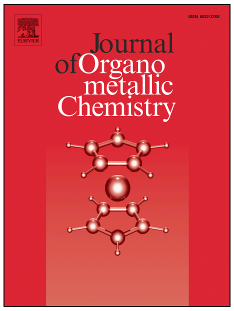


A new N–heterocyclic carbene palladium complex immobilized on nano silica: An efficient and recyclable catalyst for Suzuki–Miyaura C–C coupling reaction

Zari Pahlevanneshan, Majid Moghadam, Valiollah Mirkhani, Shahram Tangestaninejad, Iraj Mohammadpoor-Baltork, Hossein Loghmani-Khouzani

PII: S0022-328X(16)30052-3

DOI: 10.1016/j.jorganchem.2016.02.019

Reference: JOM 19403

To appear in: *Journal of Organometallic Chemistry*

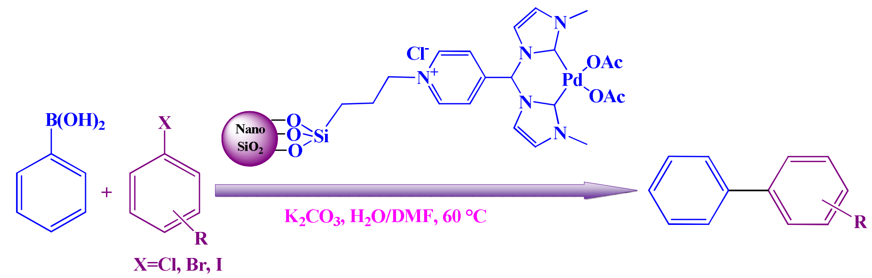
Received Date: 27 April 2015

Revised Date: 3 February 2016

Accepted Date: 11 February 2016

Please cite this article as: Z. Pahlevanneshan, M. Moghadam, V. Mirkhani, S. Tangestaninejad, I. Mohammadpoor-Baltork, H. Loghmani-Khouzani, A new N–heterocyclic carbene palladium complex immobilized on nano silica: An efficient and recyclable catalyst for Suzuki–Miyaura C–C coupling reaction, *Journal of Organometallic Chemistry* (2016), doi: 10.1016/j.jorganchem.2016.02.019.

A new catalytic system based on Pd-NHC complex of (4-pyridyl)*bis*(imidazolyl)methane supported on nanosilica is introduced. This heterogeneous catalytic system exhibited excellent activity in the Suzuki–Miyaura coupling reaction of various aryl halides with phenylboronic acid, and was reusable several times without significant loss of its catalytic activity.


B(OH)$_2$
X
R
X=Cl, Br, I
Nano SiO$_2$
Si
Cl$^-$
N$^+$
N
Pd
OAc
OAc
K$_2$CO$_3$, H$_2$O/DMF, 60 °C
R

A new *N*–heterocyclic carbene palladium complex immobilized on nano silica: An efficient and recyclable catalyst for Suzuki–Miyaura C–C coupling reaction

Zari Pahlevanneshan, Majid Moghadam,* Valiollah Mirkhani,* Shahram Tangestaninejad, Iraj Mohammadpoor–Baltork, Hossein Loghmani-Khouzani

Department of Chemistry, Catalysis Division, University of Isfahan, Isfahan 81746–73441, Iran

Abstract– A new catalytic system based on Pd–NHC complex utilizing (4–pyridyl)*bis*(imidazolyl)methaneas a bidentate NHC ligand supported on nano–silica is introduced. The catalyst was characterized by FT–IR spectroscopy, thermogravimetric analysis, field emission scanning electron microscopy, energy dispersive X–ray analysis, transmission electron microscopy and elemental analysis. This heterogeneous catalytic system exhibited excellent activity in the Suzuki–Miyaura coupling reaction of various aryl halides with phenylboronic acid, and was reusable several times without significant loss of its catalytic activity.

Keywords: *Palladium(II) N–heterocyclic carbene complex; Heterogeneous catalyst; Nano–silica; C–C coupling reactions; Aaryl halides.*

1. Introduction

N–Heterocyclic carbene (NHC) ligands with strong σ–donor and weak π–acceptor properties have received much attention in the design of homogeneous catalysts because of their binding ability to any transition metal regardless of their oxidation states that lead to stronger bonds with metal centers compared to most classical ligands. The NHC complexes are resistant to decomposition, and thermally

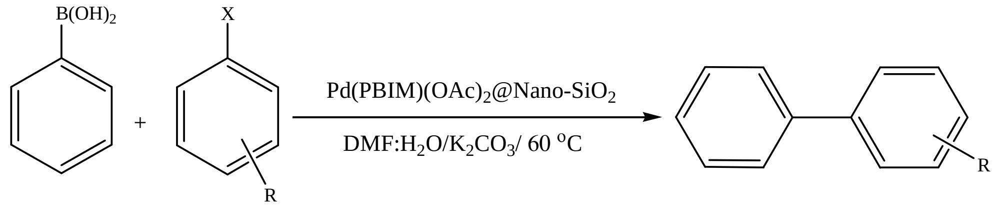
---

*Corresponding authors: Tel: +98–31–3793–4920; fax: +98–31–36689732; e–mails: moghadamm@sci.i.ac.ir (M. Moghadam); mirkhani@sci.ui.ac.ir (V. Mirkhani).

stable. On the other hand, the catalytic active site is better protected within the inner metal coordination sphere [1–5]. These properties make them the only class of ligands that can be used instead of widely used phosphine ligands [6]. Due to their unique catalytic activity, these compounds have attracted increasing attention in both academic and industrial fields [7,8]. NHC complexes as homogeneous catalysts have been used in a number of organic transformations such as olefin metathesis, and C–C and C–N bond formation reactions [9–13]. Therefore, discovery of catalytic properties of Pd–NHC complexes in the Mizoroki–Heck and Suzuki–Miyaura cross–coupling reactions is of great importance since these reactions provide many vast applications in the synthesis of natural products, numerous drugs and high performance modern organic materials [14–18].

Despite the wide application of these homogeneous catalysts inorganic transformations, their recycling is almost complicated and their separation is very difficult. Moreover, in consequence of toxicity of palladium residuals, acceptable limits of palladium traces in pharmaceuticals were set usually as ppm level. Application of supported catalysts can solve this problem [19–22]. In this regard, the immobilization of Pd–NHC complexes on polystyrene [23] or silica [24,25] has been reported. Meanwhile, utilizing of nano–supports in this case has attracted considerable interest due to their high activity and environmental acceptability [26]. Silica or modified silica–supported catalysts are good alternatives to traditional homogeneous catalysts; they are environmentally friendly, have excellent (chemical and thermal) stability, good accessibility, and good dispersion of catalytic active sites [27].

In continuation of our previous work using supported catalysts in organic synthesis [28–32], here we wish to describe the synthesis of a new NHC palladium complex supported on nano–silica, $Pd(PBIM)(OAc)_2$@Nano–SiO_2, and its application as a new heterogeneous and recoverable catalyst in the Suzuki–Miyaura C–C coupling reaction (Scheme 1).



Scheme 1. Suzuki–Miyaura C–C Coupling reaction catalyzed by Pd(PBIM)$(OAc)_2$@Nano–SiO_2

2. Experimental

The chemicals used in this work were purchased from Fluka and Merck chemical companies. The DR FT–IR spectra were recorded by a Jasco 6300 spectrophotometer. ^{1}H and ^{13}C NMR (400 and 100 MHz) spectra were recorded on a Bruker Avance 400 MHz spectrometer using $CDCl_3$ as solvent. Thermogravimetric analysis (TGA) was carried out on a Mettler TG50 instrument under air flow at a uniform heating rate of 10 ^{o}Cmin^{-1} in the range 30–600 ^{o}C. The scanning electron micrographs, equipped with an energy dispersive X–ray analysis (EDX) detector were taken on a Hitachi S–4700 field emission–scanning electron microscope (FE–SEM). The Pd content of the catalyst was determined by a Perkine Elmer ICP analyzer. Substances were quantified by gas chromatography (GC) on an Agilent GC 6890 equipped with a 19096C006 80/100 WHP packed column and a flame ionization detector (FID). Elemental analysis was performed on a LECO, CHNS–932 analyzer. The transmission electron microscopy (TEM) was carried out on a Zeiss EM10C transmission electron microscope operating at 100 kV. The silica was activated and chloropropylated by known procedures [33,34]

2.1. Synthesis ofPd(PBIM)$(OAc)_2$@Nano–SiO_2

*2.1.1. Synthesis of (4–pyridyl)bis(imidazolyl)methane (**1**)*

The (4–pyridyl)*bis*(imidazolyl)methane was prepared using the procedure reported for preparation of (2–pyridyl)*bis*(imidazolyl)methane [35]. In a typical procedure, a mixture of 1,1–carbonyldiimedazole (0.88 g, 5.42 mmol), 4–pyridinecarboxaldehyde (0.52 mL, 5.42 mmol) and $CoCl_2.6H_2O$ (6.2 mg, 0.026

mmol) was stirred at 80 ^{o}C for 14 h. The mixture was allowed to cool to room temperature, dissolved in CH_2Cl_2 (6 mL) and extracted with water (2×6 mL). Then, the organic layer was dried over Na_2SO_4 and the solvent was evaporated. The crude product was purified by column chromatography, eluted with CH_2Cl_2/CH_3OH (9:1) afforded the desired compound as a red oil. Yield: 0.158 g (80%).

^{1}H NMR ($CDCl_3$, 400MHz): 8.84 (s, 2H), 8.46 (d, *J*= 6.0 Hz, 1H), 7.81 (s, 1H), 7.52 (d, *J*= 31.6 Hz, 2H), 6.92 (d, *J*= 33.2, 2H), 6.86 (d, *J*= 7.2 Hz, 2H), 6.79 (d, *J*= 5.2, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz):150.6, 144.0, 136.8, 135.1, 130.4, 121.7, 121.2, 118.0, 68.4. FT–IR (KBr disc): 1599 (m), 1480 (m), 1224 (s), 1069 (s), 823 (m), 776 (s), 724 (s) cm^{-1}.

2.1.2. Preparation of Pd(PBIM)(OAc)$_2$@Nano–SiO$_2$

The chloropropylated nano–SiO_2 (1 g) was added to a solution of compound (**1**)(675 mg, 3 mmol) and NaI (3 mmol, 450 mg) in dry THF (40 mL). The reaction mixture was stirred under reflux conditions overnight. The yellow solid material was separated by filtration, washed with hot THF for 12 h in a Soxhlet apparatus to remove the unreacted starting materials, and then dried in a vacuum oven at 50 ^{o}C. For preparation of NHC ligand, the silica supported (4–pyridyl)*bis*(imidazolyl)methane (1 g) was reacted with methyl iodide in dry THF (30 mL). The slurry was stirred at 80 ^{o}C for 20 h and then filtered off. The corresponding solid was washed with DMF and ethanol, and then dried under reduced pressure. C: 10.5 H: 3.3 N: 2.01.

The final nano catalyst, Pd(PBIM)$(OAc)_2$@Nano–SiO_2, was obtained by addition of $Pd(OAc)_2$ (100 mg, 0.44 mmol) to a dispersed mixture of silica supported NHC (1 g) in DMSO (10 mL) under argon atmosphere at room temperature. Next, the mixture was stirred for 5 h at 60 ^{o}C and then allowed to proceed for an additional 40 min at 100 ^{o}C. The resulting catalyst washed with ethanol (3×20 mL) to remove the unreacted $Pd(OAc)_2$, and finally dried under air.

2.2. General procedure for Suzuki–Miyaura cross–coupling reaction catalyzed by Pd(PBIM)(OAc)$_2$@Nano–SiO$_2$

A mixture of aryl halide (1 mmol), phenylboronic acid (1.3 mmol), K_2CO_3 (276 mg, 2 mmol) and catalyst (0.004 g, 0.1 mol% Pd) in DMF/H_2O (4 ml, 2:1) was stirred at 60 °C under air atmosphere. The progress of the reaction was monitored by GC. After completion of the reaction, ethyl acetate (15 ml) was added and the catalyst was filtered. The organic phase was washed with H_2O (2×10 ml), dried over anhydrous $MgSO_4$ and evaporated. The residue was recrystallized from ethyl acetate: ether (1:3) to afford the pure product.

3. Results and discussion

3.1. Characterization of Pd(PBIM)(OAc)$_2$@Nano–SiO$_2$ catalyst

The preparation of the catalyst follows the steps shown in Scheme 2. First, 4–pyridinecarbaldehyde was reacted with 1,1–carbonyldiimidazole to produce the (4–pyridyl)*bis*(imidazolyl)methane (**1**). Then, this compound was attached to 3–chloropropylated nano–silica. In the next step, this solid was treated with MeI for preparation of NHC ligand. Finally, the supported palladium catalyst, Pd(PBIM)(OAc)$_2$@Nano–SiO$_2$, was obtained by the reaction of nano–silica supported NHC ligand with Pd(OAc)$_2$.

Previously, it is reported that in the methylation of (2–pyridyl)*bis*(imidazolyl)methane, only the nitrogens of imidazole rings were methylated while the pyridyl nitrogen was not methylated [35]. This can be attributed to the steric hindrance at 2-position for methylation. While this is not true in the case of (4–pyridyl)*bis*(imidazolyl)methane and all nitrogens can be methylated (Scheme 3). Therefore, we proposed two probable structures for supported catalyst.

The prepared catalyst was characterized by elemental analysis, FT–IR spectroscopy, SEM, TEM, ICP and thermal analyses. The nitrogen content of the catalyst was 1.44 mmol/g. This value shows that the amount of ligand on the nano–silica is 0.29 mmol/g. The Pd loading of the catalyst, measured by ICP, showed a value of about 0.25 mmol/g of catalyst. The FT–IR spectrum of the catalyst showed absorption bands at 1106 cm^{-1} (Si–O–Si), 798 cm^{-1} (C–Pd) absorption frequency, 1653 cm^{-1}(C=N), 1623 cm^{-1}(C=C), 1741 cm^{-1} (C=O) and 2935 cm^{-1} (C–H stretching vibration).

The thermal stability of the catalyst was also evaluated by TGA–DTG. As the thermogram shows, the weight loss below 600 °C is 15.2 for Pd(PBIM)(OAc)$_2$@Nano–SiO$_2$. The weight loss begins from 250 °C which approved that the catalyst is thermally stable below 250 °C. This observation can be attributed to the formation of a stable Pd complex (Fig. 1). The SEM image showed that the shape of silica nanoparticles is spherical (Fig. 2). The presence of the palladium was also confirmed by the EDX detector coupled to the SEM (Fig. 3). Transmission electron microscopy (TEM) confirmed the nanometer dimensions of the catalyst particles and also shows that the Pd catalyst has been dispersed on the silica nanoparticles (Fig. 4). As shown in the particle size histogram, the average size of the nanoparticles is about 8–12 nm (Fig. 5).

3.2. Suzuki–Miyaura cross–coupling of aryl halides with phenylboronic acid in the presence of Pd(PBIM)(OAc)$_2$@Nano–SiO$_2$

The catalytic activity of prepared catalyst was investigated in the Suzuki–Miyaura cross–coupling of aryl halides with phenylboronic acid. The coupling of 4–iodoanisole with phenylboronic acid was chosen as model reaction and the reaction conditions such as kind of base and solvent, temperature and catalyst amount were optimized (Table 1). Different amount of catalyst was used and the best result was obtained with 0.1 mol% of the catalyst (entries 1–4). In the absence of catalyst, no product was detected. When the model reaction was carried out at room temperature, only 49% of corresponding product was observed (entry 6). The highest yield was observed at 60 ºC. Different bases such as NEt$_3$, Na$_3$PO$_4$ and K$_2$CO$_3$ were used in the model reaction. Amongst them, K$_2$CO$_3$ was found to be the most efficient base. Comparison of inorganic bases utilized showed that carbonate base was more stable than the other one and an organic base like Et$_3$N was not as efficient as K$_2$CO$_3$ (entries 3, 8–10).

Different aqueous solvents such as DMF, DMSO, EtOH and toluene were used as reaction media and the best result was obtained in aqueous DMF (entries 3 and 11–13).

To confirm the thermal stability of the catalyst, the catalyst was heated for 1 h at 250 ^{o}C in an oven and then, this catalyst was used in the reaction of 4–iodoanisole with phenylboronic acid under the optimized reaction conditions. No obvious decrease in the catalytic activity was observed.

The applicability of this method was examined in Suzuki–Miyaura cross–coupling of aryl halides with phenylboronic acid. As can be seen from Table 2, under the optimized reaction conditions, different aryl halides were reacted with phenylboronic acid to produce the substituted biphenyls. Different aryl iodides, bromides and chlorides bearing electron–donating and electron–withdrawing groups reacted efficiently with phenylboronic acid and the desired cross–coupling products were produced in high yields. As expected; aryl iodides were found to be more reactive than aryl bromides and chlorides. When 2-bromotoluene (a more sterically crowded aryl halide) was used for the reaction with phenylboronic acid, the yield decreased to 80% (entry 9) while in the case of bromobenzene the yield was 93% (entry 8). On the other hands, when 4–methoxyphenylboronic acid was used instead of phenylboronic acid, the reaction times were longer compared to unsubstituted aryl halides (entries 6, 12 and 14).

3.3. Catalyst recovery and reuse

The recovery and reuse of a heterogeneous catalyst are of great importance from industrial, economical and green chemistry points of view. Therefore, the reusability of the catalyst was investigated using a mixture of 4–iodoanisole (1.0 mmol), phenylboronic acid (1.3 mmol), K_2CO_3 (2.0 mmol), and catalyst (0.1 mol%) at 60 ^{o}C. After completion of the reaction, the catalyst was filtered and washed thoroughly with acetone, diethyl ether and water, successively, and reused with fresh 4–iodoanisole and phenylboronic acid. The results are summarized in Table 3. As can be seen, the catalyst was recovered and recycled several times without loss of its catalytic activity remarkably. The amount of Pd leached was determined by ICP analysis. It was observed that only small amounts of Pd are leached in the first run and no Pd was detected in the filtrates after first run.

Acknowledgements

The authors are grateful to the Research Council of the University of Isfahan for financial support of this work.

References:

[1] W. A. Herrmann, Angew. Chem. Int. Ed. 41 (2002) 1291–1309.

[2] W. A. Herrmann, C. Kocher, Angew. Chem. Int. Ed. Engl. 36 (1997) 2162–2187.

[3] E. Peris, R. H. Crabtree, Coord. Chem. Rev. 248 (2004) 2239–2246.

[4] S. Díez–Gonzalez, N. Marion, S. P. Nolan, Chem. Rev. 109 (2009) 3612–3676.

[5] M. Alcarazo, T. Stork, A. Anoop, W. Thiel, A. Fürstner, Angew. Chem. Int. Ed. 49 (2010) 2542–2546.

[6] F. Glorius (Ed.) N–Heterocyclic Carbenes in Transition Metal Catalysis, Topics in Organomettalic Chemistry, Springer–Verlag, Berlin/Heidelberg, Germany, 2007, Vol. 21.

[7] S. Budagumpi, R. A. Haque, A.W. Salman, Coord. Chem. Rev. 256 (2012) 1787–1830.

[8] L. R. Titcomb, S. Caddick, F. G. N. Cloke, D. J. Wilson, D. McKerrecher, Chem. Commun. (2001) 1388–1389.

[9] M. Poyatos, J. A. Mata, E. Peris, Chem. Rev. 109 (2009) 3677–3707.

[10] A. H. Hoveyda, J. Org. Chem. 79 (2014) 4763–4792.

[11] J. S. Kingsbury, A. H. Hoveyda, J. Am. Chem. Soc. 127 (2005) 4510–4517.

[12] W. J. Sommer, M. Weck, Coord. Chem. Rev. 251 (2007) 860–873.

[13] N. Debono, A. Labande, E. Manoury, J. C. Daran, R. Poli, Organometallics 29 (2010) 1879–1882.

[14] Y. H. Chang, Z. Y. Liu, Y. H. Liu, S. M. Peng, J. T. Chen, S. T. Liu, Dalton Trans. 40 (2011) 489–494.

[15] T. Tu, H. Mao, C. Herbert, M. Z. Xu, K. H. Dotz, Chem. Commun. 46 (2010)7796–7798.

[16] S. Gu, H. Xu, N. Zhang, W. Chen, Chem. Asian J. 5 (2010) 1677–1686.

[17] N. Marion, S. P. Nolan, Acc. Chem. Res. 41 (2008) 1440–1449.

[18] G. C. Fortman, S. P. Nolan, Chem. Soc. Rev. 40 (2011) 5151–5169.

[19] Y. Uozumi, Top. Curr. Chem. 242 (2004) 77–112.

[20] D. Z. Yuan, Q. Y. Zhang, J. B. Dou, Catal. Commun. 11 (2010) 606–610.

[21] M. Choi, D. H. Lee, K. Na, B. W. Yu, R. Ryoo, Angew. Chem. Int. Ed. 48 (2009) 3673–3676.

[22] D. K. Yi, S. S. Lee, J. Y. Ying, Chem. Mater. 18 (2006) 2459–2461.

[23] N. T. S. Phan, D. H. Brown, P. Styring, Tetrahedron Lett. 45 (2004) 7915–7919.

[24] N. Gurbuz, I. Ozdemir, B. Cetinkaya, T. Seckin, Appl. Organomet. Chem. 17 (2003) 776–780.

[25] S. Paul, J. H. Clark, J. Mol. Catal. A: Chem. 215 (2004) 107–111.

[26] J. Y. Jung, J. B. Kim, A. Taher, M. J. Jin, Bull. Korean Chem. Soc. 30 (2009) 3082–3084.

[27] P. M. Price, J. H. Clark, D. J. Macquarrie, J. Chem.Soc., Dalton Trans. (2000) 101–110.

[28] M. Moghadam, S. Tangestaninejad, V. Mirkhani, B. Karami, N. Rashidi, H. Ahmadi, J. Iran. Chem. Soc. 3 (2006) 64–68.

[29] A. Landarani Isfahani, I. Mohammadpoor–Baltork, V. Mirkhani, A. R. Khosropour, M. Moghadam, S. Tangestaninejad, R. Kia, Adv. Synth. Catal. 355 (2013) 957–972.

[30] F. Sadegh, O. Bagheri, M. Moghadam, V. Mirkhani, S. Tangestaninejad, I. Mohammadpoor–Baltork, J. Organomet. Chem. 759 (2014)46–57.

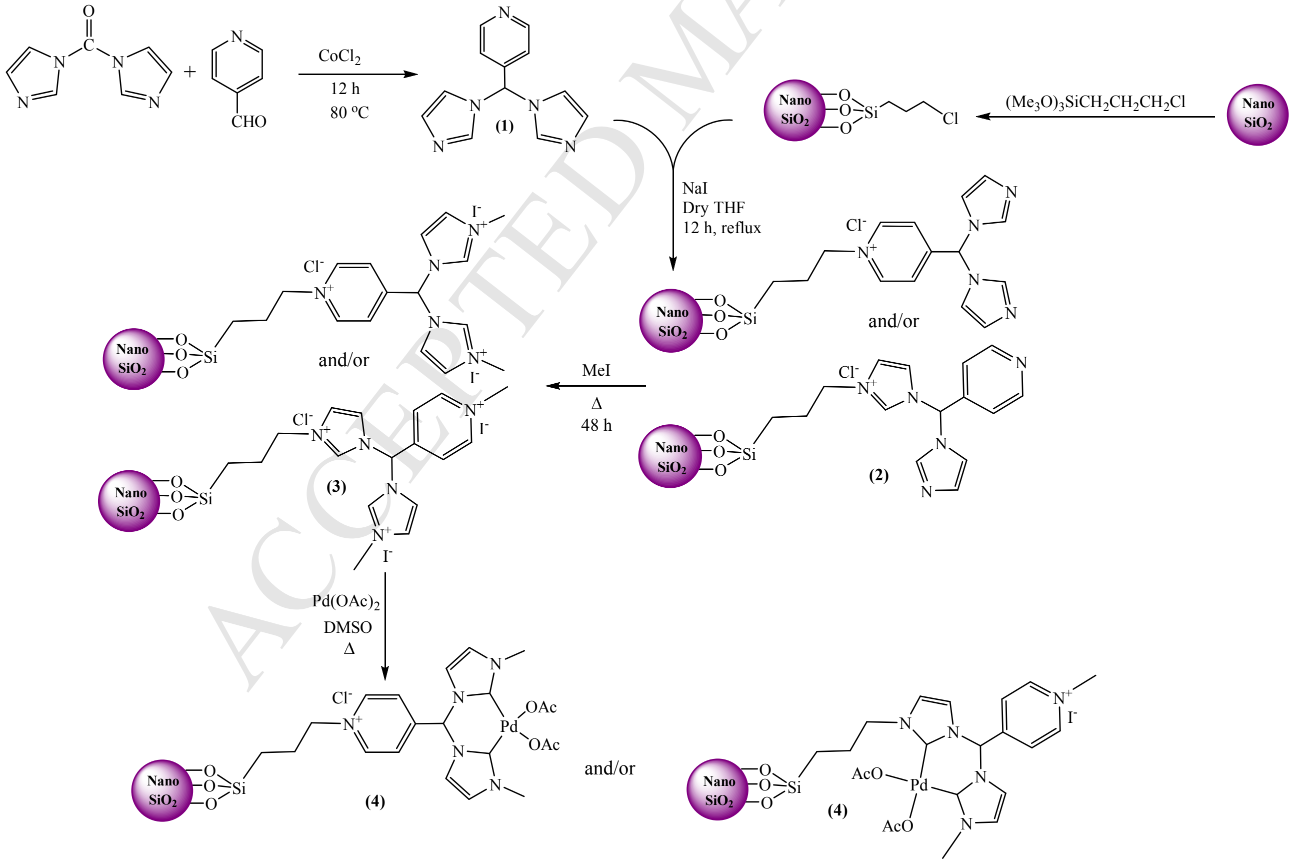
[31] M. Ghotbinejad, A. R. Khosropour, I. Mohammadpoor–Baltork, M. Moghadam, S. Tangestaninejad, V. Mirkhani, J. Mol. Catal. A: Chem. 385 (2014) 78–84.

[32] Z. Pahlevanneshan, M. Moghadam, V. Mirkhani, S. Tangestaninejad, I. Mohammadpoor–Baltork, A. R. Khosropour, Appl. Organomet. Chem. 2015, DOI 10.1002/aoc.3297

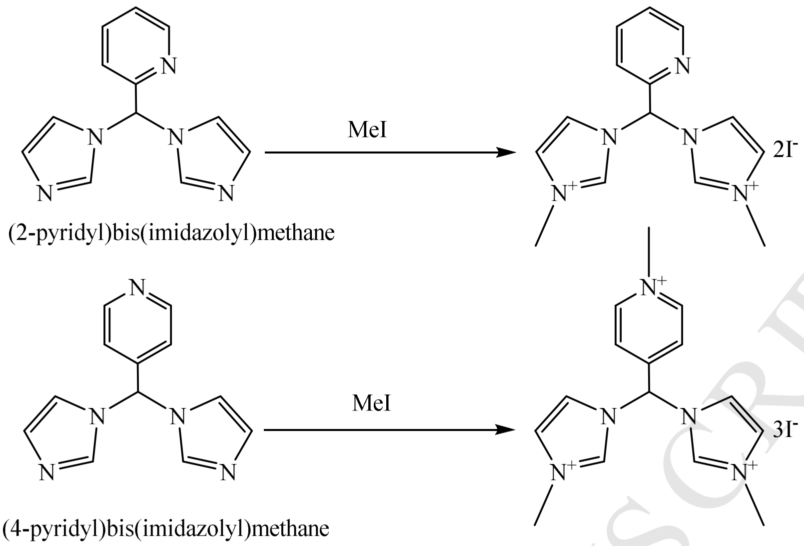
[33] B. Karimi, A. A. Safari, J. Organomet. Chem. 693 (2008) 2967–2970.

[34] M. E. Mahmoud, M. M. El–Essawi, S. A. Kholeif, E. M. I. Fathalla, Anal. Chim. Acta 525 (2004) 123–132.

[35] E. Mas–Marza, M. Sanau, E. Peris, J. Organomet. Chem. 690 (2005) 5576–5580.



Scheme 2. Preparation route for the catalyst



Scheme 3. Methylation of (2–pyridyl)*bis*(imidazolyl)methane and (4–pyridyl)*bis*(imidazolyl)methane

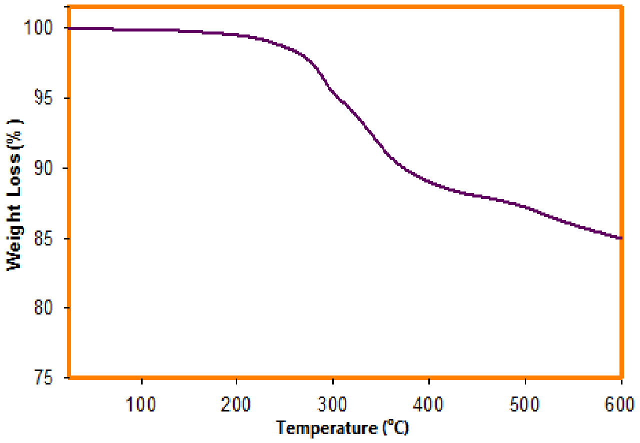


Fig. 1. TGA curve for compound (**3**)

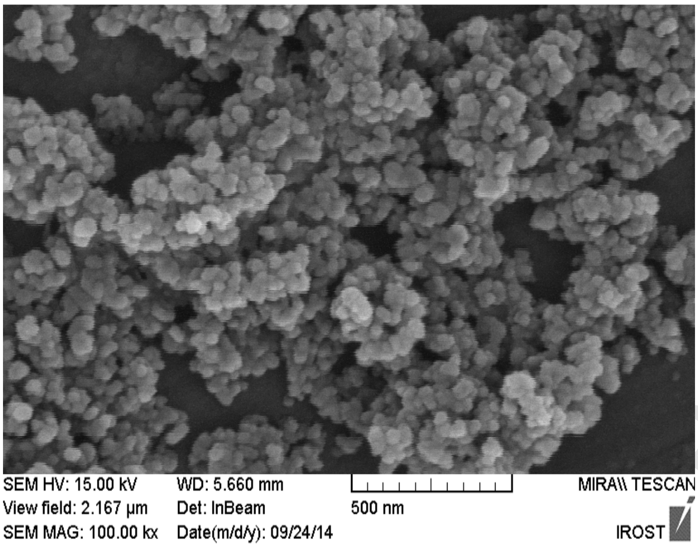


Fig. 2. SEM images of catalyst

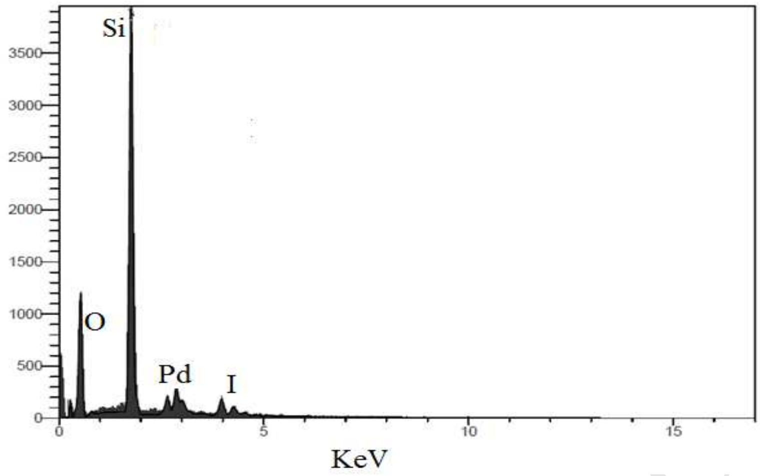


Fig. 3. SEM–EDX spectrum of catalyst

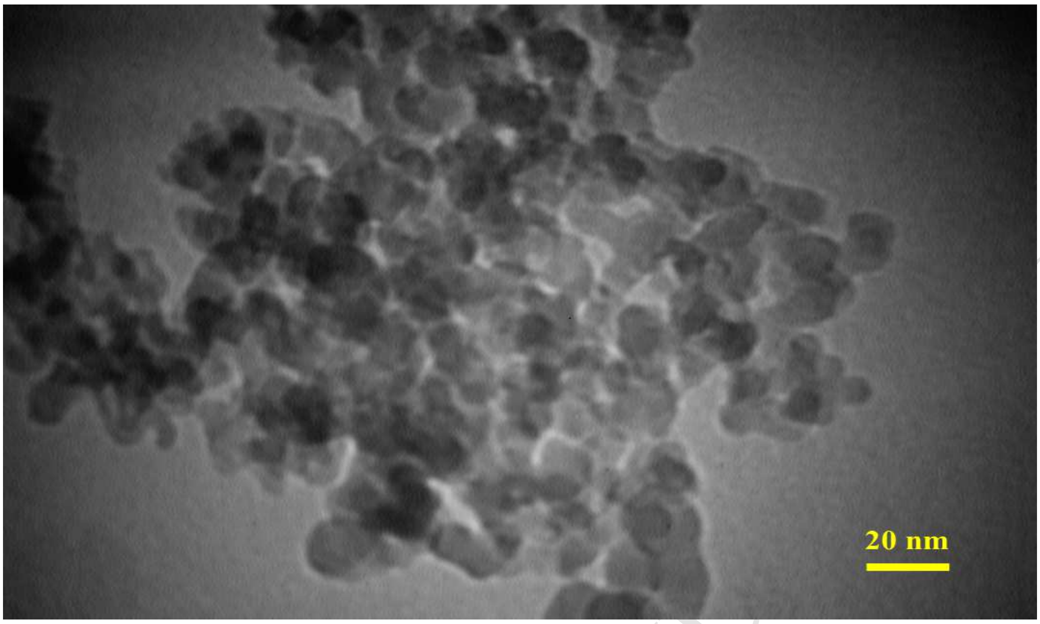


Fig. 4. TEM image of catalyst

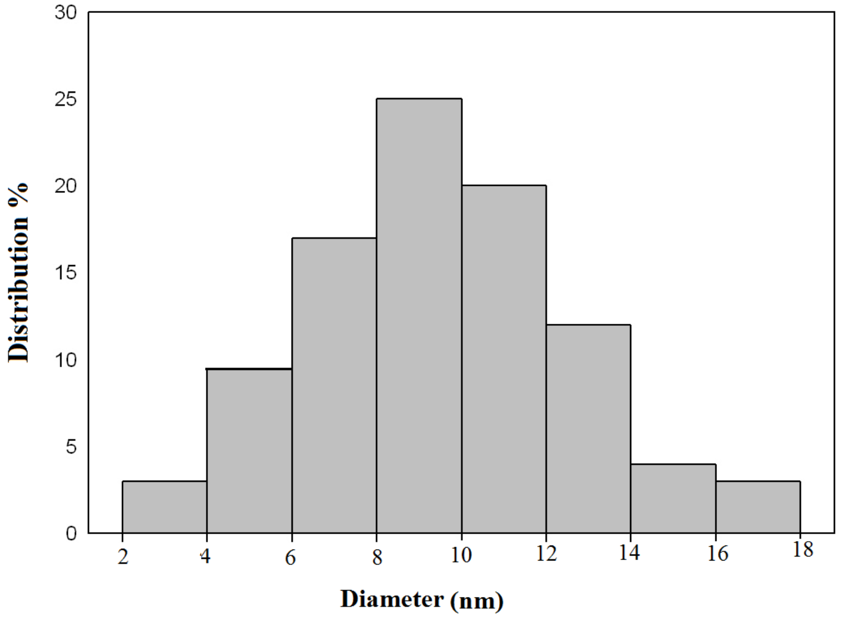
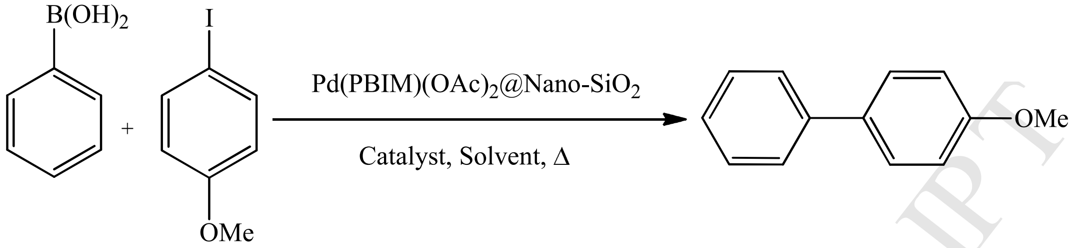


Fig. 5. Particle size distribution histogram of catalyst

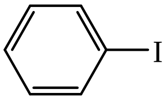
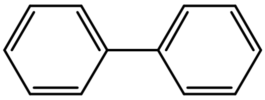
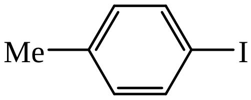
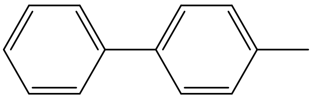
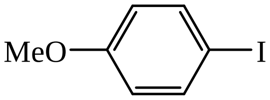
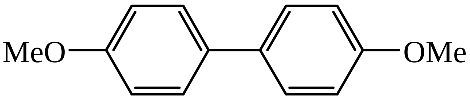
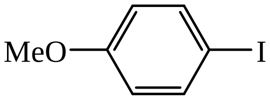
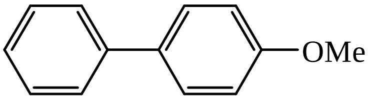
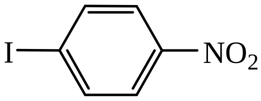
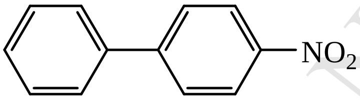
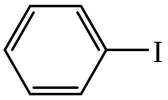
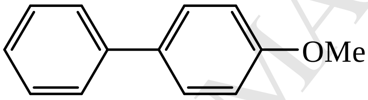
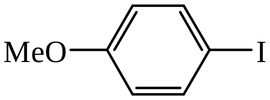
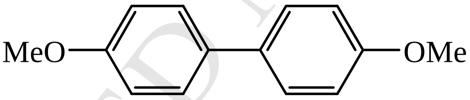
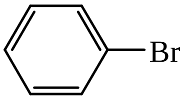
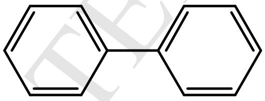
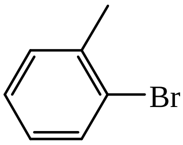
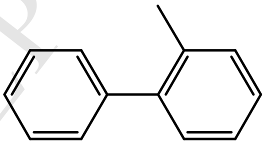
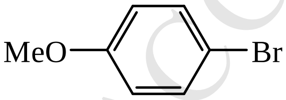
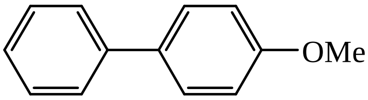
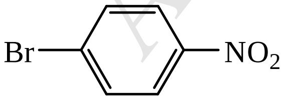
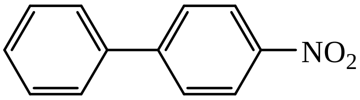
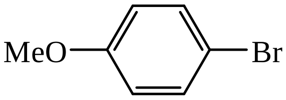
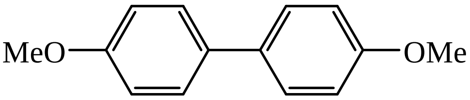
Table 1. Optimization of conditions in the Suzuki–Miyaura reaction of 4–iodoanisole and phenylboronic catalyzed by Pd(PBIM)$(OAc)_2$@Nano–SiO_2.[a]

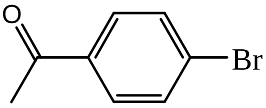
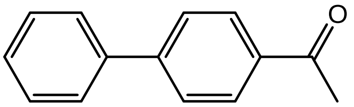
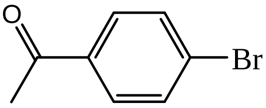
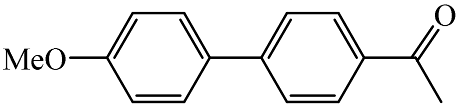
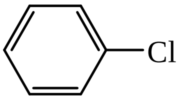
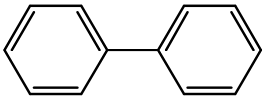
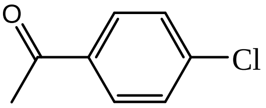
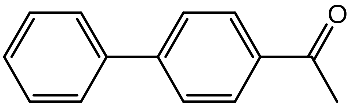
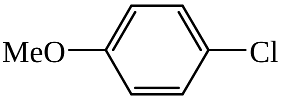
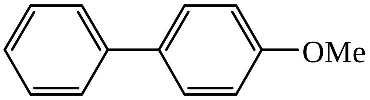
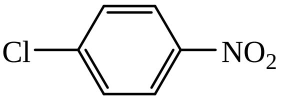
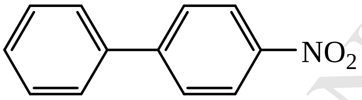


Entry	Solvent	Pd (mol%)	Base	T (°C)	Time (h)	Yield (%)[b]
1	DMF: H_2O (2:1)	0	K_2CO_3	60	5	0
2	DMF: H_2O (2:1)	0.01	K_2CO_3	60	2	30
3	DMF: H_2O (2:1)	0.1	K_2CO_3	60	1	99
4	DMF: H_2O (2:1)	0.5	K_2CO_3	60	0.7	100
5	DMF: H_2O (2:1)	0.1	K_2CO_3	90	0.5	8vhl7
6	DMF: H_2O (2:1)	0.1	K_2CO_3	r.t.	4	49
7	DMF: H_2O (2:1)	0.1	K_2CO_3	40	2	89
8	DMF: H_2O (2:1)	0.1	No Base	60	4	6
9	DMF: H_2O (2:1)	0.1	Na_3PO_4	60	1.5	75
10	DMF: H_2O (2:1)	0.1	NEt_3	60	2	32
11	DMSO: H_2O (2:1)	0.1	K_2CO_3	60	1	90
12	EtOH: H_2O (2:1)	0.1	K_2CO_3	60	1	75
13	Toluene: H_2O (2:1)	0.1	K_2CO_3	60	1	34

[a] Reaction conditions: 4–Iodoanisole (1 mmol), phenylboronic acid (1.3 mmol), base (2 mmol), solvent (4 ml) under air atmosphere.
[b] Yields determined by GC.

Table 2. Suzuki–Miyaura cross–coupling reaction of aryl halides and phenylboronic acid catalyzed by Pd(PBIM)(OAc)$_2$@Nano–SiO$_2$.[a]

Entry	Aryl halide	Product	Time (h)	Yield (%)[d]
1			0.9	98
2			0.92	97
3[d]			1.7	93
4			1	99
5			0.8	99
6[d]			1.5	91
7			1.7	93
8			1.3	93
9			1.3	80
10			1.4	87
11			1	93
12[d]			2.5	81

13			0.95	99
14[d]			1.8	90
15			1.6	68
16			1.5	99
17			2	31
18			1.4	97

---

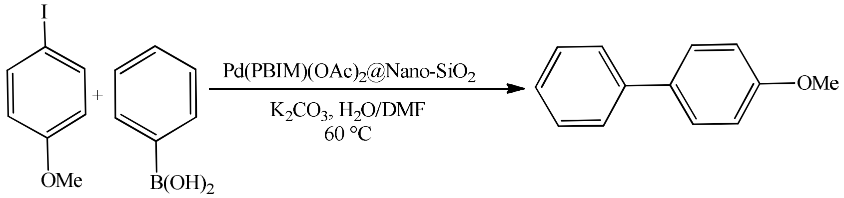
[a] Reaction conditions: Aryl halide (1 mmol), phenylboronic acid (1.3 mmol), K_2CO_3 (2 mmol), DMF/H_2O (2:1, 4 ml) under air.

[b] 60 °C, catalyst (0.1 mol% Pd).

[c] Yields determined by GC.

[d] Using 4–methoxyphenylboronic acid.

Table 3. Recycling and reuse of Pd(PBIM)(OAc)$_2$@Nano–SiO$_2$in the Suzuki–Miyaura reaction.[a]



Entry	Pd(PBIM)(OAc)$_2$@Nano–SiO$_2$[b]	
	Yield (%)[c]	Pd leached (%)[d]
1	99	0.12
2	92	–
3	92	–
4	90	–
5	88	–

[a] Reaction conditions: 4–Iodoanisole (1 mmol), phenylboronic acid (1.3 mmol), K$_2$CO$_3$ (2 mmol), DMF/H$_2$O (2:1, 4 ml) under air.

[b] 60 °C, catalyst (0.1 mol% Pd), 60 min.

[c] Yields determined by GC.

[d] Determined by ICP.

▶ A new NHC palladium complex supported on nano–silica was prepared ▶ This heterogeneous catalyst was characterized ▶ This catalyst was highly active in the Suzuki-Miyaura reaction ▶ The catalyst was reusable.