Full paper

Applied Organometallic Chemistry

Received: 30 December 2015 Revised: 12 March 2016 Accepted: 10 April 2016 Published online in Wiley Online Library

(wileyonlinelibrary.com) DOI 10.1002/aoc.3503

Flexible, dicationic imidazolium salts for *in situ* application in palladium-catalysed Mizoroki–Heck coupling of acrylates under aerobic conditions†

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The synthesis, characterization and *in situ* catalytic performance of new unsymmetric *N*,*N*′-disubstituted imidazolium-based dicationic salts in Mizoroki–Heck coupling of acrylates with aryl bromides under aerobic conditions are described. A series of flexible dicationic salts with varying steric and electronic properties were synthesized in good to excellent yields. All the salts were well characterized using spectroscopic techniques. X-ray diffraction analysis of two salts with the same dicationic backbone and different counter anions shows that the ligand adopts two different conformations which are influenced by the nature of the anion. Thus, the ligand is capable of changing its conformation according to the change in environment due to its flexible nature. All the synthesized imidazolium salts were found to be active in *in situ* palladium-catalysed Mizoroki–Heck coupling under aerobic conditions. Amongst the salts, the hydroxyl-functionalized imidazolium salt, incorporating the features of both bidentate chelating *O*,*O* ligand and carbene, shows the maximum catalytic activity. A variety of aryl and heteroaryl methyl and ethyl cinnamates were synthesized using these imidazolium salts as preligands. In addition, NMR studies confirm *in situ* generation of normal *N*-heterocyclic carbenes from the C-2 position of imidazol-2-ylidene ring. The mercury poisoning test was also performed to ascertain the nature of catalytically active palladium species. Aerobic conditions, low catalytic loading (0.5 mol%), shorter reaction times, broad functional group tolerance and good to excellent isolated yields are some of the significant features of the novel catalytic systems described here. Copyright © 2016 John Wiley & Sons, Ltd.

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Keywords: imidazolium salts; *N*-heterocyclic carbenes (NHCs); C–C bond forming reactions; Mizoroki–Heck coupling; palladium catalysis

Introduction

Palladium-catalysed Mizoroki–Heck coupling of olefins[1,2] is popular amongst organic chemists for carbon–carbon bond formation due to its wide applications in the synthesis of useful pharmaceuticals, conducting polymers, UV screens, natural products, etc.[3–5]

Traditional phosphine ligands[6,7] have limited synthetic utility due to high cost, toxicity and sensitivity towards air and moisture. However, in the last decade, a number of azolium salts functionalized with imidazoles, benzimidazoles and pyrazoles, *N*-heterocyclic carbenes (NHCs), oxazolines, Schiff bases, pyridines and amines have been developed as successful phosphine-free ligands for Mizoroki–Heck reactions, including those incorporating azolium salts into chelate as well as pincer scaffolds.[8–21] These ligands circumvent many limitations associated with the use of phosphine igands, and also avoid excessive use of ligands and high loadings of palladium. However, most of these require inert conditions or preformation of palladium complexes for an effective Mizoroki–Heck reaction. Therefore, development of novel ligands for direct *in situ* application in palladium catalysis under aerobic conditions is important.

Also, it has been reported that charged ligands lead to increased ionophilicity in comparison to the conventional neutral ligands and can prevent the commonly encountered problems of leaching of metal catalysts and difficulty in separation of metal catalyst from reaction product.[21–23] Thus, we decided to design ligands incorporating dicationic imidazolium species for direct *in situ* application in palladium-catalysed Mizoroki-Heck reaction.

Our preligand design strategy involved the synthesis of unsymmetric *N*,*N*′-disubstituted imidazolium salts by introduction of polyfunctionality which could offer (*O*,*O*)- or (*N*,*N*)-bidentate chelation. Dissymmetrization not only fine-tunes the steric and electronic properties of the ligand but also permits introduction of chelatization, hemilability, polyfunctionality, shielding effects, etc., which further influences catalyst stability, reactivity and selectivity.[24] Furthermore, a pyridine ring, which is well known to show cooperative effects[12,25–30] during catalysis, was introduced on the ligand. However, the direct attachment of pyridine to imidazole unit would make the ligand structure rigid.[31] Therefore, the pyridine ring was appended onto the imidazole nucleus through a short methylene spacer which could release the strain and increase the flexibility of the basic scaffold. Functional groups such as hydroxyl and ammonium were introduced as the *N*-alkyl side arms of the imidazole–pyridine scaffold with varied chain lengths of the linkers to provide flexibility in chelation to the metal centre during catalysis and increase the solubility in polar solvents.

Herein we describe the design and synthesis of a series of novel unsymmetric *N*,*N*′-disubstituted imidazolium salts with varying

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† *This paper is dedicated to Professor Sakae Uemura on the occasion of his 75th birthday*

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steric and electronic properties and their *in situ* catalytic performance in the synthesis of methyl and ethyl cinnamates under aerobic conditions.

Experimental

General

Unless otherwise noted, all reactions were carried out under aerobic conditions. Solvents were dried according to standard procedures. All chemicals were obtained from commercial sources and were used without further purification. Reactions were monitored with Merck Silica 60 F_{254} (0.040–0.063 mm) TLC plates. The ^{1}H NMR and ^{13}C NMR spectra were recorded with a JEOL-JNM-ECX-400P spectrometer using DMSO-d_6. Infrared (IR) spectra were recorded with a PerkinElmer FTIR Spectrum 2000 spectrophotometer using KBr pellets. Melting points were determined with a Buchi M-560 melting point apparatus and are uncorrected. High-resolution mass spectra were measured using a high-resolution TOF instrument with electrospray ionization (ESI). The starting precursor 3-(1*H*-imidazol-1-ylmethyl)pyridine (**1**) was synthesized according to an earlier reported procedure.[32]

X-ray Structure Analysis

Single-crystal X-ray data were collected with an Oxford X Calibur CCD diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at low temperature (150 K). The structures were solved using SIR-92 and refined by the full matrix least squares technique on F^2 using the SHELXL-97[33] program within the WinGX v. 1.70.01 software package. All hydrogen atoms were fixed at the calculated positions with isotropic thermal parameters and all non-hydrogen atoms were refined anisotropically. Crystal data and details of the data collection are summarized in Table 1.

Table 1. Crystallographic data for imidazolium salts **2** and **3**

	2	**3**
Empirical formula	$C_{13}H_{19}Br_2N_3O_2$	$C_{13}H_{19}BrF_6N_3O_2P$
Formula weight	409.13	474.19
Temperature (K)	298(2)	150(2)
Crystal system	Orthorhombic	Monoclinic
Space group	Pna21	P21/n
Unit cell dimensions	a = 12.7725(11) Å	a = 5.8667(3) Å
	b = 5.4177(5) Å	b = 28.275(2) Å
	c = 23.493(2) Å	c = 10.9211(7) Å
	α = 90°	α = 90°
	β = 90°	β = 89.713(5)°
	γ = 90°	γ = 90°
Volume (Å^3)	1625.6(3)	1811.6(2)
Z	4	4
$\rho_{(calc)}$ (mg m^{-3})	1.672	1.739
Reflections collected	4800	6891
Independent reflections	2688	3109
R(int.)	0.0200	0.0147
Data/restraints/parameters	2688/3/188	3109/2/241
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0288	R_1 = 0.0302
	wR_2 = 0.0603	wR_2 = 0.0721
R indices (all data)	R_1 = 0.0354	R_1 = 0.0345
	wR_2 = 0.0619	wR_2 = 0.0739
GOF on F^2	0.975	1.048
Largest difference peak	0.366	0.690
Hole (e Å^{-3})	−0.299	−0.378

Syntheses

*Synthesis of 3-(2-hydroxyethyl)-1-((1-(2-hydroxyethyl)pyridin-1-ium-3-yl)methyl)-1H-imidazolium bromide (**2**)*

A mixture of **1** (10.0 mmol, 1.596 g) and 2-bromoethanol (30.4 mmol, 3.802 g) in dry acetonitrile (30 ml) was stirred at 50 °C for 4 days. The precipitated solid was filtered and washed thrice with acetonitrile. The solid was further purified by reprecipitation from acetone–methanol affording **2** as a hygroscopic pale yellow solid. Yield: 3.869 g (94%); m.p. 184–186 °C. IR (KBr, cm^{-1}): 3305, 3272, 3135, 3066, 3033, 2927, 1637, 1574, 1560, 1501, 1451, 1406, 1379, 1174, 1065, 1054, 779, 687, 650. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 9.39 (s, 1H, H2), 9.26 (s, 1H, H8), 9.04 (d, 1H, J = 6.6 Hz, H12), 8.67 (d, 1H, J = 8.0 Hz, H10), 8.25-8.21 (m, 1H, H11), 7.89 (s, 1H, H5), 7.83 (s, 1H, H4), 5.75 (s, 2H, H6), 5.25–5.19 (br s, 2H, O*H*), 4.68 (t, 2H, J = 5.1 Hz, H13), 4.24 (t, 2H, J = 5.1 Hz, H15), 3.88 (t, 2H, J = 5.1 Hz, H14), 3.73 (t, 2H, J = 5.1 Hz, H16).^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 145.48 (C10), 145.27 (C12), 145.16 (C8), 137.21 (C2), 134.87 (C9), 127.73 (C11), 123.38 (C4), 122.30 (C5), 63.36 (C13), 59.78 (C14), 59.08 (C16), 51.96 (C15), 48.03 (C6). HRMS (ESI-TOF) m/z: $[M-2Br-H]^+$; calcd for $C_{13}H_{18}N_3O_2$: 248.1388, found: 248.1388.

*Synthesis of 3-(2-hydroxyethyl)-1-((1-(2-hydroxyethyl)pyridin-1-ium-3-yl)methyl)-1H-imidazolium bromide hexafluorophosphate (**3**)*

A mixture of imidazolium salt **2** (0.69 mmol, 0.284 g) and potassium hexafluorophosphate (1.38 mmol, 0.254 g) in water (10 ml) was stirred at room temperature for 4 days. Addition of methanol to the same solution followed by stirring at room temperature for 24 h resulted in precipitation of a white solid. The solid was filtered, washed with acetone and dried *in vacuo* to afford **3** as white solid. Yield: 0.326 g (99%); m.p. 138–140 °C. IR (KBr, cm^{-1}): 3336, 3060, 3036, 2973, 1569, 1561, 1507, 1477, 1450, 1414, 1157, 1065, 862, 835, 744, 558. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 9.32 (s, 1H, H2), 9.17 (s, 1H, H8), 9.01 (d, 1H, J = 6.6 Hz, H12), 8.62 (d, 1H, J = 8.0 Hz, H10), 8.22-8.20 (m, 1H, H11), 7.82 (s, 1H, H5), 7.79 (s, 1H, H4), 5.69 (s, 2H, H6), 5.25 (t, 1H, J = 5.1 Hz, H15), 5.18 (t, 1H, J = 5.1 Hz, H18), 4.64 (t, 2H, J = 5.1 Hz, H13), 4.21 (t, 2H, J = 5.1 Hz, H16), 3.85 (q, 2H, J = 5.1 Hz, H14), 3.71 (q, 2H, J = 5.1 Hz, H17). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 145.45 (C10), 145.32 (C12), 145.10 (C8), 137.24 (C2), 134.96 (C9), 127.83 (C11), 123.44 (C4), 122.35 (C5), 63.52 (C13), 59.86 (C14), 59.14 (C17), 51.99 (C16), 48.20 (C6). HRMS (ESI-TOF) m/z: $[M-Br-PF_6-C_2H_5O+H]^+$; calcd for $C_{11}H_{15}N_3O$: 205.1209, found: 205.0882.

*Synthesis of 3-(3-hydroxypropyl)-1-((1-(3-hydroxypropyl)pyridin-1-ium-3-yl)methyl)-1H-imidazolium bromide (**4**)*

A mixture of **1** (4.42 mmol, 0.702 g) and 3-bromopropanol (13.2 mmol, 1.835 g) in dry acetonitrile (20 ml) was stirred at 50 °C for 4 days. The solvent was then removed *in vacuo* and the residue was washed three times with acetonitrile. The resulting viscous residue was stirred in hexane–acetone (2:1) at room temperature for 1 day. The solvent was then decanted off affording **4** as a highly hygroscopic pale yellow solid. Yield: 1.390 g (72%); m.p. 132–134 °C. IR (KBr, cm^{-1}): 3393, 3086, 2954, 2885, 1638, 1561, 1508, 1481, 1458, 1245, 1163, 1070, 949, 826. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 9.36 (s, 1H, H2), 9.26 (s, 1H, H8), 9.11 (d, 1H, J = 6.6 Hz, H12), 8.61 (d, 1H, J = 8.0 Hz, H10), 8.21-8.19 (m, 1H, H11), 7.86–7.84 (m, 2H, H5 and H4), 5.68 (s, 2H, H6), 4.68 (t, 2H,

J = 7.3 Hz, H13), 4.25 (t, 2H, *J* = 7.3 Hz, H17), 3.48–3.42 (m, 4H, H15 and H19), 2.12–2.06 (m, 2H, H14), 1.99–1.92 (m, 2H, H18). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 145.83 (C10), 145.50 (C12), 145.26 (C8), 137.42 (C2), 135.56 (C9), 128.83 (C11), 123.83 (C4), 123.12 (C5), 59.86 (C13), 57.90 (C15), 57.86 (C19), 49.04 (C6), 47.47 (C17), 33.47 (C14), 32.41 (C18). HRMS (ESI-TOF) *m/z*: $[M-2Br-H]^+$; calcd for $C_{15}H_{22}N_3O_2$: 276.1707; found: 276.1762.

*Synthesis of 3-(3-ammoniopropyl)-1-((1-(3-ammoniopropyl)pyridin-1-ium-3-yl) methyl)-1H-imidazolium bromide (**5**)*

A mixture of **1** (1.13 mmol, 0.180 g) and 3-bromopropylamine hydrobromide (1.03 mmol, 0.226 g) in dry acetonitrile (5 ml) was stirred at room temperature for 2 days. The solvent was then decanted off and the viscous residue was thoroughly washed with acetonitrile. The residue was further purified by reprecipitation from chloroform–methanol affording **5** as a dark brown viscous liquid. Yield: 0.307 g (97%). IR (KBr, cm^{-1}): 3413, 3043, 2046, 1623, 1478, 1167, 751. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 9.58 (s, 1H, H2), 9.50 (s, 1H, H8), 9.22 (d,1H, *J* = 5.9 Hz, H12), 8.75 (d, 1H, *J* = 8.1 Hz, H10), 8.28-8.25 (m, 1H, H11), 8.02–7.93 (m, 8H, H5, H4, H16 and H20), 5.78 (s, 2H, H6), 4.80 (t, 2H, *J* = 6.6 Hz, H13), 4.35 (t, 2H, *J* = 6.6 Hz, H17), 2.89 (br s, 4H, H15 and H19), 2.32–2.29 (m, 2H, H14), 2.18–2.14 (m, 2H, H18). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 146.22 (C10), 145.24 (C12 and C8), 137.57 (C2), 135.59 (C9), 128.96 (C11), 123.47 (C4), 123.28 (C5), 58.69 (C13), 48.99 (C6), 46.95 (C17), 36.21 (C19), 36.04 (C15), 28.72 (C14), 27.6 (C18). HRMS (ESI-TOF) *m/z*: $[M-3Br-H]^+$; calcd for $C_{16}H_{30}BrN_5$: 371.1685; found: 371.1009.

*Synthesis of 3-ethyl-1-((1-(ethyl)pyridin-1-ium-3-yl)methyl)-1H-imidazolium bromide (**6**)*

A mixture of **1** (4.03 mmol, 0.642 g) and ethyl bromide (12.18 mmol, 1.328 g) in dry acetonitrile (20 ml) was stirred at 50 °C for 4 days. The precipitated solid was filtered and washed thrice with acetonitrile. The solid was purified by reprecipitation from acetone–methanol affording **6** as a light brown hygroscopic solid. Yield: 0.972 g (64%); m.p. 228–230 °C. IR (KBr, cm^{-1}): 3055, 3021, 2979, 1574, 1500, 1475, 1461, 1173, 872, 797, 752, 686. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 9.44 (s, 1H, H2), 9.35 (s, 1H, H8), 9.13 (d, 1H, *J* = 6.4 Hz, H12), 8.63 (d, 1H, *J* = 8.7 Hz, H10), 8.21-8.17 (m, 1H, H11), 7.89–7.82 (m, 2H, H5 and H4), 5.68 (s, 2H, H6), 4.63 (q, 2H, *J* = 7.3 Hz, H13), 4.18 (q, 2H, *J* = 7.3 Hz, H15), 1.53 (t, 3H, *J* = 7.3 Hz, H14), 1.41 (t, 3H, *J* = 7.3 Hz, H16). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 145.81 (C10), 145.33 (C12), 145.07 (C8), 137.25 (C2), 135.69 (C9), 128.60 (C11), 123.18 (C4), 123.08 (C5), 57.13 (C13), 48.69 (C6), 45.01 (C15), 16.71 (C14), 15.38 (C16). HRMS (ESI-TOF) *m/z*: $[M-2Br-H]^+$; calcd for $C_{13}H_{18}N_3$: 216.1490; found: 216.1493.

General Procedure for Mizoroki–Heck Reaction

In a typical experiment, aryl halide (5.0 mmol) and alkyl acrylate (10.0 mmol) were added to a mixture of imidazolium salt **2** (0.5 mol%), Et_3N (5.0 mmol) and $PdCl_2$ (0.5 mol%) in dimethylformamide (DMF; 2 ml). The reaction mixture was stirred at 130 °C for 4 h. On completion, the reaction mixture was treated with water and extracted with ethyl acetate (3 × 10 ml). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered and evaporated. The residue was then purified by column chromatography on silica gel using petroleum ether–ethyl acetate as the eluent to give the desired product.

The characterization data for compounds **9** and **10** were in entire agreement with those reported in the literature.[8–21,34]

General Procedure for NMR Tube Reactions

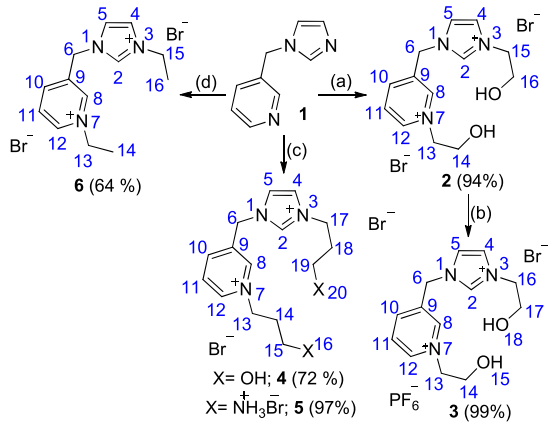
Compounds **7a** (0.062 mmol) and **8a** (0.0125 mmol) were added to a mixture of imidazolium salt **2** (0.062 mmol), Et_3N (0.062 mmol) and $PdCl_2$ (0.062 mmol) in DMSO-d_6 (0.5 ml). The reaction mixture was stirred at 130 °C and monitored using ^{1}H NMR and ^{13}C NMR spectroscopy at different time intervals.

General Procedure for Mercury Poisoning Test

In a typical experiment, aryl halide (5.0 mmol) and alkyl acrylate (10.0 mmol) were added to a mixture of imidazolium salt **2** (0.5 mol%), Et_3N (5.0 mmol) and $PdCl_2$ (0.5 mol%) in DMF (2 ml). The reaction mixture was stirred at 130 °C for 5 min. After 5 min, 300 equiv. of Hg(0) was added and the reaction mixture was stirred at 130 °C for 4 h. On completion, the reaction mixture was treated with water and extracted with ethyl acetate (3 × 10 ml). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered and evaporated. The residue was then purified by column chromatography on silica gel using petroleum ether–ethyl acetate as the eluent to give the desired product.

Results and Discussion

The synthetic methodology employed for the unsymmetric imidazolium salts is outlined in Scheme 1. The reaction of **1** with 2-bromoethanol and 3-bromopropanol in dry acetonitrile afforded the hydroxyl-functionalized imidazolium salt **2** and its homologue **4**, respectively, as pale yellow hygroscopic solids in good to excellent yields (72–94%). The ammonium-functionalized salt **5** was isolated as a dark brown viscous liquid after reaction of **1** with 3-bromopropylamine hydrobromide at room temperature in excellent yield (97%). Further, bromide counter-anion exchange in **2** with 2 equiv. of hexafluorophosphate afforded **3** as a slightly hygroscopic white solid in 99% yield. The bromide counter-anion exchange was confirmed using ^{1}H NMR and ^{13}C NMR spectroscopy.



Scheme 1. Synthesis of imidazolium salts **2**–**6**. Reagents and conditions: (a) $BrCH_2CH_2OH$, CH_3CN, 50°C; (b) KPF_6, H_2O–MeOH, r. t.; (c) $BrCH_2(CH_2)_2X$, CH_3CN, 50 °C or r.t.; (d) $BrCH_2CH_3$, CH_3CN, 50°C.

The characteristic singlet corresponding to NC*H*N proton of imidazolium ring showed an upfield shift from 9.39 ppm in **2** to 9.31 ppm in **3**. The presence of PF_6^- anion in **3** was further confirmed by the appearance of a very strong absorption peak at 835 cm^{-1} in the IR spectrum. However, the fact that only one counter-anion exchange had occurred was confirmed using single-crystal X-ray studies. The imidazolium salt **6**, which is a non-functionalized analogue of **2**, was synthesized similarly in good yield (64%).

X-ray Diffraction Studies

Crystals of **2** and **3** suitable for X-ray diffraction analysis were grown from methanol–ethyl acetate (1:1) mixture. Compound **2** crystallized in orthorhombic space group Pna21 whereas **3** crystallized in monoclinic space group P21/n. In **2**, the ligand backbone adopted a helical shape with the two hydroxyl protons of the same molecule being involved in hydrogen bonding interactions with bromide ions of different molecules (2.391 Å). In contrast, in **3** the ligand backbone adopted a folded shape. Exchange of one bromide counter anion with hexafluorophosphate flipped the orientation of the hydroxyl groups in **3** (Fig. 1). As a result, both the hydroxyl protons moved closer to interact with the same bromide ion in **3**. The Br^- anion showed H···Br bonding interactions with both hydroxyl protons H1 (2.421 Å) and H2 (2.423 Å) whereas PF_6^- formed H···F bonds with H9 (2.497 Å) of imidazolium ring and H5 (2.494–2.589 Å) of pyridinium ring. Additionally, the molecules packed in a symmetric fashion such that the imidazolium rings of one layer oriented themselves in face-to-face orientation with those of the parallel layer at a separation of 5.418–5.867 Å with no π–π stacking interactions (Figs S1–S4, supporting information). Thus, the counter-anion exchange revealed the high flexibility of the designed dicationic ligand backbone, in adopting different shapes according to the environment, which can be exploited for coordination to a metal centre during catalysis.

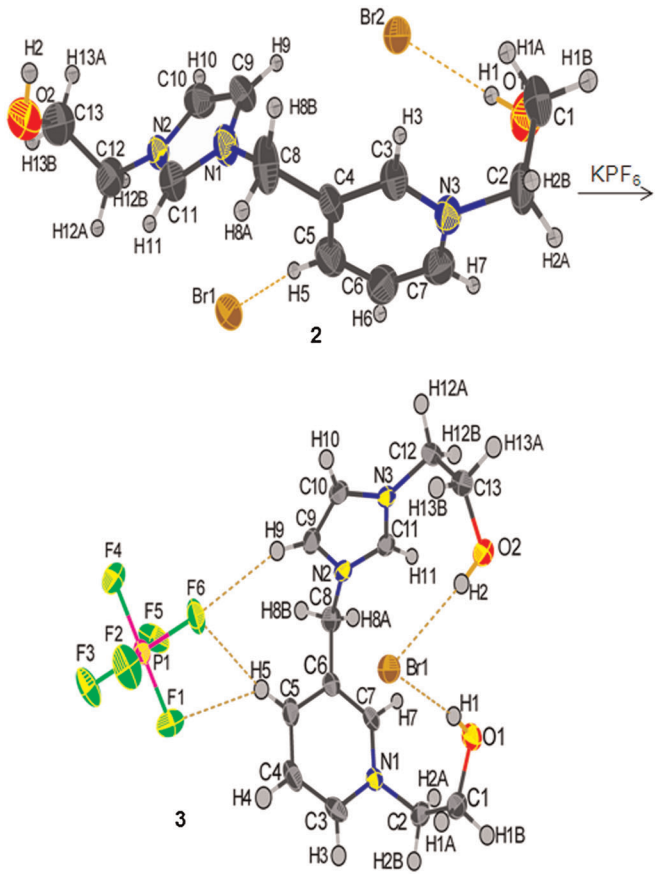
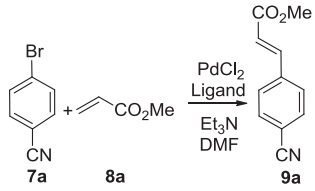


Figure 1. Molecular structures of imidazolium salts **2** and **3** before and after counter-anion exchange, respectively (50% probability ellipsoids). The dotted lines represent the hydrogen bonding interactions.

Mizoroki–Heck Reaction

We began our work with the coupling of 4-bromobenzonitrile (**7a**) with methyl acrylate (**8a**) under a set of chosen reaction conditions. Initially, the reaction was performed in the absence of any ligand, which furnished only 65% yield of methyl (*E*)-3-(4-cyanophenyl)acrylate (**9a**) (Table 2, entry 1). Addition of PPh_3 enhanced the yield to 71% (Table 2, entry 2). The starting precursor **1** furnished 80% yield of **9a** (Table 2, entry 3). Next, the imidazolium salts (**2**–**6**) were tested as preligands in the chosen model Mizoroki–Heck reaction (Table 2, entries 4–8). Different reactivities were observed for the structurally different imidazolium salts. Use of the hydroxyethyl-functionalized imidazolium salt **2** in combination with $PdCl_2$ resulted in the formation of a homogeneous orange-coloured solution and significantly increased the activity of palladium catalyst, affording the coupling product **9a** in 96% yield at low catalytic loading of 0.5 mol% in a short reaction time of 4 h (Table 2, entry 4). However, use of imidazolium salt **3**, with similar imidazolium skeleton but heterogeneous counter anions, resulted in slight precipitation of palladium black affording 92% yield of **9a** (Table 2, entry 5). Also, the length of the alkyl chain of *N*-substituents in imidazolium salts had a direct influence on the reactivity and stability of the *in situ* generated catalyst. The presence of propyl group in place of ethyl group in imidazolium salt **4** resulted in very significant palladium black precipitation, and hence reduced product yield (70%; Table 2, entry 6). Also, the ammonium-functionalized imidazolium

Table 2. Screening of imidazolium salts in model Mizoroki–Heck reaction[a]



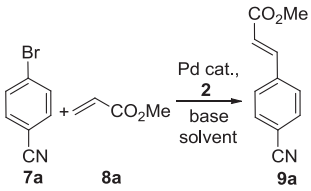
Entry	Ligand	Yield (%)[b]
1	—	65
2	PPh_3	71
3	**1**	80
4	**2**	96
5	**3**	92
6	**4**	70
7	**5**	83
8	**6**	90

[a]Reaction conditions: **7a** (5.0 mmol), **8a** (10.0 mmol), Et_3N (5.0 mmol), DMF (2.0 ml), 130°C, 4 h, under aerobic conditions.
[b]Isolated yield.

salt **5** produced **9a** in only 83% yield (Table 2, entry 7). Interestingly, the imidazolium salt **6**, which is a non-functionalized analogue of **2**, also underwent an effective coupling of 90% despite very great precipitation of palladium black (Table 2, entry 8). These observations suggested that the availability of multiple ligations in **2** could be a reason for the excellent performance of the *in situ* generated palladium catalyst. Also, the presence of hydroxyl functional group and appropriate length of the alkyl chain of *N*-substituents in imidazolium salts are crucial for their activity. Importantly, all the ligands exhibited complete regioselectivity in producing the *trans*-isomer exclusively with no *cis*- or *gem*-coupling product formation. So, imidazolium salt **2** was used as preligand for further studies.

The other reaction conditions such as base, solvent and time were also subjected to optimization. A variety of organic and inorganic bases were examined (Table 3). Use of weak bases such as $NaHCO_3$, Na_2CO_3, NaOAc and K_2CO_3 afforded 47–92% yields of **9a** (Table 3, entries 2–5). Strong bases such as NaOH and KOH afforded low yields due to hydrolysis of the ester product (78 and 39%, respectively; Table 3, entries 6 and 7). So, Et_3N remained to be the base of choice. Furthermore, a base-free reaction afforded only 5% yield giving strong evidence for the crucial role played by the base in such coupling reactions (Table 3, entry 8).

Table 3. Optimization of Reaction Conditions using model Mizoroki-Heck reaction[a]



Entry	Pd catalyst	Base	Solvent	Temp. (°C)	Yield (%)[b]
1	$PdCl_2$	Et_3N	DMF	130	96
2	$PdCl_2$	$NaHCO_3$	DMF	130	47
3	$PdCl_2$	Na_2CO_3	DMF	130	92
4	$PdCl_2$	NaOAc	DMF	130	86
5	$PdCl_2$	K_2CO_3	DMF	130	81
6	$PdCl_2$	NaOH	DMF	130	78
7	$PdCl_2$	KOH	DMF	130	39
8	$PdCl_2$	—	DMF	130	5
9	$PdCl_2$	Et_3N	NMP	130	90
10	$PdCl_2$	Et_3N	CH_3CN	80	2
11	$PdCl_2$	Et_3N	H_2O	100	6
12	$PdCl_2$	Et_3N	MeOH	80	11
13	$PdCl_2$	Et_3N	DMSO	130	33
14[c]	$PdCl_2$	Et_3N	DMF	130	93
15[d]	$PdCl_2$	Et_3N	DMF	130	72
16[e]	$PdCl_2$	Et_3N	DMF	130	91
17[f]	$PdCl_2$	Et_3N	DMF	130	87
18	$Pd(OAc)_2$	Et_3N	DMF	130	91
19	$Pd_2(dba)_3$	Et_3N	DMF	130	87
20	$PdCl_2(CH_3CN)_2$	Et_3N	DMF	130	87
21[g]	$PdCl_2$	Et_3N	DMF	130	52

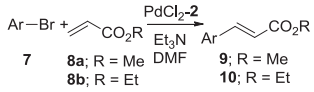
[a]Reaction conditions: **7a** (5.0 mmol), **8a** (10.0 mmol), Pd salt (0.5 mol %), imidazolium salt **2** (0.5 mol%), base (5.0 mmol), solvent (2 ml), 4 h, under aerobic conditions.
[b]Isolated yield.
[c]1 ml of DMF.
[d]4 ml of DMF.
[e]2 h.
[f]8 h.
[g]0.1 mol% catalytic loading.

Investigation of solvents showed DMF to be the most productive. *N*-methyl-2-pyrrolidone (NMP) as solvent afforded 90% conversion (Table 3, entry 9). The reactions in other solvents such as CH_3CN, H_2O, MeOH and DMSO resulted in large amounts of palladium black precipitation, and thus much reduced yields of **9a** were observed (2–33%; Table 3, entries 10–13). Any decrease or increase in the volume of DMF reduced the yield (93 and 72%, respectively; Table 3, entries 14 and 15). Further shortening of the reaction time from 4 to 2 h reduced the yield to 91% (Table 3, entry 16). Also, extending the reaction time to 8 h resulted in *ca* 10% decrease in the isolated yield (87%; Table 3, entry 17). Other palladium salts such as $Pd(OAc)_2$, $Pd_2(dba)_3$ and $PdCl_2(CH_3CN)_2$ were also examined; however, maximum catalytic performance was observed with $PdCl_2$ in combination with imidazolium salt **2** at 0.5 mol% catalytic loading (Table 3, entries 18–20). An attempt to replace palladium salt with comparatively cheaper $Ni(OAc)_2{\cdot}4H_2O$ did not result in any coupling reaction. Further reduction in catalytic loading to 0.1 mol% reduced the yield to 52% (Table 3, entry 21). So, the best conversion was achieved in the reaction of 4-bromobenzonitrile with methyl acrylate in the presence of Et_3N as base using 0.5 mol% loading of $PdCl_2$ and imidazolium salt **2** in 2 ml of DMF at 130 °C in 4 h under aerobic conditions. It is noteworthy that under these reaction conditions, 4-bromobenzonitrile could be coupled in excellent yield without any poisoning of the catalyst in contrast to phosphine-based preligands reported by Hong and co-workers under inert atmosphere.[35]

Mizoroki–Heck coupling reactions of aryl bromides with acrylates

After optimizing the reaction conditions, various aryl bromides were examined in the coupling reaction with methyl and ethyl acrylate (Table 4). The coupling reaction proceeded smoothly with aryl bromides bearing electron-withdrawing groups affording moderate to excellent yields of the corresponding methyl and ethyl cinnamates (Table 4, entries 1–12). A variety of functional groups such as CN, NO_2, CHO, $COCH_3$, COPh and CF_3 on the aryl bromides were well tolerated. Different reactivities were observed with *ortho*-, *meta*- or *para*-isomers, the *ortho*-derivatives giving generally lower conversions (Table 4, entries 3–5 and 6–8). These results are in agreement with general observations related to lower reactivity of *ortho*-substituted aryl halides in such cross-coupling reactions for steric reasons.[36] However, the reaction of *o*-bromobenzaldehyde with acrylates afforded unexpected doubly substituted deformylated products along with the expected *o*-formyl cinnamates.[34] The heteroaryl bromides 2-bromothiophene and 3-bromopyridine furnished low to moderate yields of the coupling products (Table 4, entries 13 and 14). The aryl bromide without any additional functional group on benzene ring afforded the corresponding methyl cinnamate in only16% yield (Table 4, entry 15). Furthermore, the presence of electron-donating groups such as OCH_3 and CH_3 in benzene ring deactivated the coupling with acrylates resulting in no product formation. Even increased reaction time (up to 24 h) or higher catalytic loading (5 mol%) could not enhance the reactivity of deactivated aryl bromides. Also, no product formation occurred with 4-chlorobenzonitrile, owing to the high bond strength of the C–Cl bond.

Table 4. Scope of aryl bromides in coupling with methyl and ethyl acrylate[a]



7 **8a**; R = Me **8b**; R = Et **9**; R = Me **10**; R = Et

Entry	7	Yield (%)[b]	
		R = Me	R = Et
s	4-NCPhBr	96	94
2	3-NCPhBr	79	89
3	4-O_2NPhBr	95	96
4	3-O_2NPhBr	84	98
5	2-O_2NPhBr	54	25
6	4-OHCPhBr	90	77
7	3-OHCPhBr	53	53
8[c]	2-OHCPhBr	28	26
9	4-H_3COCPhBr	84	65
10	3-H_3COCPhBr	30	26
11	4-PhOCPhBr	75	22
12	4-F_3CPhBr	84	39
13	2-Bromothiophene	32	36
14	3-Bromopyridine	42	73
15	PhBr	16	—

[a]Reaction conditions: **7** (5.0 mmol), **8a/8b** (10.0 mmol), $PdCl_2$ (0.5 mol%), imidazolium salt **2** (0.5 mol%), Et_3N (5.0 mmol), DMF (2 ml).
[b]Isolated yield.
[c]NMR calculated yield.

Mizoroki–Heck reaction of 4-bromobenzonitrile with methyl acrylate. Recycling of catalyst

The recovery and reuse of catalysts are highly desirable aspects of metal-catalysed reactions due to the high cost of metal catalysts, as well as for prevention of contamination of products with toxic metals. The recycling ability of the $PdCl_2$–imidazolium salt **2** catalytic system was investigated in the Mizoroki–Heck reaction of 4-bromobenzonitrile with methyl acrylate in DMF at 130 °C for 4 h (Fig. 2). After the first cycle, the product was extracted with ethyl acetate (3 × 10 ml). The water layer comprising $PdCl_2$/imidazolium salt/$Et_3NH^+Br^-$ left after the first run was dried and charged with fresh substrate and base. Again, the coupling reaction was performed under the same experimental conditions.

The catalytic system showed a decrease in catalytic activity with each run without any palladium black precipitation. Thus, the reduced product yield could be due to increased viscosity of the reaction mixture caused by accumulation of the salt formed from Et_3N after each run.

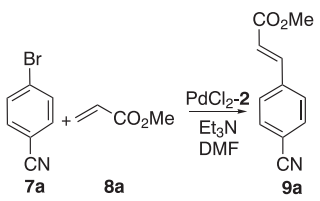


Figure 2. Recycling of catalyst in model Mizoroki–Heck reaction. Reagents and conditions: $PdCl_2$ (0.5 mol%), imidazolium salt **2** (0.5 mol%), Et_3N, DMF, 130°C, 4 h.

Mizoroki–Heck reaction of 4-bromobenzonitrile with methyl acrylate. ^1H NMR studies

In order to explore the interaction of the imidazolium salt **2** with the palladium centre, the reaction of **7a** with **8a** was performed in DMSO-d_6 in an NMR tube in the presence of Et_3N at 130 °C for 2 h under aerobic conditions using stoichiometric amounts of $PdCl_2$ and imidazolium salt **2**. The reaction was monitored using ^1H NMR and ^{13}C NMR spectroscopy (Fig. 3).

After 2 h, the ^1H NMR spectrum displayed a new set of signals parallel to those of the imidazolium salt **2** wherein the new signal for the most acidic H2 proton of imidazol-2-ylidene ring was conspicuously absent from the newly generated set of signals, thus pointing towards the most plausible coordination of the C2 carbenic carbon of imidazol-2-ylidene ring to palladium. Further, ^1H NMR spectroscopy revealed that the NHC was bound in the normal mode: the ^1H NMR spectrum of the newly generated catalytic species showed two new singlets at 7.53 and 7.36 ppm, typical for H4 and H5 present at the back side of the imidazol-2-ylidene ring.[37] It is noteworthy that the NC*H*N proton signal did not disappear in the absence of $PdCl_2$ under the same reaction conditions at 130 °C in DMSO-d_6. Moreover, the ^{13}C NMR analysis of reaction mixture showed a new signal at 165.9 ppm, which can be attributed to $C_{carbene}$–Pd bond formation (supporting information).Thus, NMR studies confirmed the *in situ* generation of normal NHCs from the C-2 position of imidazol-2-ylidene ring and the formation of $C_{carbene}$–Pd bond.

Mercury Poisoning Test for Imidazolium Salt 2

To further investigate the nature of catalytically active palladium species, we performed the mercury poisoning test by adding Hg (0) in excess, which amalgamates with Pd(0) and suppresses its catalytic activity.[38] Thus, in a representative experiment, the reaction between 4-bromobenzonitrile and methyl acrylate was carried out under standard conditions employing $PdCl_2$–salt **2** in the presence of a large excess of elemental mercury (in a molar ratio of 300:1 Hg/Pd). Hg(0) was added after 5 min of reaction and the reaction mixture was stirred for 4 h. A yield of 84% was isolated in comparison to 96% formed in an analogous experiment without Hg(0), thus showing formation of stable homogeneous palladium catalysts with imidazolium salt **2** which continued the reaction even after the addition of mercury. However, the partial decrease in catalytic activity in the presence of Hg(0) points towards the formation of small amounts of Pd (0) nanoparticles in the reaction mixture.

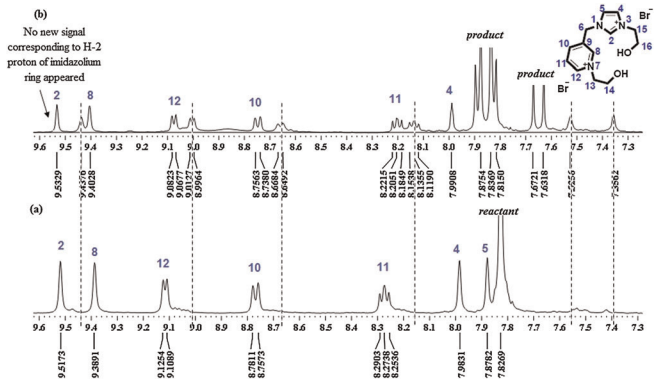


Figure 3. Partial ^1H NMR spectra recorded in DMSO-d_6 at (a) 0 h and (b) 2 h.

These results are also in agreement with the NMR studies, which also showed formation of *in situ* Pd–NHC complex during the catalytic reaction.

Conclusions

The synthesized imidazolium salts were found to be efficient phosphine-free preligands for palladium-catalysed Mizoroki–Heck reaction under aerobic conditions. The nature of the imidazolium salts had a noticeable impact on their catalytic performance. The hydroxyl-functionalized imidazolium salt **2**, incorporating the features of both bidentate chelating *O,O* ligand and carbene, successfully catalysed the Mizoroki–Heck reactions for a variety of aryl bromides with high activity and stability under aerobic conditions. Also, the catalytic system showed good tolerance to a variety of functional groups present in aryl bromides but failed to catalyse the reaction with aryl chlorides. The good to excellent yields isolated for a variety of methyl and ethyl cinnamates using low catalytic loadings under aerobic conditions in a short reaction time provide evidence for the practical utility of these catalytic systems. All the imidazolium salts used in this study produced the *trans*-product selectively; therefore, their use can be extended to other regio- or stereoselective reactions. The NMR investigations with the hydroxyl-functionalized salt showed *in situ* generation of NHC from C-2 position of imidazol-2-ylidene ring and the formation of $C_{carbene}$–Pd bond. Further structural modifications in the imidazolium salts for improving catalytic efficiency are currently underway in our laboratory.

Acknowledgements

We gratefully acknowledge financial support from the University of Delhi, India. P.G. also acknowledges the Council for Scientific and Industrial Research, India for Junior and Senior Research Fellowships. The authors are grateful to USIC-CIF, University of Delhi for single-crystal X-ray diffraction, HRMS and NMR spectral data.

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