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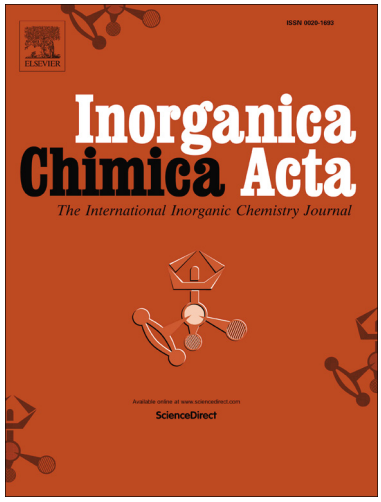

Research paper

Carbon-carbon bond formation catalyzed by PEPPSI Pd-NHC

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Carbon-carbon bond formation catalyzed by PEPPSI Pd-NHC

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ABSTRACT

Five new palladium complexes were efficiently synthesized from the reaction of benzimidazolium salts, potassium carbonate (K_2CO_3) and palladium chloride ($PdCl_2$) in pyridine (for **3-5**) or 3-chloropyridine (for **6** and **7**). The synthesized complexes were characterized and tested in Suzuki-Miyaura cross-coupling reaction as catalysts. In the presence of catalysts **3-7**, biaryl products were obtained in moderate yields when phenylboronic acid was used as boronic acid derivative. However, the coupling of thianaphthene-2-boronic acid with 1-chloro-4-nitrobenzene generated low yields although a longer period of time was used in comparison to the coupling of phenylboronic acid with aryl chlorides.

Keywords: *N*-Heterocyclic carbene; PEPPSI complex; Palladium; Suzuki-Miyaura cross-coupling reaction; Catalyst.

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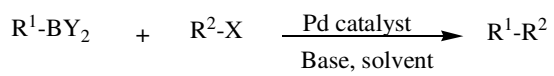
1. Introduction

N-heterocyclic carbene (NHC) metal complexes have been known for the last fifty years [1] and they have been tested in a range of fields [2-8]. The application of metal complexes containing NHC has attracted much attention recently, in particular as catalysts in carbon-carbon (C-C) and carbon-nitrogen (C-N) bond forming reactions [2, 3, 9-11]. For example, the uploading of low amounts of these compounds as catalysts has been found to be very effective for Suzuki-Miyaura cross-coupling [9].

Suzuki-Miyaura cross-coupling reaction is mostly used to synthesize substituted biphenyls and poly-olefins and can be described as a coupling of boronic acid derivatives (R^1-BY_2) with mesylate, halide or triflate (R^2-X) using a palladium catalyst in the presence of a base (Scheme 1) [12, 13]. One of the important aspects of this reaction is that green solvents, especially water, can be used which are inexpensive, non-flammable, non-toxic and can be easily separated from organic products. This additionally increases the value and importance of this reaction.



Scheme 1. General definition of Suzuki-Miyaura cross-coupling [12].

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Herein, we tested the catalytic properties of five newly synthesized benzimidazole-based **P**yridine **E**nhanced **P**recatalyst **P**reparation **S**tabilization and **I**nitiation (PEPPSI) Pd-NHC complexes in Suzuki-Miyaura cross-coupling reaction for the formation of biaryl products. Two different boronic acid derivatives (thianaphthene-2-boronic acid and phenylboronic acid) and various aryl chlorides (4-chloroacetophenone, 4-methoxy-1-chlorobenzene, 4-chlorotoluene and 1-chloro-4-nitrobenzene) were used for this coupling reaction. Catalysts **3-7** were mucher effective in the all coupling of phenylboronic acid with aryl chlorides than the coupling of thianaphthene-2-boronic acid with 1-chloro-4-nitrobenzene at 80 ^{o}C.

2. Experimental

2.1. General considerations

All reactions and purifications for the preparation of **1-7** were carried out under ambient conditions in 100 mL Schlenk tubes. All reagents and solvents were purchased from Sigma-Aldrich (Interlab A.S., USA), Scharlau (Barcelona, Spain) and Merck (Darmstadt, Germany), and were used without further purification. ^{1}H and ^{13}C NMR spectra were performed in $CDCl_3$ solvent and were recorded using a Bruker-300 or 400 MHz Ultra Shield instrument. Chemical shifts (δ) were given in ppm relative to tetramethylsilane (TMS). Coupling constants (*J*) were given in hertz (Hz). ^{1}H NMR signals are labeled as singlet (s), doublet (d), pentet (p) and multiplet (m). An Agilent Technologies 6890N Network GC system was used for the catalytic experiment measurements. An Electrothermal-9200 melting point apparatus was used for measuring melting points. A Shimadzu FT-IR 8400 spectrophotometer was used for recording the FT-IR spectra of compounds.

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2.2. New palladium complexes

2.2.1. General preparation of compounds, 3-7

The benzimidazolium salts used in this study were synthesized as described previously [14, 15]. Compounds **3-7** were prepared from the reaction of **2** (1 mmol), $PdCl_2$ (1 mmol) and K_2CO_3 (5 mmol) in pyridine or 3-chloropyridine (3 mL) for 16 h at 80 ^oC. The solvent was removed under vacuum. The obtained complexes were washed with diethyl ether (3 x 5 mL) and dried under vacuum and had different colors. These benzimidazole-based complexes were stable against atmospheric moisture and air. Compounds **3-7** were further characterized by ^1H NMR, ^{13}C NMR, FT-IR and were soluble in organic solvents such as chloroform and dichloromethane.

2.2.2. Data for the complexes

2.2.2.1. For [1-phenyl-3-(3,4,5-trimethoxybenzyl)benzimidazol-2-ylidene](pyridyl)palladium(II) dichloride, 3

1-phenyl-3-(3,4,5-trimethoxybenzyl)benzimidazolium chloride (0.2 g, 1 mmol), K_2CO_3 (0.34 g, 5 mmol) and $PdCl_2$ (0.086 g, 1 mmol) in pyridine (3 mL) were stirred at 80 ^oC for 16 h. After the reaction was finished, 10 mL of dichloromethane was added to the reaction medium. The resulting solution mixture was filtered on silica gel and through a pad of celite in order to remove unreacted $PdCl_2$. The solvent in the reaction medium was removed and dried under vacuum. The reaction yielded as a cream colored solid ($C_{28}H_{27}N_3O_3Cl_2Pd$: 630.86 g/mol), which was washed thrice with 5 mL of diethyl ether. Yield: 150 mg, 48.9%; m.p.: 198-199 ºC; color: cream; IR: 1234.3 (C-O); 1409.9 (CN); 2831.3, 2912.3 and 2993.3 (aliphatic C-H); 3058.9 cm^{-1} (aromatic C-H). ^1H NMR (300 MHz, 298 K, $CDCl_3$), δ: 3.85 and 3.89 [m, 9 H, $NCH_2C_6H_2(OCH_3)_3$-3,4,5]; 6.25 [s, 2 H, $NCH_2C_6H_2(OCH_3)_3$-3,4,5]; 7.03-8.87 (m, 16 H, Ar-*H*). ^{13}C NMR (75 MHz, 298 K, $CDCl_3$), δ: 53.68, 56.65 and 60.85

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[$NCH_2C_6H_2(OCH_3)_3$-3,4,5]; 65.87 [$NCH_2C_6H_2(OCH_3)_3$-3,4,5]; 105.47, 111.16, 111.58, 123.76, 123.80, 124.49, 125.01, 127.96, 129.38, 129.63, 130.53, 133.97, 136.01, 137.01, 137.82, 138.07, 138.64, 151.16, 153.36 and 153.69 (Ar-*C*); 164.71 (N*C*N).

2.2.2.2. For [1-phenyl-3-(2,3,5,6-tetramethlbenzyl)benzimidazol-2-ylidene] (pyridyl)palladium(II) dichloride, 4

Complex **4** ($C_{29}H_{29}N_3Cl_2Pd$: 596.89 g/mol) was synthesized under the same conditions and procedure as for **3**, from 1-phenyl-3-(2,3,5,6-tetramethylbenzyl)benzimidazolium chloride (0.2 g, 1 mmol), K_2CO_3 (0.37 g, 5 mmol) and $PdCl_2$ (0.094 g, 1 mmol) in pyridine (3 mL). Yield: 210 mg, 66.3%; m.p.: 275-276 ºC; color: cream; IR: 1446.5 (CN); 2964.4 (aliphatic C-H); 3022.2 and 3080.1 cm^{-1} (aromatic C-H). ^1H NMR (300 MHz, 298 K, $CDCl_3$), δ: 2.25 and 2.38 [m, 12 H, $NCH_2C_6H(CH_3)_4$-2,3,5,6]; 6.42 [s, 2 H, $NCH_2C_6H(CH_3)_4$-2,3,5,6]; 6.99-8.83 (m, 14 H, Ar-*H*). ^{13}C NMR (75 MHz, 298 K, $CDCl_3$), δ: 16.53 and 20.63 [$NCH_2C_6H(CH_3)_4$-2,3,5,6]; 51.19 [$NCH_2C_6H(CH_3)_4$-2,3,5,6]; 110.89, 111.60, 123.12, 123.58, 124.41, 125.01, 128.18, 129.30, 129.50, 130.20, 132.71, 134.36, 134.49, 135.25, 135.90, 137.12, 137.96, 149.35 and 151.14 (Ar-*C*); 164.41 (N*C*N).

2.2.2.3. For [1-phenyl-3-(2,3,4,5,6-pentamethylbenzyl)benzimidazol-2-ylidene](pyridyl)palladium(II) dichloride, 5

Complex **5** ($C_{30}H_{31}N_3Cl_2Pd$: 610.91 g/mol) was synthesized under the same conditions and procedure as for **3**, from 1-phenyl-3-(2,3,4,5,6-pentamethylbenzyl)benzimidazolium chloride (0.2 g, 1 mmol), K_2CO_3 (0.35 g, 5 mmol) and $PdCl_2$ (0.09 g, 1 mmol) in pyridine (3 mL). Yield: 160 mg, 51.1%; m.p.: 202-204 ºC; color: cream; IR: 1479.3 (CN); 2912.3

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(aliphatic C-H); 3006.8 cm^{-1} (aromatic C-H). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$), δ: 2.22-2.43 [m, 15 H, $NCH_2C_6(CH_3)_5$-2,3,4,5,6]; 5.29 [s, 2 H, $NCH_2C_6(CH_3)_5$-2,3,4,5,6]; 6.35-8.83 (m, 14 H, Ar-*H*). ^{13}C NMR (100 MHz, 298 K, $CDCl_3$), δ: 16.45, 17.08, 17.49, 18.02 and 42.33 [$NCH_2C_6(CH_3)_5$-2,3,4,5,6]; 51.88 [$NCH_2C_6(CH_3)_5$-2,3,4,5,6]; 108.39, 109.18, 110.80, 111.77, 120.85, 121.85, 123.70, 124.35, 126.11, 127.55, 128.63, 129.60, 130.23, 133.17, 134.59, 135.19, 136.18, 137.16, 137.89, 149.86, 151.15, 152.31 and 153.36 (Ar-*C*); 164.30 (N*C*N).

2.2.2.4. For [1-phenyl-3-((2,3-dihydrobenzo[b][1,4]dioxin-2-yl)methyl)benzimidazol-2-yliden](3-chloropyridyl)palladium(II) dichloride, 6

Complex **6** ($C_{27}H_{22}N_3Cl_3O_2Pd$: 633.26 g/mol) was synthesized under the same conditions and procedure as for **3**, from 1-phenyl-3-((2,3-dihydrobenzo[*b*][1,4]dioxin-2-yl)methyl) benzimidazolium bromide (0.2 g, 1 mmol), K_2CO_3 (0.33 g, 5 mmol) and $PdCl_2$ (0.08 g, 1 mmol) in 3-chloropyridine (3 mL). Yield: 150 mg, 50.2%; m.p.: 191-193 ºC; color: light brown; IR: 1255.6 and 1259.4 (C-O); 1488.9 (CN); 2964.4 (aliphatic C-H); 3030.0 cm^{-1} (aromatic C-H). ^{1}H NMR (400 MHz, 298 K, $CDCl_3$), δ: 4.54 [d, *J*: 8.0 Hz, 2 H, $NCH_2CHCH_2O_2C_6H_4$]; 5.05 [p, *J*: 8.0 Hz, 1 H, $NCH_2CHCH_2O_2C_6H_4$]; 5.39 [d, *J*: 8.0 Hz, 2 H, $NCH_2CHCH_2O_2C_6H_4$]; 6.88-8.90 (m, 17 H, Ar-*H*). ^{13}C NMR (100 MHz, 298 K, $CDCl_3$), δ: 48.87 [NCH_2CHCH_2O]; 65.25 [NCH_2CHCH_2O]; 72.13 [NCH_2CHCH_2O]; 111.29, 117.56, 121.68, 122.16, 123.85, 124.96, 125.94, 127.92, 128.28, 129.65, 132.67, 135.09, 135.75, 136.89, 138.12, 142.34, 143.10, 149.86, 150.88 and 151.47 (Ar-*C*); 163.80 (N*C*N).

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2.2.2.5. For [1-phenyl-3-naphthalen-1-ylmethylbenzimidazol-2-ylidene](3-chloropyridyl)palladium(II) dichloride, 7

Complex **7** ($C_{29}H_{22}N_3Cl_3Pd$: 625.28 g/mol) was synthesized under the same conditions and procedure as for **3**, from 1-phenyl-3-naphthalen-1-ylmethylbenzimidazolium chloride (0.2 g, 1 mmol), K_2CO_3 (0.37 g, 5 mmol) and $PdCl_2$ (0.09 g, 1 mmol) in 3-chloropyridine (3 mL). Yield: 70 mg, 20.8%; m.p.: 197-198 ºC; color: dark brown; IR: 1402.2 (CN); 2912.3 and 2970.2 (aliphatic C-H); 3058.9 cm^{-1} (aromatic C-H). ^1H NMR (400 MHz, 298 K, $CDCl_3$), δ: 5.66 [s, 2 H, NC*H*$_2$C$_{10}$H$_7$]; 6.78-8.89 (m, 20 H, Ar-*H*). ^{13}C NMR (100 MHz, 298 K, $CDCl_3$), δ: 65.88 [NC*H*$_2$C$_{10}$H$_7$]; 108.75, 109.11, 111.51, 121.56, 122.02, 123.32, 124.72, 125.23, 125.76, 126.06, 126.89, 127.70, 128.00, 128.86, 129.10, 129.73, 131.21, 132.86, 133.89, 134.74, 137.99 and 138.84 (Ar-*C*); 151.41 (N*C*N).

2.3. General procedure for the Suzuki-Miyaura reaction

A typical Suzuki-Miyaura cross-coupling reaction was performed using 1 mmol aryl chloride, 1.5 mmol boronic acid derivative, 2 mmol base, 0.008 mmol compounds **3-7** as catalyst and N,N-dimethylformamide (DMF)-water (H_2O) (2-2 mL) as solvent in a 25 mL Schlenk flask . This mixture was heated in an oil bath for the duration of the desired reaction time. After the 5 mL of hexane and 1 mL of ethyl acetate were added to the reaction medium, the solution was filtered using a mini-column for purification. The purity and yield of the compounds was checked by GC. The yields were related to the unreacted aryl chlorides.

3. Results and Discussion

3.1. Synthesis of PEPPSI Pd-NHC complexes, 3-7

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Compounds **3-7** were prepared from benzimidazolium salts, K_2CO_3 and $PdCl_2$ in pyridine (for **3-5**) or 3-chloropyridine (for **6** and **7**) (Scheme 1) as described previously [3, 4]. The Pd-NHC complexes (**3-7**) were characterized by FT-IR, ^1H and ^{13}C NMR spectroscopic methods. In the ^1H NMR spectra, benzylic proton (NC*H*$_2$) was resonated at low fields δ 6.25, 6.42, 5.29, 4.54 and 5.66 cm^{-1} for **3-7**, respectively. The absence of NC*H*N signal proton in a downfield for **3-7** indicated the successful formation of NHC complexes. The structure of expected complexes was further verified with the ^{13}C NMR: the carbene carbon resonance (for metal bound carbon atom in 2-position, N*C*N-Pd) shifted significantly downfield at δ 164.71, 164.41, 164.30, 163.80 and 151.41 ppm for **3-7**, respectively. Specifically, this signal was observed in the upfield area for benzimidazolium salts compared to that of the metal complexes [14, 15]. In addition, benzylic carbon (N*C*H$_2$) was resonated at δ 65.87, 51.19, 51.88, 48.87 and 65.88 cm^{-1} for **3-7**, respectively. Lastly, the FT-IR data indicated the presence of $\nu_{(CN)}$ at 1409.9, 1446.5, 1479.3, 1488.9 and 1402.2 cm^{-1} for **3-7**, respectively. The same band appeared in a different region for benzimidazolium salts; in between 1500 and 1595 cm^{-1} [14, 15]. The structures of the complexes **3**-**7** derived benzimidazolium salts were verified by the appearance of this band in different regions.

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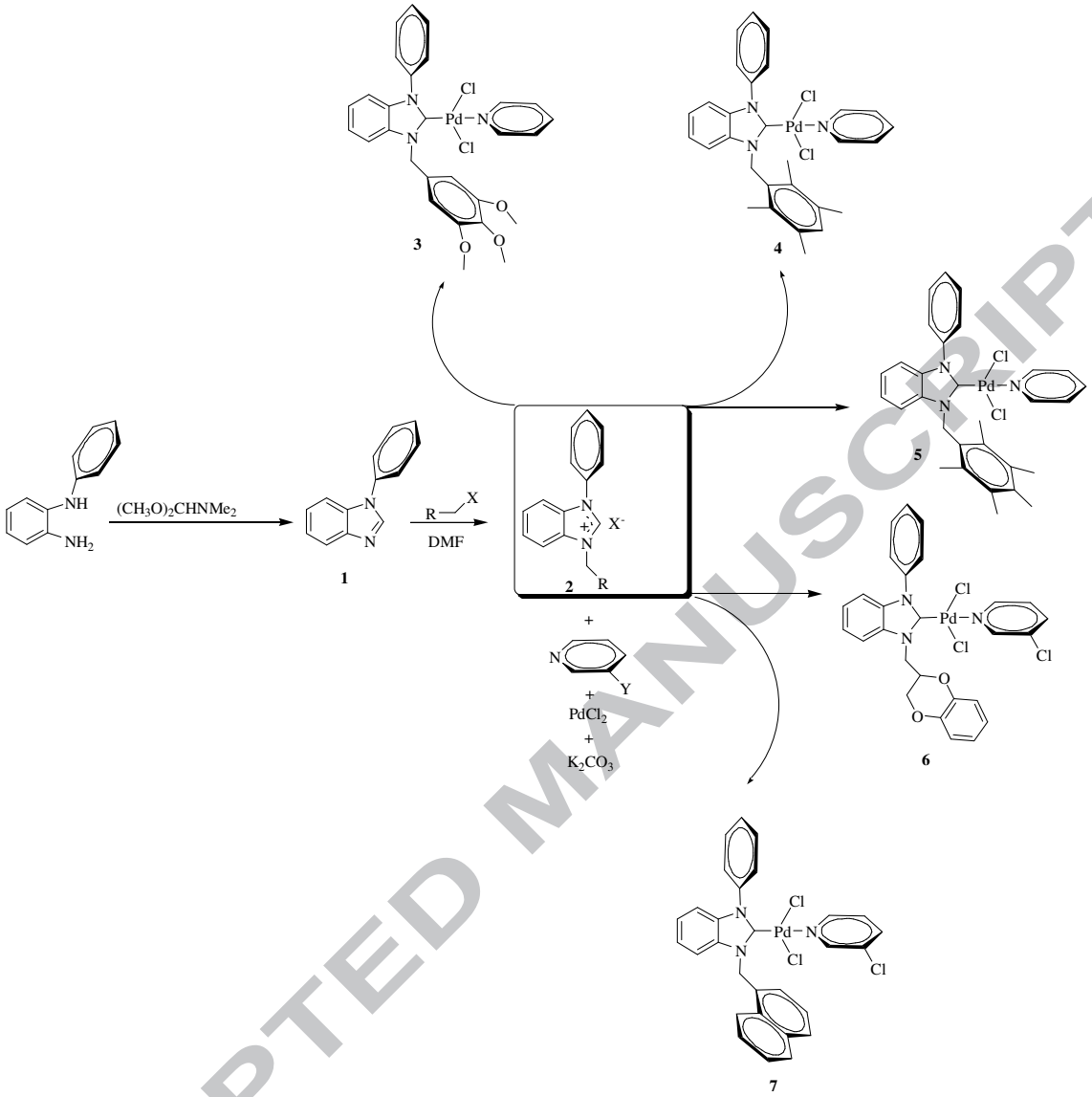

Scheme 1. Synthesis of new PEPPSI Pd-NHC complexes.

3.3. Catalytic applications of synthesized compounds in Suzuki-Miyaura coupling reaction

The air stable compound **3** was tested for its catalytic activity in order to determine a suitable reaction time for the formation of biaryl product from phenylboronic acid (1.5 mmol) with 4-chloroacetophenone (1.0 mmol) under very mild reaction conditions using K_2CO_3 (2.0 mmol) as an inorganic base and a mixture of DMF/H_2O (2/2 mL) as solvent.

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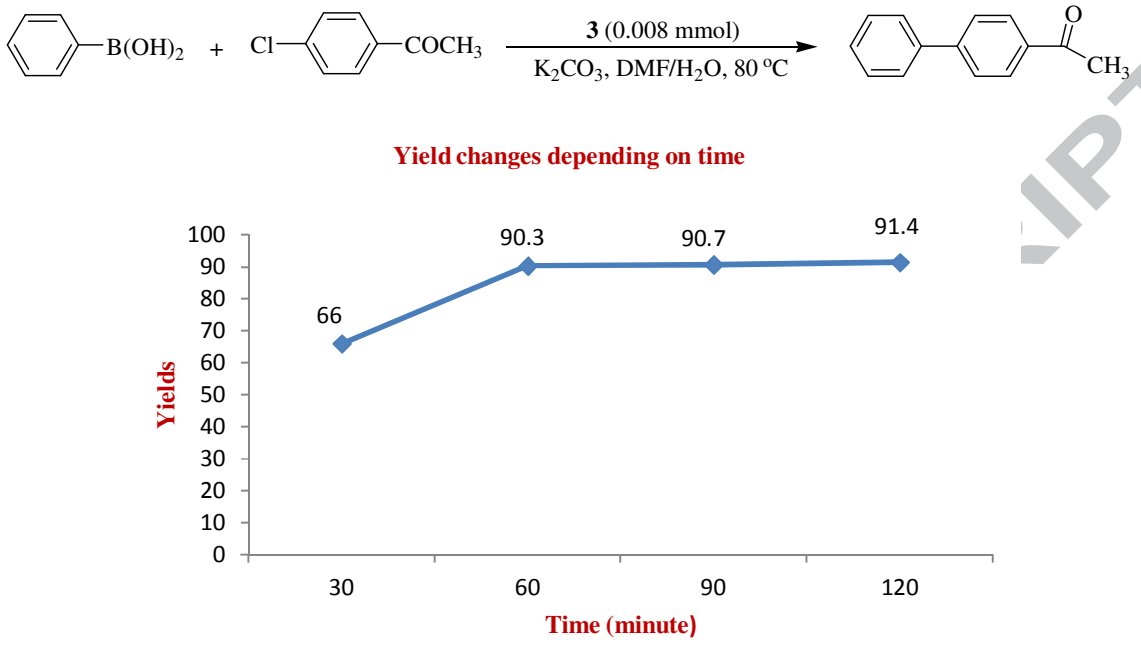
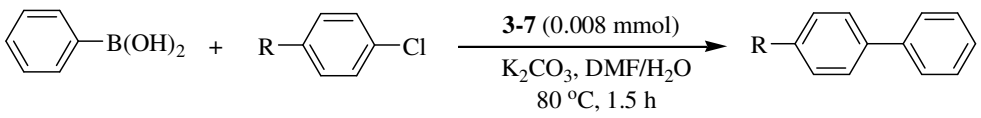
Fig. 1. The effect of time on Suzuki-Miyaura cross-coupling of phenylboronic acid with 4-chloroacetophenone as catalyzed by **3**.



Time-screening experiments showed that the reaction resulted in only a 66% yield in 30 minutes, but the yield was 91% when the reaction time was extended until 2 h (Fig. 1). Nevertheless, the yield remained almost the same between 1 h to 1.5 h and it was mostly completed in an hour with a high yield (Fig. 1).

Table 1

Suzuki-Miyaura cross-coupling of phenylboronic acid with three different aryl chlorides. [a, b]



Entry	R	Pd-NHC	Yield
1	CH_3	4	67
2	CH_3	5	30

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3	CH_3	6	21
4	CH_3	7	99.9
5	OCH3	3	43
6	OCH3	4	99.9
7	OCH_3	5	47
8	OCH_3	6	54
9	OCH_3	7	95
10	$COCH_3$	3	91
11	$COCH_3$	4	98
12	$COCH_3$	5	95
13	$COCH_3$	6	99
14	$COCH_3$	7	90

[a]Reaction condition: phenylboronic acid (1.5 mmol), aryl chlorides (1.0 mmol), K_2CO_3 (2.0 mmol), **3-7** (0.008 mmol), DMF-H_2O (2-2 mL). [b]Yields were determined by GC.

After determining a suitable reaction time for the formation of the C-C bond, the synthesized complexes were tested for their catalytic qualities in the coupling reaction of phenylboronic acid with different aryl chlorides for 1.5 h at 80 °C. When 4-chlorotoluene as aryl halide was used, a better result was obtained from the catalyst **7** compared to that of the catalysts **4**-**6** under the same experimental conditions (Table 1, entry 4). The yield was 99% (Table 1, entry 4). Among the five complexes **3-7,** 2,3,5,6-tetramethylbenzyl substituted with compound **4** displayed the top catalytic activity for the coupling of 4-chloroanisole with phenylboronic acid (Table 1, entry 6). Naphthalen-1-ylmethyl substituted with compound **7** was also found to be very effective in the coupling of 4-methoxy-1-chlorobenzene with phenylboronic acid (Table 1, entry 9). However, 2,3,4,5,6-pentamethylbenzyl substituted with compound **5** and ((2,3-dihydrobenzo[*b*][1,4]dioxin-2-yl)methyl) substituted with compound **6** showed lower catalytic activities for the same coupling reaction (Table 1, entries 2, 3, 7 and 8). Finally, catalyst properties of these complexes were tested in the carbon-carbon bond formation of 4-chloroacetophenone with phenylboronic acid. All catalyst candidates gave very high activity in this coupling reaction. Surprisingly, even compounds **5** and **6** exhibited potential catalyst properties for this reaction as opposed to earlier two couplings (Table 1, entries 2 and 3).

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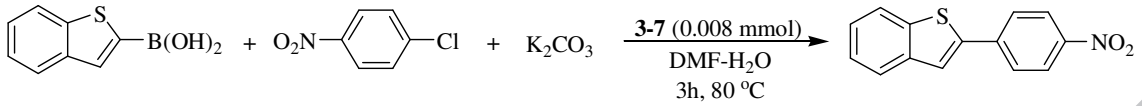
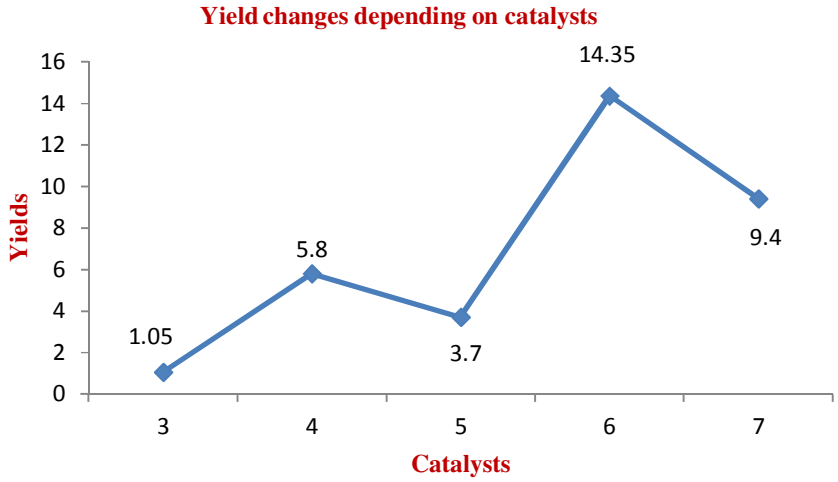
Fig. 2. Suzuki-Miyaura cross-coupling of thianaphthene-2-boronic acid with 1-chloro-4-nitrobenzene. [a, b]





In the cross-coupling of 1-chloro-4-nitrobenzene (1.0 mmol) with thianaphthene-2-boronic acid (1.5 mmol), complexes **3-7** showed a wide range of catalytic properties with varying yields from 1.05 to 14.05% after 3 h at 80 °C in DMF-H_2O (2-2 mL) mixture with compound loadings of 0.8 mmol % and 2 mmol of K_2CO_3 (Fig. 2). Compounds **6** and **7** containing the 3-chloropyridine group showed better catalytic activities than those of compounds **3-5** containing pyridine groups. Higher reaction yield for the product 2-(4-nitrophenyl)benzo[*b*]thiophene was obtained when compound **6** containing the ((2,3-dihydrobenzo[*b*][1,4]dioxin-2-yl)methyl) group was used compared to the rest of the compounds (Fig. 2).

4. Conclusion

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Several new PEPPSI Pd-NHC complexes were synthesized, characterized and their catalytic activities were determined. Overall, compounds **3-7** demonstrated good catalytic activities for the coupling of phenylboronic acid with 4-chloroacetophenone in a Suzuki-Miyaura reaction. However, lower catalytic activities were observed for the coupling reactions of 1-chloro-4-nitrobenzene with thianaphthene-2-boronic acid although the reaction was maintained for a longer period of time. Finally, the compound **7** displayed superior catalytic properties compared to the other complexes and is a good candidate to use as a catalyst in C-C bond forming reactions.

Acknowledgments

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References

[1] H.W. Wanzlick, H.J. Schönherr, Angew. Chem., Int. Ed. Engl., 7 (1968) 141-142.
[2] 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, 429 (2015) 34-38.
[3] S. Akkoç, Y. Gök, İ.Ö. İlhan, V. Kayser, N-Methylphthalimide-substituted benzimidazolium salts and PEPPSI Pd–NHC complexes: synthesis, characterization and catalytic activity in carbon–carbon bond-forming reactions, Beilstein Journal of Organic Chemistry, 12 (2016) 81-88.
[4] S. Akkoç, İ. Özer İlhan, Y. Gök, P.J. Upadhyay, V. Kayser, In vitro cytotoxic activities of new silver and PEPPSI palladium N-heterocyclic carbene complexes derived from benzimidazolium salts, Inorganica Chimica Acta, 449 (2016) 75-81.
[5] M. Dangalov, P. Petrov, N.G. Vassilev, Fluxional allyl Pd(II) and Pt(II) complexes of NHC ligands derived from substituted 1,8-naphthalimides - Synthesis and structure elucidation, Journal of Organometallic Chemistry, 824 (2016) 104-117.
[6] M. Shaikh, M. Sahu, P.K. Gavel, G.R. Turpu, S. Khilari, D. Pradhan, K.V.S. Ranganath, Mg-NHC complex on the surface of nanomagnesium oxide for catalytic application, Catalysis Communications, 84 (2016) 89-92.
[7] G. Süss-Fink, P.R. Raithby, Competition between N□H and C□H activation in the thermolysis of Os3(CO)11[NHC(CH)2)5]. The molecular structure of Os3(CO)9(μ2-H)2- [μ3-NHC(CH)24C], Inorganica Chimica Acta, 71 (1983) 109-114.
[8] J. Streuff, K. Muñiz, Efficient synthesis of fumaric amides through cross-metathesis of acrylic amides with the NHC Grubbs ruthenium catalyst, Journal of Organometallic Chemistry, 690 (2005) 5973-5978.

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[9] F. Izquierdo, M. Corpet, S.P. Nolan, The Suzuki–Miyaura Reaction Performed Using a Palladium–N-Heterocyclic Carbene Catalyst and a Weak Inorganic Base, European Journal of Organic Chemistry, 2015 (2015) 1920-1924.
[10] S. Yaşar, Ç. Şahin, M. Arslan, İ. Özdemir, Synthesis, characterization and the Suzuki–Miyaura coupling reactions of N-heterocyclic carbene–Pd(II)–pyridine (PEPPSI) complexes, Journal of Organometallic Chemistry, 776 (2015) 107-112.
[11] A. Mohan, V. Ramkumar, S. Sankararaman, Synthesis and structures of (−) menthyl and (+) neomenthyl substituted enantio pure bis(1,2,3-triazol-5-ylidene)PdI2 complexes and PEPPSI type (1,2,3-triazol-5-ylidene) (pyridine)PdI2complexes. Comparison of catalytic activities for C–C coupling, Journal of Organometallic Chemistry, 799–800 (2015) 115-121.
[12] D. Zhang, Q. Wang, Palladium catalyzed asymmetric Suzuki–Miyaura coupling reactions to axially chiral biaryl compounds: Chiral ligands and recent advances, Coordination Chemistry Reviews, 286 (2015) 1-16.
[13] N. Miyaura, A. Suzuki, Palladium-Catalyzed Cross-Coupling Reactions of Organoboron Compounds, Chemical Reviews, 95 (1995) 2457-2483.
[14] S. Akkoc, Y. Gok, Synthesis and characterization of 1-phenyl-3-alkylbenzimidazol-2-ylidene salts and their catalytic activities in the Heck and Suzuki cross-coupling reactions, Journal of Coordination Chemistry, 66 (2013) 1396-1404.
[15] Y. Gök, S. Akkoç, S. Albayrak, M. Akkurt, M.N. Tahir, N-Phenyl-substituted carbene precursors and their silver complexes: synthesis, characterization and antimicrobial activities, Applied Organometallic Chemistry, 28 (2014) 244-251.

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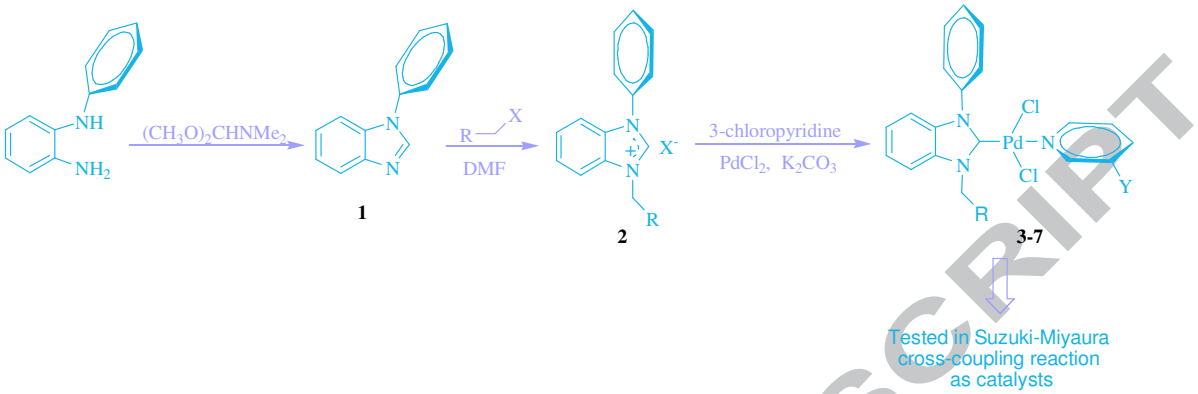
GRAPHICAL ABSTRACT



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Highlights

- New PEPPSI Pd-NHC complexes (**3**-**7**) were efficiently synthesized and characterized.
- These complexes were tested in Suzuki-Miyaura cross-coupling reaction as catalysts.
- Biaryl products were obtained in moderate yields in the presence of catalysts **3**-**7**.

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