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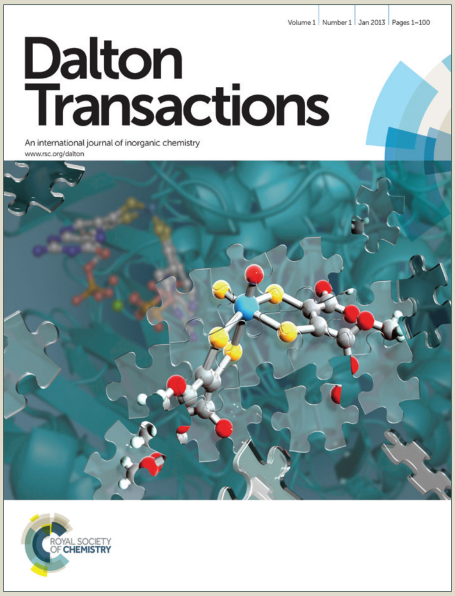

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ARTICLE

Novel Polymer Containing Phosphorus-Nitrogen Ligands for Stabilization of Palladium Nanoparticles: Efficient and Recyclable Catalyst for Suzuki and Sonogashira Reactions in Neat Water

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New polymer containing phosphorus and nitrogen ligands was successfully synthesized, characterized and used for stabilization of higly monodispersed palladium nanoparticles having an average diameter of 2-3 nm . The thermally stable heterogeneous catalyst was successfully applied in Suzuki-Miyaura and copper-free Sonogashira-Hagihara coupling reactions of aryl halides under low palladium loading conditions. Reactions were proceeded in neat water without using any organic co-solvents. The catalyst was successfully recycled for sample Suzuki-Miyaura reaction for nine consecutive times with small drops in catalytic activity.

Introduction

Nowadays, palladium catalyzed coupling reactions have found to play an important role in organic transformations.[1] During the last decades, numerous efficient homogeneous catalysts have been developed for different palladium catalyzed coupling reactions.[2] However, as palladium is one of the most toxic and expensive transition metals, growing interest has been paid in development of heterogeneous and recoverable palladium catalysts.[3] This issue is becoming more important, when small quantities of toxic palladium species cause major environmental problems, though the products obtained by palladium catalyzed reactions have wide spread applications in pharmaceutical industries. Therefore, heterogenization of palladium catalysts is extremely important from both the environmentally sustainable chemical processes and economic standpoints. In recent years, various successful methods which use palladium on various supports such as polymers,[4] modified silicas,[3a] magnetite,[5] mesoporous materials,[6] ionic liqiuids[7], and graphene[8] were developed. In this regard, challenging subjects for investigation include designing new heterogeneous catalytic systems with concomitant mild reaction conditions, using low amount of expensive palladium species, shortening of the reaction times, improving the low reactivity of aryl bromides and chlorides and conducting reactions in green solvents such as water.

Suzuki-Miyaura reaction, which is a cross coupling reaction between aryl, vinyl, or alkyl halides or pseudo-halides and organoboron reagents is one of the well-known and advanced palladium catalyzed reactions for the formation of different types of compounds, particularly biaryls.[9] Sonogashira coupling reaction is another important palladium catalyzed reaction for the formation of aryl-alkynes and conjugated enynes *via* the coupling of vinyl or aryl halides or triflates with terminal alkynes.[10] Ligands having phosphorus atoms are excellent ligands for stabilization of palladium species during coupling reactions.[11] Along this line, phosphorus-based polymers are one of the promising supports for the stabilization of palladium catalysts in coupling reaction.[12] Furthermore, existence of electronically hard nitrogen adjacent to electronically soft phosphorous (P,N ligands) modifies property of the ligand during a catalytic cycle. Phosphorus with π-acceptor character stabilizes low oxidation state metal whereas σ-donor ability of the nitrogen makes the metal more prone to oxidative addition reactions.[13]

Recently, we have reported the synthesis and characterization of 4-aminophenyl diphenylphosphinite[14] and 2-aminophenyl diphenylphosphinite.[15] *Para* isomer was used as a heterogeneous phosphinite in different organic transformation and *ortho* isomer was used as a ligand in palladium catalyzed Heck-Mizoroki,[15] Suzuki-Miyaura[16] and Sonogashira-Hagihara[17] coupling reactions. Despite the efficiency of the reported method, using high amount of expensive palladium catalyst and performing reactions at high temperature are the drawbacks of this method. Herein, we report synthesis and characterization of new polymer containing phosphorus and nitrogen ligands for stabilization of palladium nanoparticles in Suzuki-Miyaura and Sonogashira-Hagihara coupling reactions in aqueous media under low palladium loading conditions.

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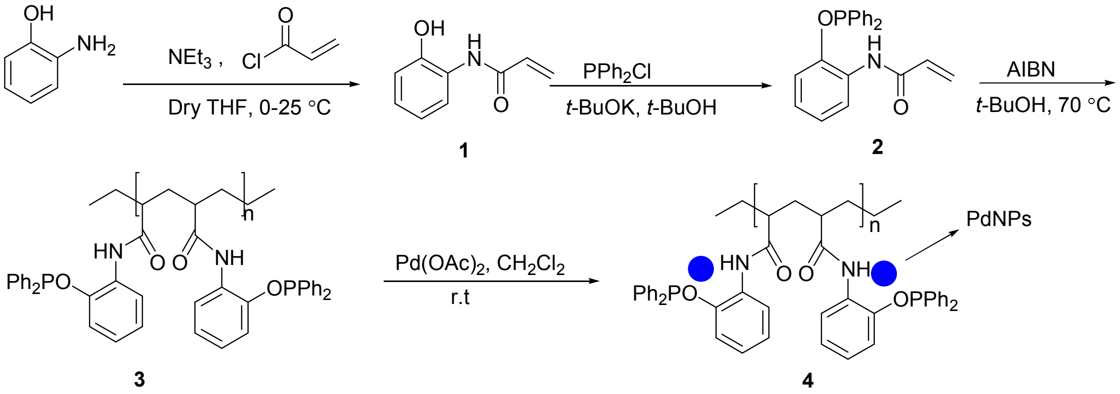
Results and discussion

The stages of catalyst preparation are summarized in Scheme 1. Briefly, 2-aminophenol was reacted with acryloyl chloride in the presence of Et_3N as a base in dry THF to produce *N*-(2-hydroxyphenyl) acrylamide (**1**). The obtained product (**1**) was characterized using ^{1}H NMR, ^{13}C NMR and FT-IR analysis (supporting information). Reaction of compound (**1**) with chlorodiphenylphosphine (PPh_2Cl) in the presence of *t*-BuOK as a base in *t*-BuOH produced phosphinite monomer (**2**) which was characterized using ^{1}H NMR, ^{13}C NMR and ^{31}P NMR (supporting information). Polymerization of phosphinite (**2**) was easily achieved using 2,2'-azobisisobutyronitrile (AIBN) as a initiator in *t*-BuOH for 24 h at 70 °C and afford final polymer (**3**). The final catalyst (**4**), polymer supported palladium nanoparticles was obtained by dissolving $Pd(OAc)_2$ in CH_2Cl_2 and treating it with polymer (**3**) for 24 h at room temperature.



Scheme 1. Synthesis steps of the catalyst

TG analysis of the polymer (**3**) indicated negligible leaching of organic groups and thermal stability of polymer up to 200˚C with three weight losses between 25-700˚C (Figure 1, supporting information). The first weight loss is related to physically absorbed water and organic solvents. The second weight loss (57.67%) occurred between 100-400˚C which may be related to the loss of 2-aminophenyl diphenyl phosphinite from the polymeric structure and third weight loss (28.82%) can be attributed to the decomposition of polymer residue.

SEM image of catalyst (Figure 2, supporting information) showed formation of large sheets in micro scale dimension (as clearly observed in TEM images). In addition, energy dispersive spectroscopy (EDS) analysis of catalyst obtained from SEM, confirm presence of Pd species in the structure of catalyst (Figure 1). Presence of palladium in final catalyst was also confirmed using atomic absorption spectroscopy (AAS) which showed 0.08 mmolg^{-1} of palladium content.

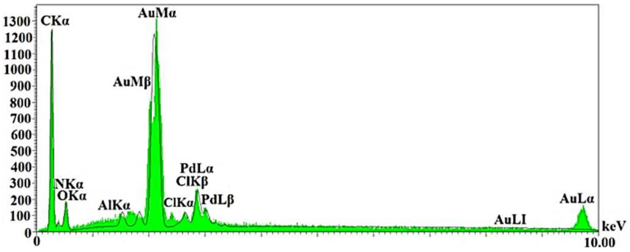


Fig. 1 EDS spectrum of the catalyst

TEM images of catalyst (**4**) indicated formation of uniform and small size Pd nanoparticles with an average diameter of 2-3 nm. It is worth mentioning that formation of palladium nanoparticles was achieved without using any reducing agents (Figure 2). The HR-TEM analysis (Figure 2c) shows the presence of lattice fringes with *d*-spacing value of 0.23 nm corresponding to the (111) plane of Pd. The (111) plane of Pd matches well with the SAED pattern revealing the (111) planes as the dominant plane for crystal growth. Figure 5f shows the selected area diffraction pattern (SAED) analysis with prominent ring pattern corresponding to hexagonal Pd structure. The diffraction pattern shows prominent rings with interplanar spacing values of 0.23, 0.19, and 0.15 nm corresponding to (111), (200), and (220) planes respectively for Pd (JCPDS no. 46-1043).

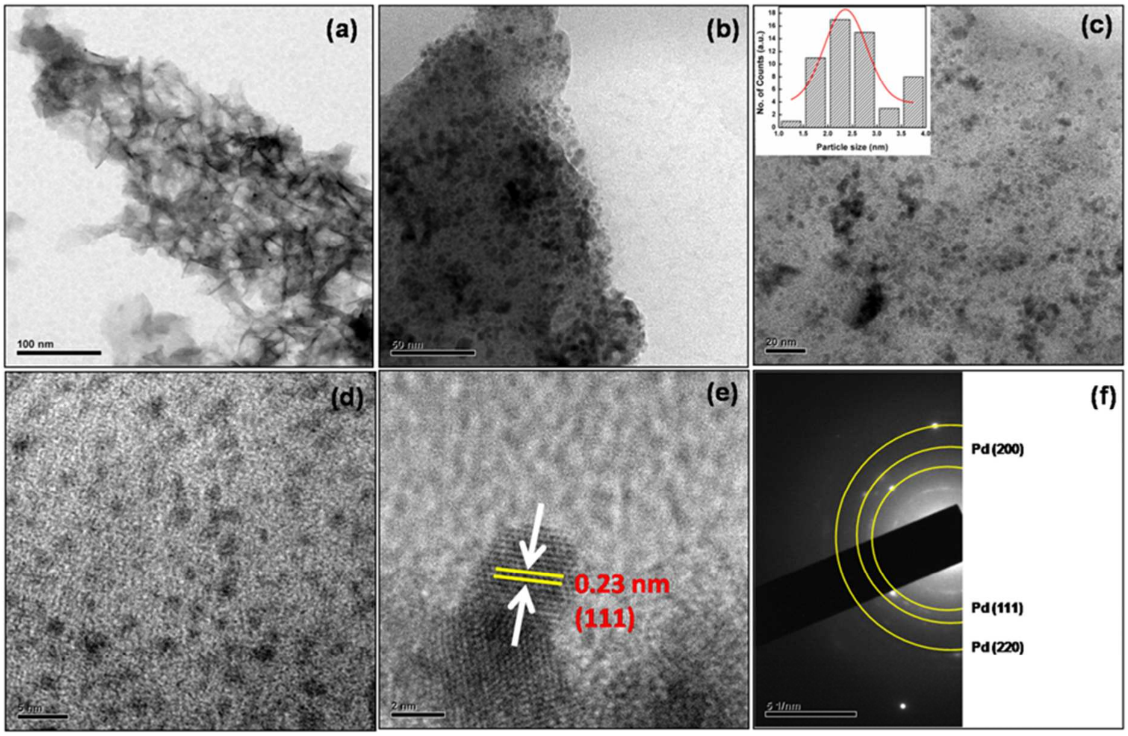


Fig. 2 (a-e) Representative HRTEM images and (f) SAED pattern of catalyst (**4**).

Formation of the Pd(0) catalyst was also confirmed by the solid UV-Vis spectrum which showed complete conversion of Pd(II) to Pd(0) by the absence of the peak at 420 nm which belongs to Pd(II) species (Figure 3).[18]

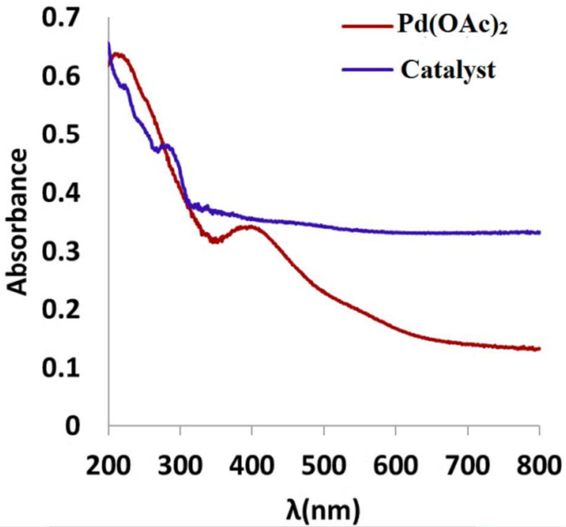


Fig. 3 Solid UV-Vis spectrum of the catalyst and $Pd(OAc)_2$

X-ray diffraction (XRD) analysis of catalyst (**4**) showed formation of Pd(0) nanoparticles by appearing Bragg's reflections related to palladium in 2θ= 40.1, 46.7, 68.1, 82.1 (Figure 4).[19]

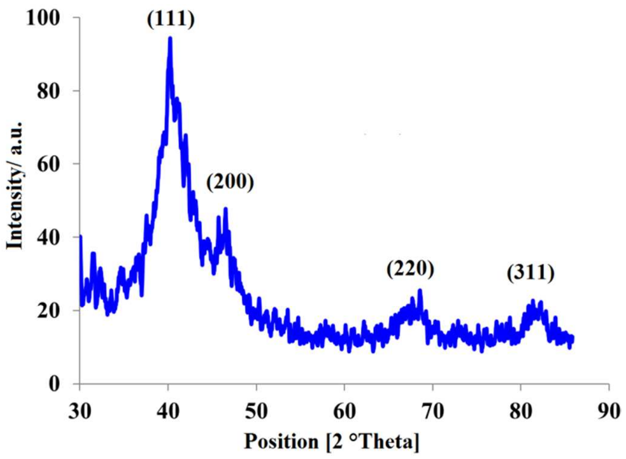


Fig. 4. XRD pattern of the catalyst

Formation of Pd(0) nanoparticles was also approved by color changing of polymer and $Pd(OAc)_2$ mixture from orange to dark brown during the catalyst synthesis (Figure 5). The color change indicated activation of Pd catalyst by intraction of phosphorus and nitrogen ligands of polymer with $Pd(OAc)_2$.[20]

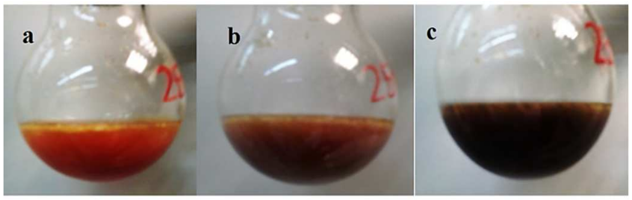
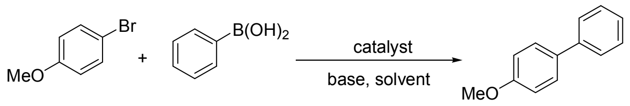


Fig. 5 Preparation of Pd catalyst a) after 1 min, b) after 3 min, c) after 5 min

The catalytic activity of prepared polymer supported catalyst (**4**) was evaluated in Suzuki-Miyaura coupling reaction of aryl halides. Primarily, reaction of less reactive 4-bromoanisol with phenylboronic acid in the presence of catalyst under different reaction conditions such as different solvents and bases was studied. Study of reaction using different bases in water at 25-60°C revealed that using K_2CO_3 as a base, 0.08 mol% of palladium catalyst at 60 °C are the most efficient reaction conditions (Table 2, entry 9). However, we have also studied the model reaction in the absence of base (Table 2, entry 10), using 0.08 mol% of $Pd(OAc)_2$ (Table 2, entry 11) and in the absence of Pd using 20 mg of polymer **3** (Table 2, entry 12). Results indicated that reactions did not proceed efficiently and starting material was intact. Using K_2CO_3 in other solvents such as DMF, CH_3CN, EtOH, toluene, 1,4-dioxane and THF gave low yields for the reaction (Table 1, entries 18-23).

Table 1 Screening of different reaction conditions for the reaction of 4-bromoanisole with phenylboronic acid in the presence of catalyst.[a]



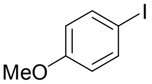
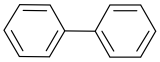
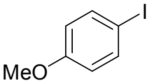
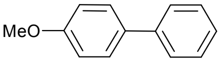
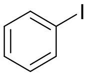
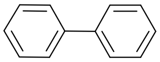
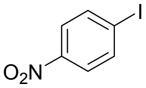
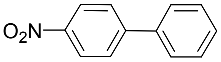
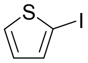
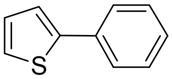
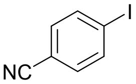
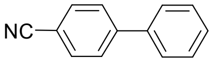
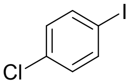
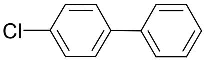
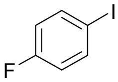
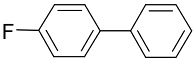
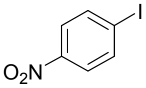
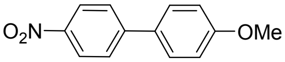
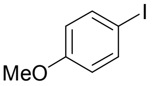
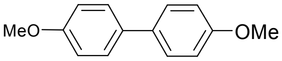
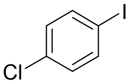
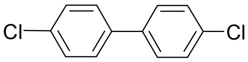
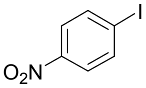
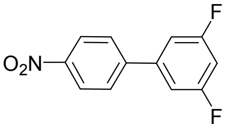
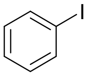
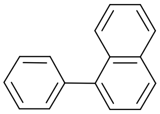
Entry	Cat mol%	Base	Solvent	Temp.(ºC)	Time(h)	Yield[b]
1	0.08	DABCO	H_2O	25	5	27
2	0.08	K_2CO_3	H_2O	25	5	10
3	0.08	K_2CO_3	H_2O	40	5	32
4	0.08	DABCO	H_2O	40	5	42
5	0.08	*t*-BuOK	H_2O	40	5	64
6	0.08	Et_3N	H_2O	40	5	45
7	0.08	K_3PO_4	H_2O	60	2	52
8	0.08	Et_3N	H_2O	60	2	85
9	0.08	K_2CO_3	H_2O	60	2	88
10	0.08	-	H_2O	60	2	5[c]
11	0.08	K_2CO_3	H_2O	60	2	7[d]
12	-	K_2CO_3	H_2O	60	2	2[e]
13	0.08	NaOAc	H_2O	60	2	5
14	0.08	*t*-BuOK	H_2O	60	2	74
15	0.08	DABCO	H_2O	60	2	83
16	0.04	K_2CO_3	H_2O	60	2	75
17	0.02	K_2CO_3	H_2O	60	2	40
18	0.08	K_2CO_3	DMF	60	2	22
19	0.08	K_2CO_3	CH_3CN	60	2	26
20	0.08	K_2CO_3	EtOH	60	2	57
21	0.08	K_2CO_3	Toluene	60	2	21
22	0.08	K_2CO_3	Dioxane	60	2	20
23	0.08	K_2CO_3	THF	60	2	14

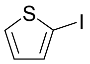
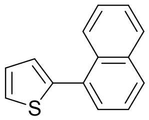
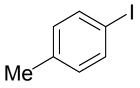
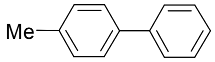
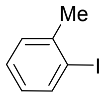
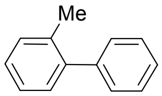
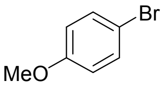
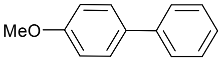
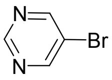
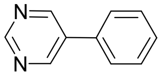
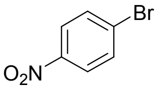
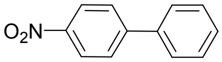
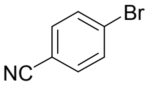
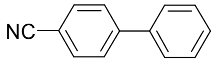
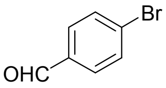
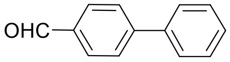
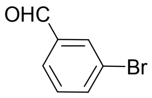
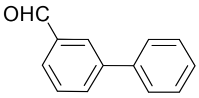
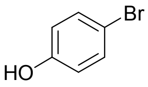
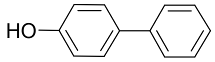
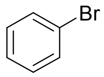
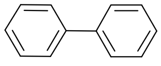
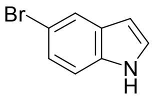
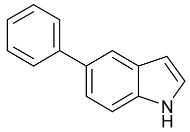
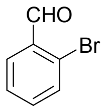
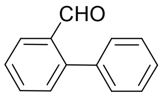
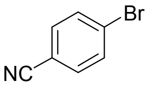
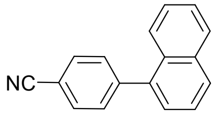
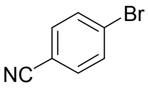
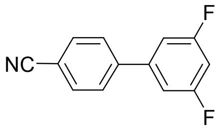
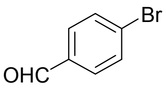
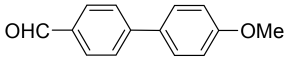
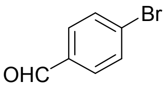
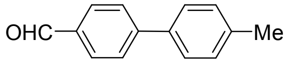
[a] Reaction conditions: 4-bromoanisole (1 mmol), phenylboronic acid (1.5 mmol), base (1.5 mmol), solvent (2 mL), catalyst (0.08 mol% Pd). [b] GC yields. [c] Reaction in the absence of base. [d]Reaction using 0.08 mol% $Pd(OAc)_2$. [e] Reaction in the absence of Pd and using 20 mg polymer **3**.

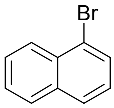
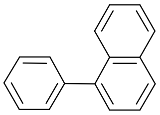
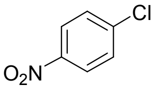
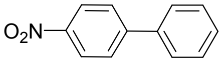
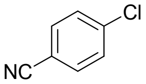
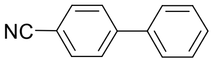
With the optimized reaction conditions in hand, K_2CO_3 as base, H_2O as solvent and 0.08 mol% Pd, substrate scope of the Suzuki-Miyaura coupling reaction was investigated for the reaction of structurally different aryl halides with arylboronic acids (Table 2). Reaction of 4-iodoanisol under optimized reaction conditions was completed at 5 minutes therefore, we decided to studied reactions of aryl iodides at room temperature under similar optimized reaction conditions to aryl bromides.

Table 2 Suzuki-Miyaura cross-coupling reaction of structurally different aryl halides and arylboronic acids

$$Ar^1X + Ar^2B(OH)_2 \xrightarrow[t\text{-BuOK, } H_2O]{\text{catalyst}} Ar^1\text{–}Ar^2$$

Entry	Ar^1	Ar^2	Temp. (ºC)	Time	Product	Yield (%)[b]
1		Ph	60	0.1		96
2		Ph	25	8		89
3		Ph	25	5		83
4		Ph	25	0.5		94
5		Ph	25	6		82
6		Ph	25	1		97
7		Ph	25	2		87
8		Ph	25	2		96
9		$4\text{-}MeOC_6H_4$	25	1		84
10		$4\text{-}MeOC_6H_4$	25	3		80
11		$4\text{-}ClC_6H_4$	25	3		90
12		3,5 difluorophenyl	25	8		83
13		1-Naphtyl	25	3		89

14		1-Naphtyl	25	3		92^c
15		Ph	25	3		96
16		Ph	25	3		87^c
17		Ph	60	2		84
18		Ph	60	9		82
19		Ph	60	3		99
20		Ph	60	1		95
21		Ph	60	1		94
22		Ph	60	1		94
23		Ph	60	7		97
24		Ph	60	10		97
25		Ph	60	10		81
26		Ph	60	1		88
27		1-naphtyl	60	5		93
28		3,5-difluorophenyl	60	9		86
29		4-OMeC$_6$H$_4$	60	2		94
30		4-MeC$_6$H$_4$	60	1		95

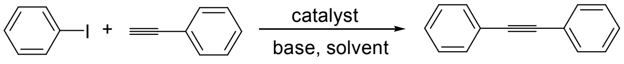
31		Ph	60	10		73
32		Ph	100	24		71[d]
33		Ph	100	24		90[d]

[a]Reaction conditions: ArX (1 mmol), phenylboronic acid (1.5 mmol), base (1.5 mmol), solvent (2 mL), catalyst (0.08 mol% Pd). [b]Isolated yields. [c]GC yields. Using 0.3 mol% Pd catalyst and 1 mmol TBAB

As shown in Table 2, the coupling reaction between aryl iodides containing electron-donating groups (Table 2, entries 1-2, 10, 15-16) and electron withdrawing groups (Table 2, entries 4, 6-8) as well as thienyl iodide (Table 2, entry 5) with phenylboronic proceeded effectively to give the corresponding biaryl products in high to excellent yields. Reactions of aryl bromides carrying both electron donating (Table 2, entries 17, 23) and electron withdrawing groups (Table 2, entries 19-22, 26-30) were performed well and desired coupling products were obtained in high to excellent isolated yields. It is worth mentioning that reaction of 5-bromopyrimidine and 5-bromoindole as heterocyclic aryl bromides afforded high isolated yields (Table 2, entries 18, 25). Different substituted arylboronic acids like 4-methoxyphenyl, 4-tolyl, 4-chloro, 3,5-difluoropheny, and 1-naphthylboronic acids with aryl bromides and iodides gave high to excellent isolated yields (Table 2, entries 9-14, 27-30). Reactions of aryl chlorides such as 4-chloro-benzonitrile and nitrobenzene under optimized reaction conditions were sluggish. However, increasing of reaction temperature to 100 °C afforded 71 and 90 isolated yields respectively (Table 2, entries 32-33).

In continue, the application of novel polymer supported Pd NPs (**4**) was studied in Sonogashira-Hagihara coupling reaction of aryl bromides and iodides under copper free reaction conditions. In order to find optimized reaction conditions, reaction of iodobenzene with phenylacetylene in the presence of 0.16 mol% catalyst and different solvents and bases were studied. Results of Table 3 indicated that using DABCO as a base and H_2O as a solvent at 60 °C is the most suitable reaction conditions (Table 3, entry 7).

Table 3 Screening of different reaction conditions for the reaction of iodobenzene with phenylacetylene in the presence of catalyst.

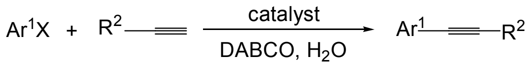


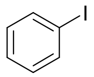
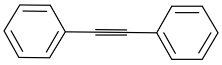
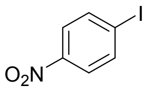
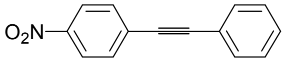
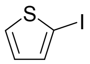
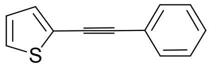
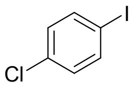
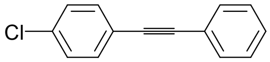
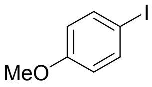
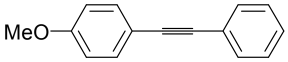
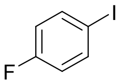
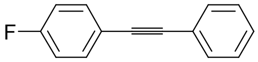
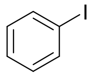
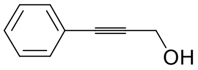
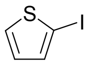
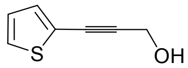
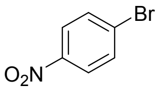
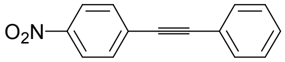
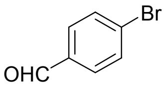
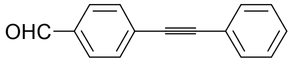
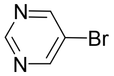
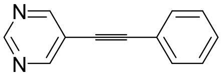
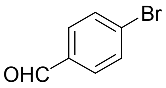
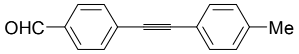
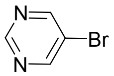
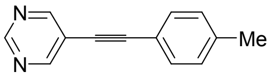
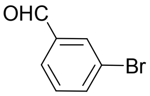
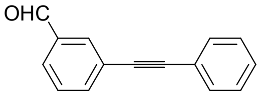
Entry	Base	Solvent	Temp.(°C)	Time(h)	Yield(%)[a]
1	K_2CO_3	H_2O	60	12	3
2	Et_3N	H_2O	60	12	10
3	NaOAc	H_2O	60	12	7
4	K_3PO_4	H_2O	60	12	5
5	*t*-BuOK	H_2O	60	12	4
6	DABCO	H_2O	60	12	65
7	DABCO	H_2O	60	24	89
8	DABCO	H_2O	50	12	54
9	DABCO	H_2O	r.t	12	26
10	DABCO	CH_3CN	60	24	73
11	DABCO	Toluene	60	24	5
12	DABCO	EtOH	60	24	53
13	DABCO	Dioxane	60	24	86

[a] GC yields

We have applied optimized reaction conditions for the reactions of structurally different aryl halides with different terminal alkynes such as phenylacetylene, propargyl alcohol and 4-ethynyltoluene (Table 4). Results indicated that aryl iodides were reacted efficiently and desired alkyne products were obtained in high to excellent yields under copper free conditions. However, reactions of aryl bromides at 60 °C were proceeded sluggish therefor, reaction temperature was increased to 100 °C and 1 mmol tetrabutylammonium bromide (TBAB) was added. Under these conditions, reactions of aryl bromides were proceeded well and afford desired products in high to excellent yields. All attempts to carry out the reaction of aryl chlorides were unsuccessful and starting materials were isolated intact.

Table 4. Sonogashira-Hagihara coupling reactions of structurally different aryl iodides and bromides with alkynes



Entry	Ar^1	R^2	Temperature	Time(h)	Product	Yield(%)^b
1		C_6H_5-	60	24		84
2		C_6H_5-	60	2		99
3		C_6H_5-	60	2		99
4		C_6H_5-	60	12		78
5		C_6H_5-	60	6		85
6		C_6H_5-	60	2		95
7		CH_2OH	60	3		90
8		CH_2OH	60	1		88
9		C_6H_5-	100	24		88
10		C_6H_5-	100	24		80
11		C_6H_5-	100	14		84
12		4-MeC_6H_4-	100	48		98
13		4-MeC_6H_4-	100	24		77
14		C_6H_5-	100	48		84

^{a}Reaction conditions: ArX (1 mmol), alkyne (1.5 mmol), base (1.5 mmol), solvent (2 mL), catalyst (0.16 mol% Pd). ^{b} Isolated yields

The recyclability of the catalyst is important factor for evaluation of catalyst from economical and green chemistry stand points of views. Thus, we have studied recycling of the catalyst for the reaction of 4-bromobenzonitrile and phenylboronic acid under optimized reaction conditions. After completion of the reaction in each run, heterogeneous catalyst was isolated with filtration and after washing with diethyl ether and drying was used for another batch of the reaction. Recycling experiments indicated that the catalyst can be successfully used during nine consecutive runs with small drops in catalytic activity (Figure 7).

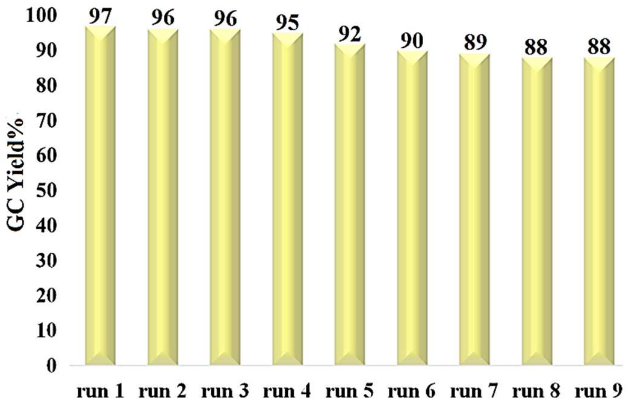


Fig. 7 Recycling of catalyst for the reaction of 4-bromobenzonitrile and phenylboronic acid.

TG analysis of catalyst after 3rd run showed thermal stability of polymer structure during the reaction. Also, atomic absorption spectroscopy of reaction mixture after 3rd run indicated that only 4% of palladium was leached to the reaction medium. In order to get information about leaching of Pd, we have repeated recycling experiment under argon atmosphere. Result showed that after 3rd run, amount of leaching was decreased to 1.8% under preserving catalytic activity. Probably, under air, palladium nanoparticles get oxidize to Pd(II) easier than inert atmosphere and produced soluble Pd(II) species can leach to the reaction mixture.[21]

Conclusion

In summary, we have demonstrated the synthesis and characterization of a Pd NPs supported thermally stable heterogeneous polymer containing phosphorus and nitrogen ligands and its application for the Suzuki-Miyaura and Sonogashira-Hagihara coupling reaction. All the reactions were conducted in the air in water without the use of an organic co-solvent. The heterogeneous catalyst can easily be recovered by filtration and can be reused for nine consecutive times with small loss of efficiency.

Synthesis of N-(2-hydroxyphenyl)acrylamide (1).

Acryloyl chloride (10 mmol, 0.85 mL) was added to a flask containing solution of 2-aminophenole (10 mmol, 1.09 g) in dry THF (20 mL) at 0 °C under argon atmosphere. Then, Et_3N (10 mmol, 1.4 mL) was added drop wise at 0 °C and mixture was stirred for 2h at room temperature. Then, reaction mixture was filtered to separate produced triethylammonium chloride salt. After evaporation of THF, crude product was purified using column chromatography using hexane and ethyl acetate as eluent. The pure product was obtained in 95% isolated yield.

Synthesis of phosphinitemonomer 2

N-(2-hydroxyphenyl)acrylamide (**1**) (10 mmol,) was added to a flask containing *t*-BuOK (10.1 mmol, 1.1 g) and *t*-BuOH (30 mL) and mixture was stirred for 10 min at room temperature. Then, chlorodiphenylphosphine (10.1 mmol, 2.2 g) was added drop wise under argon atmosphere and mixture was stirred for 12 h at room temperature. Then, hexane (20 mL) was added to the reaction mixture to precipitate phosphinite product. The solid material was filtered and washed with water (10 mL) and hexane (20 mL) to produce crude phosphinite (**2**) in 90% isolated yield. The compound was crystalized using ethyl acetate and hexane to produced pure phosphinite (**2**) in 81% yield.

Synthesis of phosphinite polymer 3

Phosphinite monomer (**2**) (5 mmol, 1.7 g) was dissolved in *t*-BuOH (50 mL) and AIBN (0.085 g, 0.5% w/w) was added to mixture under argon protection. The mixture was stirred for 24 h at 70 °C under argon atmosphere. Then, *t*-BuOH was evaporated and obtained pale yellow solid was washed with H_2O (10 mL) and hexane (30 mL) and dried in oven for 24 h at 80 °C.

Synthesis of polymer supported palladium nanoparticles

1 g of polymer (**3**) was sonicated in 5 mL CH_2Cl_2 for 5 min. To the resulting mixture $Pd(OAc)_2$ (0.1 mmol, 22 mg) was added and stirred for 24 h at room temperature. Then, mixture was filtered and solid catalyst washed with 5 mL CH_2Cl_2 and 10 mL hexane and dried under vacuum for 24 h. Atomic absorption spectroscopy showed 0.08 $mmolg^{-1}$ of palladium which is 80% loading of palladium on polymer.

General procedure for Suzuki-Miyaura coupling reaction

ArX (1mmol), $ArB(OH)_2$ (1.5 mmol), K_2CO_3 (1.5 mmol), catalyst (10 mg, 0.08 mol% Pd), and H_2O (2 mL) were added to a 5 mL flask and mixture was stirred under air at 25-100 °C (according to aryl halide) for appropriate reaction time. The progress of the reactions was monitored by GC and TLC analysis. After completion of the reaction, reaction mixture was washed with ethyl acetate (5×1 mL) and organic solvent was evaporated to obtain crud biaryl product. Further purification was achieved using column chromatography using hexane and ethyl acetate as eluent.

General procedure for Sonogashira-Hagihara coupling reaction

Alkyne (1.5 mmol), ArX (1mmol), DABCO (1.5 mmol), and TBAB (1mmol, for aryl bromides) were added to a flask containing catalyst (20 mg, 0.16 mol% Pd) and H_2O (2 mL). Reaction mixture was stirred at 60 °C for aryl iodides and 100 °C for aryl bromides for appropriate reaction time. The progress of the reaction was monitored by GC analysis. After completion of the reaction, reaction mixture was washed with ethyl acetate (5×1 mL) and organic solvent evaporated.

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Novel Polymer Containing Phosphorus-Nitrogen Ligands for Stabilization of Palladium Nanoparticles: Efficient and Recyclable Catalyst for Suzuki and Sonogashira Reactions in Neat Water