

# Use of a recyclable poly(*N*-vinyl carbazole) palladium(II) complex catalyst: Heck cross-coupling reaction under phosphine-free and aerobic conditions

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**Abstract** A novel pathway for cross-coupling reaction of terminal alkenes with aryl halides (Heck cross-coupling) has been described using a new phosphine-free poly(*N*-vinyl carbazole) anchored palladium(II) complex as catalyst in aerobic conditions. The catalyst was found to be highly active for the couplings of a variety of substituted and non-substituted aryl halides with terminal alkenes and to smoothly afford the corresponding desired products in good to excellent yields. The catalyst can be reused at least six times without noticeable decrease in catalytic activity.

## Introduction

The Heck reaction [1–3], a Pd-catalyzed C–C coupling between aryl halides and terminal alkenes, is a robust and efficient method for carbon–carbon bond formation and remains a flourishing area of research [4, 5]. The reaction has been applied to many areas, including natural products [6–8] and fine chemicals synthesis [9–11]. Usually, aryl halides are reacted with alkenes in the presence of palladium and a suitable base. Soluble palladium compounds, generally phosphine palladium complexes, are the most efficient catalysts for the Heck reaction [12–18]. However, phosphine ligands are expensive, toxic, unrecoverable and sensitive to air and moisture and therefore environmentally unfavorable. The development of catalyst systems with

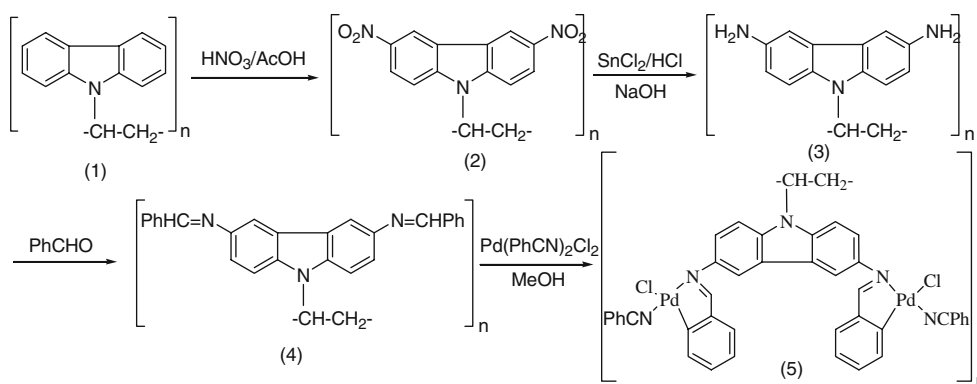
non-phosphine ligands [19–30] is now of practical interest and thus has been receiving great attention. With the development of green chemistry, the design and preparation of green catalysts have attracted much attention recently, among which heterogeneous catalysts have been widely employed [31–36]. The immobilization of metal catalysts on solid supports has become a valuable tool for the efficient separation of organic products and catalyst recycling. Polymers play a significant role in this area, offering different ways of metal attachment to the polymer matrix via covalent or non-covalent bonding, through hydrogen bridges, as well as through ionic, hydrophobic or fluorophilic interactions [37–41].

The recent discovery of polymer-based Schiff base ligands and of their effectiveness as catalysts offers an opportunity to develop phosphine-free heterogeneous catalysis. Several authors have recently reported polymer-anchored palladium complexes active for the Heck reaction under phosphine-free conditions. Schubert and coworkers reported stabilized palladium nanoparticles in star-shaped block copolymers [42]. Steel et al. described palladium *N*-heterocyclic carbene complexes anchored to polymers, and it was claimed that a true heterogeneous recyclable catalyst was functioning [43].

The excellent catalytic activity of poly (*N*-vinyl carbazole) anchored Pd(II) complex for the hydrogenation reactions of various organic substrates prompted us to extend our investigations into other catalytic reactions. In the present work, we have examined the catalytic activity of poly (*N*-vinyl carbazole) anchored Pd(II) complex in the Heck cross-coupling reaction between aryl halides and terminal alkenes under phosphine-free reaction conditions. The effects of various reaction parameters for optimization of the reaction conditions were also studied. This polymer-anchored metal complex exhibited high catalytic

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**Scheme 1** Synthesis of the polymer-anchored Pd(II) complex

performance and can be easily recovered and reused without significant loss of catalytic activity.

## Experimental

All the reagents were analytical grade and used as such without further purification. Solvents were purified and dried according to standard procedures. Poly (*N*-vinyl carbazole) (Art.No. 368350–5) was purchased from Aldrich; [Pd(PhCN)<sub>2</sub>Cl<sub>2</sub>], Pd(OAc)<sub>2</sub> and PdCl<sub>2</sub> were procured from Arora Matthey. Other reagents were purchased from Merck.

The palladium content was determined by Varian, USA, AA240 atomic absorption spectrophotometer (AAS). A Perkin–Elmer, USA, 2400C elemental analyzer was used to collect microanalytical data (C, H and N). Surface morphology of functionalized polystyrene ligand and metal complex was analyzed using a scanning electron microscope (ZEISS EVO40, England) equipped with EDX facility. Fourier transform infrared (FTIR) spectra for the catalyst and its precursors were recorded over the wave number range from 400 to 4,000 cm<sup>-1</sup> on a Perkin–Elmer, USA, FTIR 783 spectrophotometer using KBr pellets. UV–Vis spectra were taken using a Shimadzu, Japan, UV-2401PC double beam spectrophotometer having an integrating sphere attachment for solid samples. The thermal stability of the immobilized catalyst was determined using a Mettler Toledo, Switzerland, TGA/DTA 851e instrument. The reaction products were analyzed using a Varian, USA, 3400 gas chromatograph equipped with a 30 m CP-SIL8CB capillary column and a flame ionization detector. All reaction products were identified by using an Agilent, USA, GC–MS (QP-5050) equipped with a 30 m HP-5 ms capillary column.

## General experimental procedure for Heck reaction

To a suspension of polymer-anchored palladium(II) catalyst in DMF (10 mL), aryl halide (1.0 mmol), alkene

(2.0 mmol), K<sub>2</sub>CO<sub>3</sub> (1.5 mmol), 0.5 mol% of catalyst and dodecane as internal standard were added, and the reaction mixture was stirred at 80 °C under air. To study the progress of the reaction, the reaction mixtures were collected at different time intervals and quantified by GC analysis. At the end of the reaction, the catalyst was separated by simple filtration. The filtrate was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, concentrated, and the residue was purified by flash column chromatography on silica gel. The product was analyzed by GC–MS. All the prepared compounds are known and were compared with authentic samples.

## Preparation and characterization of poly (3,6-dibenzaldimino-*N*-vinylcarbazole) Pd(II) complex catalyst

The outline for the preparation of the poly (*N*-vinylcarbazole) anchored palladium(II) complex, [Pd(C<sub>6</sub>H<sub>4</sub>CH=N-Pol)(PhCN)Cl] (Pol=poly-*N*-vinylcarbazole) is shown in Scheme-1. The functionalized poly(*N*-vinyl carbazole amine) (3) was prepared according to the method of King and Sweet [44]. The polymer-anchored ligand (4) was prepared by the reaction of poly(*N*-vinyl carbazole) amine (3 g) with benzaldehyde (10 mL) in dry toluene (30 mL) medium under reflux condition for 72 h in nitrogen atmosphere. For the preparation of poly (*N*-vinyl carbazole) anchored palladium(II) complex (5), a methanolic solution (25 mL) of Pd(PhCN)Cl (0.7 g) was mixed with poly(3,6-dibenzaldimino *N*-vinyl carbazole) ligand (2 g), and the reaction mixture was first stirred for 24 h at room temperature and then refluxed for 12 h [45].

Due to insolubility of the [Pd(C<sub>6</sub>H<sub>4</sub>CH=N-Pol)(PhCN)Cl] complex in all common organic solvents, its structural investigation was limited only to its physico-chemical properties, SEM-EDX, TGA-DTA, IR and UV–Vis spectral data (Scheme 1). The complete incorporation of the organic substructure in the material was confirmed by elemental

**Table 1** Analytical data of the functionalized polymer and the Pd(II) complex

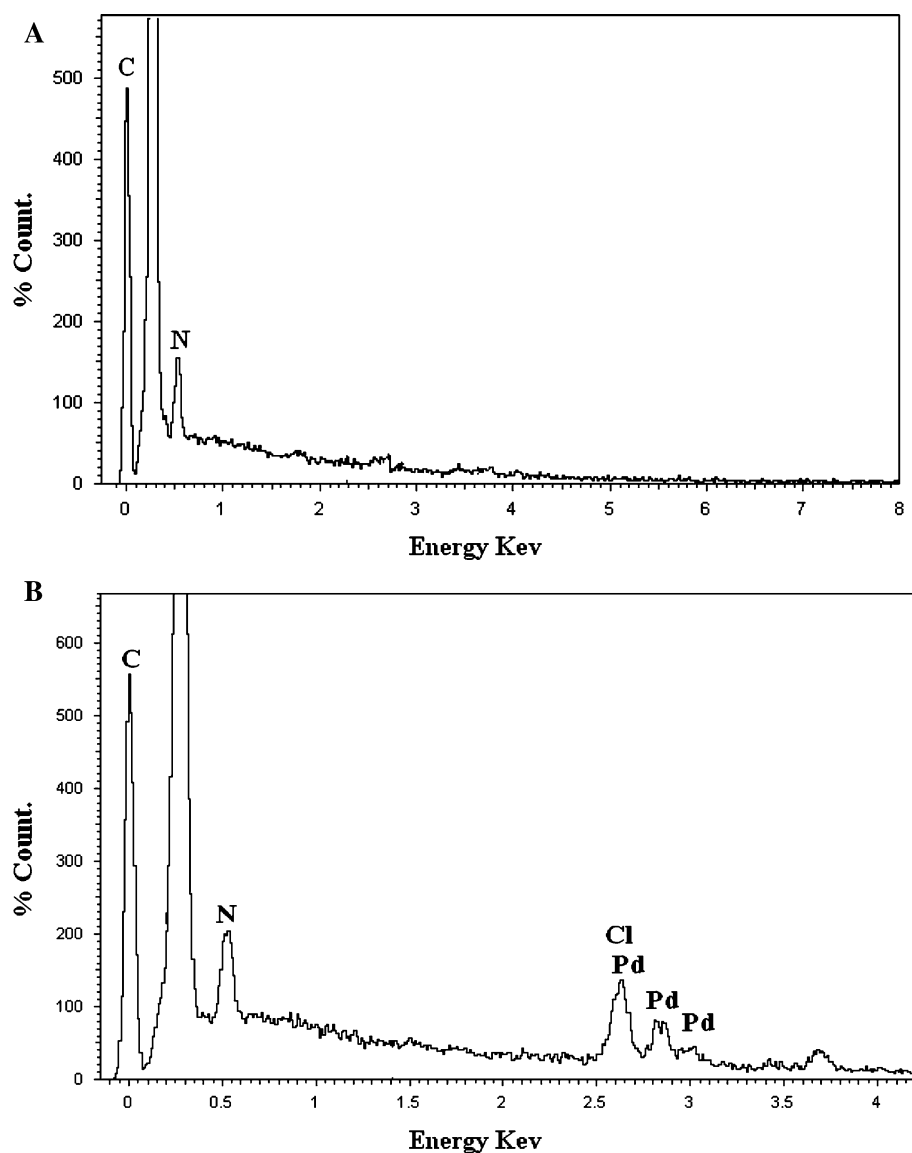
Compound	Color	Cl %	C %	H %	N %	Pd %
Pol	Faint Yellow		87.1	5.7	7.2	
Pol-NO <sub>2</sub>	Yellowish brown		76.0	4.5	10.2	
Pol-NH <sub>3</sub> Cl	Yellow	7.9	73.9	5.2	10.0	
Pol-NH <sub>2</sub>	Yellow		81.8	5.6	11.1	
[(C <sub>6</sub> H <sub>4</sub> CH=N-Pol)(PhCN)Cl]	Yellow		84.7	5.3	8.9	
[Pd(C <sub>6</sub> H <sub>4</sub> CH=N-Pol)(PhCN)Cl]	Yellowish brown	3.0	73.9	4.4	8.2	12.8

Pol = poly-*N*-vinylcarbazole

analysis (Table 1). The metal content of [Pd(C<sub>6</sub>H<sub>4</sub>CH=N-Pol)(PhCN)Cl] complex determined by AAS suggested 12.80 wt% metal loading in the immobilized palladium complex. The SEM images of polymer-anchored ligand and metal complex clearly show the morphological change, which occurred on the surface of the polymer matrix after loading of the metal. EDX data also support the metal attachment on the surface of polymer matrix (Fig. 1).

The catalyst is thermally stable up to 280 °C. The IR spectrum of poly(3,6-dibenzaldimino *N*-vinyl carbazole) showed characteristic IR peak at 1,630 cm<sup>-1</sup> that may be assigned to the C=N stretching vibration of imine, which on complexation shifted toward lower frequency to 1,620 cm<sup>-1</sup> suggesting bond formation between Pd and ligand. Other characteristic peaks at 1,590 cm<sup>-1</sup> ( $\nu$ -C=C-stretching, aromatic), 720 cm<sup>-1</sup> (orthometallation) [46],

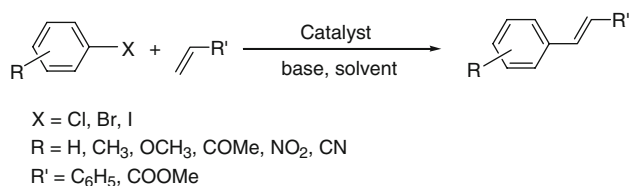
**Fig. 1** EDX spectra of poly (3,6-dibenzaldimino *N*-vinyl carbazole) ligand (a) and poly (3,6-dibenzaldimino *N*-vinyl carbazole) palladium(II) complex (b)



2,290  $\text{cm}^{-1}$  ( $\nu\text{-C}\equiv\text{N}$  of benzonitrile), 455  $\text{cm}^{-1}$  ( $\nu\text{ Pd-N}$ ) [47] and 355  $\text{cm}^{-1}$  ( $\nu\text{ Pd-Cl}$ ) [48] also support the formation of the palladium(II) complex. The UV–Vis spectra provided further evidence for the presence of palladium on polymer support. The absorption maxima at 305 nm may be attributed to the  $\pi \rightarrow \pi^*$  transition in the carbazole and the phenyl moieties, and the absorption at higher range (374, 434 nm) is due to the  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions of the imine system in conjugation with the aromatic nuclei. The Pd(II) carbazole complex shows the bands at 465 and 340 nm which may be assigned to  $^1\text{A}_{1g} \rightarrow ^1\text{A}_{2g}$  and  $^1\text{A}_{1g} \rightarrow ^1\text{B}_{1g}$  transitions, respectively [49].

### Heck cross-coupling reactions

To explore the catalytic activity of the present catalyst, we examined the Heck cross-coupling reaction. Generally, Heck reactions are conducted with a tertiary phosphine ligand. The toxicity of phosphines make them unfavorable and environmentally unacceptable. To address these concerns, we performed the Heck reaction under phosphine-free reaction condition. We began our investigation into Heck coupling reaction with the present catalyst using the coupling of bromobenzene with styrene as a model



**Scheme 2**

reaction. Since the performance of a successful metal-catalyzed cross-coupling reaction is known to be governed by a number of factors, at first the effects of various metal precursors, bases, solvents, temperatures and catalyst concentrations on the Heck cross-coupling reaction employing [Pd(C<sub>6</sub>H<sub>4</sub>CH=N-Pol)(PhCN)Cl] catalyst were surveyed. All the reactions were carried out under air (Scheme 2).

The influences of various metal salts, Pd(OAc)<sub>2</sub>, PdCl<sub>2</sub> and Pd(PhCN)<sub>2</sub>Cl<sub>2</sub> anchored with poly(3,6-dibenzaldimino *N*-vinylcarbazole) ligand were first studied. The use of Pd(OAc)<sub>2</sub> or PdCl<sub>2</sub> as a metal precursors resulted in moderate conversion of bromobenzene, whereas Pd(PhCN)<sub>2</sub>Cl<sub>2</sub> exhibited complete conversion at 80 °C (Table 2, entries 1–3). Therefore, Pd(PhCN)<sub>2</sub>Cl<sub>2</sub> was taken as a metal precursor, and further catalytic runs were studied with this catalyst, [Pd(C<sub>6</sub>H<sub>4</sub>CH=N-Pol)(PhCN)Cl]. Using metal salts without any ligand gave partial conversion of the desired product (Table 2, entries 4–6). No coupling reaction was observed without catalyst (Table 2, entry 7).

As the palladium compounds are so expensive, the amount used is an important criterion to estimate the value of a catalyst. In order to observe effect of catalyst concentrations on the conversion of bromobenzene and yield of desired product, the reactions catalyzed by [Pd(C<sub>6</sub>H<sub>4</sub>CH=N-Pol)(PhCN)Cl] at different concentrations from 0.1 to 1.0 mol% have been studied. The results are summarized in Table 2. From these results, it is seen that reactions at lower catalyst concentration (0.1 mol% of Pd) resulted in poorer conversion (Table 2, entry 8). The catalytic activity increased with an increase in the palladium concentration, and best results were obtained at catalyst concentration of 0.5 mol% Pd (Table 2, entry 3). A further increase in catalyst concentration (from 0.5 to 1.0 mol%

**Table 2** Effect of metal precursor and catalyst concentration in Heck cross-coupling reactions

Entry	Catalyst	Cat. Conc. (mol% of Pd)	Conversion <sup>a</sup> (%)
1.	[Pd(C <sub>6</sub> H <sub>4</sub> CH=N-Pol)Cl <sub>2</sub> ]	0.5	71
2.	[Pd(C <sub>6</sub> H <sub>4</sub> CH=N-Pol)(OAc) <sub>2</sub> ]	0.5	78
3.	[Pd(C <sub>6</sub> H <sub>4</sub> CH=N-Pol)(PhCN)Cl]	0.5	90
4.	PdCl <sub>2</sub>	5.0	45
5.	Pd(OAc) <sub>2</sub>	5.0	39
6.	Pd(PhCN) <sub>2</sub> Cl <sub>2</sub>	5.0	46
7.	None	–	No reaction
8.	[Pd(C <sub>6</sub> H <sub>4</sub> CH=N-Pol)(PhCN)Cl]	0.1	8
9.	[Pd(C <sub>6</sub> H <sub>4</sub> CH=N-Pol)(PhCN)Cl]	0.25	67
10.	[Pd(C <sub>6</sub> H <sub>4</sub> CH=N-Pol)(PhCN)Cl]	0.75	90
11.	[Pd(C <sub>6</sub> H <sub>4</sub> CH=N-Pol)(PhCN)Cl]	1.0	90

Reaction conditions: Bromobenzene (1.0 mmol), styrene (2.0 mmol), K<sub>2</sub>CO<sub>3</sub> (1.5 mmol), DMF (6 mL), catalyst (0.5 mol% of Pd); All the reactions were carried out in air

<sup>a</sup> Conversion of reactant was determined by GC and GCMS analysis using dodecane as internal standard

**Table 3** Heck cross-coupling reactions using [Pd(C<sub>6</sub>H<sub>4</sub>CH=N-Pol)(PhCN)Cl] complex at various solvents

Entry	Solvent	Time (h)	Temperature (°C)	Conv. <sup>a</sup> (%)
1.	DMF	8	30	0
2.	DMF	8	40	09
3.	DMF	8	50	24
4.	DMF	8	60	56
5.	DMF	8	70	82
6.	DMF	8	80	90
7.	DMSO	8	80	88
8.	THF	12	Reflux	21
9.	MeOH	12	70	46
10.	ACN	12	Reflux	38
11.	Toluene	24	Reflux	Trace
12.	DCM	24	Reflux	Trace

Reaction conditions: Bromobenzene (1.0 mmol), styrene (2.0 mmol), K<sub>2</sub>CO<sub>3</sub> (1.5 mmol), DMF (6 mL), catalyst (0.5 mol% of Pd); All the reactions were carried out in air

<sup>a</sup> Conversion of reactant was determined by GC and GCMS analysis using dodecane as internal standard

Pd) did not significantly improve the conversion (Table 2, entries 10, 11).

Reaction temperature is another important factor for Heck reaction. In general, Heck cross-coupling reaction requires high reaction temperature. It was found that a temperature below 80 °C was not suitable for this cross-coupling as a poor conversion was obtained at 40–70 °C (Table 3, entries 2–5). At room temperature, no cross-coupled product was detected in the reaction medium (Table 3, entry 1). However, good efficiency was reached

when the reaction temperature was 80 °C (Table 3, entry 6).

Solvent plays a crucial role for effective cross-coupling reaction. To verify the solvent effect in Heck cross-coupling reactions, a series of reactions were investigated by taking the model reaction in different solvents. The reaction conducted in polar solvent medium like DMF or DMSO was found to be most effective (Table 3, entries 6, 7). The use of THF, MeOH and ACN as solvents led to slower reactions (Table 3, entries 8–10), and no desired cross-coupling products were observed while reactions were carried out in toluene and dichloromethane (Table 3, entries 11, 12). Consequently, DMF was chosen as the medium of choice for this coupling.

To determine the reactivity of the catalyst in various bases, bromobenzene was chosen as the initial coupling partner in combination with styrene as a model reaction for investigation into the optimal base. Various inorganic and organic bases such as Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, NaOH, NaOAc, KOH, Et<sub>3</sub>N and NaO<sup>t</sup>Bu were examined. As shown in Table 4, the best performance was observed with K<sub>2</sub>CO<sub>3</sub> (Table 4, entry 2). Other inorganic bases like Na<sub>2</sub>CO<sub>3</sub>, NaOH, NaOAc and KOH gave reasonable conversions leading to 35–74% yields (Table 4, entries 1, 3–5). The yield was noticeably low when organic bases such as Et<sub>3</sub>N and NaO<sup>t</sup>Bu were employed (Table 4, entries 6, 7). No conversion of the reactants was observed in the absence of base (Table 4, entry 8). The catalytic performance of the coupling reaction was also greatly affected by the base–substrate molar ratio employed. The Heck cross-coupling reaction with the present catalyst was carried out under various base–substrate molar ratios and conditions. The results are shown in Table 4 (entries 2, 9–11). The best

**Table 4** Heck cross-coupling reactions using [Pd(C<sub>6</sub>H<sub>4</sub>CH=N-Pol)(PhCN)Cl] complex at various bases and base–substrate ratios

Entry	Base	Base–substrate ratio	Time (h)	Temperature (°C)	Conv. <sup>a</sup> (%)
1.	Na <sub>2</sub> CO <sub>3</sub>	1.5:1	8	80	74
2.	K <sub>2</sub> CO <sub>3</sub>	1.5:1	8	80	90
3.	NaOH	1.5:1	8	80	38
4.	NaOAc	1.5:1	8	80	49
5.	KOH	1.5:1	8	80	35
6.	Et <sub>3</sub> N	1.5:1	8	100	16
7.	NaO <sup>t</sup> Bu	1.5:1	8	100	11
8.	No base	–	8	80	No reaction
9.	K <sub>2</sub> CO <sub>3</sub>	0.5:1	8	80	25
10.	K <sub>2</sub> CO <sub>3</sub>	1:1	8	80	59
11.	K <sub>2</sub> CO <sub>3</sub>	2:1	8	80	90

Reaction conditions: Bromobenzene (1.0 mmol), styrene (2.0 mmol), K<sub>2</sub>CO<sub>3</sub> (1.5 mmol), DMF (6 mL), catalyst (0.5 mol% of Pd); All the reactions were carried out in air

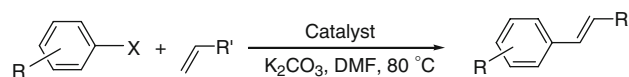
<sup>a</sup> Conversion of reactant was determined by GC and GCMS analysis using dodecane as internal standard

yield was achieved with 1.5:1 base–substrate ratio (Table 4, entry 2).

On the basis of the above optimized reaction conditions, the coupling reactions between a variety of aryl halides and alkenes were investigated (Scheme 2). The results are summarized in Table 5. Both aryl iodides and aryl bromides could react with aromatic or aliphatic terminal alkenes to give the corresponding coupling products with

good to excellent yields. As shown in Table 5, the coupling of activated and deactivated aryl iodides and alkenes proceeded in high yields and more rapidly than aryl bromides. Non-substituted aryl bromide gave moderate yield of coupled product (Table 5, entries 7, 23). Activated aryl bromide like *p*-bromonitrobenzene and *p*-bromoacetophenone bearing electron withdrawing group reacted with styrene and methyl acrylate to generate the corresponding

**Table 5** Heck reaction of aryl halides with terminal alkenes using [Pd(C<sub>6</sub>H<sub>4</sub>CH=N-Pol)(PhCN)Cl] complex catalyst



Entry	Aryl halides	Alkenes	Product <sup>a</sup>	Time (h)	Conv. <sup>b</sup> (%)	Yield <sup>c</sup> (%)
1.	Iodo benzene	Styrene	Stilbene	5	100	100
2.	<i>p</i> -Iodotoluene	Styrene	4-Methylstilbene	6	96	96
3.	<i>p</i> -Iodoanisole	Styrene	4-Methoxystilbene	6	97	97
4.	<i>p</i> -Iodonitrobenzene	Styrene	4-Nitrostilbene	5	99	99
5.	<i>p</i> -Iodoacetophenone	Styrene	4-Acetylstilbene	5	99	99
6.	<i>p</i> -Cyaniodobenzene	Styrene	4-Cyanostilbene	5	98	97
7.	Bromobenzene	Styrene	Stilbene	8	90	90
8.	<i>p</i> -Bromotoluene	Styrene	4-Methylstilbene	12	88	87
9.	<i>p</i> -Bromoanisole	Styrene	4-Methoxystilbene	12	87	87
10.	<i>p</i> -Bromonitrobenzene	Styrene	4-Nitrostilbene	8	95	95
11.	<i>p</i> -Bromoacetophenone	Styrene	4-Acetylstilbene	8	96	95
12.	<i>p</i> -Cyanobromobenzene	Styrene	4-Cyanostilbene	10	95	94
13.	2-Bromopyridine	Styrene	2-Styrylpyridine	16	81	78
14.	1-Bromonaphthalene	Styrene	1-Styrylnaphthalene	16	86	86
15.	<i>o</i> -Bromonitrobenzene	Styrene	2-Nitrostilbene	24	85	83
16.	Chlorobenzene	Styrene	Stilbene	24	Trace	Trace
17.	Iodo benzene	Me acrylate	Methylcinnamate	6	100	100
18.	<i>p</i> -Iodotoluene	Me acrylate	Methyl-4-methylcinnamate	6	94	94
19.	<i>p</i> -Iodoanisole	Me acrylate	Methyl-4-methoxycinnamate	6	90	90
20.	<i>p</i> -Iodonitrobenzene	Me acrylate	Methyl-4-nitrocinnamate	6	93	93
21.	<i>p</i> -Iodoacetophenone	Me acrylate	Methyl-4-acetylcinnamate	6	96	96
22.	<i>p</i> -Cyaniodobenzene	Me acrylate	Methyl-4-cyanocinnamate	6	91	91
23.	Bromobenzene	Me acrylate	Methylcinnamate	12	86	86
24.	<i>p</i> -Bromotoluene	Me acrylate	Methyl-4-methylcinnamate	12	80	80
25.	<i>p</i> -Bromoanisole	Me acrylate	Methyl-4-methoxycinnamate	12	84	84
26.	<i>p</i> -Bromonitrobenzene	Me acrylate	Methyl-4-nitrocinnamate	10	88	88
27.	<i>p</i> -Bromoacetophenone	Me acrylate	Methyl-4-acetylcinnamate	10	91	91
28.	<i>p</i> -Cyanobromobenzene	Me acrylate	Methyl-4-cyanocinnamate	12	92	92
29.	1-Bromonaphthalene	Me acrylate	Methyl-(3-naphthalene-5-yl)acrylate	16	80	80
30.	<i>o</i> -Nitrobromobenzene	Me acrylate	Methyl-3-nitrocinnamate	24	76	76

Reaction conditions: arylhalide (1.0 mmol), alkene (2.0 mmol), K<sub>2</sub>CO<sub>3</sub> (1.5 mmol), DMF (6 mL), catalyst (0.5 mol% of Pd); all the reactions were carried out in air

<sup>a</sup> Products were identified by comparison of their IR and <sup>1</sup>HNMR spectral data those reported in the literature (whenever possible)

<sup>b</sup> Conversion of reactant was determined by GC and GCMS analysis using dodecane as internal standard

<sup>c</sup> In all the coupling reactions, only *E*-stereochemistry was observed

**Table 6** Comparison of catalytic activity of the present catalyst in the Heck cross-coupling reaction with other related reported systems

Reaction	Catalyst	Reaction conditions	Yield%	Reference
(Bromobenzene + Styrene)	[Pd(C <sub>6</sub> H <sub>4</sub> CH=N-Pol)(PhCN)Cl]	K <sub>2</sub> CO <sub>3</sub> , DMF, 0.5 mol% catalyst, 80 °C, 8 h	90	Present
	Silylated PdNHC complex	Et <sub>3</sub> N, 0.013 mmol Pd, reflux DMF	70	19a
	MCM-41 Pd	Bu <sub>3</sub> N, 0.0187 mol% Pd, 170 °C, 72 h, NMP	20	19b
	Si-As-Pd (0)	Bu <sub>3</sub> N, <i>p</i> -xylene, 140 °C, 12 h, 0.03 mmol of Pd	54	19c
(Bromobenzene + Me acrylate)	[Pd(C <sub>6</sub> H <sub>4</sub> CH=N-Pol)(PhCN)Cl]	K <sub>2</sub> CO <sub>3</sub> , DMF, 0.5 mol% catalyst, 80 °C, 10 h	86	Present
	NHC-Pd(II)	Na <sub>2</sub> CO <sub>3</sub> , DMA, 1.0 mol% catalyst, 160 °C, 18 h	48	19d
	Silylated PdNHC complex	Et <sub>3</sub> N, 0.013 mmol Pd, reflux DMF	82	19a
	Pd(TMHD) <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub> , DMF, 12 h, 80 °C, 5 mol% catalyst	60	19e

product in good yields (Table 5, entries 10, 11, 26, 27). For deactivated aryl bromides, *p*-bromoanisole and *p*-bromotoluene bearing electron donating group in their *para* position, lower yields were obtained under the present reaction conditions (Table 5, entries 8, 9, 24, 25). The coupling of *ortho*-substituted bromobenzene having nitro group gave the corresponding coupling product with styrene and methyl acrylate in 83 and 76% yield, respectively (Table 5, entries 15, 30). Sterically hindered 1-iodonaphthalene was found to react efficiently under the present reaction conditions (Table 5, entries 14, 29). Heteroaryl bromides, such as 2-bromopyridine, also coupled effectively with styrene providing 78% coupled product (Table 5, entry 13). However, reactivity toward chloroarenes, which was observed by others [50, 51], was not achieved with our catalyst system. Displacement of styrene to methyl acrylate gave lower yields. The entire obtained product was *E*-stereochemistry, which was identified by GC–MS and <sup>1</sup>HNMR.

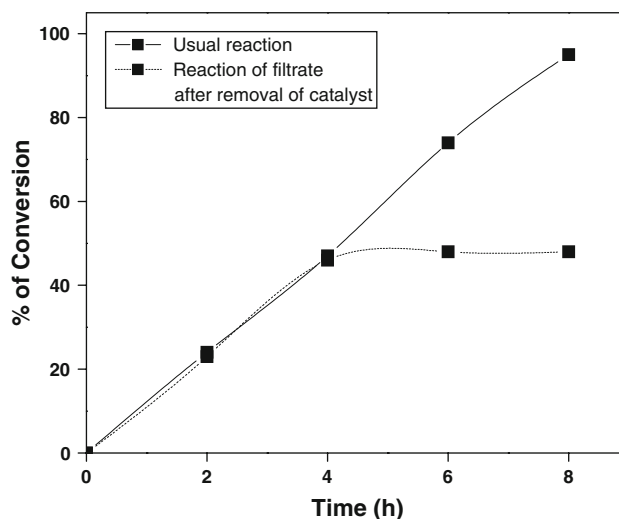
### Comparison of catalytic activity with other reported systems

Table 6 provides a comparison of the results obtained for our present catalytic system with those reported in the literature. From the table, it is seen that present catalyst exhibited higher conversions and yields compared to the other reported systems [52–56]. Reactions conducted at lower temperature and shorter reaction time were required for the Heck cross-coupling reactions using our catalyst.

### Heterogeneity test

Heterogeneity and the palladium leaching of the present catalyst were examined by the “Hot filtration test” for the Heck reaction of 4-bromonitrobenzene and styrene. Figure 2 shows the leaching experiment during the reaction over polymer-anchored palladium catalyst. After

continuing the reaction for 4 h, the catalyst was removed by filtration using Whatmann filter paper, and the resulting filtrate was subjected to heating for further 4 h reaction. Gas chromatographic analysis of the filtrate solution showed that there was no significant increase in conversion, whereas the catalyst containing portion gave 90% conversion after 4 h reaction (Fig. 2). Palladium leaching was also studied by atomic absorption spectroscopic analysis, indicating that the liquid part of Heck reaction mixture contained less than 0.5 ppm palladium. These results mean that the catalysis by leached palladium is negligible. The efficient catalytic performance is due to the polymer-anchored metal complex not due to leached palladium metal in the solvent.



**Fig. 2** Leaching experiment of poly(*N*-vinyl carbazole) anchored Pd(II) complex catalyst toward the Heck cross-coupling reaction. Reaction conditions: 4-Bromonitrobenzene (1.0 mmol), styrene (2.0 mmol), catalyst (0.5 mol% Pd), K<sub>2</sub>CO<sub>3</sub> (1.5 mmol), DMF (6 mL)

## Reuse of the catalyst

Another notable advantage of the heterogeneous catalyst with this reaction was the reuse of the catalyst. Recycling studies were performed with the present catalyst using the reaction of 4-bromonitrobenzene with styrene. After the first run, the solid catalyst was separated from the reaction medium by simple filtration, washed with dichloromethane and finally dried at 40 °C under reduced pressure. After separation and washing, the heterogeneous catalysts were used for the same reactions under the same reaction conditions as for the initial run without any regeneration procedure. The catalyst was recycled six times to give yields of 95, 93, 93, 91, 91 and 89% consecutively. This reaction conversion shows that the immobilized catalyst can be repeatedly used without any apparent decrease in its catalytic activity and selectivity.

## Conclusions

In summary, we have synthesized a new phosphine-free heterogeneous palladium catalyst  $[\text{Pd}(\text{C}_6\text{H}_4\text{CH}=\text{N}-\text{Pol})(\text{PhCN})\text{Cl}]$ , which is highly efficient for the Heck cross-coupling reactions of aryl halides with terminal alkenes. The catalyst was found to be air-stable, active and non-polluting under the various reaction conditions screened. The mild reaction conditions, simple experimental procedure, rapid conversion, excellent yields and reusability of the catalyst are notable advantages of the method. High efficiency and economy gain by simple reaction processing and easy recovery and reuse of the catalyst make it an ideal protocol from an industrial point of view.

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