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Suzuki-Miyaura C-C coupling reaction catalysed by homogeneous and nanosilica supported palladium(II) *N*-heterocyclic carbene complex derived from 3,5-di(1-imidazolyl)pyridine

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A new palladium *N*-heterocyclic carbene complex using 3,5-di(1H-imidazol-1-yl)pyridine(**1**) as precursor was prepared. The complex was immobilized on3-chloropropylated nanosilica as support and characterized by FT-IR spectroscopy, thermogravimetric analysis, field emission scanning electron microscopy, energy dispersive X-ray analysis, transmission electron microscopy and elemental analysis. The prepared catalyst was used as a heterogeneous catalyst in the Suzuki–Miyaura coupling reaction of various aryl halides with phenylboronic acid and the corresponding biphenyls were produced in high yield. The catalyst was recyclable under aerobic condition without significant loss of activity

Introduction

Application of *N*-heterocyclic carbenes (NHCs) as ligands and their metal complexes have received wide attention recently. The strong σ–donor ability, ease of preparation and effective binding ability of these ligands to most transition metals make them the only class of ligands that has been able to challenge the widely employed tertiary phosphines.[1–8] *N*-Heterocyclic carbenes (NHCs) derived from the replacement of the proton at C-2 in an imidazolium salt by a metal have been known for many years but interest was dormant until Arduengo et al. isolated the free imidazolidene carbene in 1991. NHCs transition metal complexes as homogeneous catalysts have been wildly employed in organic transformations such as coupling reactions such as Suzuki-Miyaura,[9–11] Heck,[12,13] and Kumada reactions,[14] as well as the Buchwald–Hartwig amination.[15] In particular, 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 opportunities for the synthesis of substituted arenes which are used for production of pharmaceuticals and agrochemicals. Interestingly, applying these reactions minimize the steps compared to classical organic syntheses.[16-27]

However, homogeneous catalysts have wide applications in organic transformations but these catalysts are not often used in industrial processes mainly due to their low chemical and thermal stability and their low potential to provide recyclable systems. Application of supported catalysts can solve this problem. In this regard, polymer supported catalysts have received much attention due to the stability and uniformity of the obtained materials, and the possibility of easier product/catalyst separation, combining the advantages of homogeneous and heterogeneous catalysis.[28-31] For instance, the immobilization of Pd–NHCs on polystyrene[32] or silica[33] has been reported. Meanwhile, utilizing of nano-supports in this case has attracted considerable interest due to their high activity and environmental acceptability.[34] 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.[35]

In continuation of our previous work using supported catalysts in organic synthesis,[36-40], here we report the synthesis and characterization of a new NHC palladium complex, its immobilization on 3-chloropropylated nanosilica and

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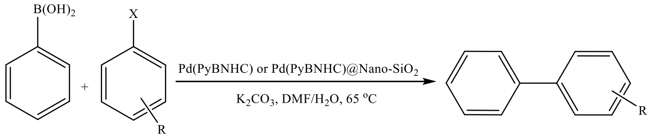
application of homogeneous and heterogeneous catalysts in the Suzuki-Miyaura C-C coupling reactions (Scheme 1).

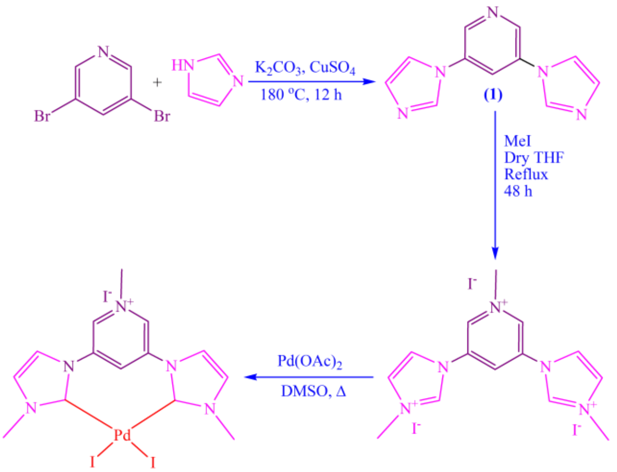


Scheme 1 Suzuki-Miyaura C-C coupling reaction catalyzed by Pd(PyBNHC) or Pd(PyBNHC)@Nano-SiO$_2$

Results and discussion

Preparation and characterization of catalysts

The preparation route for homogeneous catalyst is shown in Scheme 2. As can be seen, the 3,5-di(1H-imidazol-1-yl)pyridine was prepared and methylated by methyl iodide. Finally this methylated compound, 1,1'-(pyridine-3,5-diyl)*bis*(3-methyl-1H-imidazol-3-ium) iodide, was complexed with Pd(OAc)$_2$ to produce the homogeneous diiodo-3,5-di(3-methylimidazol-1-yl)methylpyridinium iodide) palladium(II).

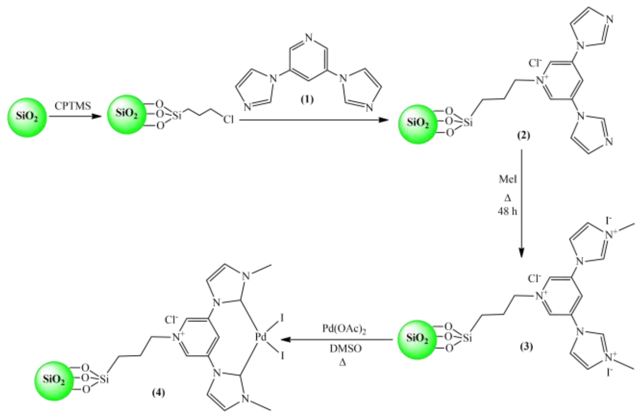


Scheme 2 Preparation route for the diiodo-(3,5-di(3-methylimidazol-1-yl)methylpyridinium iodide)palladium(II) catalyst

The catalyst was characterized by FT-IR, ^{1}H- and ^{13}C NMR spectroscopies and also elemental analysis (see experimental section).

The preparation path for heterogeneous catalyst is depicted in Scheme 3. First, 3,5-di(1H-imidazol-1-yl)pyridine was attached to the surface 3-chloropropylated nanosilica and methylated with MeI for preparation of NHC ligand. In the next step, the heterogeneous catalyst, Pd(PyBNHC)@Nano-SiO$_2$ (**4**), was obtained by the reaction of nanosilica supported NHC ligand with Pd(OAc)$_2$.

The size and surface morphologies of the **(4)** were directly visualized by FE-SEM (Fig. 2). As can be seen, the nano-SiO$_2$ particles are spherical and have diameters in the range of 40 to 80 nm. The presence of the palladium was also confirmed by the EDX detector coupled to the SEM (Fig. 3). Further characterization of (**4**) was performed by transmission electron microscopy (TEM). The TEM images of (**4**) showed well-defined particles of Pd complex dispersed in nanosilica matrix (Fig. 4).



Scheme 3 Preparation route for the Pd(PyBNHC)@Nano-SiO$_2$ catalyst

The ICP analysis showed that 0.30 mmole of Pd was anchored on 1 g of heterogeneous catalyst. The nitrogen content of the catalyst was 2.22% that shows the amount of ligand on the nanosilica is 0.32 mmol/g. In the diffuse reflectance FT-IR, the bands at 1094 cm^{-1} (Si–O–Si), 808 cm^{-1} (C–Pd), 1605 cm^{-1} (C=N), and 2956 cm^{-1} (C–H stretching vibration) proved the attachment of catalyst on the surface of nano SiO$_2$. The TGA–DTG analysis of the catalyst shows thermal stability below 260 °C and the weight loss is 16.4 below 600 °C. This observation can be attributed to the formation of a stable Pd species (Fig. 1).

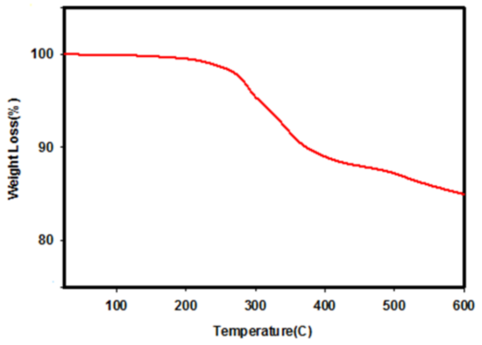


Fig. 1. TGA curve for compound (**3**)

Investigation of catalytic activity of both catalysts in the C-C coupling reactions

The catalytic activities of both homogeneous and heterogeneous catalysts were investigated in the Suzuki–Miyaura cross-coupling of aryl halides with phenylboronic acid. As shown in Table 1, the reaction conditions such as kind of base and solvent, temperature and catalyst amount were optimized in the coupling of 4-iodoanisole with phenylboronic acid in the presence of Pd(BNHC)@Nano-SiO_2. Different amount of catalyst was used and the best result was obtained with 0.15 mol% of the catalyst (entries 1-4). In the absence of catalyst, no product was detected in the reaction mixture. This coupling reaction was found to be highly sensitive to the reaction temperature (entries 4-7). When the model reaction was carried out at room temperature, only 48% of corresponding product was observed (entry 6). A reaction temperature of 65 °C was found to be optimal for the model reaction. Different bases such as NEt_3, Na_3PO_4 and K_2CO_3 were used in the model reaction. Amongst them, K_2CO_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 NEt_3 was not as efficient as K_2CO_3 (entries 4 and 8-10). Then, the same reaction was carried out in different aqueous/organic media. Different aqueous solvents such as DMF, DMSO, EtOH and *i*-PrOH and toluene were used as reaction media and the best result was obtained in aqueous DMF (entries 4 and 11-14).

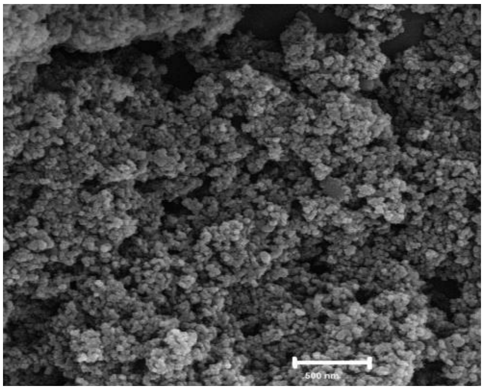


Fig. 2. SEM image of Pd(PyBNHC)@Nano-SiO_2

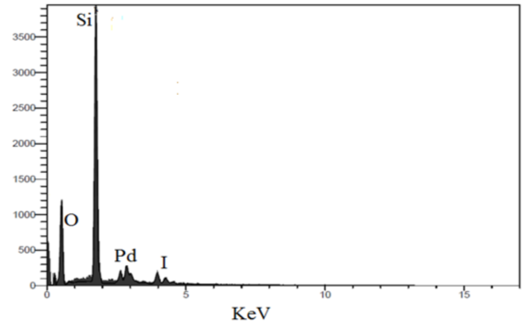


Fig. 3. SEM-EDX spectrum of Pd(PyBNHC)@Nano-SiO_2 catalyst

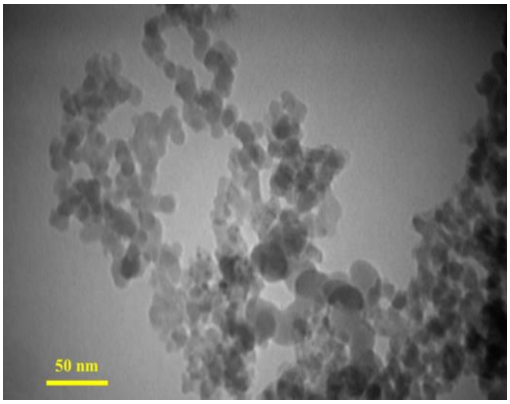
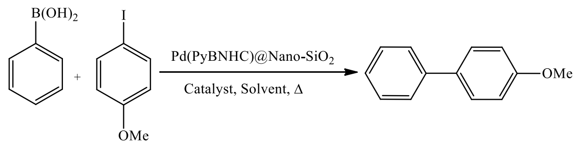


Fig. 4. TEM image of heterogeneous Pd(PyBNHC)@Nano-SiO_2 catalyst

Table 1. Optimization of conditions in the Suzuki-Miyaura reaction of 4-iodoanisole and phenylboronic acid catalyzed by Pd(PyBNHC)(@Nano-SiO_2.[a]



Row	Solvent	Pd (mol%)	Base	T (°C)	Time (h)	Yield (%)[b]
1	DMF: H_2O	0	K_2CO_3	65	6	0
2	DMF: H_2O	0.01	K_2CO_3	65	1.7	32
3	DMF: H_2O	0.15	K_2CO_3	65	0.8	99
4	DMF: H_2O	0.5	K_2CO_3	65	0.6	100
5	DMF: H_2O	0.15	K_2CO_3	85	0.6	100
6	DMF: H_2O	0.15	K_2CO_3	r.t.	5	48
7	DMF: H_2O	0.15	K_2CO_3	40	2.3	89
8	DMF: H_2O	0.15	No Base	65	5	9
9	DMF: H_2O	0.15	Na_3PO_4	65	1.5	77
10	DMF: H_2O	0.15	NEt_3	65	2	34
11	DMSO: H_2O	0.15	K_2CO_3	65	1	92
12	EtOH: H_2O	0.15	K_2CO_3	65	1	78
13	*i*-PrOH: H_2O	0.15	K_2CO_3	65	1	81
14	Toluen: H_2O	0.15	K_2CO_3	65	1	37

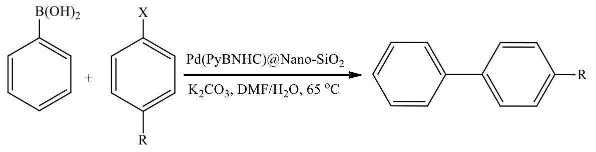
[a] Reaction conditions: 4-Iodoanisole (1 mmol), phenylboronic acid (1.4 mmol), base (3 mmol), solvent/H_2O (5 ml, 2:1) under air atmosphere.

[b] Yields were determined by GC.

Therefore, aryl halide (1 mmol), phenylboronic acid (1.4 mmol), K_2CO_3 (3 mmol) and Pd(BNHC)@Nano-SiO_2 (**4**) (0.15 mol%Pd) in DMF/H_2O (5 ml, 2:1) at 65 °C were selected as optimized conditions. Under these optimized conditions, different aryl halides were reacted with phenylboronic acid to produce the substituted biphenyls. 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, 4-chloroanisole was used in this reaction, only 21% of the corresponding product was produced (entry 12).

In order to show the effect of supporting on the catalytic activity, all reactions were repeated using diiodo-(3,5-di(3-methylimidazol-1-yl)methylpyridiniumiodide)palladium(II) complex as homogeneous catalyst using aryl halide (1 mmol), phenylboronic acid (1.4 mmol), K_2CO_3 (3 mmol) and homogenous palladium (II) complex (1 mol% Pd) in DMF/H_2O (5 ml, 2:1) (Table 3). The same trend observed for heterogeneous catalyst was also observed for homogeneous counterpart.

Table 2. Suzuki-Miyaura cross-coupling reaction of aryl halides and phenylboronic acid catalyzed by Pd(PyBNHC)@Nano-SiO_2.[a]



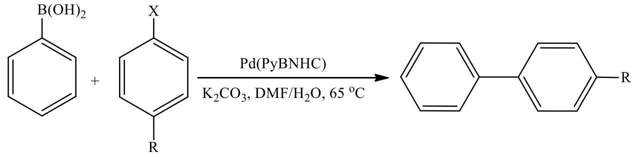
Entry	X	R	Time (h)	Yield (%)[b,c]	TOF (h^{-1})
1	I	H	0.8	96(92)	800
2	I	Me	0.93	98(93)	702
3	I	MeO	0.8	99(96)	825
4	I	NO_2	1	99(92)	660
5	Br	H	1.4	92(89)	438
6	Br	MeO	1.5	87(82)	387
7	Br	NO_2	1	91(87)	606
8	Br	Ac	0.93	98(93)	653
9	Cl	H	1.7	69(65)	270
10	Cl	Ac	1.5	98(92)	435
11	Cl	NO_2	1.5	97(91)	431
12	Cl	OMe	2	21(18)	70

[a] Reaction conditions: Aryl halide (1 mmol), phenylboronic acid (1.4 mmol), K_2CO_3 (3 mmol), catalyst (0.15 mol% Pd), DMF/H_2O (2:1, 5 ml).

[b] Yields were determined by GC.

[c] The yields in the parentheses refer to isolated yields.

Table 3. Suzuki-Miyaura cross-coupling reaction of aryl halides and phenylboronic acid catalyzed by Pd(PyBNHC).[a]



Entry	X	R	Time (h)	Yield (%)[b]	TOF (h^{-1})
1	I	H	0.3	97	323
2	I	Me	0.31	98	316
3	I	MeO	0.2	99	495
4	I	NO_2	0.37	99	267
5	Br	H	0.45	82	182
6	Br	MeO	0.5	87	174
7	Br	NO_2	0.9	92	102
8	Br	Ac	0.8	82	102
9	Cl	H	1	76	76
10	Cl	Ac	1.4	98	70
11	Cl	NO_2	1.5	81	54

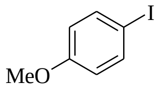
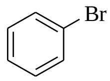
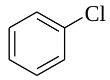
[a] Reaction conditions: Aryl halide (1 mmol), phenylboronic acid (1.4 mmol), K_2CO_3 (3 mmol), catalyst (1 mol% Pd), DMF/H_2O (2:1, 5 ml), 65 °C.

[b] Yields were determined by GC.

[c] The yields in the parentheses refer to isolated yields.

Comparison of the turnover frequencies of (TOF) of both catalysts showed that the heterogeneous catalyst is more reactive than the homogeneous one. This can be attributed to the dispersion of catalyst on nanosilica bearing high surface area which in turn facilitates the accessibility of catalytic active sites. To stress this point, some of the reactions were carried out at equal times (0.3 and 0.8 h) and also using 0.15 mol% of catalyst. The results showed that the heterogeneous catalyst is much more efficient than the homogeneous counterpart (Table 4).

Table 4. Comparison of catalytic activity of both catalysts in the Suzuki-Miyaura reaction.[a]

Aryl halide	Pd(PyBNHC)		Pd(PyBNHC)@Nano-SiO_2	
	Yield (%)[b]		Yield (%)[b]	
	0.3 h	0.8 h	0.3 h	0.8
	38	63	57	96
	22	49	34	71
	2	15	12	43

[a] Reaction conditions: Aryl halide (1 mmol), phenylboronic acid (1.4 mmol), K_2CO_3 (3 mmol), catalyst (0.15 mol% Pd), DMF/H_2O (2:1, 5 ml).

[b] Yields were determined by GC.

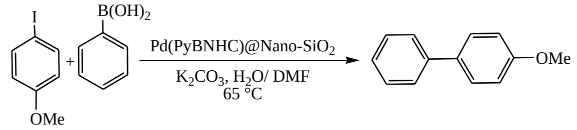
Catalyst recovery and reuse

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 (1.4 mmol), K_2CO_3 (3 mmol), and catalyst (0.15 mol%) at 65 °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 5. As can be seen, the catalyst was recovered and recycled several times without remarkable loss of its catalytic activity. 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.

Conclusion

In conclusion, Suzuki-Miyaura C-C coupling reaction catalysed by homogeneous and nanosilica supported palladium(II) *N*-heterocyclic carbene complex derived from 3,5-di(1-imidazolyl)pyridine was carried out. Both homogeneous and heterogeneous catalysts were applied in the Suzuki–Miyaura coupling of aryl iodide, bromides and chlorides with phenylboronic acid and the corresponding biphenyls were produced in good to excellent yield (69-99% except for 4-chloroanisole). As expected, aryl iodides and bromides were more reactive than chloride one. Despite the higher catalytic activity of homogeneous catalyst, it could not be reused even one time while the heterogeneous catalyst was reused five consecutive times without significant loss of its activity.

Table 5. Investigation of recycling of Pd(PyBNHC)@Nano-SiO_2 in the Suzuki-Miyaura reaction.[a]



Entry	Yield (%)[b]	Pd leached (%)[c]
1	99	0.11
2	93	-
3	92	-
4	90	-
5	87	-

[a]Reaction conditions: 4-Iodoanisole (1 mmol), phenylboronic acid (1.4 mmol), K_2CO_3 (3 mmol), catalyst (0.15 mol% Pd), DMF/H_2O (2:1, 5 ml), 65°C, 0.8 h.

[b]Yields were determined by GC.

[c]Determined by ICP.

Experimental

Materials and methods

All the reagents were obtained from commercial sources. The DRFT-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. The morphological features were obtained on a Hitachi S–4700 field emission–scanning electron microscope (FE–SEM), equipped with an energy dispersive X-ray analysis (EDAX) detector. Thermogravimetric analysis (TGA) was carried out on a Mettler TG50 instrument under air flow at a uniform heating rate of 10 °Cmin^{-1} in the range 30-600 °C. Elemental analysis was performed on a LECO, CHNS-932 analyzer. The mass spectrum of palladium complex was recorded on a Shimadzo LCMS-2010 EV. The transmission electron microscopy (TEM) was carried out on a Zeiss EM10C transmission electron microscope operating at 100 kV. GC analyses were performed on an Agilent GC 6890 equipped with a 19096C006 80/100 WHP packed column and a flame ionization detector (FID). The GC yields were calculated by the “internal standard addition” method and in this manner anisole was used as internal standard. The compound of 3,5-di(1H-imidazol-1-yl)pyridine was prepared according to the literature method.[41]

Synthesis of diiodo-3,5-di(3-methylimidazol-1-yl)methylpyridiniumiodide)palladium(II) complex

For preparation of NHC ligand, (**L**), 3,5-di(1H-imidazol-1-yl)pyridine (211 mg, 1 mmol) was reacted with excess methyl iodide in dry THF (30 mL) to produce the 1,1'-(pyridine-3,5-diyl)*bis*(3-methyl-1H-imidazol-3-ium) iodide. The mixture was stirred at 80 °C for 24 h and then filtered off. The corresponding solid was washed with DMF and ethanol, and then dried under reduced pressure. Yield: 0.554 g (87%). M.p.: 270 °C. FT-IR (KBr pellet): absorption frequency in 1634 cm^{-1} (C=N), 1605 cm^{-1}(C=C) and 2869 cm^{-1}(C–H stretching vibration). ^{1}H NMR (D_2O, 400 MHz): 9.74 (s, 1H), 9.39 (s, 1H), 9.01 (d, J= 2.4 Hz, 1H), 8.54 (t, J= 2 Hz, 1H), 8.11 (d, J= 2.4 Hz, 1H), 7.94 (d, J= 2.0 Hz, 2H), 7.77 (d, J= 2.4 Hz, 1H), 7.66 (d, J= 2.0 Hz, 1H), 4.02 (s, 3H), 3.98 (s, 6H).^{13}C NMR (D_2O, 100 MHz): 34.5, 36.5, 37.0, 121.8, 121.9, 124.9, 125.0, 125.8, 126.2, 132.5, 133.4, 136.2, 141.6, 144.3. Anal. found: C, 27.17;H, 2.93; N,11.35. Calc. for $C_{14}H_{18}N_5I_3$: C, 27.05; H, 2.89; N, 11.27.

The palladium complex of 1,1'-(pyridine-3,5-diyl)*bis*(3-methyl-1H-imidazol-3-ium) iodide was straightforwardly synthesized by *in situ* deprotonation of the imidazolium salt precursor (**L**)(318 mg, 0.5 mmol) with palladium acetate (112 mg, 0.5 mmol) in DMSO. The mixture was stirred for 5 h at 60 °C and then allowed to proceed for an additional 40 min at 100 °C until a red mixture was obtained. The remaining DMSO was then removed in *vacuo* to give an orange solid which was washed with ethanol and CH_2Cl_2 (3×20 mL) to remove the unreacted $Pd(OAc)_2$, and finally dried under air. Yield:185 mg (50%). ^{1}H NMR (DMSO-d_6, 400 MHz): 6.78 (d, J= 2.0 Hz, 1H), 6.69 (d, J= 2.0 Hz, 1H), 6.13 (t, J= 2.0 Hz, 1H), 5.71 (d, J= 2.0 Hz, 1H), 5.69 (d, J= 2.0 Hz, 1H), 5.43 (d, J= 2.0 Hz, 1H), 5.41 (d, J= 2.0 Hz, 1H), 1.75 (s, 9H). ^{13}C NMR (DMSO-d_6, 100 MHz): 35.2, 37.3, 37.8, 122.8, 122.9, 125.3, 125.9, 126.7, 127.1, 135.2, 140.1, 140.3 163.4, 165.2. LC-MS (ESI+) m/z): 742.77 $[M+H+1]^+$. Anal. found: C, 22.71; H, 2.28; N, 9.52. Calc. for $C_{14}H_{16}N_5I_3Pd$: C, 22.68; H, 2.18; N, 9.45.

Synthesis of Pd(PyBNHC)@Nano-SiO_2

The silica was activated and chloropropylated by known procedures.[42] In a round-bottomed flask equipped with a condenser and a magnetic stirrer, chloropropylated nanosilica (1 g), 3,5-di(1H-imidazol-1-yl)pyridine (211 mg, 1 mmol) and NaI (3 mmol, 450 mg) in dry THF (40 mL) was stirred under reflux conditions overnight. The yellow solid material was separated by filtration, washed with hot THF for12 h in a Soxhlet apparatus to remove the unreacted starting materials, and then dried in a vacuum oven at 50 °C. For preparation of supported NHC ligand, the nanosilica supported 3,5-di(1H-imidazol-1-yl)pyridine (1 g) was reacted with methyl iodide in dry THF (30 mL). The slurry was stirred at 80 °C for 24 h and then filtered off. The corresponding solid was washed with DMF and ethanol, and then dried under reduced pressure. C: 8.53, H: 1.49, N: 2.22. The final nanocatalyst, Pd(PyBNHC)@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 °C and then allowed to proceed for an additional 40 min at 100 °C. The resulting catalyst washed with ethanol (3×20 mL) to remove the unreacted $Pd(OAc)_2$, and finally dried under air.

General procedure for Suzuki–Miyaura cross-coupling reaction

A mixture of aryl halide (1 mmol), phenylboronic acid (1.4 mmol), K_2CO_3 (3 mmol) and Pd(PyBNHC)@Nano-SiO_2, (0.15 mol% Pd) in DMF/H_2O (5 ml, 2:1) was stirred at 65 °C under air atmosphere. After completion of the reaction, the catalyst was separated by centrifugation and the products were extracted with ethyl acetate (2×15 mL). The organic phase was separated and dried over $MgSO_4$, and evaporated under reduced pressure. The residue was recrystallized from ethyl acetate and ether (1: 3) to afford the pure product.

Recovery and reuse of nanosilica-supported Pd catalyst

Due to the importance of recovery and reuse of heterogeneous catalysts, the reusability of the catalyst (**4**) was investigated in the reaction of 4-iodoanisole (1 mmol) with phenylboronic acid in the presence of (1.4 mmol), K_2CO_3 (3 mmol) and heterogeneous catalyst (0.15 mol%) at 65 ^{o}C. After completion of the reaction, the reaction mixture was worked-up as described above. The filtered catalyst was successively reused in the same reaction. The amount of Pd leached was determined by ICP analysis using a Perkine Elmer ICP analyzer.

Acknowledgements

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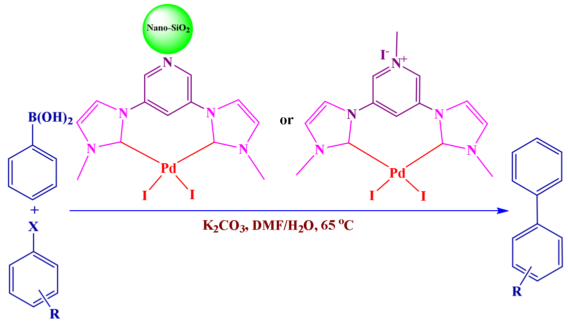

Efficient Suzuki-Miyaura C-C coupling reaction catalysed by palladium(II) NHC complex derived from 3,5-di(1-imidazolyl)pyridine under homogeneous and heterogeneous conditions is reported.