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Room-Temperature Suzuki-Miyaura Reaction Catalyzed by Palladium Nanoparticles in Lactate-Anion Ionic Liquid

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A palladium nanoparticle catalyst (PdNPs@[Bmim]Lac) has been prepared by a simple, mild and efficient chemical approach using 1-butyl-3-methylimidazolium lactate ([Bmim]Lac) ionic liquid) as a stabilizer. This catalyst exhibits excellent activity, stability, recyclability and simple manipulation in Suzuki-Miyaura reactions at room temperature in air.

Keywords palladium nanoparticles, room temperature, Suzuki-Miyaura reaction, lactate anion, ionic liquid

Introduction

The palladium-catalyzed Suzuki-Miyaura coupling reaction is one of the most powerful tools for the formation of C—C bonds in preparing biaryl compounds, such as natural products, pharmaceuticals, and polymers.[1] Palladium nanoparticles (PdNPs) are attracting much interest due to their enhanced catalytic activity that arises from their high surface area and rotational degrees of freedom caused by their nanoscale dimensions.[2] Nevertheless, PdNPs show a tendency for self-agglomeration, resulting in a decrease of catalytic activity during reaction processes.[3] To circumvent this problem, one of the most attractive methods is currently the preparation of PdNPs in the presence of stabilizers.[4] Ionic liquids (ILs) have emerged as important stabilizing and recyclable agents for metal NPs, simultaneously avoiding the use of highly toxic solvents.[5] Hence, transition metal NPs stabilized by ILs have been extensively employed for hydrogenation, oxidation, C—C coupling reactions, and so on.[6] For instance, ILs with imidazolium cations displaying a high degree of 3-D structural organization have been used as "entropic drivers" (the so-called IL effect) for the preparation of a plethora of well-defined and extensively ordered nanoscale structures.[7] Meanwhile, the anionic component of an IL is also an important factor with regard to controlling of the size and shape of PdNPs.[8] To date, halogen-anion ILs have been predominantly adopted as stabilizers for the preparation of metal NP catalysts for reactions such as Suzuki-Miyaura coupling.[9] However, halides are the most common and persistent contaminants to environment. For example, fluorinated-anion ILs display high cytotoxicity due to their high susceptibility to hydrolysis with the formation of corrosive HF.[10] Furthermore, most Suzuki-Miyaura reactions in ILs typically require an inert atmosphere or elevated temperature with limited substrate scope.[11] From the economic and environmental aspect, ambient temperature catalysis has become high importance, considering both needs for low cost energy and thermal instability of substrates.[12] Thus, there is an urgent need for the development of highly active nanocatalysts stabilized by halogen-free anions ILs which can catalyze Suzuki-Miyaura reaction under mild reaction condition.

In this context, we report herein the desired preparation of a 1-butyl-3-methylimidazolium-lactate IL-stabilized PdNPs catalyst (PdNPs@[Bmim]Lac), which shows high activity in catalyzing the Suzuki-Miyaura reaction at room temperature (r.t.) in air. Lactate was selected as the anion of the IL on the basis of following considerations. First, the naturally-occurring lactate anion is non-toxic and pharmaceutically acceptable, and remains inactive toward microorganisms.[13] Second, the electron-donating hydroxyl and carboxyl groups of the lactate anion are able to interact with surface metal atoms, thus further stabilizing PdNPs.[5b] Third, the hydroxyl group of the lactate anion might be helpful for the formation of monodisperse PdNPs showing enhanced dispersibility in protic solvents.

Experimental

General

Palladium acetate [$Pd(OAc)_2$, $w(Pd) = 47.5\%$, reagent grade], methanol (HPLC grade) and ethanol (anhydrous) were obtained from Acros (Belgium). [Bmim]Lac,

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1-butyl-3-methylimidazolium acetate ([Bmim]CH_3COO), 1-butyl-3-methylimidazolium propionate ([Bmim]C_2H_5COO), 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF_4) and 1-butyl-3-methylimidazolium glycolate ([Bmim]$HOCH_2COO$) ($>$99%, reagent grade) were purchased from Chengjie Co., Ltd (Shanghai, China). Aryl halides (reagent grade) and arylboronic acids (reagent grade) were from Darui Co., Ltd (Shanghai, China). Other reagents (analytic grade) were purchased from Guangzhou Reagent Factory (Guangzhou, China). All chemicals were used as received without further purification.

UV-vis absorption measurement (UV/Vis) spectra were obtained on a Shimadzu UV-2450 spectrophotometer using methanol as solvent. The transmission electron microscopy (TEM) micrographs were recorded on a Tecnal^{TM} G2 F30 transmission electron microscope at 300 kV. Samples were prepared by directly dropping the mixture of PdNPs and IL/ethanol solution onto carbon-coated Cu grids. X-Ray diffraction (XRD) analysis was performed in a Bruke D8 advance by using Cu Kα radiation (λ=0.15418 nm) and operating at 40 kV and 40 mA. X-Ray photoelectron spectroscopy (XPS) measurements were carried on a Thermo Scientific Escalab 250 spectrometer by using non-monochromatic Al Kα radiation and C1s (284.8 eV) as the internal standard. The mixture of PdNPs and IL was coated on the glass slice for XPS and XRD analysis after the removal of ethanol by a rotary evaporator at r.t. Melting points were recorded on an Electrothermal X6 microscopic digital melting point apparatus. Products of Suzuki-Miyaura reactions were analyzed by NMR (Bruker DRX 400 MHz instrument; DMSO-d_6 as solvent and TMS as the internal standard) and gas chromatography-mass spectrometry (GC-MS, Shimadzu QP 2010; capillary column: 30 m×0.25 mm×0.25 μm, helium as the carrier gas and identified by the NIST 08 MS library). The palladium contents of the samples were determined quantitatively by atomic absorption spectroscopy (AAS) on a HITACHI Z-5000 instrument.

Preparation of PdNPs@[Bmim]Lac

0.3 mmol of $Pd(OAc)_2$, 60 mL of EtOH and 6.0 mmol of [Bmim]Lac were added to a 150 mL round-bottom flask and stirred at r.t. condition. The color of reaction mixture changed from bright yellow to black indicating the achievement of PdNPs@[Bmim]Lac.

General procedure for the Suzuki-Miyaura reaction

Aryl halide (1.0 mmol), arylboronic acid (1.1 mmol), $Na_3PO_4 \cdot 12H_2O$ (3.0 mmol), prepared PdNPs@[Bmim]Lac (1.0 mol% Pd) and $EtOH/H_2O$ (V : V=2 : 1; 6.0 mL) were added to a 15 mL round-bottom flask and stirred at r.t. in air. The end of reaction was tracked by TLC (thin layer chromatography). After completion of the reaction, the mixture was extracted by hexane (15 mL×3) after the removal of the solvent by a rotary evaporator. The combined extracts were dried with anhydrous Na_2SO_4 overnight, filtered and the hexane was removed by a rotary evaporator. The products were further purified by recrystallization with ethanol. The identification was conducted by ^{1}H, ^{13}C NMR and GC-MS analysis (see Supporting Information).

Recyclability of the catalyst

The recyclability of the catalytic system was investigated by choosing the coupling of 4-bromoanisole with phenylboronic acid as a model reaction. After one run, the reaction mixture was extracted by hexane (15 mL×3) after the removal of the solvent by a rotary evaporator. Then, the resulting residual mixture was used for the next run.

Results and Discussion

Characterization of PdNPs@[Bmim]Lac

The reduction progress of Pd(II) ion to Pd(0) in the preparation of PdNPs@[Bmim]Lac was confirmed by UV/Vis absorption measurement (Figure 1). UV/Vis absorption spectra show two characteristic absorption peaks at 249 and 380 nm before reduction, corresponding to the absorbances of imidazolium ring[14] of IL and Pd(II) ions.[15] With the reduction proceeding, the peak at 380 nm reduced gradually but the absorbance increased due to the enhancement of surface plasmon scattering.[16] The peak at 380 nm disappeared completely and a broad continuous absorption was observed, indicating complete reduction of Pd(II) ions to Pd(0).[17]

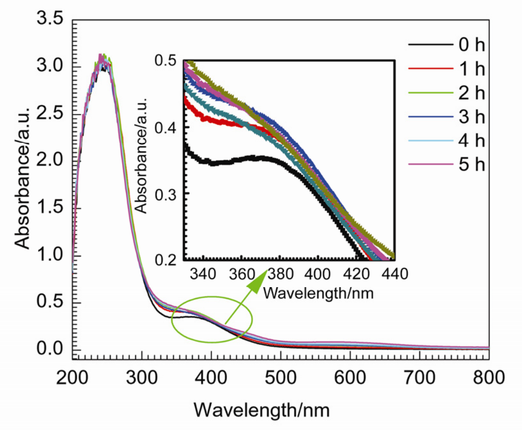


Figure 1 UV/Vis spectra of the mixture at different reduction stages.

TEM shows that the obtained PdNPs (Figure 2a) are well dispersed with an average particle size of (1.50±0.39) nm. Several crystalline planes were distinguishable and the interplanar distances were measured from the Fast Fourier Transform (FFT) (Figure 2b) and the corresponding crystalline planes were specified. The interplanar distance with the value of 0.228 nm matches well with (111) planes in face-centered cubic (fcc) Pd.[18] According to "lattice-matching model",[19] lactate anions are effective for coordinating the Pd(111) face of a metal nanocluster.

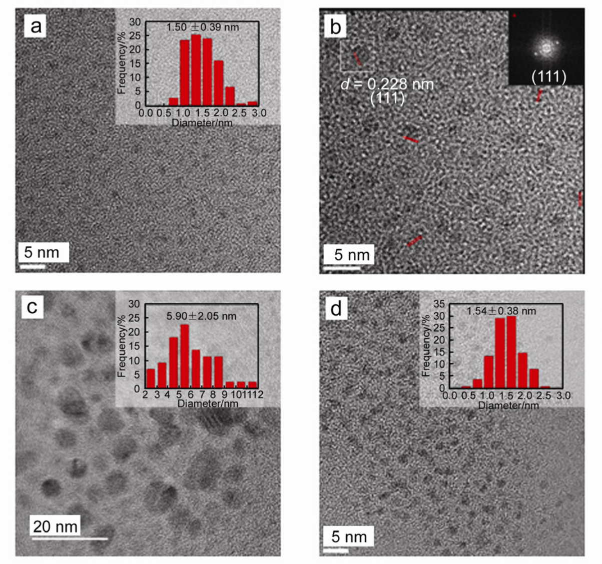


Figure 2 (a) TEM image of fresh PdNPs@[Bmim]Lac catalyst; (b) HRTEM image and Fast Fourier Transforms (FFT, top right images); (c) TEM image of $Pd(OAc)_2$ and [Bmim]Lac after cross-coupling (Table 2, Entry 2); (d) TEM image of PdNPs@[Bmim]Lac catalyst after six cycles.

As shown in Figure 3, XRD pattern of the PdNPs does not show any diffraction peak of Pd metal. The Bragg reflection at 21.85° corresponds to diffraction peak of SiO_2 of glass slice.[20] TEM analysis shows the presence of PdNPs of about 1.5 nm. The particle size of PdNPs might be too small to form long range ordering so that XRD diffraction, which works on periodicity, could not be detected.[18,21]

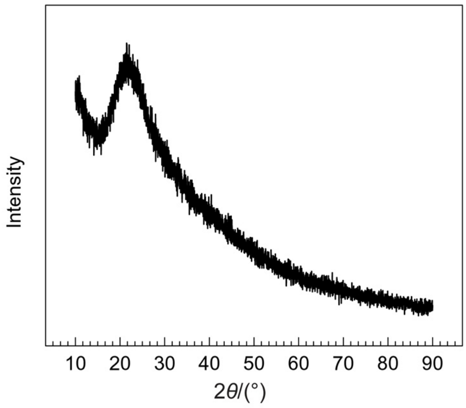


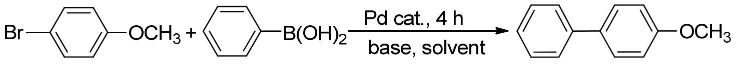
Figure 3 XRD patterns of PdNPs@[Bmim]Lac on glass slice.

Catalytic studies

The coupling of 4-bromoanisole with phenylboronic acid was employed as a model reaction for screening of the parameters of the Suzuki-Miyaura reaction catalyzed by PdNPs@[Bmim]Lac (Table 1). Initially, various solvents were screened, keeping the other parameters fixed, those were Na_2CO_3 as the base, 70 ℃ as the reaction temperature, and PdNPs@[Bmim]Lac (2.0 mol% Pd) as the catalyst. Anhydrous solvents such as toluene (PhMe), *N*,*N*-dimethylformamide (DMF) and EtOH give low yields of less than 30% (Entries 1—3). Organic/aqueous mixed solvent enhances the yield significantly (Entry 4). Water plays an important role in the reactions, having a solubilizing effect on the inorganic bases and aiding the dispersibility of the IL with hydroxyl groups. Similar result has been observed in literature.[22] A mixed solvent of $EtOH/H_2O$ ($V:V=2:1$) achieves a good yield of 79% (Entry 4). So $EtOH/H_2O$ was then used for the screening of different bases (Entries 5—9). The highest yield of 99% was obtained when $Na_3PO_4{\cdot}12H_2O$ was used (Entry 9). Notably, since EtOH was employed as the solvent in both the preparation of the catalyst and the coupling reaction steps, the prepared catalysis system can be directly deployed in the coupling reaction without further work-up when $EtOH/H_2O$ was used. In the investigation of reaction temperature (Entries 10—12), it is gratifying to find that the coupling proceeds well at r.t., giving 99% yield (Entry 12). Finally, we assessed the influence of catalyst loading on this reaction (Entries 13—18). The coupling reaction does not proceed in the absence of the Pd catalyst (Entry 13). The low loading of PdNPs can catalyze this reaction prominently (Entry 14), but it is time-consuming to obtain the acceptable product yield (Entry 15). Hence, 1.0 mol% was the suitable loading of catalyst while maintaining a 99% yield of the product (Entry 18).

In order to gain further insights into the catalytic mechanism of as prepared PdNPs catalyst, a series of control experiments were carried out under optimized conditions (Table 2), namely catalyst (1.0 mol% of Pd), $EtOH/H_2O$ ($V:V=2:1$) as solvent and $Na_3PO_4{\cdot}12H_2O$ as a base at r.t. At first, $Pd(OAc)_2$ without ILs offers a moderate yield with the formation of less-active palladium black (Entry 1). Direct addition of $Pd(OAc)_2$ and [Bmim]Lac to the reaction system leads to a low yield of 63% (Entry 2). Under this condition, the Pd(II) species is reduced by ethanol to Pd metal with uncontrolled size (Figure 2c). These findings clearly indicate that very small size of the prepared PdNPs plays an important role for the catalytic activity. Then, the effect of a series of ILs with different anions was evaluated. The use of acetate, propionate, and tetrafluoroborate anions instead of lactate anion results in apparently lower yields (Entries 3—5). Interestingly, yield of 99% can be obtained by the use of PdNPs@[Bmim]$HOCH_2COO$ (Entry 6) due to the similar structure of glycolate anion as that of lactate anion (Entry 7). Low yield of 68% is obtained with the formation of Pd black while NaLac was used for the replacement of [Bmim]Lac (Entry 8). It has reported that a three-dimensional network formed by anions and the imidazolium ring cations of ILs brings metal NPs with the needed electrostatic and steric stabilization.[9a] Hence, it is thought that [Bmim]Lac comprised with the hydroxyl group is able to strengthen

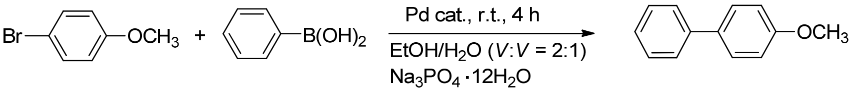
Table 1 Optimization of the reaction conditions[a]



Entry	Base	Solvent (*V* ∶ *V*)	*T*/℃	[Pd]/mol%	Yield[b]/%
1	Na_2CO_3	PhMe	70	2.0	16
2	Na_2CO_3	DMF	70	2.0	18
3	Na_2CO_3	EtOH	70	2.0	25
4	Na_2CO_3	$EtOH/H_2O$ (2 ∶ 1)	70	2.0	79
5	K_2CO_3	$EtOH/H_2O$ (2 ∶ 1)	70	2.0	68
6	KOAc	$EtOH/H_2O$ (2 ∶ 1)	70	2.0	76
7	K_3PO_4•$3H_2O$	$EtOH/H_2O$ (2 ∶ 1)	70	2.0	79
8	NaOH	$EtOH/H_2O$ (2 ∶ 1)	70	2.0	89
9	Na_3PO_4•$12H_2O$	$EtOH/H_2O$ (2 ∶ 1)	70	2.0	99
10	Na_3PO_4•$12H_2O$	$EtOH/H_2O$ (2 ∶ 1)	60	2.0	99
11	Na_3PO_4•$12H_2O$	$EtOH/H_2O$ (2 ∶ 1)	40	2.0	99
12	Na_3PO_4•$12H_2O$	$EtOH/H_2O$ (2 ∶ 1)	25	2.0	99
13	Na_3PO_4•$12H_2O$	$EtOH/H_2O$ (2 ∶ 1)	25	0	0
14	Na_3PO_4•$12H_2O$	$EtOH/H_2O$ (2:1)	25	0.25	40
15[c]	Na_3PO_4•$12H_2O$	$EtOH/H_2O$ (2 ∶ :1)	25	0.25	79
16	Na_3PO_4•$12H_2O$	$EtOH/H_2O$ (2 ∶ 1)	25	0.5	90
17	Na_3PO_4•$12H_2O$	$EtOH/H_2O$ (2 ∶ 1)	25	0.75	93
18	Na_3PO_4•$12H_2O$	$EtOH/H_2O$ (2 ∶ 1)	25	1.0	99

[a] Conditions: 4-bromoanisole (1.0 mmol), phenylboronic acid (1.1 mmol), base (3.0 mmol), solvent (6.0 mL) in air for 4 h. [b] Determined by GC analysis (hexamethylbenzene as an internal standard). [c] The reaction time is 8 h.

Table 2 Results of control experiments[a]



Entry	Pd catalyst	ILs or salts		Yield[b]/%
		Cation	Anion	
1	$Pd(OAc)_2$	—	—	80
2	$Pd(OAc)_2$ and [Bmim]Lac	$[Bmim]^+$	Lac^-	63
3	PdNPs@[Bmim]CH_3COO	$[Bmim]^+$	CH_3COO^-	81
4	PdNPs@[Bmim]C_2H_5COO	$[Bmim]^+$	$C_2H_5COO^-$	79
5	PdNPs@[Bmim]BF_4	$[Bmim]^+$	BF_4^-	58
6	PdNPs@[Bmim]$HOCH_2COO$	$[Bmim]^+$	$HOCH_2COO^-$	99
7	PdNPs@[Bmim]Lac	$[Bmim]^+$	Lac^-	99
8	$Pd(OAc)_2$@NaLac	Na^+	Lac^-	68

[a] Conditions: 4-bromoanisole (1.0 mmol), phenylboronic acid (1.1 mmol), Na_3PO_4•$12H_2O$ (3.0 mmol), $EtOH/H_2O$ (*V* ∶ *V*=2 ∶ 1, 6.0 mL), and catalyst (1.0 mol% of Pd) in air for 4 h. [b] Determined by GC analysis (hexamethylbenzene as an internal standard).

this network. Moreover, the nature of the Pd surface was analyzed by XPS (Figure 4) as both the catalyst preparation and the coupling reaction were carried out in air. Peaks at 334.2 and 339.4 eV can be attributed to Pd $3d_{5/2}$ and Pd $3d_{3/2}$ of Pd(0).[23] Peaks at 335.5 and 340.8 eV corresponded to binding energies of Pd $3d_{5/2}$ and Pd $3d_{3/2}$ of Pd(II) in PdO, respectively.[24] It is found that partial oxidation of the PdNP surfaces to PdO occurred during the reaction. However, no obvious detrimental effect on the activity of the PdNPs was observed as an oxide layer has a significant stabilizing effect on metal NPs[9b] and fresh PdNP surfaces can be continuously generated through reduction by the ethanol solvent.[25]

To test the generality of this PdNPs@[Bmim]Lac catalyst, couplings of various aryl halides and aryl

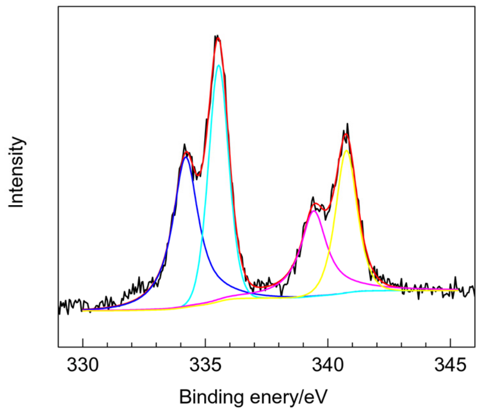
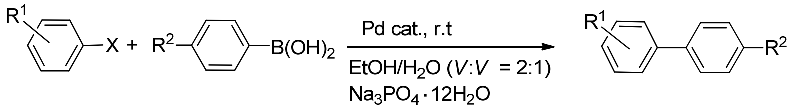
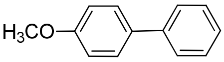
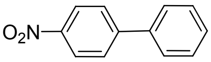
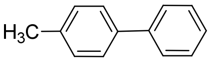
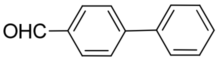
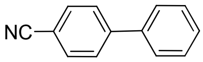
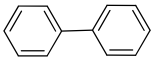
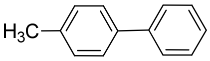
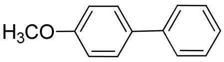
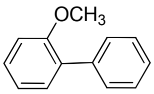


Figure 4 XPS spectra of PdNPs@[Bmim]Lac.

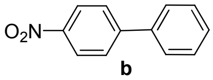
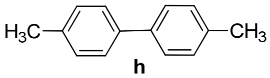
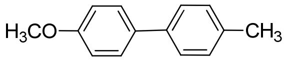
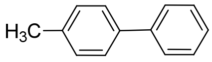
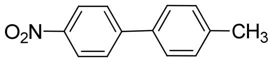
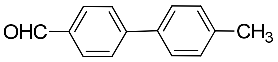
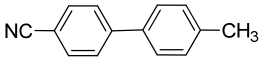
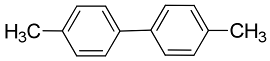
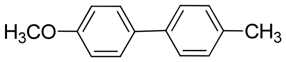
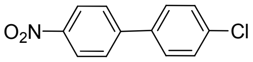
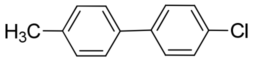
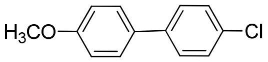
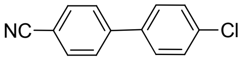
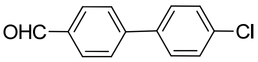
boronic acids were investigated under the optimized conditions (Table 3). It is noteworthy that the PdNPs@[Bmim]Lac catalyst shows high efficiency and good functional group tolerance. Aryl bromides and iodides bearing electron-donating (CH_3, OCH_3), electron-neutral (H), and electron-withdrawing (NO_2, CHO, CN) groups are all efficiently coupled with phenylboronic acid to afford the desired biaryls in good to excellent yields at r.t. (Entries 1—10). However, 2-bromoanisole is coupled in a lower yield due to the effect of steric hindrance (Entry 8 vs. Energy 9). In addition, the coupling reaction can be efficiently accomplished with aryl boronic acids bearing electron-donating (CH_3) or electron-withdrawing groups (Cl) (Entries 11—23).

Table 3 Reaction scope[a]



Entry	X	R^1	R^2	Time/h	Product	Yield[b]/%
1	I	4-OCH_3	H	4	 **a**	99
2	I	4-NO_2	H	4	 **b**	93
3	I	4-CH_3	H	4	 **c**	99
4	Br	4-CHO	H	4	 **d**	98
5	Br	4-CN	H	4	 **e**	93
6	Br	H	H	4	 **f**	94
7	Br	4-CH_3	H	4	 **c**	92
8	Br	4-OCH_3	H	4	 **a**	99
9	Br	2-OCH_3	H	6	 **g**	87

Continued

Entry	X	R^1	R^2	Time/h	Product	Yield[b]/%
10	Br	4-NO_2	H	4	 b	98
11	I	4-CH_3	4-CH_3	4	 h	99
12	I	4-OCH_3	4-CH_3	4	 i	92
13	Br	H	4-CH_3	4	 c	90
14	Br	4-NO_2	4-CH_3	4	 j	97
15	Br	4-CHO	4-CH_3	4	 k	99
16	Br	4-CN	4-CH_3	4	 l	90
17	Br	4-CH_3	4-CH_3	4	 h	86
18	Br	4-OCH_3	4-CH_3	5	 i i	93
19	I	4-NO_2	4-Cl	4	 m	90
20	Br	4-CH_3	4-Cl	4	 n	91
21	Br	4-OCH_3	4-Cl	4	 o	94
22	Br	4-CN	4-Cl	4	 p	84
23	Br	4-CHO	4-Cl	4	 q	91

[a] Conditions: aryl halide (1.0 mmol), arylboronic acid (1.1 mmol), $Na_3PO_4 \cdot 12H_2O$ (3.0 mmol), $EtOH/H_2O$ ($V:V=2:1$, 6.0 mL), and PdNPs@[Bmim]Lac (1.0 mol% of Pd) in air. [b] Isolated yield based on aryl halide.

To the best of our knowledge, this PdNPs@[Bmim]Lac system exhibits outstanding catalytic activity among the reported catalysts used for the Suzuki-Miyaura coupling reaction in ILs in terms of catalyst loading (1.0 mol% Pd) at r.t. condition. PdNPs or Pd-ligand complexes in ILs have been widely reported to efficiently catalyze the Suzuki-Miyaura coupling of aryl bromides and iodides with phenylboronic acid. However, these coupling reactions require high temperatures up to 100 ℃, high catalyst loadings, or environmentally unfriendly solvents.[26] The activity of the present catalyst is also comparable to that of a recently reported PdNPs-phosphine ligand catalyst.[27] It is thought that the carboxyl and hydroxyl groups of the lactate anion can provide sufficient stabilization and aid the dispersion of the PdNPs, as hydroxyl-functionalized ILs have been demonstrated to facilitate the formation of near-monodisperse NPs and to enhance their stability.[18,28]

The reusability of our prepared catalyst was next investigated in the coupling of 4-bromoanisole with phenylboronic acid under the optimized condition. As shown in Figure 5, the catalyst is still of high catalytic activity without obvious decrease. A TEM image of the catalyst after the sixth run (Figure 2d) indicates that the mean diameter of the NPs (1.54±0.38 nm) is very close to that of the fresh sample (Figure 2a, 1.50±0.39 nm). AAS shows that about 0.2% of the total palladium appears in the hexane extract. It is interesting to see that the recovered catalyst after eight runs could still give the similar yield of product as fresh catalyst at the longer reaction time (9th run).

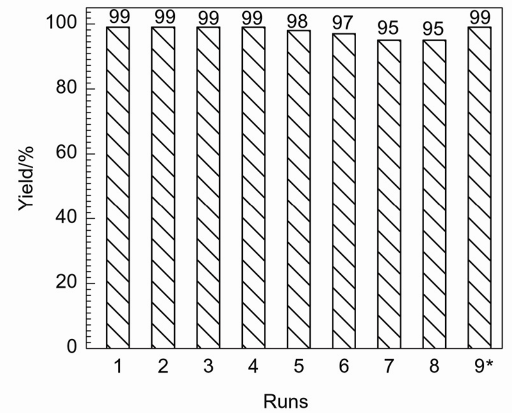


Figure 5 Recycling tests for the model reaction. Reaction conditions: 4-bromoanisole (1.0 mmol), phenylboronic acid (1.1 mmol), $Na_3PO_4 \cdot 12H_2O$ (3.0 mmol), $EtOH/H_2O$ ($V:V=2:1$; 6.0 mL) and catalyst (1.0 mol% of Pd) in air for 4 h; Isolated yield. *: The reaction time is 6 h.

Conclusions

In conclusion, a PdNPs catalyst (PdNPs@[Bmim]-Lac) stabilized by an IL with a natural, reusable, and non-toxic lactate anion has been prepared by a very simple method under mild conditions. It exhibits high catalytic activity in promoting Suzuki-Miyaura reactions at r.t. in air with an environmentally friendly solvent system. The concept of designing new metal NP catalysts employing ILs based on natural anions with coordinating and protecting groups is attractive, which would offer good prospects for the development of highly efficient, stable, and recyclable catalysts for coupling reactions. Further studies aimed at a series of organic transformations using other renewable ILs to stabilize metal NPs as well as delineation of the relevant mechanism, are currently underway in our laboratories.

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