.

[16] C. Valente, M.E. Belowich, N. Hadei, M.G. Organ, Eur. J. Org. Chem. 2010 (2010) 4343.

[17] I. Larrosa, C. Somoza, A. Banquy, S.M. Goldup, Org.Lett. 13 (2011)146.

[18] C. Dash, M.M. Shaikh, P. Ghosh, Eur. J. Inorg. Chem. (2009) 1608.

[19] W.A. Herrmann, M. Elison, J. Fischer, C. Köcher, G.R.J. Artus, Angew Chem., Int. Ed. Engl. 34 (1995) 2371.

[20] S. Akkoç, Y. Gök, M. Akkurt, M.N. Tahir, Inorg. Chim. Acta 413 (2014) 221.

[21] İ. Özdemir, Y. Gök, Ö. Özeroğlu, M. Kaloğlu, H. Doucet, Eur. J. Inorg. Chem. 12 (2010) 1798.

[22] S. Akkoç, Y. Gök, Appl. Organomet. Chem., 28 (2014) 854.

[23] S. Demir, I. Özdemir, B. Çetinkaya, H. Arslan, D. VanDerveer, Polyhedron 30 (2011) 195.

[24] T. Zhang, M. Shi, M. Zhao, Tetrahedron 64 (2008) 2412.

[25] K.H. Hoi, S. Çalimsiz, R.D.J. Froese, A.C. Hopkinson, M.G. Organ, Chem. Eur. J. 17 (2011) 3086.

[26] L. Yang, Y. Li, Q. Chen, Y. Du, C. Cao, Y. Shi, G. Pang, Tetrahedron 69 (2013) 5178.

[27] L. Benhamou, C. Besnard, E.P. Kündig, Organometallics 33 (2014) 260.

[28] M. Sayah, A.J. Lough, M.G. Organ, Chem. Eur. J. 19 (2013) 2749.

[29] A. Chartoire, X. Frogneux, A. Boreux, A.M.Z. Slawin, S.P. Nolan, Organometallics 31 (2012) 6947.

[30] M.G. Organ, S. Çalimsiz, M. Sayah, K.H. Hoi, A.J. Lough, Angew. Chem. 121 (2009) 2419-2423; Angew. Chem. Int. Ed. 48 (2009) 2383.

[31] J. Zhao, L. Yang, K. Ge, Q. Chen, Y. Zhuang, C. Cao, Y. Shi, Inorg. Chem. Commun. 20 (2012) 326.

[32] Y. Gök, S. Akkoç, S. Albayrak, M. Akkurt, M.N. Tahir, Appl. Organomet. Chem. 28 (2014) 244.

[33] Other compounds are examined in another journal.

Synopsis Absract:

- PEPPSI themed six novel palladium *N*-heterocyclic carbene complexes were synthesized.
- Their structures were characterized by elemental analysis and spectroscopic methods.
- These complexes were tested as catalysts in the direct arylation and they exhibited high catalytic activities.

Synopsis Absract:

Pyridine **E**nhanced **P**recatalyst **P**reparation, **S**tabilization and **I**nitiation (PEPPSI) themed six novel palladium *N*-heterocyclic carbene (Pd-NHC) complexes (**2a-f**) were synthesized and characterized by elemental analysis and spectroscopic methods. These novel complexes (**2a-f**) were tested as catalysts in the direct arylation of 2-*n*-propylthiazole, 2-*n*-butylthiophene and 2-*n*-butylfuran with different aryl bromides at 130 ºC for 1 h. These complexes exhibited high catalytic activities.

Graphical abstract: