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PEPPSI-type complexes with small NHC ligands obtained according to the new method efficiently catalyzed Suzuki-Miyaura reaction

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ABSTRACT

A series of 13 new PEPPSI-type complexes with small NHC ligands and differently substituted imidazoles were prepared using as substrates $[Pd(\mu\text{-}X)X(bmim\text{-}y)]_2$ dimer or imidazole complexes $PdCl_2(imidazole)_2$. Improvement of the synthetic method allowed simplification of the purification step. The obtained complexes efficiently catalyzed the Suzuki-Miyaura cross-coupling of substituted bromobenzenes and arylboronic acids in water and in ^{i}PrOH/water mixture. The observed catalytic activity was significantly better than that of $Pd(OAc)_2$ and similar to that of $Pd(IPr)Cl_2(3\text{-}Cl\text{-}py)$ in the same conditions. TEM analysis of the post-reaction mixture evidenced formation of Pd NPs of diameter ca. 3 nm, participating in the catalytic process.

1. Introduction

In past decades, since Arduengo in 1991 has isolated first stable free carbene [1], transition metal complexes with N-heterocyclic carbene ligands (NHCs) gained great attention, especially as catalysts in the cross-coupling reactions, enabling activation of the C-Cl bond under mild conditions and using green solvents [2], in particular water [2d]. Since that time, Herrmann, Nolan, Glorius and others have made a significant contribution in the development of the palladium-NHC complexes and they have provided an explanation of their role in the cross-coupling reactions [3]. In this respect, Suzuki-Miyaura reaction was intensively studied as a powerful tool for the preparation of the non-symmetric biaryls [4]. Recently the aromatic amides and esters were employed in Suzuki-Miyaura as coupling partners instead the aryl halides to obtain diaryl ketones [5].

Palladium complexes bearing bulky NHC ligands, two halides and pyridine, were introduced by Organ as PEPPSI complexes (Pyridine Enhanced Precatalyst Preparation Stabilization and Initiation) [6]. These well-defined, air and moisture stable compounds, have found many applications as efficient catalysts in C-C and C-N bond forming reactions [7]. The high catalytic activity of the PEPPSI complexes, was explained by their ability to accelerate the reductive elimination of product due to the steric hindrance of bulky NHC ligand. Furthermore, the NHC ligand, which shows strong σ-donating properties facilitates the oxidative addition of aryl halide [6]. PEPPSI-type complexes are stable and easy to handle, what distinguishes them among other palladium complexes with the carbene ligands [6]. The high catalytic activity of PEPPSI complexes motivated to investigate their analogues with non-bulky NHC ligands [8] and to apply different N-ligands as a leaving group [8,9]. Continuing our studies in this area, we present in this paper new PEPPSI-type palladium complexes bearing smaller NHC ligands and imidazoles as N-ligands. They can be obtained according to the procedure described already in the literature [10] or by the new method elaborated during these studies.

The obtained complexes were applied as the catalysts in Suzuki-Miyaura reaction in aqueous medium. The mechanism of the catalytic function of PEPPSI-type complexes in cross-coupling reactions is still under debate. In most cases, for original PEPPSI catalysts, homogeneous reaction pathway was proposed with Pd(0)-NHC complexes as catalytically active form [6,7]. However their transformation into Pd(0) nanoparticles was also evidenced for PEPPSI-type complexes with triazoles [11] and with π-acidic

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4,5-cyano-1,3-dimesitylimidazol-2-ylidene [12] as well as for the series of Pd-NHC complexes with small NHC and bulky NHC ligands [13]. These *in situ* formed Pd NPs, stabilized with NHC and N-ligands, efficiently catalyze cross-coupling reactions [11–13]. To get deeper knowledge about transformations of PEPPSI-type complexes under Suzuki-Miyaura conditions, mechanistic studies were undertaken and presented in this paper.

2. Experimental section

2.1. Methods and materials

^{1}H, ^{13}C and COSY spectra were recorded on a Bruker Avance 500 MHz instrument using $CDCl_3$ and CD_2Cl_2 as the solvents and chemical shifts were marked in ppm relative to the solvent residual signal according to the literature report [14]. Elementary analyses were carried out on the CHNS vario EL III Elementar instrument. Transmission Electron Microscopy images were recorded on a FEI Tecnai G^2 20 X-TWIN electron microscope with a LaB_6 cathode. To prepare the samples for TEM studies 2 ml of methanol was added to the mixture of the analyzed solution and the resulting suspension was ultrasonically treated for 5 min. Specimens were prepared by putting a droplet of a colloidal suspension on a carbon-coated copper microscope grid followed by evaporating the solvent under the IR lamp for 15 min. The GC-MS measurements were performed using an HP 5890 GC instrument equipped with an HP 5917 A mass detector and HP 5 capillary column with stationary phase with composition 5% diphenylpolysiloxane, 95% dimethylpolysiloxane, He was used as a carrier gas.

All imidazoles and ionic liquids, besides 1-methyl-3-(propoxymethyl)imidazolium chloride ([miop]Cl) and 1-benzyl-3-methylbenzimidazolium chloride ([bnmim]Cl) [15], were purchased from Sigma-Aldrich and used without further purification. The solvents were used without further purification.

Complexes $[PdCl_2(CH_3CN)_2]$ [16], $[Pd(imidazole)_2Cl_2]$ [16], $[Pd(\mu\text{-}X)X(bmim\text{-}y)]_2$ [13a] and $[Pd(bmim\text{-}y)_2Cl_2]$ [13b] were obtained according to the literature.

Used abbreviations of NHC ligands: [bmim-y] – 1-butyl-3-methylimidazol-2-ylidene, [bnmim-y] – 1-benzyl-3-methylimidazol-2-ylidene, [miop-y] – 1-methyl-3-(propoxymethyl)imidazole-2-ylidene, [bnmbenzim-y] – 1-benzyl-3-methylbenzimidazol-2-ylidene, [IMes] – 1,3-bis(2,4,6,-trimethylphenyl)imidazol-2-ylidene.

2.2. Synthesis of palladium PEPPSI-type complexes with different imidazole ligands from $[Pd(\mu\text{-}X)X(bmim\text{-}y)]_2$. Method A

An appropriate imidazole (0.2 mmol) was added to the mixture of $[Pd(\mu\text{-}X)X(bmim\text{-}y)]_2$ (0.1 mmol) in CH_2Cl_2 (1–2 ml). The color changed from orange to yellow immediately (in case of iodide complex from dark red to red). The mixture was stirred for 1 h at room temperature. After this time 8 ml of a hexane was added to the solution and clouding of the mixture was observed. The mixture was left for 24 h and the yellow solid was formed. The product was filtrated, washed with hexane and dried. The complexes were obtained with the yield of 80–90%.

*2.2.1. $[PdBr_2(bmim\text{-}y)(1\text{-methylimidazole})]$ **(1a)**: yield: 90%, Anal. calcd. (%) For $C_{12}H_{20}N_4Br_2Pd$: C 29.62; H 4.14; N 11.52. Found: C 29.51; H 4.06; N 11.54*

^{1}H NMR (500 MHz, $CDCl_3$, δ [ppm]): 8.15 (broad s, 1H, NCHN), 7.62 (pseudo t, 1H, NCH), 6.89 (d, 1H, NCH, $J_{HH} = 2.0$ Hz), 6.88 (d, 1H, NCH, $J_{HH} = 2.0$ Hz), 6.78 (pseudo t, 1H, NCH), 4.47 (t, 2H, NCH_2, $J_{HH} = 7.40$ Hz), 4.06 (s, 3H, NCH_3), 3.67 (s, 3H, NCH_3), 2.02 (mult, 2H, CH_2), 1.45 (mult, 2H, CH_2), 1.00 (t, 3H, CH_3, $J_{HH} = 7.40$ Hz).

^{13}C NMR (125.7 MHz, $CDCl_3$, δ [ppm]): 148.9 (NCN), 140.4 (NCHN), 130.5 (NCH) 123.0 (NCH), 121.5 (NCH), 119.9 (NCH), 51.0 (NCH_2), 38.4 (NCH_3), 34.3 (NCH_3), 32.3 (CH_2), 20.1 (CH_2), 13.9 (CH_3).

*2.2.2. $[PdBr_2(bmim\text{-}y)(1,2\text{-dimethylimidazole})]$ **(1b)**: yield: 87%, Anal. calcd. (%) For $C_{13}H_{22}N_4Br_2Pd$: C 31.19; H 4.43; N 11.19. Found: C 31.33; H 4.32; 11.02*

^{1}H NMR (500 MHz, $CDCl_3$, δ [ppm]): 7.09 (d, 1H, NCH, $J_{HH} = 1.65$ Hz), 6.87 (d, 1H, NCH, $J_{HH} = 2.0$ Hz), 6.86 (d, 1H, NCH, $J_{HH} = 2.0$ Hz), 6.74 (d, 1H, NCH, $J_{HH} = 1.65$ Hz), 4.52 (t, 2H, NCH_2, $J_{HH} = 7.65$ Hz), 4.12 (s. 3H, NCH_3), 3.55 (s, 3H, NCH_3), 2.77 (s, 3H, CCH_3), 2.11 (mult, 2H, CH_2), 1.50 (mult, 2H, CH_2), 1.04 (t, 3H, CH_3, $J_{HH} = 7.40$ Hz).

^{13}C NMR (125.7 MHz, $CDCl_3$, δ [ppm]): 151.2 (NCN), 145.7 (NCN), 127.9 (NCH), 122.8 (NCH), 121.6 (NCH), 120.7 (NCH), 51.1 (NCH_2), 38.5 (NCH_3), 33.6 (NCH_3), 32.4 (CH_2), 20.2 (CH_2), 14.5 (CCH_3), 13.9 (CH_3).

*2.2.3. $[PdBr_2(bmim\text{-}y)(1\text{-butylimidazole})]$ **(1c)**: yield: 81%, Anal. calcd. (%) For $C_{15}H_{26}N_4Br_2Pd$: C 34.08; H 4.96; N 10.60. Found: C 35.16; H 5.10; N 10.78*

^{1}H NMR (500 MHz, $CDCl_3$, δ [ppm]): 8.17 (broad s, 1H, NCHN), 7.62 (pseudo t, 1H, NCH), 6.89 (d, 1H, NCH, $J_{HH} = 1.95$ Hz), 6.88 (d, 1H, NCH, $J_{HH} = 1.95$ Hz), 6.80 (pseudo t, 1H, NCH), 4.47 (t, 2H, NCH_2, $J_{HH} = 7.65$ Hz), 4.07 (s, 3H, NCH_3), 3.90 (t, 3H, NCH_3, $J_{HH} = 7.30$ Hz), 2.02 (mult, 2H, CH_2), 1.75 (mult, 2H, CH_2), 1.45 (mult, 2H, CH_2), 1.34 (mult, 2H, CH_2), 1.00 (t, 3H, CH_3, $J_{HH} = 7.40$ Hz), 0.94 (t, 3H, CH_3, $J_{HH} = 7.40$ Hz).

^{13}C NMR (125.7 MHz, $CDCl_3$, δ [ppm]): 148.8 (NCN), 139.5 (NCHN), 130.1 (NCH) 122.89 (NCH), 121.4 (NCH), 118.5 (NCH), 50.9 (NCH_2), 47.7 (NCH_2), 38.3 (NCH_3), 32.7 (CH_2), 32.2 (CH_2), 19.9 (CH_2), 19.7 (CH_2), 13.8 (CH_3), 13.5 (CH_3).

*2.2.4. $[PdBr_2(bmim\text{-}y)(1\text{-methylbenzimidazole})]$ **(1d)**: yield: 85%, Anal. calcd. (%) For $C_{16}H_{22}N_4Br_2Pd$: C 35.81; H 4.13; N 10.44. Found: C 36.13; H 4.11; N 10.24*

^{1}H NMR (500 MHz, $CDCl_3$, δ [ppm]): 8.45 (mult, 1H, Ar), 8.29 (s, 1H, NCHC), 7.38 (mult, 3H, Ar), 6.92 (d, 1H, NCH, $J_{HH} = 1.95$ Hz), 6.91 (d, 1H, NCH, $J_{HH} = 1.95$ Hz), 4.57 (t, 2H, NCH_3, $J_{HH} = 7.65$ Hz), 4.17 (s, 3H, NCH_3), 3.85 (s, 3H, NCH_3), 2.14 (mult, 2H, CH_2), 1.53 (mult, 2H, CH_2), 1.06 (t,3H, CH_3).

^{13}C NMR (125.7 MHz, $CDCl_3$, δ [ppm]): 149.7 (NCN), 144.9 (NCHN), 140.8 (NC, Ar), 133.7 (NC, Ar), 124.2 (NCH), 123.2 (Ar), 122.9 (Ar), 121.6 (NCH), 121.4 (Ar), 109.8 (Ar), 51.11 (NCH_2), 38.5 (NCH_3), 32.4 (CH_2), 31.8 (NCH_3), 20.1 (CH_2), 13.9 (CH_3).

*2.2.5. $[PdBr_2(bmim\text{-}y)(1\text{-benzylimidazole})]$ **(1e)**: yield: 87%, Anal. calcd. (%) For $C_{18}H_{24}N_4Br_2Pd$: C 38.43; H 4.30; N 9.96. found: C 39.42; H 4.09; N 9.96*

^{1}H NMR (500 MHz, $CDCl_3$, δ [ppm]): 8.29 (broad s, 1H, NCHN), 7.66 (pseudo t, NCH, 1H), 7.36 (mult, 3H, Ar), 7.18 (mult, 2H, Ar), 6.89 (d, NCH, 1H, $J_{HH} = 1.95$ Hz), 6.88 (d, NCH, 1H, $J_{HH} = 1.95$ Hz), 6.78 (pseudo t, 1H, NCH), 5.07 (s, 2H, NCH_2), 4.47 (t, 2H, NCH_2, $J_{HH} = 7.65$ Hz), 4.07 (s, 3H, NCH_3), 2,02 (mult, 2H, CH_2), 1.45 (mult, 2H, CH_2), 1.00 (t, 3H, CH_3).

^{13}C NMR (125.7 MHz, $CDCl_3$, δ [ppm]): 148.6 (NCN), 140.1 (NCHN), 134.9 (NCH), 130.7 (Ar), 129.3 (Ar), 128.9 (Ar), 127.9 (Ar), 123.0 (NCH), 121.5 (NCH), 118.9 (NCH), 51.9 (CH_2), 51.0 (NCH_2), 38.5 (NCH_3), 32.3 (CH_2), 20.1 (CH_2), 13.9 (CH_3).

*2.2.6. $[PdBr_2(bmim\text{-}y)(1\text{-benzyl-2-methylimidazole})]$ **(1f)**: yield: 85%, Anal. calcd. (%) For $C_{19}H_{26}N_4Br_2Pd$: C 39.57; H 4.54; N 9.72. found: C 39.88; H 4.40; N 9.64*

^{1}H NMR (500 MHz, $CDCl_3$, δ [ppm]): 7.35 (mult, 2H, Ar), 7.16 (d, 1H, NCH, $J_{HH} = 1.65$ Hz), 7.07 (mult, 2H, Ar), 6.88 (d, 1H, NCH,

J_{HH} = 2.0 Hz), 6.87 (d, 1H, NCH, J_{HH} = 2.0 Hz), 6.75 (d, 1H, NCH, J_{HH} = 1.65 Hz), 5.02 (s, 2H, NCH_2), 4.52 (t, 2H, NCH_2, J_{HH} = 7.65 Hz), 4.12 (s, 3H, NCH_3), 2.76 (s, 3H, CCH_3) 2.11 (mult, 2H, CH_2), 1.49 (mult, 2H, CH_2), 1.04 (t, 3H, CH_3, J_{HH} = 7.40 Hz).

^{13}C NMR (125.7 MHz, $CDCl_3$, δ [ppm]): 150.9 (NCN), 145.8 (NCN), 135.1 (NCH), 129.3 (Ar), 128.5 (Ar), 128.3 (Ar), 127.1 (Ar), 122.8 (NCH), 121.6 (NCH), 120.0 (NCH), 50.6 (NCH_2), 51.1 (NCH_2), 38.5 (NCH_3), 32.4 (CH_2), 20.1 (CH_2), 14.8 (CCH_3), 13.9 (CH_3).

2.2.7. [PdI$_2$(bmim-y)(1-benzyl-2-methylimidazole)] ***(1g)****: yield: 82%, Anal. calcd. (%) For $C_{19}H_{26}N_4I_2Pd$: 34.03; H 3.91; N 8.35. found: C 33.65; H 3.65; N 8.35*

^{1}H NMR (500 MHz, $CDCl_3$, δ [ppm]): 7.34 (mult, 3H, Ar), 7.11 (d, 1H, NCH, J_{HH} = 1.60 Hz), 7.06 (mult, 2H, Ar), 6.90 (s, 2H, 2 x NCH), 6.77 (d, 1H, NCH, J_{HH} = 1.60 Hz), 5.04 (s, 2H, NCH_2), 4.41 (t, 2H, NCH_2, J_{HH} = 7.75 Hz), 3.99 (s, 3H, NCH_3), 2.69 (s, 3H, CCH_3), 2.06 (mult, 2H, CH_2), 1.48 (mult, 2H, CH_2), 1.03 (t, 3H, CH_3, J_{HH} = 7.40 Hz).

^{13}C NMR (125.7 MHz, $CDCl_3$, δ [ppm]): 149.2 (NCN), 145.6 (NCN), 135.1 (NCH), 128.7 (Ar), 128.5 (Ar), 126.9 (Ar), 123.3 (Ar), 123.1 (NCH), 121.5 (NCH), 120.2 (NCH), 51.5 (NCH_2), 50.6 (NCH_2), 39.2 (NCH_3), 31.6 (CH_2), 20.2 (CH_2), 15.7 (CCH_3), 13.9 (CH_3).

2.3. Synthesis of palladium PEPPSI-type complexes with different carbene ligands [PdCl$_2$(NHC)(imidazole)]. Method B

Palladium (II) complex with 1-methylimidazole ligands [$PdCl_2$(1-methylimidazole)$_2$] (0.5 mmol, 0.17 g), K_2CO_3 (1.5 mmol, 0.21 g), $MgSO_4$ (0.2 g, for drying), an appropriate imidazolium chloride (0.65 mmol) and finally a mixture of solvents CH_3CN:THF (8 ml: 5 ml) were placed in a round-bottom flask equipped with a stirring bar. The flask was capped with a rubber septum. The mixture was heated in the oil bath for 24 h at 50 °C in the air atmosphere. During that time, the color changed from yellow to greenish. After the reaction, the cooled down mixture was filtrated to remove inorganic salts. Then, the yellow solution was evaporated under vacuum and the resulting oily residue was dissolved in a minimum amount of acetone. Next, 10 ml of water was slowly added to the yellow solution and clouding of the mixture was observed. The mixture was left to evaporate acetone and to enable sedimentation of the formed precipitate. After that time, water with excess of the imidazolium chloride and 1-methylimidazole was decanted. The obtained product was washed with the water and dried under vacuum. The complexes 2f and 2 g were obtained from the appropriate imidazole and the precipitated solids required additional washing with ethyl alcohol and diethyl ether. One of the obtained complexes [$PdCl_2$(IMes)(1-methylimidazole)] (2e) was described in the literature [7b].

2.3.1. [PdCl$_2$(bmim-y)(1-methylimidazole)] ***(2a)****: yield 45%. Anal. calcd. (%) For $C_{12}H_{20}N_4Cl_2Pd$: C 36.25; H 5.07; N 14.09. Found: C 36.77; H 5.16; N 14.65*

^{1}H NMR (500 MHz, $CDCl_3$, δ [ppm]): 8.15 (broad s, 1H, NCHN), 7.50 (pseudo t, 1H, NCH), 6.88 (d, 1H, NCH, J_{HH} = 2.0 Hz), 6.86 (d, 1H, NCH, J_{HH} = 2.0 Hz), 6.80 (pseudo t, 1H, NCH), 4.52 (t, 2H, NCH_2, J_{HH} = 7.55 Hz), 4.13 (s, 3H, NCH_3), 3.67 (s, 3H, NCH_3), 2.03 (mult, 2H, CH_2), 1.45 (mult, 2H, CH_2), 1.00 (t, 3H, CH_3, J_{HH} = 7.40 Hz).

^{13}C NMR (125.7 MHz, $CDCl_3$, δ [ppm]): 150.4 (NCN), 138.6 (NCHN), 128.5 (NCH), 122.7 (NCH), 121.3 (NCH), 119.7 (NCH), 50.6 (NCH_2), 37.9 (NCH_3), 34.2 (NCH_3), 32.7 (CH_2), 19.9 (CH_2), 13.8 (CH_3).

2.3.2. [PdCl$_2$(bnmim-y)(1-methylimidazole)] ***(2b)****: yield 55%. Anal. calcd. (%) For $C_{15}H_{18}N_4Cl_2Pd$: C 41.74; H 4.20; N 12.98. Found: C 40.98; H 3.73; N 12.63*

^{1}H NMR (500 MHz, $CDCl_3$, δ [ppm]): 8.07 (broad s, 1H, NCHN), 7.52 (pseudo t, 1H, NCH), 7.48 (mult, 2H, Ar), 7.34 (mult, 3H, Ar), 6.85 (d, 1H, NCH, J_{HH} = 2.0 Hz), 6.81 (pseudo t, 1H, NCH), 6.67 (d, 1H, NCH, J_{HH} = 2.0 Hz), 5.82 (s, 2H, NCH_2), 4.17 (s, 3H, NCH_3), 3.68 (s, 3H, NCH_3).

^{13}C NMR (125.7 MHz, $CDCl_3$, δ [ppm]): 151.5 (NCN), 138.7 (NCHN), 135.7 (Ar), 129.0 (Ar), 129.1 (Ar), 128.6 (Ar), 128.5 (NCH), 123.4 (NCH), 121.1 (NCH), 119.8 (NCH), 54.7 (NCH_2), 38.1 (NCH_3), 34.4 (NCH_3).

2.3.3. [PdCl$_2$(miop-y)(1-methylimidazole)] ***(2c)****: yield 48%. Anal. calcd. (%) For $C_{12}H_{20}N_4OCl_2Pd$: C 34.84; H 4.87; N 13.55. Found: C 35.01; H 4.78; N 13.45*

^{1}H NMR (500 MHz, $CDCl_3$, δ [ppm]): 8.05 (broad s, 1H, NCH), 7.50 (pseudo t, 1H, NCH), 7.12 (d, 1H, NCH, J_{HH} = 2.0 Hz), 6.94 (d, 1H, NCH, J_{HH} = 2.0 Hz), 6.81 (pseudo t, 1H, NCH), 5.97 (s, 2H, NCH_2O), 4.16 (s, 3H, NCH_3), 3.68 (s, 3H, NCH_3), 3.67 (t, 2H, OCH_2, J_{HH} = 6.55 Hz), 1.62 (mult, 2H, CH_2), 0.91 (t, 3H, CH_3, J_{HH} = 7.40 Hz).

^{13}C NMR (125.7 MHz, $CDCl_3$, δ [ppm]): 151.6 (NCN), 138.7 (NCHN), 128.6 (NCH), 120.4 (NCH), 119.9 (NCH), 123.8 (NCH), 80.1 (NCH_2O), 71.4 (OCH_2), 38.2 (NCH_3), 34.4 (NCH_3), 22.8 (CH_2), 10.6 (CH_3).

2.3.4. [PdCl$_2$(bnmbenzim-y)(1-methylimidazole)] ***(2d)****: yield 63%. Anal. calcd. (%) For $C_{19}H_{20}N_4Cl_2Pd$: C 47.34; H 4.19; N 11.63; found: C 47.67; H4.15; N 11.18*

^{1}H NMR (500 MHz, CD_2Cl_2, δ [ppm]): 8.09 (broad s, 1H, NCHN), 7.57 (mult, 2H, Ar), 7.50 (pseudo t, 1H, NCH), 7.27–7.37 (mult, 4H, Ar), 7.44 (mult, 1H Ar), 7.16 (mult, 2H, Ar), 6.89 (pseudo t, 1H, NCH), 6.17 (s, 2H, NCH_2Ph), 4.40 (s, 3H, NCH_3), 3.70 (s, 3H, NCH_3).

^{13}C NMR (125.7 MHz, $CDCl_3$, δ [ppm]): 165.8 (NCN), 138.7 (NCHN), 135.7 (Ar), 135.3 (Ar), 134.1 (Ar), 128.5 (Ar), 128.2 (Ar) 128.1 (Ar), 123.3 (NCH), 123.2 (Ar), 119.9 (NCH), 111.5 (Ar), 110.1 (Ar), 53.1 (NCH_2Ph), 34.9 (NCH_3), 34.4 (NCH_3).

2.3.5. [PdCl$_2$(IMes)(1-methylimidazole)] ***(2e)****: yield 55%. Anal. calcd. (%) For $C_{25}H_{30}N_4Cl_2Pd$: C 53.25; H 5.36; N 9.94. found: C 52.52; H 5.48; N 9.43*

^{1}H NMR (500 MHz, CD_2Cl_2, δ [ppm]): 7.78 (s, 1H, NCHN), 7.23 (pseudo t, 1H, NCH), 7.03 (s, 2H, NCH), 7.02 (s, 4H, Ar), 6.56 (pseudo t, 1H, NCH), 3.48 (s, 3H, NCH_3), 2.36 (s, 12H, $ArCH_3$), 2.35 (s, 6H, $ArCH_3$).

^{13}C NMR (125.7 MHz, $CDCl_3$, δ [ppm]): 154.1 (NCN), 139.1 (Ar), 138.6 (NCHN), 136.5 (Ar), 135.4 (Ar), 129.3 (Ar), 124.1 (NCH), 128.7 (NCH), 119.0 (NCH), 34.1 (NCH_3), 21.3 ($ArCH_3$), 19.3 ($ArCH_3$).

2.3.6. [PdCl$_2$(bmim-y)(1-benzylimidazole)] ***(2f)****: yield 40%. Anal. calcd. (%) For $C_{18}H_{24}N_4Cl_2Pd$: C 45.64; H 5.11; N 11.83. Found: C 45.99; H 4.89; N 11.81*

^{1}H NMR (500 MHz, $CDCl_3$, δ [ppm]): 8.19 (broad s, 1H, NCHN), 7.55 (pseudo t, NCH, 1H), 7.36 (mult, 3H, Ar), 7.18 (mult, 2H, Ar), 6.88 (d, NCH, 1H, J_{HH} = 1.95 Hz), 6.87 (d, NCH, 1H, J_{HH} = 1.95 Hz), 6.80 (pseudo t, 1H, NCH), 5.07 (s, 2H, NCH_2), 4.53 (t, 2H, NCH_2, J_{HH} = 7.65 Hz), 4.14 (s, 3H, NCH_3), 2.03 (mult, 2H, CH_2), 1.46 (mult, 2H, CH_2), 1.00 (t, 3H, CH_3).

^{13}C NMR (125.7 MHz, $CDCl_3$, δ [ppm]): 150.4 (NCN), 138.3 (NCHN), 134.9 (NCH), 129.3 (Ar), 128.8 (Ar), 128.8 (Ar), 127.8 (Ar), 122.8 (NCH), 121.4 (NCH), 118.9 (NCH), 51.9 (CH_2), 50.8 (NCH_2), 38.0 (NCH_3), 32.8 (CH_2), 20.1 (CH_2), 13.9 (CH_3).

2.3.7. [PdCl$_2$(bmim-y)(1-benzyl-2-methylimidazole)] ***(2g)****: yield 40%. Anal. calcd. (%) For $C_{19}H_{26}N_4Cl_2Pd$: C 46.79; H 5.37; N 11.49. Found: C 45.94; H 4.60; N 11.07*

^{1}H NMR (500 MHz, $CDCl_3$, δ [ppm]): 7.34 (mult, 2H, Ar), 7.17 (d, 1H, NCH, J_{HH} = 1.65 Hz), 7.08 (mult, 2H, Ar), 6.86 (d, 1H, NCH, J_{HH} = 2.0 Hz), 6.85 (d, 1H, NCH, J_{HH} = 2.0 Hz), 6.74 (d, 1H, NCH, J_{HH} = 1.65 Hz), 5.00 (s, 2H, NCH_2), 4.57 (t, 2H, NCH_2, J_{HH} = 2.0 Hz),

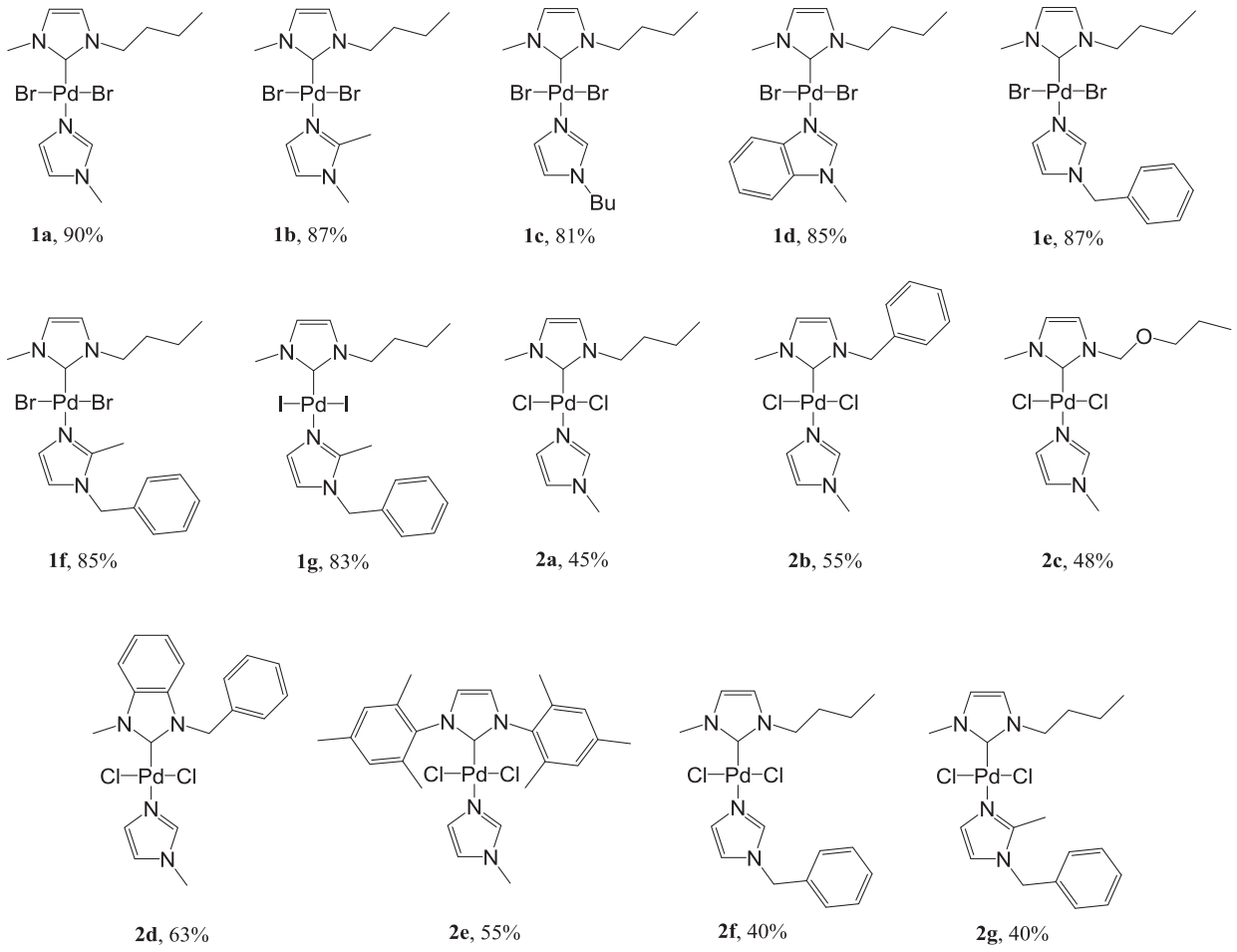


Fig. 1. Structures of PEPPSI-type palladium complexes.

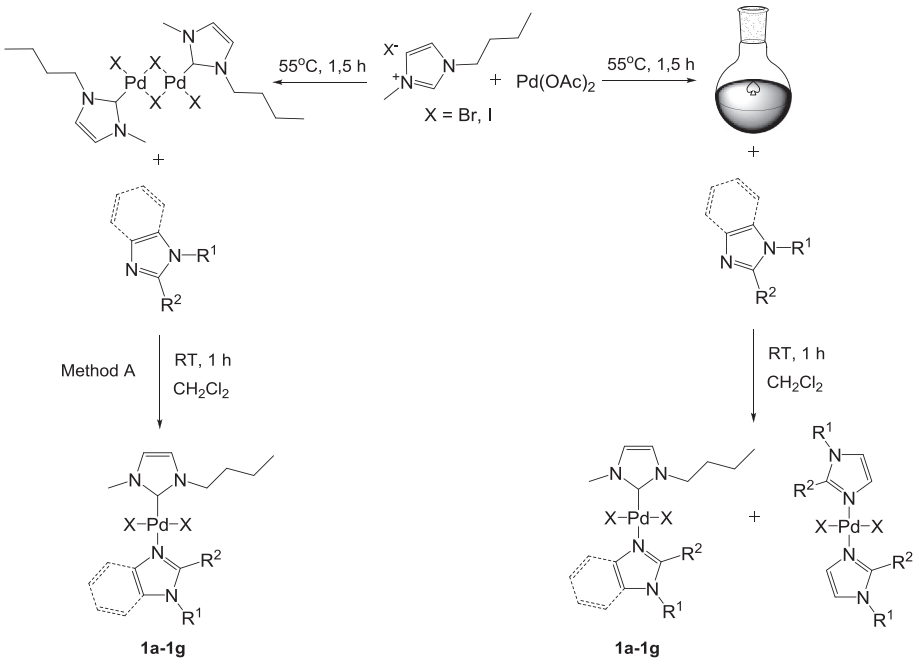


Fig. 2. Synthesis of palladium PEPPSI-type complexes with different imidazoles - method A.

4.18 (s, 3H, NCH_3), 2.77 (s, 3H, CCH_3), 2.12 (mult, 2H, CH_2), 1.51 (mult, 2H, CH_2), 1.04 (t, 3H, CH_3, $J_{HH} = 7.40$ Hz).

^{13}C NMR (125.7 MHz, $CDCl_3$, δ [ppm]): 151.5 (NCN), 145.9 (NCN), 135.0 (NCH), 129.3 (Ar), 128.5 (Ar), 128.9 (Ar), 127.9 (Ar), 122.6 (NCH), 121.4 (NCH), 119.8 (NCH), 50.8 (NCH_2), 50.6 (NCH_2), 38.0 (NCH_3), 32.9 (CH_2), 20.1 (CH_2), 14.0 (CCH_3), 13.9 (CH_3).

2.4. The Suzuki-Miyaura reaction procedure

All lab glassware and stirring bars were treated with aqua regia to remove any possible palladium contamination before applying them to catalytic reactions.

The Suzuki-Miyaura reactions were carried out in a 50 ml Schlenk tube equipped with a stirring bar. The solid substrates, phenylboronic acid (1.1 mmol, 0.134 g), K_2CO_3 (1.0 mmol, 0.138 g) and palladium catalyst (0.005 mmol) were weighed and placed in the Schlenk tube. Next, solvent (1.5 ml H_2O + 1.5 ^{i}PrOH or 3.0 ml H_2O) was added. The Schlenk tube was cooled down in the liquid nitrogen, evacuated using a membrane pump and filled with dinitrogen. This procedure was repeated three times. At the end, in the flow of dinitrogen, 2-bromotoluene (1.0 mmol, 0.17 g, 120 µl) was added. The Schlenk tube was tightly closed with a rubber septum and the reaction mixture was stirred at 80 °C for 1 h. After that time, water (3 ml) was added to facilitate phase separation, and the organic products were extracted with 21 ml of diethyl ether (3 × 7 ml, time of extraction 3 × 5 min). The extract was GC-MS analyzed with dodecane (0.44 mmol, 100 µl) as the internal standard. All the reactions were carried out at least two times.

To obtain time-profile of reaction the reaction mixture was cooled down in liquid nitrogen immediately after appropriate time (2.5 min, 5 min etc.) to stop the reaction. Next, the standard extraction was used to separate reaction products for GC analysis.

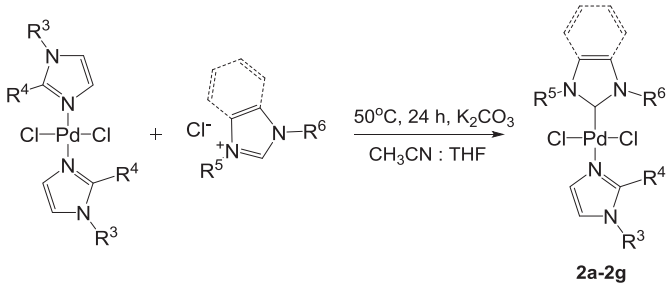


Fig. 3. Synthesis of palladium PEPPSI-type complexes with different NHC ligands - method B.

3. Results and discussion

3.1. Synthesis and structure of palladium PEPPSI-type complexes

The PEPPSI-type complexes studied in this paper are shown in Fig. 1.

The presented complexes were obtained according two different approaches.

The complexes with 1-butyl-3-methylimidazol-2-ylidene (bmim-y) and different imidazole ligands (1a-1g) were synthesized from palladium dimer $[Pd(\mu\text{-}X)X(bmim\text{-}y)]_2$ [13a,13b] (Method A, Fig. 2). Complex 2e containing the bulky NHC ligand is known and it was prepared according to the original Organ procedure [6a,6b].

The attempts to prepare complexes (1a-1g) using the *in situ* formed palladium dimer were also undertaken to avoid its isolation (Fig. 2). For this purpose, the imidazole was added to the homogeneous mixture of [bmim]Br and $Pd(OAc)_2$, and the resulted solution was stirred and heated for 1.5 h. Next CH_2Cl_2 (2 ml) was added and stirring was continued for next 1 h in room temperature. After that time the reaction mixture was diluted with CH_2Cl_2, passed through a short pad of silica gel. The obtained yellow solution was evaporated, then hexane was added to precipitate the

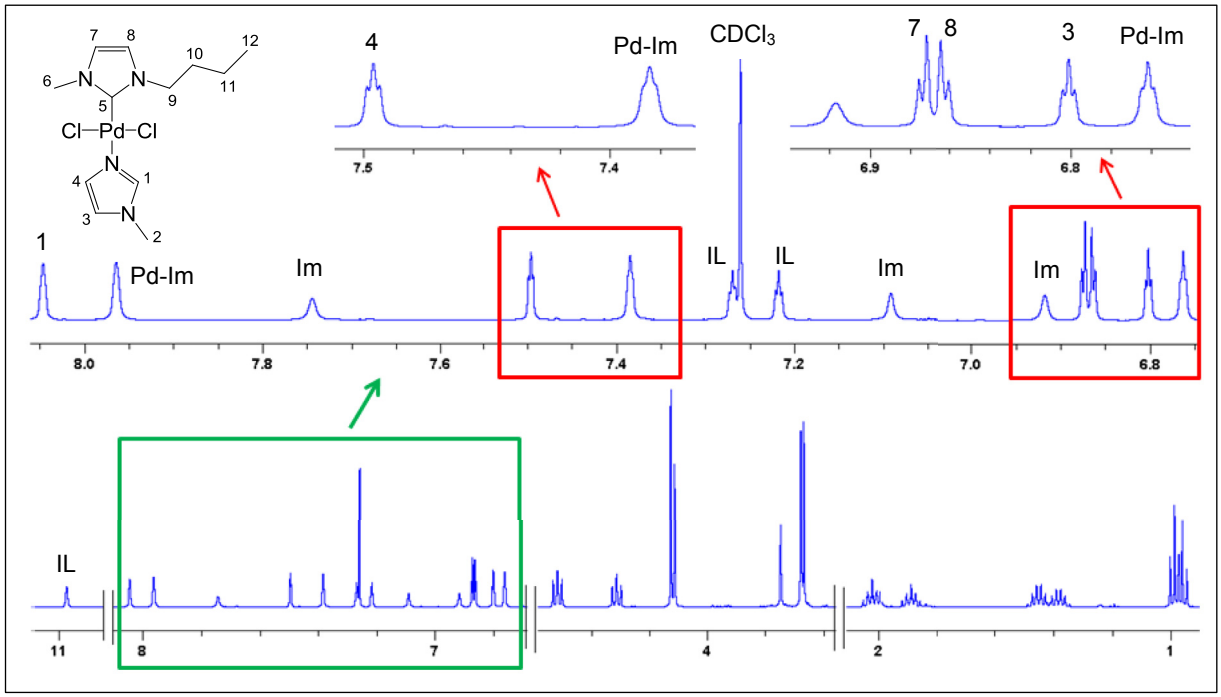


Fig. 4. ^{1}H NMR spectra recorded during synthesis of $[PdCl_2(bmim\text{-}y)(1\text{-}MeIm)]$ 1a from $[Pd(1\text{-methylimidazole})_2Cl_2]$ and bmimCl. Characteristic peaks of complex 1a, $[Pd(1\text{-methylimidazole})_2Cl_2]$ (Pd-Im), 1-butyl-3-methylimidazolium chloride (IL) and 1-methylimidazole (Im) were indicated.

solid. The NMR analysis has demonstrated that the obtained solid is a mixture of the palladium complex with imidazole ligands and the desired PEPPSI-type complex in the ratio 1:2 with predominance of the carbene complex. Exceptionally, reaction with 1-methylimidazole formed only the PEPPSI-type complex (1a). Thus, the results obtained using the isolated palladium dimer were much better and complexes with different imidazoles were isolated with 80–90% yield. However, the preparation of palladium dimer is not very efficient and the yield is 40–50%.

The complexes with different NHC ligands (2a-2g) were prepared according to the novel method using imidazole palladium complexes and imidazolium chlorides as the substrates. The syntheses were performed at the presence of K_2CO_3 which was necessary to detach proton at C2 of imidazolium chloride (Fig. 3).

During reaction, the imidazole ligand was replaced by the NHC ligand formed *in situ*, as it was confirmed by the NMR spectrum of the reaction mixture recorded after 6 h (Fig. 4). The spectrum showed characteristic peaks of the complex [$PdCl_2$(1-methylimidazole)$_2$], the formed product [$PdCl_2$(bmim-y)(1-methylimidazole)], released 1-methylimidazole and unreacted [bmim]Cl. The elaborated procedure avoided a tedious purification steps such as vacuum distillation to remove the excess of imidazole. The described method is suitable for complexes containing water-soluble N-ligands due to the step of purification/precipitation in which excess of the imidazolium chloride and the detached imidazole are removed in the aqueous phase. For complexes with water-insoluble imidazoles the obtained product has to be washed with ethyl alcohol and next with diethyl ether. Unfortunately, PEPPSI-type complexes are slightly soluble in ethyl alcohol, which causes decrease of the final yield. The complexes (2a-2g) obtained according to the new recipe were isolated with 40–63% yield, which makes this procedure competitive to the method of preparation of PEPPSI-type complexes with the smaller carbene ligands described in the literature [13a,13b]. According to the NMR spectra of the reaction mixture, all ionic liquid reacted to the desired product. Thus, the isolated yield should be improved and enhanced. Most likely, complexes 2a -2 g did not precipitate completely from acetone/water solution (see Fig. 4).

All the obtained complexes were characterized by NMR. The spectra presented some characteristic spectroscopic features. The specific peaks of carbene carbons in the ^{13}C spectra were detected for all the complexes in the downfield area (δ 149–165 ppm). The kind of the imidazole and halogen ligands has only a very small influence on the shift of the carbene carbon. Similarly, substituents present in the NHC ligand slightly affected the position of carbene carbon signal (complexes 2a, 2b, 2c, 2e), whereas the extended aromatic ring of the NHC ligand shifted the peak towards the lower field (complex 2d). For the complexes with 1-butyl-3-methylimidazol-2-ylidene the roof effect of the signals originating from the two neighboring protons of the carbene ring (N-CH=CH-N) was observed, while in the imidazolium bromide these protons showed pseudo-triplets (Fig. 5). The analysis of the spectra of complexes 1f, 1 g and 2 g; 1a and 2a; 1e and 2f containing different halogen ligands revealed an enhancement of the roof effect for signals of the mentioned protons in the following order: Cl < Br < I. For the iodine complex the protons formed singlet. The protons of the imidazole ring (N-ligand) in the complexes are observed as pseudo-triplets due to the similar values of ^3J and ^4J coupling constants. The COSY spectra confirmed the coupling between these protons. Consequently, for the complexes with the imidazole ligands substituted by the methyl group at C2 (complexes 1b, 1f, 1 g, 2 g) pseudo-triplets were not observed.

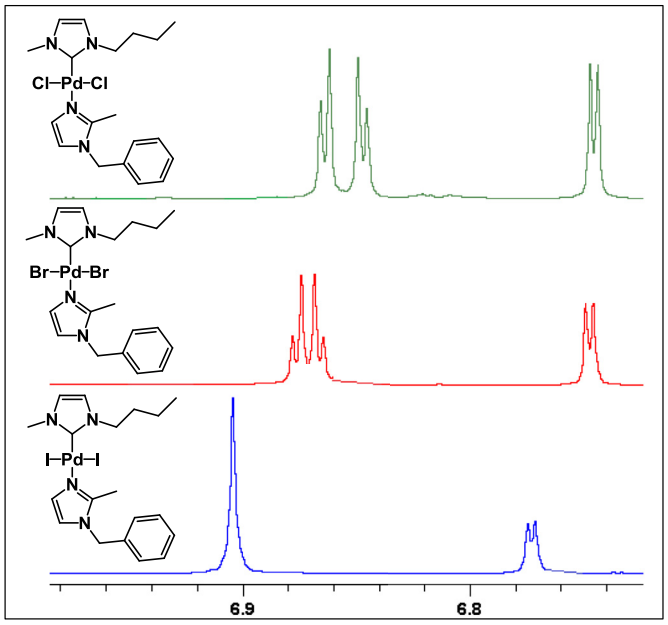
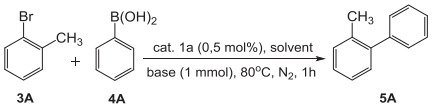


Fig. 5. Fragment of ^1H NMR for complexes 1f, 1 g and 2 g showing an enhancement of the roof effect.

3.2. Catalytic activity of PEPPSI-type palladium complexes

The obtained complexes were employed as the catalysts in Suzuki-Miyaura reaction of 2-bromotoluene and phenylboronic acid as the model substrates. The optimization of the conditions was carried out with [$PdBr_2$(bmim-y)(1-methylimidazole)] as the catalyst. During the initial studies different bases, time, temperature and loading of the catalyst were tested at 80 °C in the mixture of 2-propanol and water as the solvent (Table 1). The yield of the product obtained after 0.5 and 2 h were similar, so the next experiments were carried out in 1 h. When the effect of the base is concerned, carbonate salts provided a very good yield, bicarbonates and hydrated phosphates also worked well and moderate results

Table 1
Optimization of conditions for the model reaction of 2-bromotoluene (3A) and phenylboronic acid (4A) catalyzed by complex 1a[a].



Entry	Base	Solvent	Yield [%][b]
1	K_2CO_3	^{i}PrOH/H_2O (1:1)	97 (73[c], 77[d])
2	Na_2CO_3	^{i}PrOH/H_2O (1:1)	96
3	Cs_2CO_3	^{i}PrOH/H_2O (1:1)	98
4	$NaHCO_3$	^{i}PrOH/H_2O (1:1)	95
5	$K_3PO_4 \cdot 3H_2O$	^{i}PrOH/H_2O (1:1)	91
6	KOH	^{i}PrOH/H_2O (1:1)	74
7	NaOH	^{i}PrOH/H_2O (1:1)	75
8	K_2CO_3	H_2O	82
9	K_2CO_3	^{i}PrOH	42
10	K_2CO_3	H_2O + 150 µl ^{i}PrOH	87
11	K_2CO_3	^{i}PrOH + 150 µl H_2O	55

[a] Conditions: 1.0 mmol 3A, 1.1 mmol 4A, 0.005 mmol 1a, 1 mmol of base, 3 ml of solvent, 80 °C, N_2, 1 h.
[b] GC-MS yield of 5A averaged over at least two runs.
[c] 50 °C, 1 h.
[d] 50 °C, 4 h.

Table 2
Yield of 5A obtained in the Suzuki-Miyaura reaction at different loadings of 1a.[a]

Entry	1a mol%	Yield [%][b]	TON
1	0.01	44	4400
2	0.0625	47	752
3	0.125	97	776
4	0.25	98	392
5	0.5	97	194
6	1	95	95

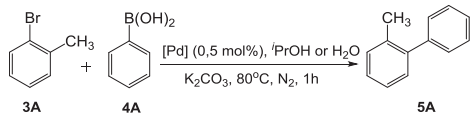
[a] Conditions: 1.0 mmol 3A, 1.1 mmol 4A, 1 mmol K_2CO_3, 3 ml ^{i}PrOH/H_2O (1:1), 80 °C, N_2, 1 h.
[b] GC-MS yield of 5A averaged over at least two runs.

were achieved in the presence of hydroxides. When the reaction was carried out at 50 °C, the complex 1a showed lower yield than at 80 °C, even if the reaction time was extended to 4 h. Under catalyst loading below 1 mol%, up to 0.125 mol%, high conversion, 95–97% was obtained. Further decrease of the 1a amount resulted in conversion decrease to 44% at 0.01 mol %. Nevertheless TON value 4400 in this case was pretty high (Table 2, entry 1 and 2). Good results were obtained using water as the solvent and further increase of the yield was noted after addition of small amount of 2-propanol. This could be explained by the increased solubility of the catalyst in 2-propanol. On the other hand, only 42% of product was formed in 2-propanol and the yield increased to 55% when small amount of water was added. Thus, the mixture of 2-propanol and water was selected as the best solvent for further studies of Suzuki-Miyaura reaction. In the next experiments the optimal conditions were used: 0.5 mol% [Pd], 1 mmol K_2CO_3, 80 °C, 1 h, 3 ml ^{i}PrOH/H_2O (1:1).

With the optimal reaction conditions in hand we have tested other palladium PEPPSI-type complexes. As it has been shown in Table 3, all of the catalysts were highly active, forming over 90% of the desired product. In this series of complexes 1c, 1 g, 2a showed slightly lower activity. The obtained results have not revealed any pronounced correlation between the structure and catalytic activity of the studied complexes. This can indicate formation of similar catalytically active palladium forms under reaction conditions. In fact, transmission electron microscopy (TEM) analysis of the reaction mixture evidenced the presence of palladium nanoparticles, most probably involved in the catalytic process.

For comparison, Suzuki-Miyaura reactions were also carried out in water, which is considered as a green solvent. In general, the yield of 2-methylbiphenyl was slightly lower than in 2-propanol/water mixture. In particular, the presence of the methyl group at C2 of imidazole resulted in a decrease of the yield of ca. 20% (complexes 1b, 1f, 2d, 2 g). In both of the solvents, ^{i}PrOH/H_2O and H_2O, complex 1c with an elongated alkyl chain of the substituent in N-position of imidazole ring exhibited lower activity. The complex 1 g with iodide ligand exhibited significantly lower activity compared to the chlorido and bromido analogues.

Table 3
Results of the Suzuki-Miyaura reaction of 2-bromotoluene (3A) and phenylboronic acid (4A) in ^{i}PrOH/H_2O and H_2O[a] catalyzed by complexes 1a-2g and other palladium precursors.

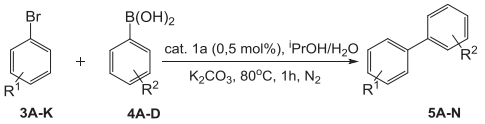


3A 4A 5A

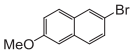
Entry	Catalyst/Catalytic system	Yield [%][b]	
		^{i}PrOH/H_2O (1:1)	H_2O
1	1a	97	83
2	1b	95	67
3	1c	87	72
4	1d	93	75
5	1e	95	87
6	1f	95	66
7	1 g	70	40
8	2a	85	81
9	2b	93	87
10	2c	92	85
11	2d	98	60
12	2e	100	67
13	2f	100	79
14	2 g	92	56
15	[$PdCl_2$(1-benzylimidazole)$_2$]	98	44
16	[$PdCl_2$(1-methylimidazole)$_2$]	–	44
17	[$PdCl_2$(1-methylimidazole)$_2$] + [bmim]Cl (0.0075 mmol)	–	33
18	[$PdCl_2$(1-methylimidazole)$_2$] + [bnmim]Cl (0.0075 mmol)[c]	–	38
19	[$PdCl_2$(1-benzylimidazole)$_2$] + [bmim]Cl (0.0075 mmol)	100	41
20	[Pd(bmim-y)$_2$$Cl_2$]	75	63
21	[Pd(bmim-y)$_2$$Cl_2$] +1-benzylimidazole (0.0075 mmol)	57	0
22	[Pd(bmim-y)$_2$$Cl_2$] +1-methylimidazole (0.0075 mmol)	–	0
23	$Pd(OAc)_2$	68	0
24	[Pd(IPr)Cl_2(3-Cl-py)]	100	81

[a] Conditions: 1.0 mmol 3A, 1.1 mmol 4A, 0.005 mmol of [Pd], 1 mmol K_2CO_3, 3 ml of solvent, 80 °C, N_2, 1 h.
[b] GC-MS yield of 5A averaged over at least two runs.
[c] [bnmim]Cl = 1-benzyl-3-methylimidazolium chloride.

Table 4
Results of the Suzuki-Miyaura reaction of aryl bromides (3A-K) and boronic acid derivatives (4A-D)[a] catalyzed by complex 1a.



3A-K 4A-D 5A-N

Entry	3 (R^1)	4 (R^2)	Yield [%][b]
1	**3A** (2-Me)	**4A** (H)	**5A** 96
2	**3B** (4-Me)	**4A** (H)	**5B** 100
3	**3C** (4-NO_2)	**4A** (H)	**5C** 100 (98[c])
4	**3D** (4-CHO)	**4A** (H)	**5D** 100 (99[c])
5	**3E** (4-CN)	**4A** (H)	**5E** 100 (99[c])
6	**3F** (4-COMe)	**4A** (H)	**5F** 100 (99[c])
7	**3G** (2-OMe)	**4A** (H)	**5G** 100 (93[c])
8	**3H** (3-OMe)	**4A** (H)	**5H** 100 (94[c])
9	**3I** (4-OMe)	**4A** (H)	**5I** 100 (95[c])
10	**3J** 	**4A** (H)	**5J** 90
11	**3K** 	**4A** (H)	**5K** 100 (92[c])
12	**3A** (2-Me)	**4B** (4-COMe)	**5L** 67[d]
13	**3A** (2-Me)	**4C** (2-Br)	**5M** 0
14	**3A** (2-Me)	**4D** 	**5N** 73[e]

[a] Conditions: 1.0 mmol 3A-K, 1.1 mmol 4A-D, 0.005 mmol of complex 1a, 1 mmol K_2CO_3, 3 ml. ^{i}PrOH/H_2O (1:1), 80 °C, N_2, 1 h.
[b] GC-MS yield of 5A averaged over at least two runs.
[c] Isolated yields.
[d] 15% of homocoupling product was also formed.
[e] 10% of homocoupling product was also formed.

The reference PEPPSI-IPr complex (Pd(IPr)Cl_2(3-Cl-py)) gave very good results in both solvents (Table 3, run 24). Interestingly, these results are very similar to these obtained with 2f catalyst containing bmim-y as NHC ligand.

The next part of the research was aimed at comparison of the activity of new complexes with their analogues formed *in situ*. In these experiments, the imidazolium salts or imidazoles were added to palladium complexes with imidazole ligands or to palladium complexes bearing NHC ligands. Interestingly, the obtained results were in most cases worse than these with pre-made compounds. Exceptionally, palladium complex with benzylimidazole ligand provided 98% of the product and the yield increased to 100% after addition of [bmim]Cl (Table 3, entry 15 and 19). It is also worth to underline that the new PEPPSI-type complexes showed much better activity in water than Pd(II)-imidazole and Pd(II)-NHC complexes. Moreover, addition of imidazole suppressed completely catalytic activity of Pd(II)-NHC complex in water (Table 3, entry 21 and 22). In contrast, PEPPSI-type complexes 2a and 2f with the same ligands provided 81 and 79% of 5A in water (Table 3, entry 8 and 13).

It is important to note that the results obtained for the complexes studied here were much better, than for the commonly used $Pd(OAc)_2$, under the applied conditions (both in ^{i}PrOH/H_2O and H_2O) (Table 3, entry 23).

The scope of the reaction was investigated under the optimal conditions with complex 1a as the catalyst. As it can be concluded from the data in Table 4, aryl bromides both with withdrawing and donating groups, were coupled with very high yields. Also the naphthalene derivatives are suitable substrates for the coupling with phenylboronic acid. The reaction with the boronic acid derivatives (Table 4, entry 12, 13 and 14) lead to 10–15% of the homocoupling products. For comparison two experiments were performed with more challenging aryl chloride, 2-chloronitrobenzene. Using 1a as catalyst and prolonged reaction time (24 h), 32% of non-symmetric biphenyl was obtained in ^{i}PrOH/H_2O. The conversion to the cross-coupling product increased to 72%

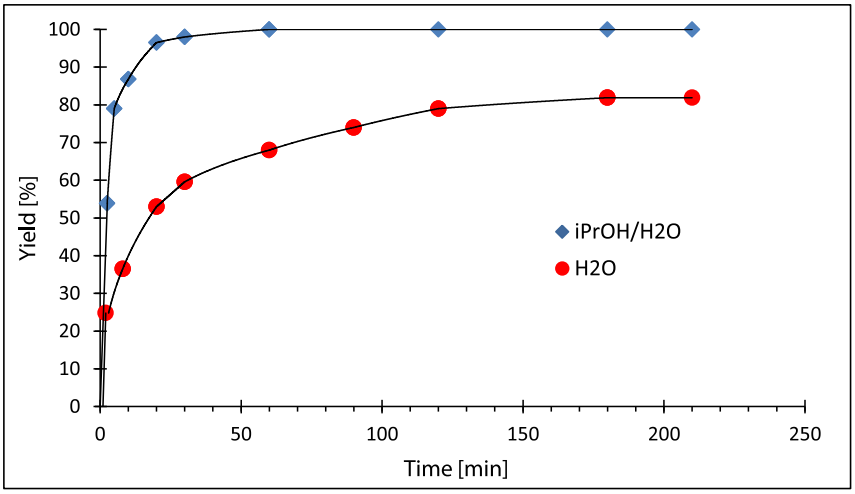


Fig. 6. Kinetic curves for the formation of product 5A in the Suzuki-Miyaura reaction performed in ^{i}PrOH/H_2O and H_2O catalyzed by complex 1f. Reaction condition: 1.0 mmol 3A, 1.1 mmol 4A, 0.005 mmol of complex 1f, 1 mmol K_2CO_3, 3 ml of solvent, 80 °C, N_2.

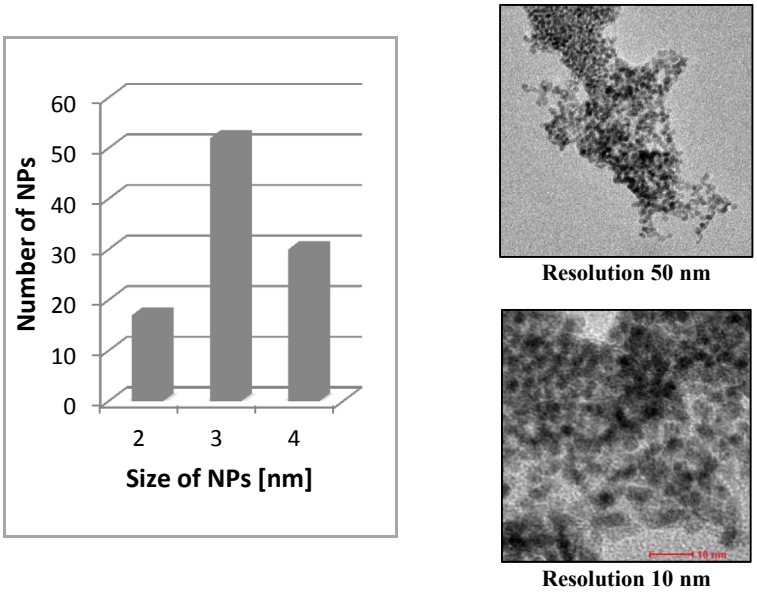


Fig. 7. TEM micrographs and distribution of Pd NPs isolated after the Suzuki-Miyaura reaction catalyzed by 0.5 mol% of complex 1a.

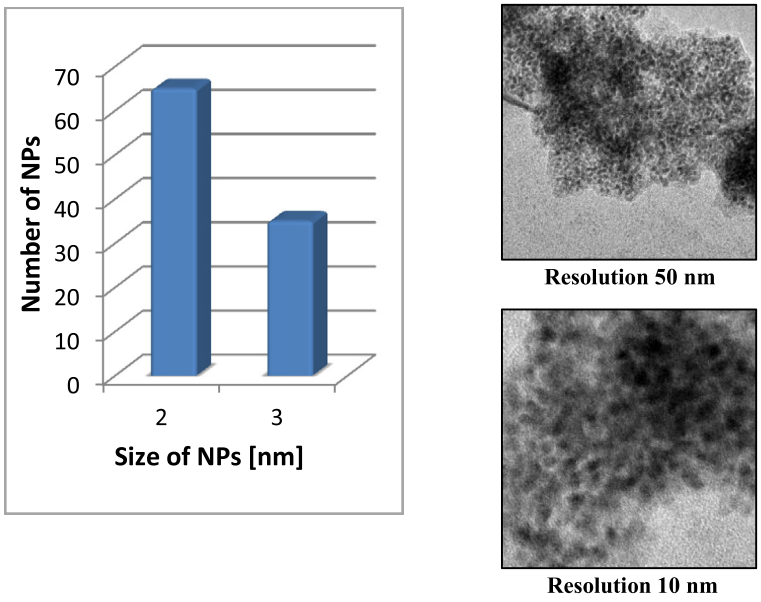


Fig. 8. TEM micrographs and distribution of Pd NPs isolated after the Suzuki-Miyaura reaction catalyzed by 0.5 mol% of complex 1f.

at 120 °C in ethylene glycol as a solvent.

For a deeper insight into kinetic of the reaction catalyzed by the complex 1f, formation of product 5A was monitored in the time in two solvents. As shown in Fig. 6reaction performed in the mixture of ^{i}PrOH/H_2O achieved 54% yield of the product just after 2 min and the yield increased to 80% after 5 min. The reaction performed in H_2O required 20 and 120 respectively to achieve the same yield of 5A.

3.3. TEM studies of the post-reaction mixture

Transmission electron microscopy (TEM) analyses were performed for the reaction mixtures obtained with complexes 1a and 1f (Figs. 7 and 8). The TEM studies confirmed the presence of palladium nanoparticles with a diameter ca. 3 nm. The lack of agglomeration could indicate on the good stabilization of nanoparticles by NHC and imidazole ligands present in the reaction mixture.

The presence of Pd NPs can suggests their involvement in the process. In order to confirm that supposition the mercury poisoning test was performed [17]. In the reaction with 300 excess of Hg(0) the conversion of substrate was 48% whereas without Hg(0) it was 95%. Thus, the partial inhibition of the reaction course was observed. This result is not sufficient to consider Pd NPs are the only catalytically active form present in the studied system. Consequently, a “cocktail” type catalytic system can be proposed [18].

4. Conclusions

The novel procedure of the synthesis of PEPPSI-type complexes with non-bulky NHC ligands and substituted imidazoles, such as N-ligand, was elaborated and successfully applied to obtain 6 new palladium complexes. Advantageously, this method enabled to simplify the purification step as well as application of substrates excess, in particular the N-ligand. The imidazole complexes, which were used as the substrates in the syntheses, were easily obtained with high yields.

The obtained new PEPPSI-type complexes with small NHC ligands presented high catalytic activity in the Suzuki-Miyaura reaction in ^{i}PrOH/water mixture and in the aqueous medium. The observed activity was much higher than activity of $Pd(OAc)_2$ and similar to that of $Pd(IPr)Cl_2$(3-Cl-py) under the same conditions. This could be explained by the effect of the NHC and imidazole ligands present in the catalytic system. These ligands efficiently stabilized Pd NPs formed during the reaction from the palladium complexes. Importantly, introduction of imidazole ligands instead of pyridines or amines, allowed to obtain better results for PEPPSI-type complexes with non-bulky NHC ligands [8]. In this context the high activity on the new palladium complexes in aqueous medium should be underlined.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.jorganchem.2018.01.033.

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