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Imidazolium ionic liquid-tagged palladium complex: an efficient catalyst for the Heck and Suzuki reactions in aqueous media†

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An air stable, water soluble, and efficient ionic liquid-tagged Schiff base palladium complex was prepared. The synthesized complex was well characterized by NMR, mass spectrometry, FT-IR, UV-visible spectroscopy and powder X-ray diffraction. The complex was used as a catalyst for the Suzuki and Heck crosscoupling reactions in water. Good to excellent yields were achieved using a modest amount of the catalyst. In addition, the catalyst can be easily reused and recycled for six steps without much loss in activity, exhibiting an example of sustainable and green methodology.

Introduction

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Palladium-catalyzed cross-coupling reactions have made a noteworthy contribution to organic synthesis as they are used to build C-C bonds.¹⁻⁴ An intriguing aspect of palladium catalysis is its broad application in synthesis; it has played a pivotal role in the synthesis of fine chemicals and advanced functional materials.⁵ Palladium-catalyzed C-C coupling reactions without the use of any ligands have been reported, but the major drawbacks associated with them are the use of toxic solvents and the requirement for high temperature and long reaction time.⁶⁻⁸ There has always been a demand for the development of a robust, efficient and cost effective catalyst that can circumvent the limitations of the existing catalysts.⁹⁻¹¹ Moreover, environmental concerns and economic considerations also make it essential to develop catalytic systems that can be recovered and recycled, especially when noxious transition metals are involved.12-14

From the standpoint of green chemistry, water is known to be a potential replacement for organic solvents.^{15–17} The major advantages associated with water are its low cost, non-flammability and low toxicity, and there is no need to desiccate substrates prior to the reaction.¹⁸ Combining the use of water as a solvent with hydrophilic metal catalysts results in easy separation and recycling of the catalyst from the product. In general, it has been observed that neutral catalysts are not retained in water and are lost during product isolation. Therefore, an effective approach is to use metal complexes with charged groups to avoid catalyst leaching into the organic layer.¹⁹

Ionic liquids are salts which have melting points below the boiling point of water, and they are solely composed of ions in their molten state. They have been termed 'designer solvents', as their properties, such as the vapor pressure, thermal stability, solubility, solvating ability etc., can be tuned as needed by appropriately varying the combination of ions. Chemists have initially focused on using them as alternative solvents to volatile organic solvents in various organic transformations.²⁰⁻²² Presently, ionic liquid chemistry is on the cutting edge of the development of sustainable processes, and has gained wide recognition due to the use of ionic liquids in a diverse range of applications.^{23,24} The concept of functionalized ionic liquids (FILs), through the incorporation of additional functional groups as part of the cation and/or anion, has recently gained remarkable interest.²⁵ FILs that are obtained by incorporating a coordination center serve a dual purpose as an immobilization solvent and a ligand to the catalyst.²⁶ Many ligands tethered to imidazolium-based ionic liquids have been reported, however, these are not room temperature ionic liquids, and needed to be dissolved in another ionic liquid for catalytic applications (Fig. 1).²⁷⁻²⁹ Wei et al. reported SiO₂-supported



Fig. 1 Ligands tethered to the imidazolium-based ionic liquid.

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imidazolium ionic liquid-immobilized PdEDTA as an efficient and reusable catalyst for the Suzuki reaction in water.³⁰ The catalytic system is solid and provides a semi-homogeneous environment for the reaction. The advantage of these types of catalysts is that they are strongly retained during product extraction.

Metal complexes of Schiff bases are the subject of detailed investigation because of their wide applications in the fields of synthesis and catalysis.³¹ As there has been extensive research focused on the modification of Schiff base ligands, and as an extension to our research on the development of ionic liquidtagged Schiff bases,³² we became interested in the synthesis of water soluble ionic liquid-tagged metal complexes, and their use as catalysts for organic transformations. Our efforts have aimed to establish methodology for C-C coupling reactions using an efficient and reusable catalyst in water and air, making the process green and economically viable. Herein, we report the synthesis and characterization of a novel imidazolium ionic liquid-tagged Schiff base complex of palladium, and its catalytic application in the Heck and Suzuki reactions in aqueous media. In comparison to other reported palladium catalyzed reactions in aqueous media,^{33,34} the catalyst works well under these conditions for water insoluble arvl halides in both the Heck and Suzuki reactions, without the aid of a phase transfer catalyst or organic solvents.

Results and discussion

Synthesis of the imidazolium ionic liquid-tagged Schiff base (4) was achieved, as depicted in Scheme 1. Selective O-alkylation of 2,4-dihydroxybenzaldehyde (1) with 1,3-dibromopropane gave 4-(3-bromopropoxy)-2-hydroxybenzaldehyde (2), which on further reaction with 1-methylimidazole resulted in the imidazolium ionic liquid-tagged aldehyde 3 in almost quantitative yield. Condensation of 3 with aniline in ethanol gave the imidazolium ionic liquid-tagged Schiff base 4 in 68% yield.32 The structure of 4 was confirmed by IR, NMR and mass spectrometry data. The FT-IR spectrum of 4 exhibited absorption bands at 1620 cm⁻¹ (C=N stretch) and 3441 cm⁻¹ (OH stretch). In the ¹H NMR spectrum of 4, a peak representing the azomethine proton (CH=N) appeared at δ 8.79, and the hydroxyl proton resonated at δ 13.77. Peaks corresponding to other protons were also shown. A peak at m/z 336.3 in the ESI-MS spectrum of 4 corresponding to the $[M - Br]^+$ ion further confirmed the structure of 4.



Scheme 1 Synthesis of the ionic liquid-tagged Schiff base.



Scheme 2 Synthesis of the ionic liquid-tagged palladium complex.

After successful synthesis of the imidazolium ionic liquidtagged Schiff base 4, it was allowed to react with palladium acetate in ethanol for 4 h to give the desired imidazolium ionic liquid-tagged palladium complex 5 in 80% yield (Scheme 2). The structure of palladium complex 5 was established by spectroscopic and mass spectrometry analysis. In the FTIR spectrum of 5, the azomethine peak was shifted towards a lower frequency than in 4, to 1596 cm⁻¹, and the peak in the region of 3400 cm⁻¹ (OH stretch) in the spectrum of 4 disappeared, which indicated that the ligand had coordinated with the metal ion through the nitrogen of the C=N group.³⁵ The ¹H and ¹³C NMR spectra of 5 were consistent with the structure of the complex. In the ¹H NMR spectrum of 5, the shift of the peak for the azomethine proton to δ 7.93 (Fig. 6, ESI[†]) and the absence of a peak for the hydroxyl proton suggested that complete complexation with the metal had occurred through the nitrogen of the C=N group and oxygen of the OH group. The MALDI mass spectrum of 5 showed a peak at m/z 777.32 that corresponds to the $[M + H - 2Br]^+$ ion (Fig. 8, ESI[†]).

The electronic spectra of 4 and the complex 5 were recorded using distilled DMSO as solvent. The free ligand 4 exhibited two absorption bands at 280 nm and 321 nm, which can be attributed to the π - π^* and n- π^* transitions of the ligand. The shift of these bands towards shorter wavelengths (264 and 304 nm, respectively), and the appearance of a new band at 395 nm in the absorption spectrum of 5 suggested complexation of 4 with palladium. The powder XRD pattern of 4 showed sharp peaks, revealing its crystalline nature (Fig. 4, ESI[†]). On complexation with the metal, the intensity of the peaks in the XRD patterns diminished and line broadening was observed, indicating a change in nature from a crystalline to amorphous state.36 The powder XRD pattern of the complex was also recorded after heating it at 200 °C for 4 h, and it was found that there was no significant change, indicating the high thermal stability of 5.

We next focused our attention on exploring the catalytic applications of 5 for carbon–carbon bond forming (Heck and Suzuki) reactions in aqueous media. Initially, the reaction conditions for the Heck reaction were optimized by performing a model reaction between iodobenzene (**6a**) and benzyl acrylate (**7a**). The results of the different reaction conditions are summarized in Table 1. It was found that carrying out the reaction at 80 °C with 1 mol% of 5 in the presence of K_2CO_3 gave benzyl cinnamate (**8aa**') in 96% yield (Table 1, entry 6). The use of an organic base, such as triethylamine, resulted in a

Table 1 Optimization of the reaction conditions for the Heck reaction catalyzed by 5^a



^{*a*} Reaction conditions: **6a** (1 mmol), **7a** (2 mmol), **5** (x mol%), base (2 mmol), water (2 mL), 4 h. ^{*b*} Isolated yield.



Scheme 3 Heck reaction catalyzed by 5 in aqueous medium.

poor yield of **8aa**', which may be attributed to the poor solubility of triethylamine in aqueous media.

With the optimized reaction conditions in hand, the scope of the Heck reaction was investigated by employing substituted aryl halides 6a-g to react with substituted olefins 7a'-f' (Scheme 3). Aryl iodides with electron-donating methyl and methoxy groups or an electron-withdrawing nitro group both reacted well under these conditions to give the desired coupled products in excellent yields (Table 2, entries 11-16). Similarly, different substituted alkenes also reacted smoothly to afford the corresponding coupled products in excellent yields. It is worth mentioning that the presence of electronwithdrawing groups on both substrates resulted in better yields compared to substrates bearing electron-donating groups. The more demanding substrates, viz. aryl bromides and aryl chlorides, were also allowed to react with styrene and benzyl acrylate under these conditions (Table 2, entries 2-3 and 6-7). To our delight, heteroaryl iodides, such as 2-iodothiophene (6e), also underwent Heck coupling with 7a' to give the corresponding coupled product 8ea' in 82% yield (Table 2, entry 17). The catalyst was found to be very effective for various substrates, including heteroaromatic halides, and gave the coupled products in good to excellent yields (76-98%) in a short reaction time. The identities of the products were confirmed by their melting points and ¹H and ¹³C NMR data, which were found to be consistent with reported values (ESI⁺).

 Table 2
 Heck reaction between aryl halides and alkenes catalyzed by 5

 in water^a
 Image: second se

S. no.	Х	Ar	R	Product	Time (h)	Yield ^b (%)
1	Ι	C_6H_5	COOCH ₂ C ₆ H ₅	8aa'	4.0	96
2	Br	C_6H_5	COOCH ₂ C ₆ H ₅	8aa'	5.5	86
3	Cl	C_6H_5	COOCH ₂ C ₆ H ₅	8aa'	6.0	82
4	Ι	C_6H_5	COOCH ₃	8ab′	3.5	96
5	Ι	C_6H_5	C ₆ H ₅	8ac′	5.5	80
6	Br	C_6H_5	C_6H_5	8ac′	6.0	79
7	Cl	C_6H_5	C_6H_5	8ac′	6.5	76
8	Ι	C_6H_5	4-CH ₃ C ₆ H ₅	8ad′	4.5	82
9	Ι	C_6H_5	4-ClC ₆ H ₅	8ae'	4.5	81
10	Ι	C_6H_5	$4-BrC_6H_5$	8af'	4.5	83
11	Ι	$4-CH_3C_6H_4$	COOCH ₂ C ₆ H ₅	8ba′	4.5	80
12	Ι	$4-NO_2C_6H_4$	COOCH ₂ C ₆ H ₅	8ca'	4.0	98
13	Ι	$4-NO_2C_6H_4$	C ₆ H ₅	8cc′	4.5	88
14	Ι	$4-NO_2C_6H_4$	4-CH ₃ C ₆ H ₅	8cd′	5.0	81
15	Ι	$4-NO_2C_6H_4$	4-ClC ₆ H ₅	8ce'	5.0	78
16	Ι	4-OCH ₃ C ₆ H ₄	COOCH ₂ C ₆ H ₅	8da'	5.0	86
17	Ι	2-C ₄ H ₃ S	COOCH ₂ C ₆ H ₅	8ea'	6.0	82

^{*a*} Reaction conditions: aryl halide (1.0 mmol), alkene (2.0 mmol), 5 (1 mol%), K_2CO_3 (2.0 mmol), deionized water (2 mL). ^{*b*} Isolated yield.

Table 3 Optimization of the reaction conditions for the Suzuki reaction catalyzed by $\mathbf{5}^a$

	+ (HO) ₂ B	5 Base, H₂O, r.t.			
6a	9a′		10aa′		
Entry	5 (mol%)	Base	Yield ^b (%)		
1	0.1	Et_3N	69		
2	0.1	NaOH	68		
3	0.1	$NaHCO_3$	71		
4	0.1	Cs_2CO_3	76		
5	0.1	K ₂ CO ₃	80		
6	0.5	K_2CO_3	80		
7	1	K_2CO_3	81		
8	3	K_2CO_3	82		
9	0.01	K_2CO_3	80		

^{*a*} Reaction conditions: **6a** (1.0 mmol), **9a**' (1.2 mmol), **5** (x mol%), base (2.0 mmol), deionized water (2 mL), 30 min. ^{*b*} Isolated yield.

Encouraged by the excellent results obtained by using 5 as a catalyst for the Heck reaction in aqueous media, we set out to optimize the reaction conditions for the Suzuki reaction in aqueous media. As the Suzuki reaction is largely affected by the amount of catalyst and the type of base used, we optimized the reaction conditions using the reaction between iodobenzene (6a) and phenylboronic acid (9a') to give biphenyl (10aa') as a model reaction. The results from various experiments are summarized in Table 3. It was found that using 0.1 mol% of 5 in the presence of K_2CO_3 as the base were the most suitable conditions for an efficient conversion at room temperature with an excellent yield of 10aa' (Table 3, entry 5). The yield of 10aa' was not affected much by increasing the concentration of the catalyst up to 3 mol% (Table 3, entries 5–8). Although 10aa' was obtained in excellent yield (80%) using 0.01 mol% of Scheme 4 Suzuki reaction catalyzed by 5 in aqueous medium.

Table 4Suzuki reaction between aryl halides (6) and arylboronic acids(9) catalyzed by 5 in water^a

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^{*a*} Reaction conditions: arylhalide (1.0 mmol), arylboronic acid (1.2 mmol), 5 (0.1 mol%), K₂CO₃ (2.0 mmol), water (2 mL). ^{*b*} Isolated yield.

5 in the presence of K_2CO_3 (Table 3, entry 9), it was not possible to recycle the catalyst after two cycles under these conditions, and thus we determined that the optimum loading for the catalyst was 0.1 mol% for the Suzuki reaction.

The scope of the Suzuki reaction catalyzed by 5 in aqueous medium was investigated by employing various aryl halides and arylboronic acids (Scheme 4). The results are summarized in Table 4. Reaction of substituted iodobenzenes (6a-e, 6h-j) with arylboronic acids gave the corresponding coupled products in good to excellent yields (65-89%). Reaction of bromobenzene (6f) and chlorobenzene (6g) with arylboronic acids also afforded good yields of the coupled products (70-76%) (Table 4, entries 2-3, 5-6, 11 and 13-14). However, the times required for the completion of the reactions for bromobenzene (6f) and chlorobenzene (6g) were longer than that for iodobenzene (6a). The method is equally applicable for aryl iodides substituted with either electron-withdrawing or electron-donating groups. For example, 4-nitro-, 4-methyl-, 4-methoxy- and 2-aminoiodobenzenes were smoothly converted to the corresponding coupled products in high yields.

The reusability of 5 was evaluated for both the model Heck and Suzuki reactions. As shown in Table 5, the catalyst could be effectively used for up to six cycles without much loss in catalytic activity. Leaching of the catalyst during extraction may Table 5 Reusability of 5 for the Heck reaction and the Suzuki reaction

Run	1	2	3	4	5	6
% Yield ^{<i>a</i>} of 8aa'	96	95	93	91	91	90
% Yield ^{<i>a</i>} of 10aa ′	80	78	77	76	74	72
^{<i>a</i>} Isolated vield.						

be one of the factors responsible for the gradual decrease in the yield of the product during recycling.

Conclusions

In summary, we have synthesized and systematically characterized a novel imidazolium ionic liquid-tagged palladium Schiff base complex, and explored its catalytic activity for the Heck and Suzuki reactions in aqueous media. The complex showed high activity and excellent yields for these reactions. The catalyst is moisture insensitive and highly stable under thermal and aerobic conditions. The reaction conditions for the ionic liquid-tagged palladium catalyzed coupling reactions are simple and effective for more challenging substrates, such as chlorides. The use of an aqueous medium and the recyclability of the catalyst are the advantages that make this method economical and environmentally friendly.

Experimental

Materials and methods

All of the reagents were purchased from Sigma-Aldrich, India, and Spectrochem Pvt. Ltd, India, and were used without additional purification. The solvents used were purchased from Merck (India) and were distilled and dried before use. Melting points were determined in open capillary tubes on a MPA120 automated melting point apparatus and are uncorrected. IR spectra were recorded on an ABB Bomen MB 3000 FTIR spectrophotometer using KBr pellets, and the electronic spectra were recorded on a Shimadzu UV-1800 UV-Vis spectrophotometer. ¹H and ¹³C NMR spectra were recorded on Bruker Heaven 11400 (400 MHz) and Varian (500 MHz) spectrometers using $CDCl_3$ and $DMSO-d_6$ as solvents, and the chemical shifts were expressed in ppm. Mass spectra were recorded on an AB SCIEX TOF/TOF 5800 spectrometer. Powder X-ray diffraction (XRD) data were obtained on a Rigaku Miniflex II diffractometer with Cu K_{α} radiation, and diffraction patterns were recorded over a range of 2θ angles from 10 to 50°. Synthesis of the ionic liquid-supported Schiff base 4 was achieved from 2,4dihydroxybenzaldehyde by following our earlier reported method.32

Synthesis of 4-(3-bromopropoxy)-2-hydroxybenzaldehyde (2). A round bottom flask containing 1,3-dibromopropane (8.0 mmol), 2,4-dihydroxybenzaldehyde (6.0 mmol) and sodium bicarbonate (6.0 mmol) in acetone (50 mL) was heated at 60 °C for 60 h. After the reaction had gone to completion, the reaction mixture was purified over a silica gel column to give pure 2 in 65% yield.

Synthesis of the ionic liquid-tagged aldehyde (3). A mixture of 1-methylimidazole (3.5 mmol) and 2 (3.5 mol) was stirred at 80 °C for 48 h to give a viscous liquid. The reaction mixture was washed with a diethyl ether–ethyl acetate mixture to give the ionic liquid-tagged aldehyde 3 in almost quantitative yield.

Synthesis of the ionic liquid-tagged Schiff base (4). A mixture containing the ionic liquid-tagged aldehyde 3 (3.0 mmol) and aniline (4.0 mmol) in ethanol (15 mL) was refluxed for 4 h. On completion of the reaction, ethanol (30 mL) was added to the reaction mixture; the solid product which formed was filtered off and washed with cold ethanol. The crude product was purified by recrystallization from ethanol–ethyl acetate (3:1 v/v).

Synthesis of the imidazolium ionic liquid-tagged palladium complex (5). The ionic liquid-tagged Schiff base 4 (672 mg, 2.0 mmol) was stirred with ethanol in a 25 mL round bottom flask for 15 min. Palladium acetate (224 mg, 1.0 mmol) was added to the resulting solution, and the mixture was refluxed for 4 h until the product had completely precipitated. After cooling, the product 5 was separated by filtration and recrystal-lized from a mixture of petroleum ether (2 mL) and methanol (15 mL).

General procedure for the Heck reaction in water

A 50 mL round bottom flask containing a mixture of aryl halide (1.0 mmol), alkene (2.0 mmol), K_2CO_3 (2.0 mmol) and 5 (1.0 mol%) in water (2 mL) was heated to a temperature of 80 °C in an oil bath. The progress of the reaction was monitored using TLC at regular time intervals. After completion of the reaction, the reaction mixture was added to water (20 mL) and extracted with ethyl acetate (3 × 10 mL). The organic layer was dried with anhydrous Na₂SO₄, and concentrated to give the crude product which was purified by column chromatography over silica gel (mesh 60–120), using *n*-hexane–ethyl acetate as an eluent. The products were analyzed by NMR spectroscopy.

General procedure for the Suzuki reaction in water

To a 50 mL round bottom flask, aryl halide (1.0 mmol), arylboronic acid (1.2 mmol), 5 (0.1 mol%), K_2CO_3 (2.0 mmol) and water (2 mL) were added, and continuously stirred at room temperature (25 °C). The progress of the reaction was monitored by means of TLC at regular 5 minute intervals. After completion of the reaction, the reaction mixture was diluted with water (20 mL) and extracted with a mixture of hexane and ethyl acetate (1:1 v/v, 3 × 10 mL). Diethyl ether was used for extraction in the cases of **10ha'**, **10ia'** and **10ja'**. The organic layer was dried with anhydrous Na₂SO₄, and then the solvent was evaporated under reduced pressure. The resulting residue was purified by column chromatography over silica gel (mesh 60–120), using *n*-hexane–ethyl acetate as an eluent, to give the desired product. The products were analyzed by NMR spectroscopy.

Reusability and recovery of the catalyst

After the first run of the reaction was completed, the product was directly extracted into the organic layer, and the catalyst which remained in the aqueous layer was reused for the next cycle of the reaction, following the same procedures as mentioned above for the Heck and Suzuki reactions.

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