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$PdCl_2$(bipy) complex—An efficient catalyst for Heck reaction in glycol–organic biphasic medium

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Abstract

The Palladium complex $PdCl_2$(bipy) (**1**) was found to be efficient in catalyzing the Heck reaction of aryl halides in a biphasic system comprising ethylene glycol along with an organic solvent. A proper tailoring of the organic phase ensured that the leaching of the catalyst to the organic phase was negligible. The catalyst was active for the Heck reaction of a number of olefins, aryl halides, in presence of organic and inorganic bases. The $PdCl_2$(bipy) catalyst was stable and could be recycled for five times without any loss in activity and selectivity. A major advantage of this work is that unlike hitherto reported biphasic systems; it does not employ a water-soluble ligand to achieve biphasic catalysis.

Keywords: Heck reaction; Biphasic catalysis; $PdCl_2$(bipy) complex; C–C coupling

1. Introduction

Catalysis employing two-phase media has been commercially exploited for a number of reactions like hydroformylation, hydrogenation, oligomerization and telomerization reactions [1–8]. Of these, the processes using aqueous phase catalysts employ sulfonated phosphine ligands bound to the central metal catalyst [9–10]. The sulfonated phosphines are invariably sensitive to the presence of oxygen and are prone to oxidation, reducing their ability to stabilize the catalysts and hence their utility as ligands. In case of the application of such biphasic media in Palladium catalyzed systems like Heck reactions, the deactivation of the phosphines can lead to the decomposition of the Palladium catalyst to the Pd metal due to insufficient stabilization of the metal, as phosphines are gradually oxidized or degenerated. It is thus necessary to obtain stable catalysts with ligands stable to oxygen for application to Heck reactions in biphasic media.

Heck reactions in aqueous or biphasic media have been reported by a number of groups [11–13]. A majority of the groups have investigated water-soluble catalysts for this purpose along with solvent mixtures comprising polar solvents like DMF, CH_3CN, DMAc, etc., along with water. The primary objective of these studies has been to homogenize the aqueous systems to achieve good conversions. As far as biphasic systems are concerned, most of the studies have utilized water-soluble phosphine based catalysts in a glycol–organic biphasic system. Bhanage et al. [10] have reported Heck reactions with various metal–TPPTS complexes in a biphasic mode using ethylene glycol and toluene. The activity of the Pd complex catalysts for Heck reaction of iodobenzene and butyl acrylate was found to be highly dependent on the ratio of Pd:TPPTS, and the catalyst could not be recycled at a Pd:TPPTS ratio of less than 1:2, due to extensive precipitation of metal. At a Pd: TPPTS, 1:4 no precipitation was observed. Pd complexes incorporating carbohydrate substituted triarylphosphine-ligands for two-phase Heck reactions have been reported by Beller et al. [14] in a xylene–ethylene glycol biphasic medium, at a Pd:phosphine ratio of 1:3. Similarly, Thorpe et al. [15] have reported synthesis of a disulfonated phosphine and its application to biphasic Pd–TPPDS catalyzed Heck reaction of iodobenzene with methyl acrylate, also in a toluene–ethylene glycol biphasic medium. In all of these systems, as mentioned earlier, a non-polar organic solvent, either toluene or xylene is used with ethylene glycol as the other phase. In a majority of these systems no detailed investigations on catalyst recycle and recovery have been reported. From the process point of view it is necessary to have a stable and non-leaching catalyst with an

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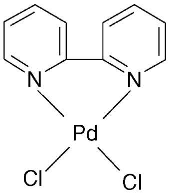
efficient catalyst recycle. This is more important in Heck reactions as even the highly stable complexes like Palladacycles are known to slowly break down to Pd metal [16]. There is definitely scope for further development of non-phosphine catalysts which have stability towards the reaction conditions employed in Heck reactions, and which is also stable in a biphasic medium, to facilitate catalyst recycle and product separation.

Cabri et al. [17] have reported that Pd complexes of bidentate nitrogen ligand such as 1,10-phenanthroline derivatives are active for Heck type reactions in homogeneous medium to give 94% product. However, surprisingly very little or no activity was observed for Heck reaction using the Pd complexes of 2,2′-bioxazoline and 2,2′-bipyridine ligands. Tsai et al. [18] have used heterogenized Palladium bipyridyl complex anchored on MCM-41 for Heck reactions as an efficient and recyclable heterogeneous catalyst with a TON up to 10^6 for each cycle. A 98% conversion of butyl acrylate was obtained in 16 h for the coupling with *p*-bromoacetophenone using this catalyst, however the system required 96 h for the *n*-butyl acrylate and iodobenzene system. The complex is also reportedly active for the Pd(II)–bipyridine catalyzed Suzuki reaction, i.e. conjugate addition of arylboronic acid to α,β-unsaturated carbonyl compounds in a homogeneous medium as reported by Lu et al. [19].

Our investigations have revealed that not only is $PdCl_2$(bipy) (**1**) an excellent and stable catalyst for Heck vinylation, but also the preferential solubility of the complex in ethylene glycol vis à vis non-polar organic media, make it a good catalyst for application in biphasic media. We report here a biphasic system using $PdCl_2$(bipy) catalyst which has been found to be active for the Heck reaction in an ethylene glycol–organic solvent system The catalyst has been recycled for five times without any loss in activity, proving the stability of the catalyst.



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The major advantage of the proposed catalyst is that biphasic catalysis is achieved by employing a conventional organic phase soluble ligand 2,2′-bipyridine unlike conventional catalysts (which have a hydrophilic moiety like that in TPPTS [10]) reported for biphasic Heck reactions. The catalyst does not require stringent oxygen free conditions, nor does it precipitate as is reported in other biphasic systems and was recycled a number of times with no loss in activity. The catalyst was retained in the glycol phase with practically no leaching to the organic phase. Although this catalyst is less efficient than P–C Palladacycle [20–21], the $PdCl_2$(bipy) catalyst provides an efficient recyclable catalyst in the biphasic system. The biphasic system was demonstrated for a number of aryl halides, olefins and in the presence of different organic and inorganic bases.

2. Experimental

$PdCl_2$, 2,2′-bipyridine, olefins and aryl halides used were procured form Aldrich USA and used without any further treatment. The solvents (*n*-octane, *p*-xylene, ethylene glycol) were obtained from Ms SDs chemicals, India. Bases used were of analytical grade, purchased from Loba chemicals, India. $PdCl_2$(bipy) (**1**) complex was synthesized as per reported procedures. Characterization of the $PdCl_2$(bipy) complex was carried out by IR, NMR and elemental analysis and was found to matched with the standard procedure [22].

2.1. Apparatus and procedure

Since the temperatures utilized for the reaction were higher than the boiling points of most of the reactants and solvents, the reactions were conducted in a high pressure autoclave of capacity 50 ml manufactured by Ms Amar Engineering, Mumbai and had facilities for withdrawal of liquid and gaseous samples. The temperature was controlled by means of electric heating. The reactor was fitted with a cooling loop for proper control of temperature.

In a typical experiment, a required amount of the olefin and the aryl halide was added to the organic phase (mixture of *n*-octane and *p*-xylene) to make the volume 15 ml. In another flask the catalyst and base were added in the required quantity to ethylene glycol (15 ml). Both these phases were then mixed thoroughly and the sample was taken for GC analysis. This mixture was then charged into the reactor and the contents were heated to the desired temperature with an agitation of 1000-rpm to ensure thorough mixing in the reactor. The reaction was continued for the desired period (generally 3 h). The progress of the reaction was monitored by intermediate sampling of the liquid contents in the reactor. A portion of the reaction mixture was repeatedly taken out from the reactor and the two phases were analysed by using a capillary gas chromatograph with flame ionization detector [Agilent 6850 series, controlled by the HP Chemstation software, on HP1 column with film thickness 0.25 μm. Initial temperature—80 °C, final temperature—250 °C]. The identification of products was done using a GC–MS [Agilent 6890N series equipped with 5973N Mass Selective Detector]. From the quantitative analysis, the conversion of the aryl halide, selectivity, turnover number (TON) and turnover frequency (TOF) were calculated by using the following formulae

$$\text{Conversion}\ (\%) = \frac{\text{Initial moles of substrate (ArX)} - \text{Final moles of substrate (ArX)}}{\text{Initial moles of substrate (ArX)}} \times 100 \tag{1}$$

$$\text{Selectivity}\ (\%) = \frac{\text{moles of product formed}}{\text{moles of substrate (ArX) consumed}} \times 100 \tag{2}$$

$$\text{TON} = \frac{\text{moles of product formed}}{\text{moles of catalyst}} \tag{3}$$

$$\mathrm{TOF}\,(\mathrm{h}^{-1}) = \frac{\text{moles of product formed}}{\text{moles of catalyst} \times \text{time (h)}} \qquad (4)$$

3. Results and discussion

3.1. Preliminary reactions and screening of solvents

In biphasic systems the role of the solvent is extremely important as the different factors regarding the solubility of the reactants in the catalyst phase and the polarity of the solvent play a major role in deciding the performance of the catalyst. To develop an efficient biphasic system the two phases have to be tailored such that they are immiscible with each other and that the catalyst is soluble in one phase, and the reactants and products are soluble in the second phase. The base used can be soluble in either phase, since the base–HX adduct or quaternary salt formed by the sequestration of the HX is either soluble in the polar phase or is present as a solid, as presented in Fig. 1. The use of ethylene glycol phase as a polar phase for solubilization of the catalyst was an obvious choice considering the literature reports on biphasic media for Heck reactions [10,14,15]. In this study the role of mixed organic solvents as the second phase was investigated. The studies were conducted using different compositions of *n*-octane and *p*-xylene as the organic phase, as this solvent system was found to be immiscible with ethylene glycol. The results are presented in Table 1. It was observed that the activity was the highest either in pure octane or xylene as solvent. However, in case of 100% *n*-octane, the product stilbene, precipitated out of the reaction medium, as the solubility of stilbene in octane is very poor. In case of xylene as the organic phase, although precipitation of the stilbene was not observed, some leaching of the catalyst to the organic phase was observed. Varying proportions of *n*-octane in *p*-xylene were studied to optimize the solvent combination. A solvent composition of 75% octane + 25% *p*-xylene (v/v) was found to give good activity (similar to that with pure octane), and also ensured no leaching of catalyst to the organic phase. In this solvent mixture the stilbene was found to be highly soluble. The results in Table 1 show a marginal drop in activity with 25% xylene as compared to 100% octane. Hence, for all screening studies the biphasic system comprising octane 75%, xylene 25% (v/v)–ethylene glycol was used. A typical concentration time profile for the Heck coupling of iodobenzene with styrene in presence of KOAc base in the optimized biphasic system is shown in Fig. 2. The consumption of iodobenzene and styrene was found to be commensurate with the stilbenes formed.

Table 1
Heck reaction of styrene and iodobenzene using $PdCl_2$(bipy) catalyst and KOAc as a base in biphasic medium using *n*-octane + *p*-xylene solvent mixtures

Sr. no.	*n*-Octane:*p*-xylene (v/v, %)	%Conversion of iodobenzene	TOF (h^{-1})
1	100:0	73	227
2	75:25	71	222
3	50:50	67	210
4	25:75	79	253
5	0:100	83	262

Reaction conditions: organic phase—15 ml: styrene (3.3 mmol) + iodobenzene (3.0 mmol) taken in *n*-octane + *p*-xylene (different composition); glycol phase—15 ml: catalyst (0.003 mmol) + base (KOAc—3.0 mmol) in ethylene glycol; 150 °C; 1000 rpm (time: 3 h). Selectivity >98% for (*cis* + *trans*) stilbene.

3.2. Screening of base

A detailed screening of bases was conducted using the $PdCl_2$(bipy) catalyst in an organic–glycol biphasic medium for the vinylation of iodobenzene with styrene. A variety of organic and inorganic bases were screened for their activity in the biphasic system, including aliphatic and aromatic organic bases

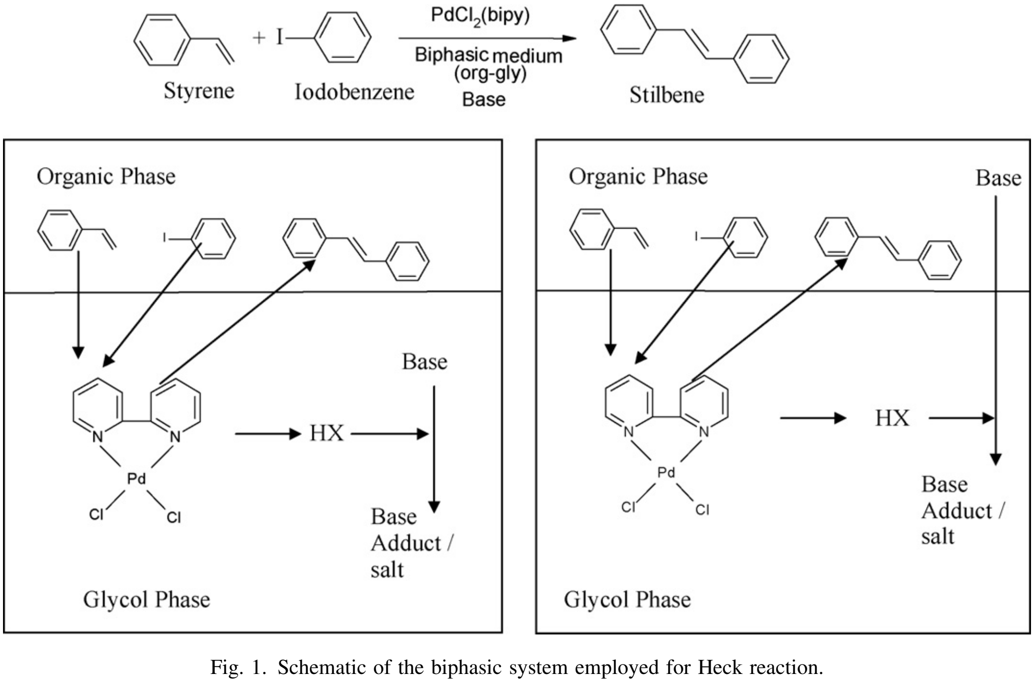

Fig. 1. Schematic of the biphasic system employed for Heck reaction.

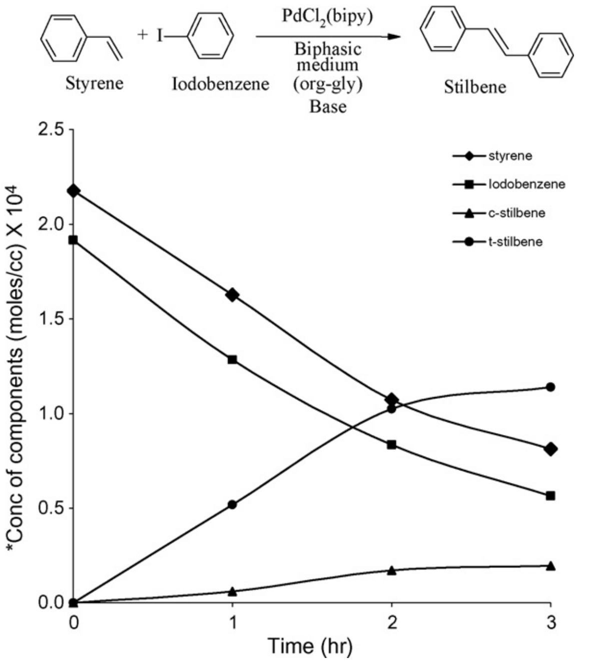

Fig. 2. Typical concentration vs. time profile of Heck reaction in biphasic medium. Reaction conditions: organic phase—15 ml: styrene (3.3 mmol) + iodobenzene (3.0 mmol) taken in *n*-octane (75%) + *p*-xylene (25%); glycol phase—15 ml: catalyst (0.003 mmol) + base (KOAc—3.0 mmol) in ethylene glycol; 150 °C; 1000 rpm (time: 3 h). Selectivity >98% for (*cis* + *trans*) product. Concentration based on volume of organic phase (15 ml) of reaction mixture.

and monovalent/divalent inorganic bases. In Heck reactions, the base can be used to neutralize the acid (HX) resulting from the formal exchange of a hydrogen atom with an aryl or vinyl group. As per the reported mechanism, the base helps in the regeneration of the active Pd(0) catalyst complex [23]. The results are shown in Fig. 3 as the TON observed for the different bases.

Amongst inorganic bases the acetates were found to have better activity compared to others. Sodium, potassium and ammonium acetates gave TONs higher than 500. Even Mg acetate was found to be active for the reaction. The carbonates of sodium and potassium were also active, and Na_2CO_3 was found to be more active than the K_2CO_3. With carbonates a high conversion of iodobenzene was observed, but, instead of desired product, i.e. stilbene, benzene was the major product indicating a dehalogenation in presence of the carbonates. The presence of benzene was confirmed by GC–MS.

The organic bases were also found to be active for the Heck reaction in the biphasic medium. Triethylamine, morpholine and piperidine gave excellent activity with TONs in the range of 450–950. However, although the highest turnover number of 943 was obtained for triethylamine, considerable dehalogenation of iodobenzene was observed. Aliphatic amines were more active than aromatic amines. Morpholine and piperidine showed better activity, as they can form the quaternary ammonium salts easily, compared to aromatic bases. As compared to other bases like pyridine, *N*-methyl pyrolidine and tribenzylamine, piperidine and triethylamine showed higher activity, as they are relatively strong bases.

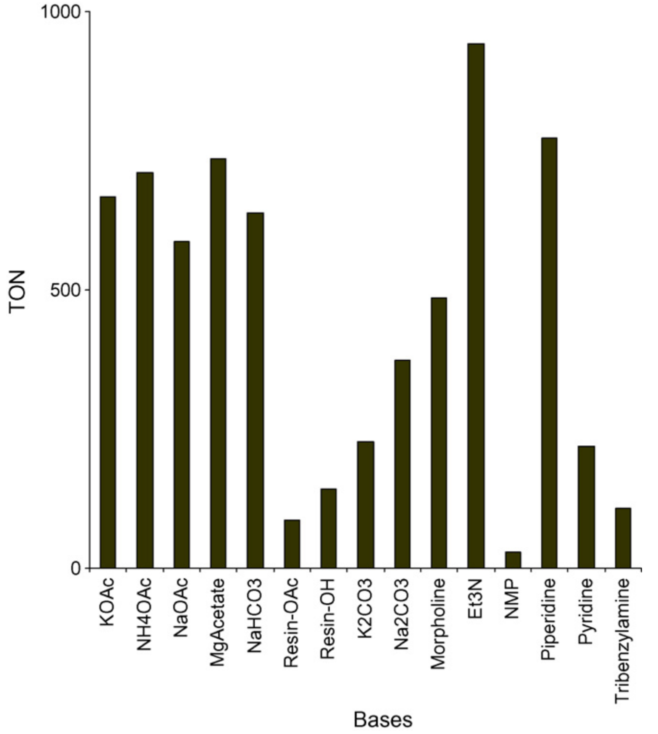

Fig. 3. TON observed for Heck reaction of iodobenzene and styrene with $PdCl_2$(bipy) catalyst using different bases in biphasic medium. Reaction conditions: organic phase—15 ml: styrene (3.3 mmol) + iodobenzene (3.0 mmol) taken in *n*-octane (75%) + *p*-xylene (25%); glycol phase—15 ml: catalyst (0.003 mmol) + base (3.0 mmol) in ethylene glycol; 150 °C; 1000 rpm (time: 3 h). Selectivity >98% for (*cis* + *trans*) product.

3.2.1. Anion exchange resins as bases

The use of anion exchange resins as bases were also investigated. The main objective for these experiments was to see whether use of solid and recyclable bases could be achieved. If successful, the removal of the base–halide adduct would be feasible, ensuring a better catalyst recycle. The anion exchange resin can then be reconverted to the original form by a separate process for further reuse. For this study –OH and –OAc exchanged resins were tested for their activity as bases for the Heck reaction. The quantity of resin used was molar equivalent of the base concentration used, calculated on the basis of their exchange capacity. The –OH resin was more active compared to the –OAc resin, with the former giving a TON of 142. In comparison a TON of 86 was observed for the –OAc resin. However, although effective as a base for the Heck reaction, the loading required for the ion exchange resin was higher compared to the other bases used.

3.3. Screening of aryl halide

The activity of $PdCl_2$(bipy) for the Heck coupling in a biphasic *n*-octane, *p*-xylene–glycol medium was assessed for the different aryl halides. For this purpose arylation of styrene was investigated in the presence of KOAc as a base. The results are shown in Fig. 4 as the TON observed for the various ArX. Table 2 shows the conversion of aryl halides and the respective TOFs for the different reactions conducted. In all the cases the

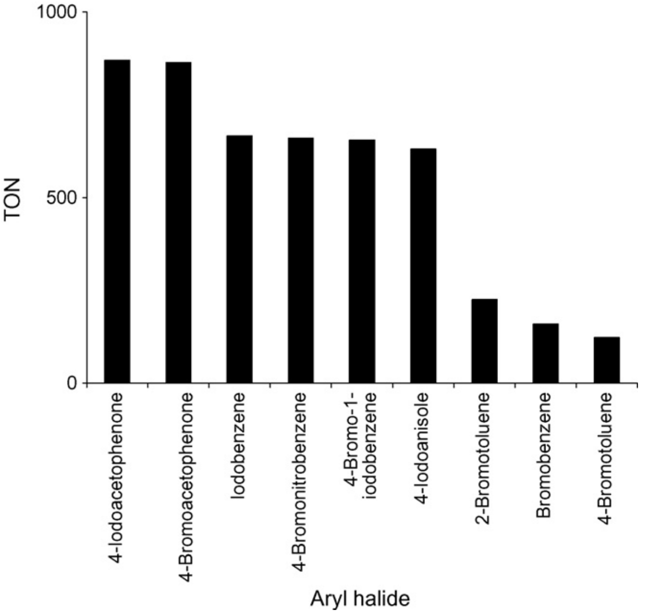

Fig. 4. TON observed for Heck reaction of various aryl halides with styrene using $PdCl_2$(bipy) catalyst and KOAc as a bases in biphasic medium. Reaction conditions: organic phase—15 ml: styrene (3.3 mmol) + ArX (3.0 mmol) taken in *n*-octane (75%) + *p*-xylene (25%); glycol phase—15 ml: catalyst (0.003 mmol) + base (KOAc—3.0 mmol) in ethylene glycol; 150 °C; 1000 rpm (time: 3 h). Selectivity >98% for (*cis* + *trans*) product.

products were analysed on GC and identification and confirmation of the product was done by using GC–MS.

Iodides were found to be more active than bromides amongst aryl halides. It was seen that catalyst showed the highest activity with 4-iodoacetophenone compared to all other compounds studied, with highest conversion of 87% and a TON of 870. With 4-bromotoluene the lowest activity was observed. It is well known that the haloarenes with substituents having a positive inductive effect are less reactive.

For the reaction of 4-bromo iodobenzene only the iodo substituent underwent reaction to produce 4-bromostilbene. Since iodoarenes are reportedly more active than the bromo derivatives, this behavior is expected. Also, no further reaction of the 4-bromo stilbene was observed within the reaction period.

It was also seen that the halides with strong electron withdrawing substituents showed a very high activity, whereas those with electron donating substituents showed poor activity. This observation is as per the general trends observed for the activities of Pd complex catalyzed Heck reactions.

Although the iodoarenes were far more active than the bromoarenes, the activity of the catalyst observed for the Heck coupling of styrene with different substrates in the biphasic medium was not exactly according to Hammett correlation observed in homogeneous reactions [24]. This is likely to be due to the varying solubilities of the substrates in the glycol phase, where the catalyst is present. The activity observed will be due to the combined effect of the substrate concentration in the glycol (catalyst) phase and the electronic properties of the substrates.

Table 2

Heck reaction of different aryl halides with styrene using $PdCl_2$(bipy) catalyst and KOAc as a base in biphasic medium

Sr. no.	Aryl halide	Conversion of aryl halide	TOF (h^{-1})
1	4-Iodoacetophenone	87	290
2	4-Bromoacetophenone	87	288
3	Iodobenzene	71	222
4	4-Bromonitrobenzene	70	220
5	4-Bromo-1-iodobenzene	69	218
6	4-Iodoanisole	67	210
7	2-Bromotoluene	21	75
8	Bromobenzene	16	53
9	4-Bromotoluene	12	41

Reaction conditions: organic phase—15 ml: styrene (3.3 mmol) + ArX (3.0 mmol) taken in *n*-octane (75%) + *p*-xylene (25%); glycol phase—15 ml: catalyst (0.003 mmol) + base (KOAc—3.0 mmol) in ethylene glycol; 150 °C; 1000 rpm (time: 3 h). Selectivity >98% for (*cis* + *trans*) product.

3.4. Screening of olefins

The activity of the $PdCl_2$(bipy) catalyst for the vinylation of iodobenzene with different olefins was studied in the *n*-octane, *p*-xylene–glycol biphasic medium in presence of KOAc as the base. The results are presented in Table 3, and the TONs for the different olefins are presented in Fig. 5. As earlier, the confirmation of the product was done by using GC–MS.

Generally it was seen that the olefins with strong electron withdrawing substituents show poor activity, whereas those with strong electron donating substituents show higher activity. This trend is opposite to that observed for aryl halides. The Heck reaction cycle reported suggests an addition of the olefin to the Pd(0) species, to form a pi-complex. Electron rich olefins will be expected to react faster than those with electron withdrawing substituents.

Acrylates were found to be more reactive than styrene derivatives. The regio selectivity of the product formed in case of acrylates favored 100% trans product, whereas with the styrene derivatives some *cis* product (<5%) is observed.

In our study, as also observed for the halides, the activity of the catalyst for different substrates in the biphasic medium was

Table 3

Heck reaction of different olefin with iodobenzene using $PdCl_2$(bipy) catalyst and KOAc as a base in biphasic medium

Sr. no.	Olefins	Conversion of iodobenzene	TOF (h^{-1})
1	Methyl acrylate	99	329
2	*n*-Butyl acrylate	98	326
3	4-Chlorostyrene	81	263
4	Styrene	71	222
5	3-Nitrostyrene	70	219
6	4-Methylstyrene	69	216
7	4-Vinyl anisole	61	194
8	4-Vinyl aniline	49	159

Reaction conditions: organic phase—15 ml: olefin (3.3 mmol) + iodobenzene (3.0 mmol) taken in *n*-octane (75%) + *p*-xylene (25%); glycol phase—15 ml: catalyst (0.003 mmol) + base (KOAc—3.0 mmol) in ethylene glycol; 150 °C; 1000 rpm (time: 3 h). Selectivity >98% for (*cis* + *trans*) product.

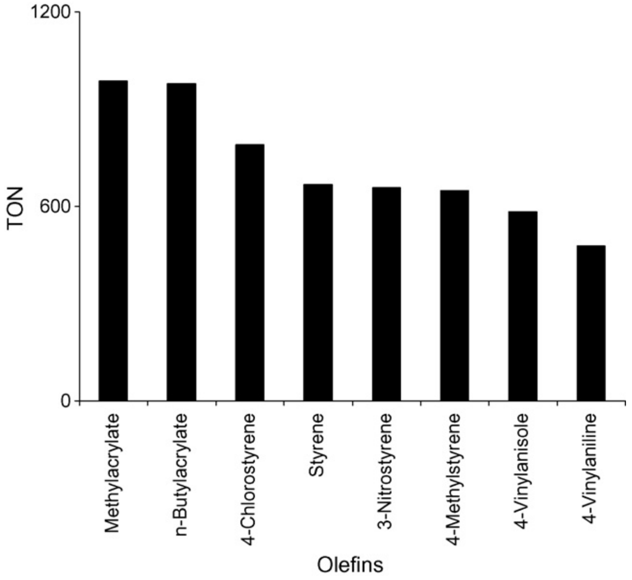

Fig. 5. TON observed for Heck reaction of different olefin with iodobenzene using $PdCl_2$(bipy) catalyst and KOAc as a bases in biphasic medium. Reaction conditions: organic phase—15 ml: olefin (3.3 mmol) + iodobenzene (3.0 mmol) taken in *n*-octane (75%) + *p*-xylene (25%); glycol phase—15 ml: catalyst (0.003 mmol) + base (KOAc—3.0 mmol) in ethylene glycol; 150 °C; 1000 rpm (time: 3 h). Selectivity >98% for (*cis* + *trans*) product.

not exactly according to Hammett correlation reported for the homogeneously catalyzed Heck reactions. The activity observed in the biphasic medium could thus be due to the combined effect of the solubility of the olefin and the role played by the various substituents on the olefins.

3.5. Catalyst recycle study for the Heck reaction using n-octane, p-xylene–glycol biphasic medium

A major advantage of the biphasic system is the ease of product separation and recycle of the catalyst. Since the objective of this study was to develop a biphasic system for an efficient recycle of catalyst, a detailed investigation was done on the recycle of catalyst using KOAc as the base. In the biphasic catalytic system developed the catalyst and glycol solvent are recycled to the next reaction, after separation of the organic phase. The glycol layer from a Heck reaction in biphasic medium of styrene and iodobenzene using $PdCl_2$(bipy) catalyst in presence of KOAc as a base was separated and recycled a number of times to ascertain the stability and activity of the catalyst. As seen in Fig. 6, the catalyst was recycled for five times with practically no loss in activity. The activity was retained over five recycles with a marginal drop in activity. Neither the precipitation of the catalyst, nor the leaching of Palladium to the aqueous phase was observed in the course of the investigations. In this study the base–HX adduct present in the glycol phase was allowed to accumulate for the next recycle. The presence of the adduct was not found to influence the activity of the catalyst. The salt also did not precipitate out of the solution.

The leaching of the catalyst to the organic phase was checked using Atomic Absorption Spectroscopy [AAS] and the concentration of Pd in the organic phase was negligible. Moreover, a recycle of the organic phase showed no activity for the Heck reaction.

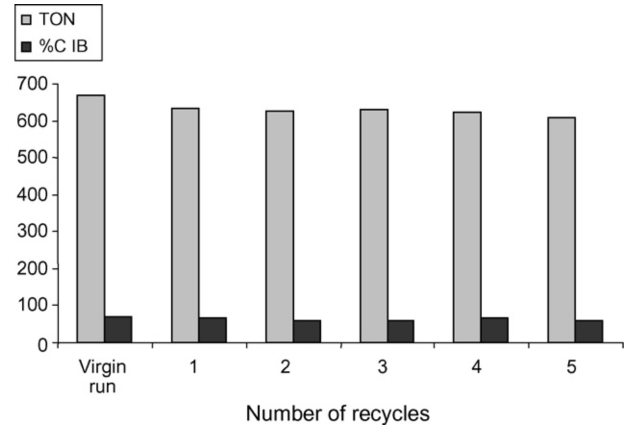

Fig. 6. Activity of $PdCl_2$(bipy) catalyst on recycle of glycol phase in a glycol–organic biphasic medium for Heck reaction of styrene with iodobenzene using and KOAc as a base. Reaction conditions: organic phase—15 ml: styrene (3.3 mmol) + iodobenzene (3.0 mmol) taken in *n*-octane (75%) + *p*-xylene (25%); glycol phase—15 ml: catalyst (0.003 mmol) + base (KOAc—3.0 mmol) in ethylene glycol; 150 °C; 1000 rpm (time: 3 h) (for recycle study the ethylene glycol layer is separated and used as it is with the fresh organic layer along with the substrates and the base).

4. Conclusions

Palladium complex consisting of chelating nitrogen ligands, i.e. 2,2′-bipyridine has been synthesized and characterized using elemental analysis, IR and NMR spectroscopy. This complex is highly active and can catalyze Heck reaction efficiently in glycol–organic biphasic medium and remarkable activity and selectivity were achieved.

$PdCl_2$(bipy) complex is found to be active for the Heck reaction in a biphasic glycol–organic solvent system. This catalyst is stable under reaction conditions in the glycol phase with negligible leaching to the organic phase. A major factor here is that the catalyst does not employ water-soluble ligands but employs conventional ligands like bipyridine. This is the first time wherein a biphasic system has been achieved for the Heck reaction, using a Pd complex containing an organic phase soluble bipyridine ligand, instead of a water-soluble ligand conventionally used. By proper tailoring of the solvent it has been possible to use the complex for application in biphasic medium. The role of different solvent compositions, olefins, aryl halides and bases has been elucidated in the biphasic system. The catalyst was recycled a number of times maintaining the activity. The role of different solvent compositions, alkenes, halides and bases has been elucidated in the biphasic system.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cattod.2007.10.043.

References

[1] W. Keim, Chem. Ing. Technol. 56 (1984) 850–853.

[2] A. Behr, W. Keim, Arab. J. Sci. Eng. 10 (1985) 377–385.

[3] C.W. Kohlpaintner, Beller M, J. Mol. Catal. 116 (1997) 259–267.

[4] B. Cornils, Topics in Current Chemistry 206 (1999) 133–152.

[5] Y. Tokitoh, N. Yoshimura, T. Higashi, K. Hino, M. Murasawa (Kuraray), EP 436 226 (1991) (Chem. Abstr. 115 (1991) 158508z).

[6] G. Mercier, P. Chabardes, Pure Appl. Chem. 66 (1994) 1509.

[7] Y. Chauvin, S. Einloft, H. Olivier, Ind. Eng. Chem. Res. 34 (1995) 1149–1155.

[8] Y. Chauvin, B. Gilbert, I. Guibard, J. Chem. Soc. Chem. Commun. (1990) 1715–1716.

[9] E.G. Kuntz, Chemtech. 17 (1987) 570–575.

[10] B.M. Bhanage, F.G. Zhao, M. Shirai, M. Arai, Tetrahedron Lett. 39 (1998) 9509–9512.

[11] N.A. Bumagin, P.G. More, I.P. Beletskaya, J. Organ. Chem. 371 (1989) 397–401.

[12] R.B. DeVasher, L.R. Moore, K.H. Shaughnessy, J. Org. Chem. 69 (2004) 7919–7927.

[13] D. Bradley, G. Williams, H. Lombard, C.W. Holzapfel, Synth. Commun. 31 (13) (2001) 2077–2081.

[14] M. Beller, J.G.E. Krauter, A. Zapf, Angew. Chem. Int. Ed. Engl. 36 (7) (1997) 772–774.

[15] T. Thorpe, S.M. Brown, J. Crosby, S. Fitzjohn, J.P. Muxworthy, J.M.J. Williams, Tetrahedron Lett. 41 (2000) 4503–4505.

[16] I.P. Beletskaya, A.V. Cheprakov, J. Organ. Chem. 689 (2004) 4055–4082.

[17] W. Cabri, I. Candiani, A. Bedeschi, R. Santi, Synlett (11) (1992) 871–872 (English).

[18] F. Tsai, C. Wu, C. Mou, M. Chao, H. Lin, S. Liu, Tetrahedron Lett. 45 (2004) 7503–7506.

[19] X. Lu, S. Lin, J. Org. Chem. 70 (2005) 9651–9653.

[20] M. Ohff, A. Ohff, M.E. van der Boom, D. Milstein, J. Am. Chem. Soc. 119 (1997) 11687–11688.

[21] W.A. Herrmann, K. Ofele, D.v. Preysing, S.K. Schneider, J. Organ. Chem. 687 (2003) 229–248.

[22] B.J. McCormick, E.N. Jaynes Jr., R.I. Kaplan, Inorg. Synth. 13 (1971) 216.

[23] C. Amatore, A. Jutand, J. Organ. Chem. 576 (1999) 254–278.

[24] C.S. Consorti, M.L. Zanini, S. Leal, G. Ebeling, J. Dupont, Org. Lett. 5 (7) (2003) 983–986.