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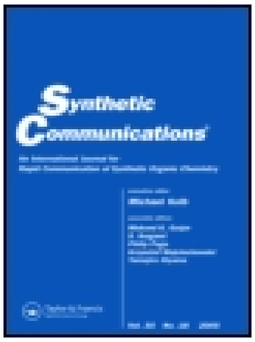

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Synthesis of palladium nanoparticles using triazolium based ionic liquids: A reusable catalyst for addition of arylboronic acids to nitrostyrenes

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ABSTRACT
Formation of stable and small-sized palladium nanoparticles of diameter 9.4 nm was accomplished by a simple heating of $Pd(OAc)_2$ in 1-octyl-1,2,4-triazolium trifluoroacetate ionic liquid under standard atmospheric hydrogen pressure. Palladium nanoparticles were characterized by XRD, SEM, TEM, and EDX analysis techniques. The application of an addition reaction of arylboronic acid to nitrostyrenes provided diaryl-substituted products in high yields. This Pd-NPs are capable of being recycled by a simple decantation procedure and reusable up to four times without any effect on its catalytic activity.

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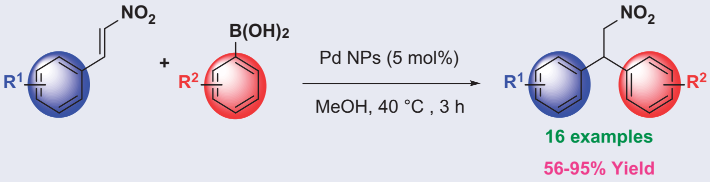
KEYWORDS
Addition reaction; arylboronic acid; ionic liquids; nitrostyrene; Pd nanoparticles

GRAPHICAL ABSTRACT



Introduction

Room temperature ionic liquids (RTIL) are environmentally benign solvents; have generated considerable attention in the direction of organic chemical reactions. The unique features of ionic liquids (ILs) are their excellent characteristics of negligible vapor pressures, high-ionic conductivity and as high-thermal stability.[1–3] These characteristics have made them novel and environmentally friendly solvents, used for enzyme-catalyzed reactions[4] as well as organic transformations. ILs have wide range of applications due to their low-melting point (as low as –80 °C) and high-thermal stability (stable up to 300 °C).[5] For the last few years, the ionic liquid (IL) field is dominated by imidazolium salts, but there are a very few triazolium compounds that can be characterized as ILs. Fluorine-based anions referred to in literature are very few in number[6,7] for the

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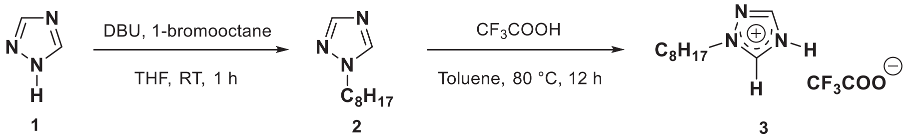


Scheme 1. Preparation of 1-octyl-1,2,4-triazolium trifluoroacetate ionic liquid.

synthesis of ILs. The parent triazoles and their derivatives found many applications in medicine and industry.[8–11]

In recent years, ILs are seen as the most advanced solvents for the organic nanoparticle synthesis with unique physical and chemical properties.[12] Among the classes of ILs, the chemistry of azolium based IL is the subject of in-depth study, particularly imidazolium based ILs.[13–15] The reason is that the imidazolium based ILs are easily tunable by means of changing substitution on nitrogen in the ring and also by using different anions.[16,17] The literature on azolium based ILs has shown the exploration of a small magnitude for the triazolium based ILs, especially 1,2,4-triazolium based ILs on their synthesis and applications in organic reactions.[18–21] Commonly used ILs are [C_4-mim]Br (where C_4 depicts the butyl group; and mim represents methylimidazole fragment), [C_4-mim][PF_6], [C_6-mim][PF_6] and so on.[22] It was reported that the use of the longer alkyl chain effectively decrease the solubility of the ionic liquid in the aqueous phase and lead to improved yields.[23] This has created interest in the subject of synthesizing C_8-triazolium based ILs using 1,2,4-triazole as the starting material (Scheme 1).[24]

Among the various metal nanoparticles (NPs), palladium nanoparticles (Pd-NPs) in ILs have recently gained considerable importance, as this methodology allows simultaneous achievement of the advantages of the elimination of highly toxic solvents and the possibility of recycling the catalyst.[25,26] In addition, it has been widely demonstrated that ILs can play a greater role than merely solubilizing reagents, as their ability to affect the nature of the catalytically active species has also been shown to be dependent on the structure of both cations and anions.[27,28]

Nacci et al. found the possibility of the use of Pd-NPs in tetraalkylammonium-based ILs, prepared from the reduction of Pd(OAc) in the presence of tetrabutylammonium acetate at 90 °C, as pre-catalysts for the Suzuki coupling of aryl halides.[29] Interestingly, the results showed the use of tetrabutylammonium hydroxide as a base significantly increased the catalytic efficiency and the reaction could be performed under mild temperatures. The replacement of tetrabutylammonium bromide (TBAB) by tetraheptylammonium bromide (THeptAB), which contains longer side chains, led to the enhancement of the Suzuki reaction, probably due to the stronger stabilization of the Pd-NPs provided by the long-chain ionic liquids.[30] Mu's group established a simple and general method for preparing poly(N-vinyl-2-pyrrolidone) (PVP)-stabilized noble metal nanoparticles in ILs. These NPs were very stable and showed high-catalytic activity and stability in the hydrogenation of olefins under mild conditions and reused the catalyst without any loss of activity.[31] Calo et al. show that the reaction of $Pd(OAc)_2$ with tetrabutylammonium acetate (TBAA), dissolved in (TBAB), leads to the fast formation of Pd-NPs, which efficiently catalyze the stereospecific reaction of cinnamates with aryl halides to provide β-aryl-substituted cinnamic esters. The role of TBAA is crucial in determining the formation of NPs and stereospecificity of the C–C coupling process.[32] Prechtl group had given a brief summary in the field of C–C cross-coupling reactions with Pd-NPs in ILs. Five exemplary model systems using the Pd-NPs/ILs approach have been presented: Heck, Suzuki, Stille, Sonogashira, and Ullmann reactions, all of which have the use of ILs as reaction media in common and the use of Pd-NPs as a reservoir for the catalytically active palladium species.[33]

Venkatesan et al. synthesized Pd(0)-NPs with a simple heating of $Pd(OAc)_2$ in 1-butyronitrile-3-methylimidazolium-N-bis(trifluoromethane sulfonyl)imide ($(BCN)MI.NTf_2$) under reduced pressure. These NPs were used as catalysts for the hydrogenation of internal alkynes at 25 °C under 1 bar of hydrogen yields *Z*-alkenes. Application of higher hydrogen pressure (4 bar) in these reactions always led to the formation of alkanes without the detection of any alkenes.[34] Calo's group reported that Palladium nanocolloids supported on chitosan which behaves as a very effective and recyclable heterogeneous catalysts in Heck reaction of aryl bromides and activated chlorides in TBAB as solvent and TBAA as a base. The stability of the catalyst allows an extensive recycle in the coupling of iodoaromatics with butyl acrylate.[35] The Pd-NPs synthesized by Safavi et al. found the NPs as highly active, recyclable, and stable catalysts for Suzuki and Heck reactions even under reflex condition. The nanocatalysts are used several times without deterioration of its catalytic activity.[36] Yang's group have developed a highly stable Pd-NPs, protected by an ionic polymer (IP) in a functionalized IL which was used as an excellent precatalyst for Suzuki, Heck, and Stille coupling reactions. This NP-IP-IL system is considered to be an alternative to the traditional palladium on carbon (Pd/C) precatalyst employing in many C–C coupling reactions under solvent-free conditions.[37] Cassol's group disclosed their results concerning the *in situ* TEM analysis of Pd-NPs dispersed in ($BMI\text{-}PF_6$) ionic liquid, before and after arylation of *n*-butyl acrylate, and the Pd leaching from the IL phase to the organic phase at different substrate conversions.[38]

Faria et al. synthesized Pd-NPs supported on a polymeric membrane, CA/Pd(0), which was found to be a highly efficient "dip catalyst" for Suzuki–Miyaura cross-coupling reactions. The CA/Pd(0) was prepared initially using the synthesis of Pd(0) by hydrogen decomposition of $Pd(acac)_2$ dissolved in $BMI\text{-}BF_4$ IL.[39] Zhao et al. established the identification of the Pd-NPs with nitrile-functionalized ILs as the active catalyst in the Stille reaction under reflux condition.[40] Lee et al. demonstrated single-walled carbon nanotubes (SWNTs), which serve as a supporting material for Pd nanoparticles generated *in situ* in IL. Pd nanocatalysts on SWNTs exhibit superior reactivity for hydrogenation of aryl ketones in IL under mild conditions and were reused about 10 times without any loss of catalytic activity.[41] Heck reactions of aryl chlorides were catalyzed by the Calo's group using ligand-free palladium acetate in a molten mixture of tetraalkylammonium ILs under aerobic conditions. Deactivated electron-rich aryl chlorides reacted with a wide array of substituted alkenes under these conditions, which thereby enabled the coupling of combinations of substrates that are generally unreactive with traditional catalysts.[42] Umpierre et al. prepared Pd-NPs using a simple hydrogen reduction in $Pd(acac)_2$ dispersed in $BMI.PF_6$IL. The ILs created an external layer around the metal NPs that controls the access of the reagents to the catalytically active sites as a function of their solubility in the ionic layer. This catalytic system [Pd-NPs embedded

$$\mathrm{Pd(OAc)_2} \xrightarrow[75\ ^{\circ}\mathrm{C},\ 1\ \mathrm{h}]{\mathrm{IL},\ \mathrm{H_2}\ (1\ \mathrm{atm})} \mathrm{Pd(0)\ Nanoparticles}$$

Scheme 2. Synthesis of Pd-NPs using triazolium based ILs.

in ILs] is one of the most effective catalysts for performing selective hydrogenation of 1,3-butadiene to 1-butene.[43]

In 2003, Huang's group summarized their results that Phenanthroline (Phen) ligand-protected Pd-NPs in [BMIM][PF_6] IL is not only used as an active and selective catalytic system but also reused many times without reducing the activity of hydrogenation of olefins under mild reaction conditions.[44] In 2004, they conducted their first study of immobilization of Pd-NPs onto a solid surface (molecular sieves) by 1,1,3,3-tetramethylguanidinium lactate (TMGL) IL. The catalytic system was used in solvent-free hydrogenation reactions and achieved unprecedented activity and stability. The combination of NPs, IL, and molecular sieves showed excellent synergistic effects in the enhancement of the activity and durability of the catalyst, and this approach found wide potential applications in transition-metal nanocatalysed reactions.[45]

In this work, the authors have synthesized Pd-NPs using novel 1-octyl-1,2,4-triazolium trifluoroacetate ionic liquid (**3**) (Scheme 2). To the best of the authors' knowledge, this is the first use of palladium nanoparticles as a catalyst for the addition reaction of aryl boronic acid to nitrostyrene. The Pd-NPs are very efficient for addition reaction and the experiments were also carried out for the reuse of the catalyst by a simple decantation procedure for further reactions. The catalyst did not show any loss in its activity, even after four runs of repeated addition reaction.

Results and discussion

In the preliminary experiments, Pd-NPs was synthesized and characterized by XRD, SEM, TEM and EDX analysis.

XRD analysis

X-ray diffraction (XRD) pattern of the Pd-NPs shown in Figure 1 confirmed the crystalline feature of the product and the mean diameter was 9.4 nm, as estimated by the Debye–Scherrer equation. The XRD patterns of the synthesized Pd-NPs clearly mentioned the main characteristic peaks, observed at 39.900°, 46.500°, 67.590°, 81.600°, and 86.720° which corresponded to the indexed planes of the crystals of Pd(0) (111), (200), (220), (311), and (222), respectively.[46]

SEM and EDX analysis

The morphology of the Pd-NPs shown in Figure 2 was determined using scanning electron microscopy (SEM). A thin film of the sample was prepared on a carbon-coated copper grid by simply dropping a very small amount of the sample on the grid. Moreover, the presence of F and Pd in the sample arising from Energy Dispersive X-ray Spectroscopy (EDX) analysis (Fig. 3) provided evidence of the possibility of strong

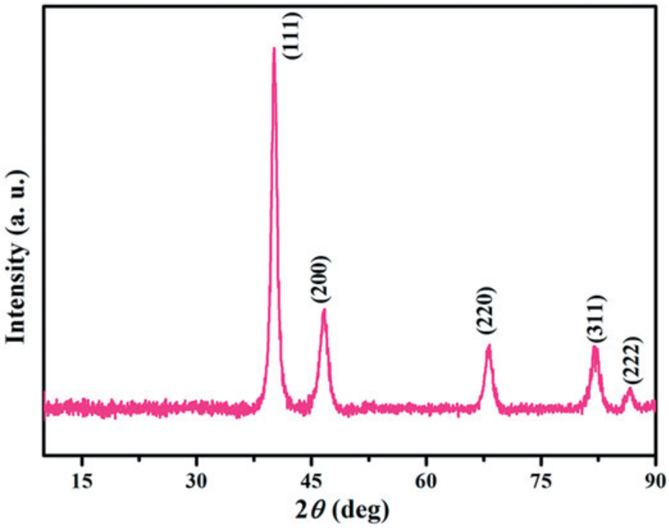


Figure 1. X-ray powder diffraction pattern of synthesized Pd-NPs.

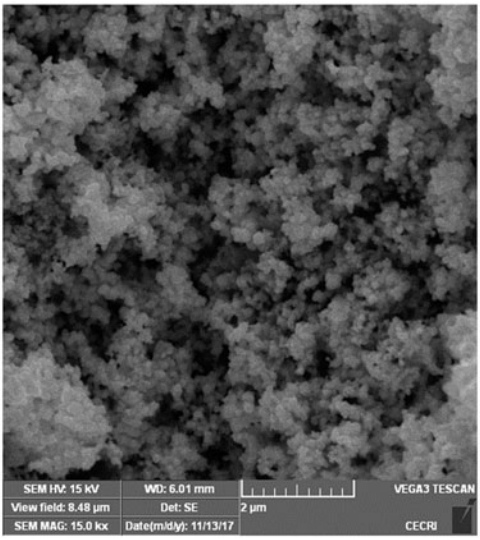


Figure 2. Scanning electron microscopy images of the synthesized Pd-NPs.

coordination or absorption from 1-octyl-1,2,4-triazolium trifluoroacetate ionic liquid on the surface of Pd-NPs even if the samples had gone through the purification procedure.

TEM and SAD analysis

In this study, topology and particle size of the NPs were characterized using transmission electron microscopy (Model Philips CM 200 instrument). The morphology of the synthesized Pd-NPs shown in Figure 4a was determined by transmission electron microscopy (TEM). The solution containing the nanoparticles was diluted and a drop of it was placed on the copper grid and allowed to dry in a vacuum. The diffraction ring

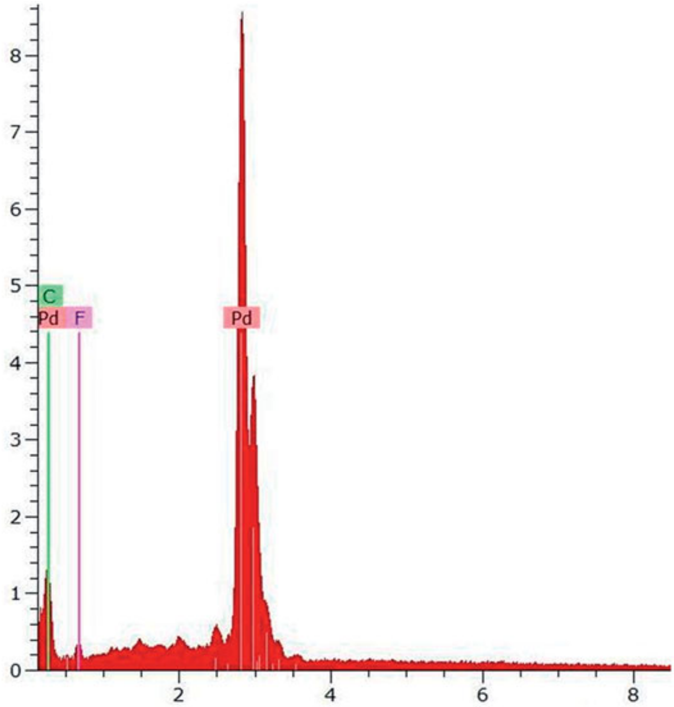


Figure 3. Energy dispersive x-ray spectrum of the synthesized Pd-NPs.

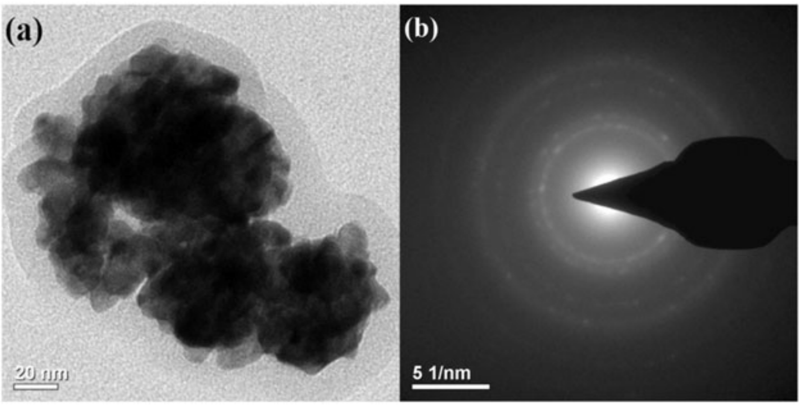
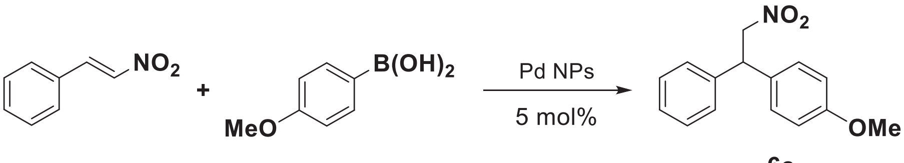


Figure 4. Transmission electron microscopy image of the synthesized Pd-NPs. (a) TEM image at 20 nm. (b) Selected area diffraction (SAD) pattern of Pd-NPs.

patterns from selected area diffraction (SAD) shown in Figure 4b confirmed the crystalline nature of the particles.

Optimization of the addition reaction

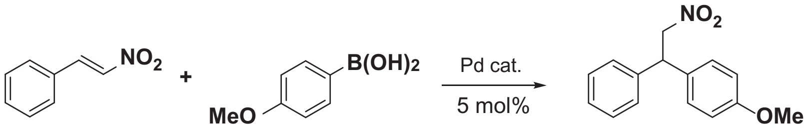
Apart from the synthetic point of view, the diaryl-substituted product of this reaction is important, in particular, due to the presence of this structural unit in a number of pharmaceutical intermediates.[47] Nevertheless, nitrostyrenes are the challenging



4 5 6c

Scheme 3. The model reaction for preparation of 1-methoxy-4-(2-nitro-1-phenylethyl)benzene.

Table 1. Screening of palladium catalysts.[a]



4 5 6c

Entry	Catalyst	Yie
1	Pd(OAc)$_2$	26
2	PdCl2	34
3	Pd2(dba)$_3$	47
4	Pd(TFA)$_2$	40
5	Pd black[b]	29
6	Pd NPs	95

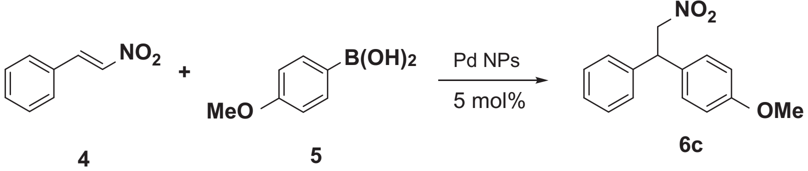
[a] Reaction conditions: Nitrostyrene (1 mmol), 4-methoxy phenylboronic acid (1.5 mmol) and Pd catalyst (5 mol%) in 3 mL MeOH at 40 °C for 3 h.

[b] Instead of ionic liquid methanol is used as a solvent.

substrate for this reaction in addition to boronic acids. Thus, the optimized conditions were determined by the reaction of simple nitrostyrene with 4-methoxy phenylboronic acid, which was selected as a model reaction (Scheme 3). The reaction conditions were optimized on the basis of catalyst study, solvent effect, time, temperature and quantity of catalyst to be used for the synthesis of 1-methoxy-4-(2-nitro-1-phenylethyl) benzene (**6c**).

The catalytic activity of various palladium sources, namely, Pd(OAc)$_2$, PdCl$_2$, Pd$_2$(dba)$_3$, Pd(TFA)$_2$ were screened for the addition reaction of 4-methoxy phenylboronic acid with nitrostyrene to compare the efficiency of the synthesized Pd-NPs. In addition, palladium black was also prepared in the absence of ionic liquid and its catalytic activity is compared in Table 1. Among the all palladium catalyst screened, Pd-NPs prepared in the presence of ionic liquid (Entry 6) gave 95% yield while using 5 mol% of the catalyst at 40 °C for 3 h, whereas entry 1–5 furnished less than 50% yield under identical condition. In order to find the role of solvents on the addition reaction, the model study was carried out using different solvents at various temperatures in the presence of 5 mol% of Pd-NPs as a catalyst. Among the different solvents studied, methanol gave excellent yields. It was evident that the reaction did not progress well at room temperature. However, a slight increase in temperature (40 °C) enhanced the rate of the reaction. Yields of the almost same quantity were obtained when the temperature was raised to 80 °C. The authors observed a maximum conversion (95%) while using methanol as a solvent at 40 °C for 3 h (Table 2, Entry 17). The time mentioned in the

Table 2. Optimization of addition reaction.[a]



Entry	Solvent	Time (h)[b]	Temperature (°C)	Yield (%)[c]
1	Toluene	24	RT	NR
2	Toluene	24	40	57
3	Toluene	24	80	58
4	CH_3CN	24	RT	NR
5	CH_3CN	24	40	52
6	CH_3CN	24	80	49
7	$CHCl_3$	24	RT	NR
8	$CHCl_3$	16	40	39
9	$CHCl_3$	16	80	40
10	CH_2Cl_2	24	RT	NR
11	CH_2Cl_2	16	40	23
12	CH_2Cl_2	16	80	21
13	EtOH	24	RT	NR
14	EtOH	6	40	72
15	EtOH	6	80	72
16	MeOH	24	RT	NR
17	MeOH	3	40	95
18	MeOH	3	80	94
19	THF	24	RT	NR
20	THF	6	40	79
21	THF	6	80	76

NR: no reaction; RT: room temperature.

[a] Reaction conditions: Nitrostyrene (1 mmol), 4-methoxy phenylboronic acid (1.5 mmol) and Pd-NPs (5 mol%).

[b] After complete conversion (confirmed by TLC).

[c] Isolated yields.

Table 3. Effect of quantity of Pd-NPs on addition reaction.[a]

Entry	Catalyst (mol%)	Yield (%)[b]
1	–	NR
2	2	70
3	3	74
4	5	95
5	10	96

NR: no reaction.

[a] Reaction conditions: Nitrostyrene (1 mmol) and 4-methoxy phenylboronic acid (1.5 mmol) in 3 mL MeOH at 40 °C for 3 h.

[b] Isolated yields.

table was periodically monitored and confirmed by TLC after a complete conversion of the reaction.

Next, the authors examined the effect of the amount of Pd-NPs to be used on the model reaction (Scheme 3). The reaction was performed in the presence of various quantities of Pd-NPs (Table 3) by fixing the solvent, time, and temperature as indicated in Table 2. The maximum conversion of the product was obtained using 5 mol% of nanocatalysts in methanol at 40 °C (Table 3, Entry 4). There was no significant increase in the conversion even when the catalyst loading was increased from 5 to 10 mol% (Table 3, Entries 4 and 5). Accordingly, the condition was optimized using 5 mol% of Pd-NPs and a study was made of the addition reaction of various nitrostyrene derivatives with substituted phenylboronic acids in methanol to give the desired products in good to excellent yields. Both electron-withdrawing and electron-donating groups were seen well tolerated for addition reaction. The results have been summarized in Table 4. Thus, the overall catalytic activity was proved to be exceptional for the addition reaction of arylboronic acid to nitrostyrene.

Conclusions

In summary, the authors have developed an environmentally benign Pd-NPs using triazolium based room temperature ionic liquids. The thermal treatment of $Pd(OAc)_2$ in 1-octyl-1,2,4-triazolium trifluoroacetate ionic liquids results in the formation of stable and highly mono-dispersed Pd-NPs. A mild and simple procedure for the addition reaction of arylboronic acid to nitrostyrene has been developed using this Pd-NPs as a catalyst. In view of the mild reaction conditions, simplicity in product separation, catalyst recovery, and reusability, this methodology could find extensive industrial applications.

Experimental section

Synthesis of ionic liquid

1-octyl-1,2,4-triazole (2): To a solution of 1,2,4-triazole (345 mg, 5 mmol) dissolved in THF (5 mL) was added 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) (0.75 mL, 5 mmol) and stirred for 0.5 h. 1-bromooctane (0.87 mL, 5 mmol) was added to this reaction mixture slowly and allowed to stir at room temperature for 1 h. The reaction was monitored by TLC. After complete conversion, the reaction mixture was washed with water (2 × 20 mL) and brine solution. The crude product was purified by column chromatography and the compound **2** was obtained.

1 -octyl-1,2,4-triazole (2)

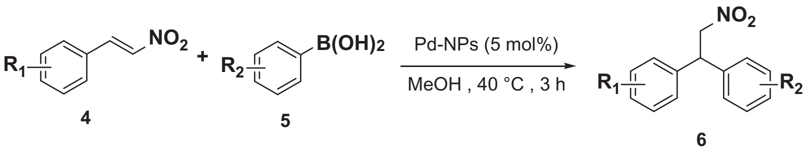
Yield 78%, viscous yellow liquid; ^1H NMR: (400 MHz, $CDCl_3$) δ (ppm): 8.03 (1 H, s), 7.92 (1 H, s), 4.14 (2 H, t, J = 8 Hz), 1.88–1.84 (2 H, m), 1.25 (10 H, t, J = 8 Hz), 0.85 (3 H, t, J = 8 Hz); ^{13}C NMR: (100 MHz, $CDCl_3$) δ (ppm): 151.7, 142.7, 49.7, 31.6, 29.7, 29.0, 28.9, 26.4, 22.5, 14.0; Anal. Calcd. for $C_{10}H_{19}N_3$: C, 66.26; H, 10.56; N, 23.18; Found: C, 65.06; H, 9.18; N, 22.79.

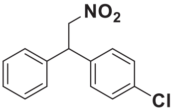
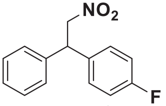
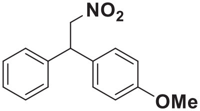
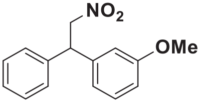
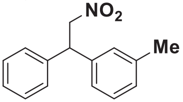
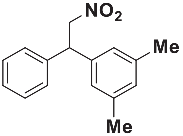
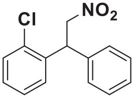
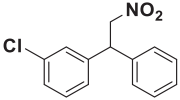
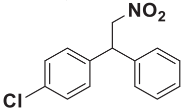
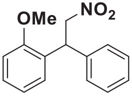
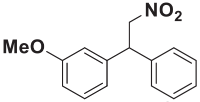
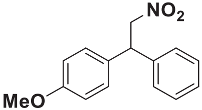
1-octyl-1,2,4-triazolium trifluoroacetate ionic liquid (3): Trifluoroacetic acid (0.38 mL, 5 mmol) was added slowly to a magnetically stirred solution of 1-octyl-1, 2, 4-triazole (906 mg, 5 mmol) in toluene (5 mL) and heated to 80 °C for 12 h (Scheme 1).[24] After complete conversion, the solvent was evaporated in vacuum and the viscous liquid was washed with hexane and dried at 45 °C under vacuum for 2 h to furnish the compound **3.**

1 -octyl-1,2,4-triazolium trifluoroacetate ionic liquid (3)

Yield 89%, viscous yellow liquid; IR (KBr, cm^{-1}): 3418, 2934, 2856, 1675, 1464, 1197, 1134, 803, 719; ^1H NMR: (400 MHz, $CDCl_3$) δ (ppm): 8.44 (1 H, t, J = 4 Hz), 8.09 (1 H,

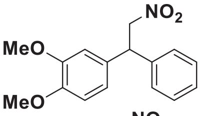
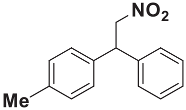
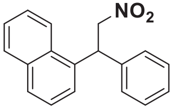
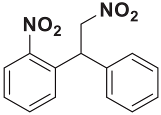
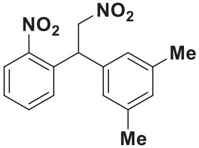
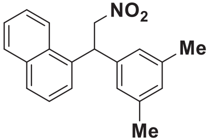
Table 4. Pd-catalyzed addition reaction of arylboronic acids to nitrostyrenes.[a]



S.No	R_1	R_2	Product	6(a–o)	Yield (%)[b]
1	H	4-Cl		6a	80
2	H	4-F		6b	56
3	H	4-OMe		6c	95
4	H	3-OMe		6d	83
5	H	3-Me		6e	91
6	H	3,5-Me		6f	91
7	2-Cl	H		6g	93
8	3-Cl	H		6h	63
9	4-Cl	H		6i	82
10	2-OMe	H		6j	87
11	3-OMe	H		6k	84
12	4-OMe	H		6l	88

(*continued*)

Table 4. Continued.

S.No	R_1	R_2	Product	6(a–o)	Yield (%)[b]
13	3,4-OMe	H		6m	82
14	4-Me	H		6n	85
15	α-naphthyl	H		6o	87
16	2-NO_2	H		6p	82
17	2-NO_2	3,5-Me		6q	90
18	α-naphthyl	3,5-Me		6r	86

[a] Reaction conditions: Nitrostyrene (2 mmol), Phenylboronic acid (3 mmol), and Pd-NPs (5 mol%) in 5 mL MeOH at 40 °C for 3 h.
[b] Isolated yields.

s), 4.22 (2 H, t, J = 8 Hz), 1.91 (2 H, t, J = 8 Hz), 1.30–1.25 (10 H, m), 0.87 (3 H, s); ^{13}C NMR: (100 MHz, $CDCl_3$) δ (ppm): 149.3, 142.0, 50.5, 31.6, 29.5, 28.9, 28.8, 26.3, 22.5, 14.0; Anal. Calcd. for $C_{12}H_{20}F_3N_3O_2$: C, 48.81; H, 6.83; N, 14.23; Found: C, 49.06; H, 6.76; N, 14.41.

Synthesis and isolation of Pd-NPs

Palladium nanoparticles were prepared by simple hydrogen decomposition (1 atm H_2, constant pressure) of $Pd(OAc)_2$ (450 mg, 2 mmol) dissolved in 3.0 mL of 1-octyl-1,2,4-triazolium trifluoroacetate ionic liquid at 75 °C for 1 h to yield a black suspension. Acetone (15–20 mL) was added, and centrifugation of this mixture yielded palladium nanoparticles (79% yield) with a diameter of 9.4 nm. These nanoparticles were washed with acetone and dried in vacuum under reduced pressure (Scheme 2).[39]

General procedure for the synthesis of 1-chloro-4-(2-nitro-1-phenylethyl)benzene (6a)

Pd-NPs (10 mg, 5 mol%) in a 25 mL round bottom flask, was taken with MeOH (5 mL). To this suspension, nitrostyrene (298 mg, 2 mmol) and 4-chloro phenylboronic

Table 5. Reusability of Pd-NPs for addition reaction.[a]

Entry	No. of runs	Yield (%)[b]
1	Fresh	95
2	First	94
3	Second	92
4	Third	92
5	Fourth	90

[a] Reaction conditions: Nitrostyrene (1 mmol) and 4-methoxy phenylboronic acid (1.5 mmol) in 3 mL MeOH at 40 °C for 3 h.

[b] Isolated yields.

acid (470 mg, 3 mmol) were added. The reaction mixture was stirred at 40 °C for 3 h under air atmosphere. Then it was filtered and the solvent was removed by a rotary evaporator under reduced pressure to afford a crude adducts, which was purified using column chromatography on silica gel using 5% ethyl acetate in hexane to give compound **6a.**

1 -chloro-4-(2-nitro-1-phenylethyl)benzene (6a)[47,48]

Yield 80%, pale yellow oil; IR (KBr, cm^{-1}): 3064, 3027, 2915, 1554, 1491, 1376, 1091, 1015, 820, 755; ^1H NMR: (400 MHz, $CDCl_3$) δ (ppm): 7.38–7.28 (5 H, m), 7.24–7.19 (4 H, m), 4.98 (2 H, d, J = 8 Hz), 4.91 (1 H, t, J = 8 Hz); ^{13}C NMR: (100 MHz, $CDCl_3$) δ (ppm): 138.7, 137.7, 133.5, 129.2 (2C), 129.1 (2C), 129.0 (2C), 127.8 (2C), 127.5, 79.0, 48.3.

Reusability study

The recycling potential of palladium nanoparticles was studied by the addition reaction successively in four runs. NPs in this experiment were recycled four times without any loss of activity. This is shown in Table 5. After complete conversion of the reaction, the Pd-NPs were separated from the reaction mixture by a simple filtration procedure and washed with EtOH to remove all organic impurities. The catalyst residue was dried at 45 °C under vacuum and the particles were reused for evaluating the performances in the cycle. The reaction mixture was again filtered for the next use and the crude product was purified using column chromatography to furnish a pure adduct.

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Disclosure statement

The authors announce no competing interest.

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