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REGULAR ARTICLE

# A new PEPPSI type N-heterocyclic carbene palladium(II) complex and its efficiency as a catalyst for Mizoroki-Heck cross-coupling reactions in water

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**Abstract.** A new air and moisture stable PEPPSI (PEPPSI: pyridine-enhanced pre-catalyst preparation, stabilisation, and initiation) themed palladium N-heterocyclic carbene (NHC) complex [Pd(L)$Br_2$(Py)] (**1**) [L: 2-flurobenzyl)-1-(4-methoxyphenyl)-1H-imidazolline-2-ylidene] was synthesized and characterized. The structure of complex **1** was determined by X-ray single-crystal analysis. The palladium center in **1** adopted a square planar geometry with carbene and pyridine ligands occupying the mutual *trans* position. The complex **1** was employed to catalyze the Mizoroki-Heck cross-coupling reactions of aryl bromides/iodides with styrene in water. To the best of our knowledge, this is the first report where a Pd-PEPPSI catalyst was successfully employed in aqueous-phase Mizoroki-Heck reaction. Good to excellent yields of cross-coupling products were obtained with a range of representative aryl bromides/iodides under relatively mild conditions (100 °C, 1 mol% of **1**).

**Keywords.** N-heterocyclic carbene; Palladium; PEPPSI; Mizoroki-Heck reaction; aqueous media.

## 1. Introduction

N-heterocyclic carbenes (NHCs) are among the most intriguing classes of ligands that have generated numerous breakthroughs in the field of organometallic chemistry and homogeneous catalysis.[1] In recent years, NHCs have been viewed as a sustainable alternative to phosphines in many Pd-catalyzed reactions, including carbon-carbon and carbon-heteroatom bond formation reactions.[2] The main advantages of the NHC systems over phosphines lie in their trouble-free syntheses, easy handling property, non-toxic behaviour, air and moisture stable properties, and tuneable catalytic activity *via* altering the stereo-electronic property of the pendant groups attached to the imidazole moiety.[3,4] Moreover, due to their strong σ-donating and poor π-accepting properties, they can produce many stable complexes compared to the analogous phosphine-based systems.[5] In the past few years, Pd-NHC systems have been increasingly used as catalysts for various types of cross-coupling reactions. Since the first report of the utilization of Pd-NHC system in Mizoroki-Heck reaction by Herrmann's group,[6] a large number of efficient catalysts bearing NHC are documented for catalyzing Heck reaction. Despite remarkable progress that has been made in this field, to date, only a few catalytic systems are effective to carry out the reaction in neat water.[7] It may be noted that water is always considered as a potentially benign solvent for organic synthesis. In this prospect, the development of a robust NHC-Pd based catalytic system for Heck

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reaction in water is of tremendous significance. Among various NHC systems, the air-stable and user-friendly pyridine stabilized complexes, so-called PEPPSI complexes (PEPPSI: pyridine-enhanced pre-catalyst preparation, stabilisation, and initiation) developed by Organ and co-workers[8] have got numerous attention as pre-catalysts for various organic reactions. The NHC ligand, because of its strong *trans* directing property, is expected to create a vacant site for substrate binding by easily releasing the labile pyridine ligand trans to NHC and thus would enhance the catalytic activities. In fact, there exist several recent reports on the utility of PEPPSI-Pd-NHC complexes in Negishi,[8] Suzuki,[9] C-N coupling,[10] Sonogashira,[11] C-H bond activation,[12] aryl amination,[13] etc. Moreover, heterogeneous NHC-Pd based systems have also been explored for the aqueous phase cross-coupling reaction like Suzuki-Miyaura reaction. To cite an example, recently Choudhury *et al.,* have reported an efficient co-ordination polymer anchored Pd-NHC system and their application as a promising catalyst in aqueous phase Suzuki reaction.[9] However, their uses in Mizoroki-Heck coupling are limited. To our knowledge, only three catalytic systems (Figure 1) are known where PEPPSI-Pd-NHC complexes are employed in Mizoroki-Heck reaction to date.[14] However, uses of environmentally unfavourable reaction media like dioxane (Shen),[14a] DMF (Crudden and Lin),[14b,c] along with high reaction temperatures (~140 °C) are the major limitations of those systems. To the best of our knowledge, there is no literature precedent available pertaining to the utility of Pd-PEPPSI-NHC complexes in the Mizoroki-Heck reaction in water, although such systems have been employed in aqueous media for other cross-coupling reactions like Suzuki,[15] Sonogashira,[11] etc. Herein, we report the synthesis and characterization of a new PEPPSI-Pd-NHC complex and its catalytic application of Mizoroki-Heck reaction in water.

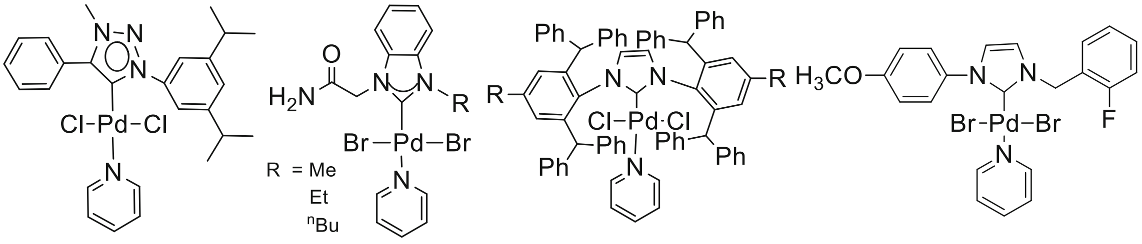
## 2. Experimental

### 2.1 *Materials and methods*

All reactions and manipulations were carried out under air atmosphere unless otherwise stated. The imidazole precursors (4-methoxyphenyl)-1H-imidazole and $PdCl_2$ were purchased from TCI and Sigma-Aldrich, respectively. All solvents, substrates for catalysis and other chemicals were purchased from various commercial firms like TCI, Acros Organics, and Merck. The NMR spectrum for the imidazolium salt **L** was recorded in $CD_3OD$, while the complex was performed in $CDCl_3$ with tetramethylsilane as an internal standard and operating on a Bruker Avance 400 MHz NMR spectrometer. High-resolution mass spectra were recorded with an Agilent 6550 iFunnel Q-TOF MS system. The GCMS spectra of the catalytic products were performed in an Agilent GC Model 7820A with a mass detector model 5975 series.

### 2.2 *Procedure for preparation of 3-(2-flurobenzyl)-1-(4-methoxyphenyl)-1H-imidazolium bromide (L)*

(4-methoxyphenyl)-1H-imidazole (174 mg, 1 mmol) and 2-fluorobenzyl bromide (1.89 mg, 10 mmol) were taken in a round bottom flask (50 mL) and the mixture was dissolved in 5 mL $CH_3CN$ and then the resulting mixture was heated at 80 °C for 48 h. The reaction mixture was allowed to come to room temperature and diethyl ether was added to obtain a precipitate. The solution was filtered and the solid residue was washed with diethyl ether thrice and then dried in vacuum. The procedure yielded 268 mg (74%) of the product as a white powder. $^1H$ NMR ($CD_3OD$, 400 MHz, $\delta$, ppm): 9.60 (s, 1H, NCHN), 7.79 (t, $J$ = 1.6 Hz, 1H, CH=CH, imidazole), 7.78 (s, CH=CH, imidazole), 7,63-7.59 (m, 3H, Ar), 7.53-7.47 (m, 1H, Ar), 7.31-7.20 (m, 2H, Ar), 7.16-7.12 (m, 2H, Ar), 5.61 (s, 2H, benzyl $CH_2$), 3.30 (s, 3H, $OCH_3$), $^{13}C$ ($CD_3OD$, 100 MHz, $\delta$, ppm) 163.72, 162.50, 161.26, 136.67, 133.14 (d, $^3J_{C,F}$ = 8.4 Hz), 132.47 (d, $^3J_{C,F}$ = 2.9 Hz), 129.21, 126.38 (d, $^4J_{C,F}$ = 3.6 Hz), 125.09, 124.30,123.73, 122.79,122.15, 117.14, 116.93, 116.43,



**(Crudden, 2012)** **(Lin, 2013)** **(Shen, 2014)** **This work**

**Figure 1.** PEPPSI-Pd-NHC precatalysts for Mizoroki-Heck reaction.

56.34, 49.63. HR-MS: [M-Br]$^+$ = 283. 16, calculated: 283.12.

### 2.3 *Procedure for the preparation of PEPPSI-Pd-NHC (1) complex*

A 50 mL flask equipped with a magnetic stir bar was charged with imidazolium salt **L** (218 mg, 0.6 mmol), $PdCl_2$ (89 mg, 0.5 mmol), $K_2CO_3$ (207 mg, 1.5 mmol), excess KBr, pyridine (5 mL). The mixture was allowed to stir at 80 °C for 48 h and then cooled to room temperature and the solvent was removed under vacuum. The residue was dissolved in dichloromethane (DCM) and purified by column chromatography, eluting with DCM/hexane (7:3). Complexes **1a** and **1** were recovered from the first and second fraction of the solvent respectively. **Complex 1**: Yield 265 mg, (70%); yellow powder; $^1$H NMR ($CDCl_3$, 400 MHz, $\delta$, ppm) 8.87 (d, $J$ = 8 Hz, 2H, py) 7.90 (t, $J$ = 7.6 Hz, 2H, Py), 7.84 (t, $J$ = 9.2 Hz, 1H, py), 7.71-7.67 (m, 1H, aromatic), 7.40-7.35 (m, 1H, aromatic), 7.27-7.24 (m, 2H, aromatic), 7.20-7.15 (m, 2H, aromatic), 7.07-7.03 (m, 2H, aromatic), 7.11 (d, $J$ =2.4 Hz, 1H, CH=CH imidazole), 6.97 (d, $J$ = 1.6 Hz, 1H, CH=CH imidazole), 5.94 (s, 2H, benzyl $CH_2$), 3.68 (s, 3H, $OCH_3$), $^{13}$C ($CDCl_3$, 100MHz, $\delta$, ppm) 162.1, 159.7, 152.5, 149.8, 149.5, 137.7, 132.5, 132.2 (d, $^3J_{C,F}$= 3.2 Hz), 130.6 (d, $^3J_{C,F}$ = 8.2 Hz), 124.7 (d, $^4J_{C,F}$ = 3.6 Hz), 124.4, 123.9, 122.2 (d, $^2J_{C,F}$ = 14.1 Hz), 121.8,115.5 (d, $^2J_{C,F}$ = 21.2 Hz), 114.2, 55.4, 48.3 (d, $^3J_{C,F}$ = 4.2 Hz); HRMS: [M-2Br-Py+H]$^+$ = 387.02, calculated = 387.02.

### 2.4 *X-ray single crystal analysis*

Single crystal X-ray diffraction: Single crystal X-ray diffractions were collected on a Bruker SMART APEX-II CCD diffractometer using Mo Kα (λ =0.71073 Å) radiation.[16] Bruker SAINT software has been employed for reducing the data and SADABS for correcting the intensities of absorption.[17] All co-crystal structures were solved and refined using SHELXL with anisotropic displacement parameters for non-H atoms. In all crystal structures, H-atoms are located experimentally, whereas C–H atoms were fixed geometrically using the HFIX command in SHELX-T.[18] The figures and packing diagrams are made using Mercury 3.9 version. No missed symmetry was observed in the final check of CIF file using PLATON.[19,20]

**Crystallographic parameters:**

Complex **1** (CCDC no: 1860391), Empirical Formula: $C_{22}H_{19}Br_2FN_3OPd$; MW (g/mol): 626.64; Crystal size: 0.25 x 0.15 x 0.11; Colour: Pale yellow; Crystal system: Monoclinic; Space group: $P2_1/c$; Cell length (in Å): *a*, 16.230(3); *b:* 8.5370(14); *c:* 33.317(5); Cell angles, α: 90; *β*: 90; *γ*: 90; Cell volume, 4599.2(13); Cell density [g/cm$^3$]: 1.811; T (K): 100K; μ (mm$^{-1}$): 4.308; GoF: 1.024; R1: 0.0343; wR2: 0.0580; Reflections collected: 69825; Unique reflections: 4807; Observed reflections: 3472.

Complex **1a** (CCDC no: 1863543), Empirical Formula: $C_{10}H_{10}Br_2N_2Pd$; MW (g/mol): 424.42; Crystal size: 0.27x0.21x0.11; Colour: Yellow; Crystal system: Triclinic; Space group: *P1*; Cell length (in Å): *a*, 5.656(3); *b:* 7.125(3); *c:* 7.784(4); Cell angles (in °), α: 79.958(4); *β*: 88.681(4); *γ*: 88.681(4); Cell volume, 307.3(3); Cell density [g/cm$^3$]: 2.293; T (K): 100K; μ (mm$^{-1}$): 4.308; GoF: 1.145; R1: 0.076; wR2: 0.2361; Reflections collected: 9344; Unique reflections: 1590; Observed reflections: 1464.

### 2.5 *General procedure for the catalytic reaction*

A round-bottomed flask (50 mL) equipped with a condenser and a magnetic stirring bar was charged with aryl halide (1 mmol), styrene (1.5 mmol), $K_2CO_3$ (3 mmol) and **1** (1 mol%) in water (3 mL) were allowed to stir at 100 °C in air. The progress of the reaction was monitored by TLC (hexane/ethyl acetate, 4:1). After completion of the reaction, the reaction mixture was cooled to room temperature. Ethyl acetate (15 mL) was added to the reaction mixture. The organic layer was washed with water (3 x 10 mL) and dried over anhydrous $MgSO_4$ and the reaction mixture was analysed with GC-MS.

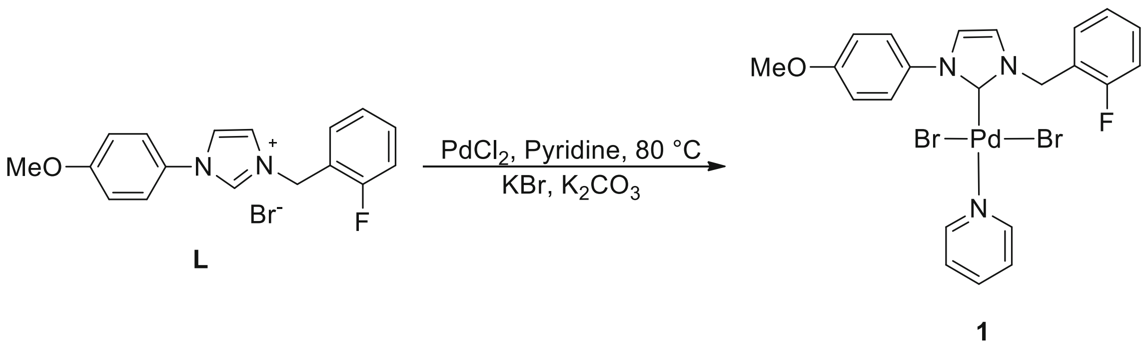
### 2.6 *Transmission electron microscopy (TEM)*

The sample was prepared by the doping of an ethanol solution of palladium black on the copper grid coated with carbon. Transmission electron micrographs were recorded on a JEOL JEM -2100 plus electron microscope.

## 3. Results and Discussion

### 3.1 *Synthesis and characterisation of ligand and complex*

The NHC salt (2-flurobenzyl)-1-(4-methoxyphenyl)-1H-imidazolium bromide (**L**) was prepared by the arylation of (4-methoxyphenyl)-1H-imidazole with 2-fluorobenzyl bromide by following a method similar to that reported by Mukherjee *et al.*[21] The structure of the **L** was assigned based on NMR ($^1$H and $^{13}$C) and mass spectral data. The ESI-MS spectrum of **L** shows the base peak at *m/z* = 283.1 corresponds to [M-Br]$^+$ ions. In the $^1$H NMR spectrum, the imidazolium proton of **L** appeared at 9.60 ppm, and the value is consistent with the literature data.[22] The $^{13}$C NMR signal of the carbene (NCN) of **L** displayed at 136.66 ppm. The PEPPSI-Pd-NHC complex **1** was synthesized by following Organs' procedure[8a] by treating $PdCl_2$ with corresponding carbene precursor (**L**) in pyridine in the



**Scheme 1.** Synthesis of PEPPSI-Pd-NHC complex **1**.

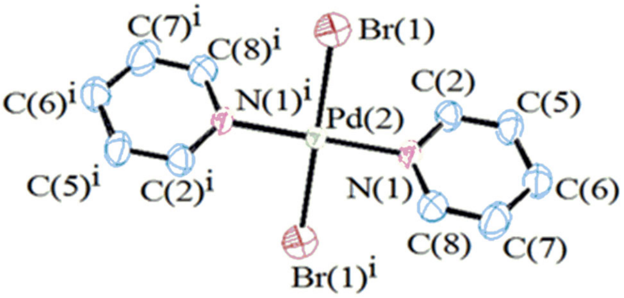


**Figure 2.** Molecular structure of **1a**.

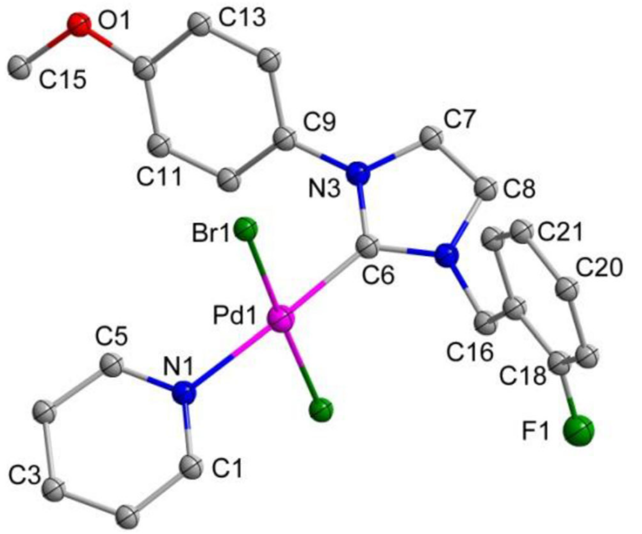


**Figure 3.** Molecular structure of **1**.

presence of $K_2CO_3$ and excess of KBr (Scheme 1). After thorough purification by column chromatography, the complex **1** was isolated in 70% yields and it is air and moisture stable and can be stored for more than six months without any noticeable decomposition. The complex is soluble in polar organic solvents like chloroform, dichloromethane, acetonitrile, and acetone. Alongside the complex **1**, a small amount of known bis-pyridine complex, *trans*-$[Pd(Br)_2(Py)_2]$ (Py = pyridine; **1a**) was also isolated as a side product. Since the molecular structure of complex **1a** is not reported, we have determined its structure by X-ray single-crystal analysis and the molecular structure is displayed in Figure 2. The X-ray quality crystals of **1a** were grown through slow diffusion of hexane into a concentrated dichloromethane solution. The complex adopts a regular square planar geometry in which the Pd center is predictably surrounded by two pyridine and two bromine ligands in mutual *trans* positions.

The molecular dimensions of the complex **1a** are more or less similar to the analogues diiodo-$[PdI_2(Py)_2]$[23] or dichloro complex *trans*-$[PdCl_2(Py)_2]$.[24] As expected, the Pd-X bond distances in the complexes *trans*-$[PdX_2(Py)_2]$ follow the trend: Pd-I (2.623 (15) Å)> Pd-Br (2.411(2) Å)> Pd-Cl (2.297(1) Å). The Pd-N bond length (2.053(9) Å) in the complex **1a** is slightly longer than that of the analogous diiodo (2.018(8) Å) or dichloro complex (2.024(6) Å). The identity of the PEPPSI-Pd-NHC complex **1** was confirmed by $^1H$, $^{13}C$ NMR and mass spectrometry. The formation of the Pd-$C_{carbene}$ bond in the complex was evident from the disappearance of the imidazolium proton (NC*H*N) signal. Other characteristic peaks of the ligand precursor, **L** were observed in the $^1H$ NMR spectrum of the complex. In the $^{13}C$ NMR, the palladium carbene carbon appeared at $\delta$ 151 ppm for the complex **1**, and the value is similar to the other reported Pd-NHC complexes.[25] Compared to the free imidazolium salt this value is shifted downfield indicating complexation. The mass spectrum of the complex **1** exhibits a low intense peak at *m/z*, 387.02 for $[M\text{-}2Br\text{-}Py+H^+]^+$. The isotopic patterns of all the *m/z* peaks of the complex **1** matched with the expected patterns. The molecular structure of the complex **1** is determined by X-ray single-crystal analysis and the molecular structure of **1** is displayed in Figure 3. The crystals suitable for X-ray analysis were grown by slow diffusion of hexane into a concentrated acetone solution of the complex **1** at room temperature. The complex crystallizes in the monoclinic space group $P2_1/c$ with two molecules in the asymmetric unit (Z = 4). The crystal data parameter is summarized in Table S1 (Supplementary Information). Molecules are arranged by weak interactions such as C–H···O, C–H···π and π···π (Figure S13, Supplementary Information) to complete the three packings. Symmetry independent molecule runs along [010] axis *via* π···π interactions. Two such molecular tapes are held together by weak C-H···O and C–H···π interactions (Figure 4). The C-H···F interaction plays an important role to complete the molecular packing. The Pd metal in the complex **1** adopts a distorted square planar environment with carbene and pyridine occupying mutual *trans* position (Figure 3). The Pd-$C_{carbene}$ (1.973(7) Å) and Pd-$N_{py}$ (2.106(6) Å) bond distances in **1** are comparable to those reported for other PEPPSI-Pd-NHC complexes.[11a,26] It is interesting to note that Pd−N distance in the complex **1** is much longer than the Pd-N distance in the complex **1a** (2.053(9) Å) which is attributed to the strong *trans* influence of the NHC ligand (Table S1, Supplementary Information). The $C_{Carbene}$−Pd−$N_{py}$ and Br-Pd-Br bond angles are at 176.71(3) and 177.81(4) consistent with distorted square planar geometry of the metal center. The crystal is stabilized by weak interactions namely C2-H···Br3, C22-H···O1 and C27-H···F1 H-bonds as shown in Figure S13 (Supplementary Information).

### 3.2 *Mizoroki-Heck reaction catalysed by Pd-PEPPSI complex*

The proposed Mizoroki-Heck reactivity of our catalyst **1** was investigated in model reaction between bromobenzene and styrene in common solvents such as *N*,*N*-dimethylformamide (DMF), toluene, tetrahydrofuran (THF) and water, in the presence of base $K_2CO_3$ and complex 1 (1.0 mol%) at a temperature mentioned in Table 1 for 24 h. To our disappointment, no desired product was obtained (Table 1, entries 1-4). However, there are literature precedents available that the additions of tetra-n-butyl ammonium bromide (TBAB), as an additive, effectively improve the reactivity in Heck coupling reactions.[27] This prompted us to examine the catalytic performance of the complex **1** in presence of TBAB and we were pleased to find that addition of TBAB (1.5 equivalents) in the model system significantly improved the conversion of product to 84% for the complex **1** (1 mol%) in water under air in presence of $K_2CO_3$ base (2 equivalents) (Table 1, entry 8). The conversion of the product could be further increased to 95% by simply increasing the $K_2CO_3$ concentration from 2 to 3 equivalents (Table 1; entry 9). As demonstrated in Table 1, only THF (Entry 7) can show comparable results with $H_2O$, while much lower conversions are obtained with solvents like DMF and toluene (entries 5 & 6). It is important to note that in the absence of catalyst, no conversion was observed (Table 1; entry 10). Since water is environmentally benign solvent compared to THF,[28] therefore, optimisation of other reaction variables such as catalyst loadings, bases, temperatures, etc. was carried out in water under refluxing condition in presence of TBAB and the results are displayed in Table 1. To find out the best base for our system, we have tested the commonly available inorganic bases like $Na_2CO_3$, KOH, NaOH and $KO^tBu$ using complex **1** as a catalyst. It has been observed that activities of $K_2CO_3$ and $Na_2CO_3$ are comparable, (entries 8 & 15) while NaOH showed the lowest activity (entry 16). The temperature optimization study reveals that a temperature of 100 °C is essential to obtain nearly quantitative conversion of the product (entry 9). When the temperature was decreased to 80 °C, a substantial drop in the conversion of the product was noticed (entry 11). In fact, at room temperature, the reaction did not proceed at all. Like temperatures, the catalyst loadings and the reaction times also have some impact on our catalytic system. When the catalyst loading was reduced from 1 mol% to 0.5 mol%, the product conversion was decreased to 59% (entry 14). The optimal condition for our catalytic system stands out to be: 1 mol% **1**, $K_2CO_3$ (3 equivalents) as a base, TBAB (1.5 equivalents), water as the solvent, 100 °C as the reaction temperature. It is interesting to note that under optimized conditions when the efficiency of the bis-pyridine complex **1a** was examined in the model reaction; no product was formed substantiating the PEPPSI influence in the catalytic process (entry 19).

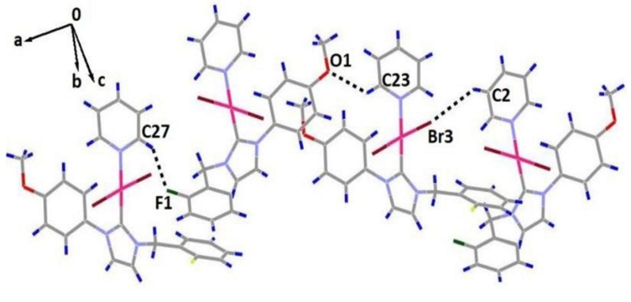
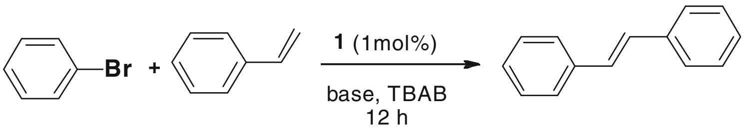


**Figure 4.** Symmetry independent molecules of **1** form a chain along [010] axis.

**Table 1.** Optimization of reaction variables for Pd-PEPPSI complex **1** catalyzed Mizoroki-Heck cross-coupling reactions[a].



| Entry | T (°C) | Solvent | Base | Additive | Conversion[b] |
|---|---|---|---|---|---|
| 1 | 140 | DMF | $K_2CO_3$ | – | 0 |
| 2 | 100 | $H_2O$ | $K_2CO_3$ | – | 0 |
| 3 | 100 | Toluene | $K_2CO_3$ | – | 0 |
| 4 | 66 | THF | $K_2CO_3$ | – | 0 |
| 5 | 140 | DMF | $K_2CO_3$ | TBAB | 11 |
| 6 | 110 | Toluene | $K_2CO_3$ | TBAB | 25 |
| 7 | 66 | THF | $K_2CO_3$ | TBAB | 82 |
| 8 | 100 | $H_2O$ | $K_2CO_3$ | TBAB | 84 |
| 9 | 100 | $H_2O$ | $K_2CO_3$ | TBAB | 95 |
| 10 | 100 | $H_2O$ | $K_2CO_3$ | TBAB | 00[c] |
| 11 | 80 | $H_2O$ | $K_2CO_3$ | TBAB | 45 |
| 12 | 60 | $H_2O$ | $K_2CO_3$ | TBAB | 41 |
| 13 | 30 | $H_2O$ | $K_2CO_3$ | TBAB | 00 |
| 14 | 100 | $H_2O$ | $K_2CO_3$ | TBAB | 59[d] |
| 15 | 100 | $H_2O$ | $Na_2CO_3$ | TBAB | 78 |
| 16 | 100 | $H_2O$ | NaOH | TBAB | 42 |
| 17 | 100 | $H_2O$ | KOH | TBAB | 48 |
| 18 | 100 | $H_2O$ | KOtBu | TBAB | 56 |
| 19 | 100 | $H_2O$ | $K_2CO_3$ | TBAB | 00[e] |

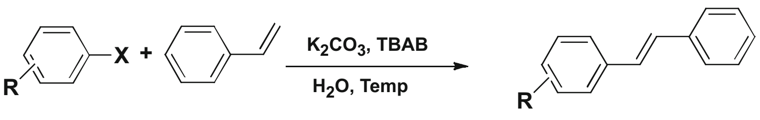
[a]Reaction condition: 1 mmol bromobenzene, 1.5 mmol styrene, 1.5 mmol TBAB, base (2 mmol, entries 1-8, 3 mmol, entries 9-19) and 1 mol% **1** are heated for 12 h at mentioned temperature. [b]Conversion is determined by GC, [c]absence of **1** [d]**1** (0.5 mol%), [e]Complex **1a**.

To check the general applicability of our catalytic system, we have explored the catalytic performance of our complex **1** for a range of representative aryl bromides and iodides. It is observed that both electron-donating (Table 2; entries 3, 4, 8, 10) and electron-withdrawing para and meta substituted (entries 5-7 & 11-13) aryl bromides/iodides fairly react with styrene to give corresponding coupling products in moderate to excellent yields. However, ortho-substituted aryl halides reluctant to participate in the reaction as the conversion of the product gave only 18% when 2-iodotoluene was employed as a coupling partner (Entry 9). Usually, the reactions with aryl iodides required less reaction time compared to corresponding aryl bromides (entry 3 vs 4; entry 11 vs 12). Our system failed to activate chloroarenes and heteroaryl halides as substrates in water (entries 14-16).

It may be important to mention that there is literature evidence[29] where Pd-NHC complexes often generate Pd nanoparticles under catalytic condition. Hence, we were intrigued to see if any such nanoparticles were generated in our case. However, in our case, no nanoparticles were generated as observed by transmission electron microscopy (TEM) analysis (Figure S14, Supplementary Information).

Based on the literature reports,[28] we proposed a plausible reaction pathway in Scheme 2. It is well-documented that Pd-NHC complexes bearing throw-away ligands in the presence of TBAB, forms an anionic complex, TBA[(NHC)$PdBr_3$] which in turn acts as an active precatalyst in the reaction. Thereafter, at high temperature, in the presence of $K_2CO_3$, NHC-Pd (II) complex reduced to corresponding NHC-Pd(0) and in our case, possibly formed $[(NHC)\ Pd(0)Br]^-$ that could initiate the reaction. After the formation of the catalytically active Pd(0) species, the catalytic cycle could be summarised by four main steps, namely, oxidative addition of aryl halide to palladium center, co-ordination of substrates styrene, migratory insertion and β-hydride syn elimination to deliver the product.

**Table 2.** Pd-PEPPSI complex catalyzed Mizoroki-Heck cross-coupling reactions of different aryl halides with styrene[a].



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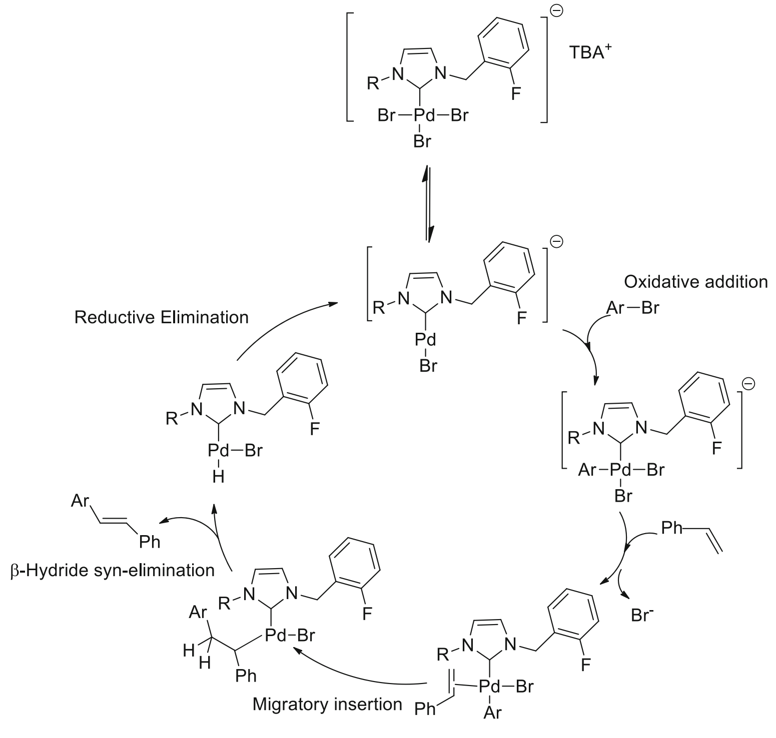
| Entry | R | X | Time (h) | Conversion (%)[b] |
|---|---|---|---|---|
| 1 | H | Br | 12 | 95 (90)[c] |
| 2 | H | I | 5 | 96 |
| 3 | 4-OMe | Br | 12 | 82 |
| 4 | 4-OMe | I | 5 | 93 |
| 5 | 4-$NO_2$ | Br | 12 | 91 |
| 6 | 4-$NO_2$ | I | 5 | 92 |
| 7 | 3-$NO_2$ | Br | 12 | 75 |
| 8 | 4-$CH_3$ | Br | 12 | 90 |
| 9 | 2-$CH_3$ | I | 12 | 18 |
| 10 | 3-$CH_3$ | I | 5 | 82 |
| 11 | 4-$COCH_3$ | Br | 12 | 100 (94)[c] |
| 12 | 4-$COCH_3$ | I | 5 | 100 |
| 13 | 4-CHO | Br | 12 | 97 (92)[c] |
| 14 | H | Cl | 12 | Trace |
| 15 | 4-$NO_2$ | Cl | 12 | Trace |
| 16 | 2-Bromopyridine |  | 12 | Trace |

[a]Conditions: Aryl halide (1 mmol), styrene (1.5 mmol), $K_2CO_3$ (3 mmol), $H_2O$ (3 mL), TBAB (1.5 mmol), reaction time: 5-12 h; 1 (1.0 mol%), Temp: 100 °C; [b]Conversion is determined by GC. [c]Isolated yields.



**Scheme 2.** Possible mechanism for the PEPPSI Pd-NHC catalysed Mizoroki-Heck reaction.

## 4. Conclusions

In summary, we have reported the synthesis of an air and moisture stable PEPPSI-Pd-NHC complex and explored its catalytic potential for Mizoroki-Heck cross-coupling reaction. The structure of the complex **1** was determined by X-ray single-crystal analysis. Present studies represent the first use of PEPPSI-Pd-NHC catalyst for the Mizoroki-Heck cross-coupling reactions in aqueous media where good-to-excellent yields of cross-coupling products are obtained.

## Supplementary Information (SI)

Figures S1–S21, Table S1 and CIF files are available at www.ias.ac.in/chemsci.

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**Conflicts of interest** There are no conflicts to declare.

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