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Cite this: *RSC Adv.*, 2026, **16**, 27300

Novel catalytic properties of pyridyl-bonded Pd-catalysts in cross-couplings of aryl halides with phenyl boronic acid under aerobic conditions

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Received 8th April 2026
Accepted 6th May 2026

DOI: 10.1039/d6ra02949c

rsc.li/rsc-advances

A new series of stable, easily accessible, efficient and recyclable phosphine free Pd-catalysts have been developed for their catalytic activity using Suzuki–Miyaura cross-coupling as model reaction system. The 2-benzoylpyridine-*N*(4)-substitutedthiosemicarbazones form compounds of composition, $[\mathrm{Pd}\{(2\text{-py-N})(\mathrm{Ph})\mathrm{C{=}N{-}N{=}C(-S)-N^4HR}\}\mathrm{Cl}]$ (R =H, Me, Et, Ph), which have been labeled as Cat **1**(H), Cat **2**(Me), Cat **3**(Et) and Cat **4**(Ph) – based on *R*-substitution at $-\mathrm{N^4HR}$. The catalytic activity of these complexes with central core, {Pd(NNS-L)Cl}, has been explored by using simple aryl bromides and aryl iodides as substrates for S-M coupling reactions. Thus the C–C cross-couplings of a series of aryl halides (R–X), Ph–X, $p\text{-NC}{-}C_6H_4{-}X$, $p\text{-MeO}{-}C_6H_4{-}X$ and $p\text{-Me}{-}C_6H_4{-}X$ (X = Br, I), with phenyl boronic acid have been successfully carried out in the presence of a Pd-catalyst using K_2CO_3 base in aqueous ethanol medium at 50 °C under aerobic conditions. Each catalyst activated C–Br and C–I bonds of aryl halides and formed di-aryl products, Ph–Ph, $p\text{-NC}{-}C_6H_4{-}Ph$, $p\text{-MeO}{-}C_6H_4{-}Ph$ and $p\text{-}H_3C{-}C_6H_4{-}Ph$, from both type of halides with high isolated yields and TON. The reactivity of C–X bonds of aryl halides ($Y{-}C_6H_4{-}X$; X = Br, I) towards oxidation addition varied in the order: Y = CN > H > MeO ~ Me (Y is trans to X). These are initial, preliminary studies that may enable future work establishing these complexes as promising catalysts for related transformations. The catalytic system has interesting key features such as aqueous ethanol media, recyclability, and phosphine-free nature.

Introduction

The carbon–carbon cross-coupling reactions of aryl halides with organoboronic acids are useful in the synthesis of a variety of di-aryl products and the substituted aromatic compounds.[1–3] The synthesis of organic compounds is important for various industrial applications, such as making building blocks of polymers, natural products, agrochemicals and pharmaceuticals.[1,4–13] The cross-coupling reactions generally make use of Pd based catalysts and the success of a reaction depends on the characteristics of a catalyst used. In literature one type of catalysts used in Suzuki–Miyaura C–C couplings comprise phosphine based complexes such as $Pd(PPh_3)_4$,[14] or a palladium-complex with a hemi-labile phosphine-P,O ligand.[15] The ligand free Pd-nanoclusters.[2] heterogeneous MOF supported Pd-nanoparticles,[3] or thiosemicarbazone induced palladium-nanoparticles,[16] form another category of catalysts used in the reactions. Furthermore, it is interesting to note that there is a surge in the use of thiosemicarbazone based complexes as catalysts owing to the low cost and easy synthesis of the ligands as well as their metal complexes (Fig. 1. General structure I of thiosemicarbazone ligands).[13,17–19] Thus, several Pd-complexes of the thio-ligands such as salicylaldehyde thiosemicarbazones,[20,21] benzaldehyde thiosemicarbazo-nes,[22–24] carbohydrate based thiosemicarbazones,[25,26] pyridoxalthiosemicabazones,[27] and sulfon-ated thiosemicarbazones,[28] have been used as catalysts in C–C cross coupling and other allied coupling reactions.

The coupling reactions using catalysts have one or more limitations, such as limited recycling of catalysts, low stability of a catalyst, oxidation of the Pd-bonded phosphine, the difficulty to separate a catalyst from a product mixture, requirement of high boiling solvents (*e.g.* dioxane, toluene, DMF, PEG *etc.*), and necessity of using inert atmosphere.[14–16,20–28] Such limitations make it necessary for the search of new catalysts with better properties, such as stability, recyclability, ease of separation from the product, low boiling green solvents and normal atmospheric conditions. Furthermore, it may be noted that due to the limitations of the catalysts,[1–3] the industrial applications of the Suzuki–Miyaura cross-coupling reactions remain challenging.[1–3,29–34] For example, one issue deals with the presence of Pd metal in products of pharmaceutical importance, prepared using catalysts based on nanoparticles/clusters.[1–3] Further, the well-tailored catalysts are needed to drive C–C coupling reactions to produce biofuels which are usually energy-consuming reactions.[35] Likewise, there are efforts for conversion of terrestrial biomass-derived substrates into fuels

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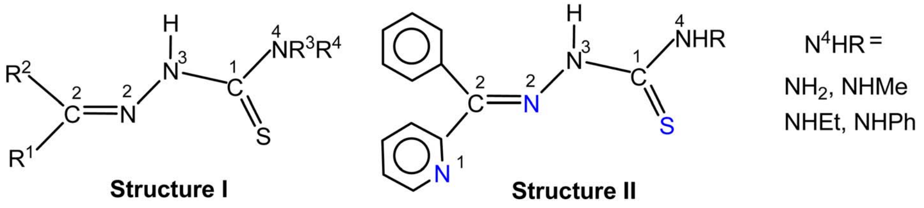


Fig. 1 General and pyridine based thiosemicarabzones (structures I and II).

and useful chemicals, in order to find potential alternatives and substitutes for current fossil-based fuels and chemicals.[36]

In view of the above background, it was planned to study the catalytic activity of phosphine free coordination compounds of palladium(II), particularly using pyridine based thiosemicarbazones (*e.g.* Structure **II**, Fig. 1). Suzuki–Miyaura coupling was chosen as a model reaction, but the applicability of these catalysts is not necessarily limited to this transformation. The present studies make a starting point for broader future applications. The choice of using specifically pyridine based thiosemicarbazone ligands has its origin linked to their unusual chemical activity such as stabilization of $\mathrm{Cu^{II}}$–iodide bonds,[37,38] formation of novel tri-nuclear $\mathrm{Cu^{II}}$–$\mathrm{Ru^{II}}$–$\mathrm{Cu^{II}}$ complexes,[39] as well as first discrete octahedral Hg(II) complex with anionic pyridine carbaldehdye thiosemicarbazone.[40] In the present study, pyridyl-bonded Pd-complexes of 2-benzoylpyridine-*N*(4)-substituted thiosemicarbazones, having terdentacy (*N*,*N*,*S*), are investigated for their catalytic activity, using Suzuki–Miyaura cross-couplings as model reaction system.

Materials and methods

The chemicals, such as phenylboronic acid, bromobenzene, *p*-cyano-bromobenzene, *p*-methoxy-bromobenzene, *p*-methyl-bromobenzene, iodobenzene, *p*-cyano-iodobenzene, *p*-methoxy-iodobenzene, *p*-methyl-iodobenzene, potassium carbonate, sodium carbonate, potassium hydroxide, sodium hydroxide, ethanol, ethyl acetate, acetonitrile, methanol, acetic acid, and chloroform were of AR grade. The $\mathrm{PdCl_2}$, 2-benzoyl pyridine {(2-py)(Ph)C═O}, thiosemi -carbazide {$\mathrm{NH_2}$–NH–C(═S)–$\mathrm{NH_2}$}, *N*(4)-methyl thiosemicarbazide{$\mathrm{NH_2}$–NH–C(═S)–$\mathrm{N^4HMe}$}, N(4)-ethyl thiosemicarbazide{$\mathrm{NH_2}$–NH–C(═S)–$\mathrm{N^4HEt}$} and *N*(4)-phenyl thiosemicarbazide {$\mathrm{NH_2}$–NH–C(═S) $\mathrm{N^4HPh}$}, were procured from Aldrich (general details – s1).

The ligands were prepared by the reaction of a 2-benzoylpyridine with a thiosemicarbazide in ethanol solvent along with 20–30 mL water, and a few drops of acetic acid, as represented in Fig. 2.[41,42] Coordination compounds of palladium(II) chloride with 2-benzoyl – pyridine N(4) – substitutedthiosemicarbazones, labeled as Cat **1**(H), Cat **2**(Me) Cat **3**(Et) and Cat **4**(Ph) (Fig. 3), have been prepared by our group,[41,42] as well as, by other groups using different methods.[43–46] These complexes characterized using X-ray crystallography and other techniques,[41–46] have been studied for their cytotoxic activity by Beraldo *et al.*[43] The novelty here lies in evaluating their catalytic activity (physical properties of catalysts – s2).

Selection of base and temperature for catalytic reactions

In order to make a selection of the base and temperature, a few experiments were performed (Table s1). We selected the reaction of bromobenzene with phenylboronic acid in aqueous ethanol as a model reaction. Further, the use of ethanol–water solvent system was considered relatively green and easy to remove unlike the high boiling solvents such as DMSO or DMF. Among the catalysts, Cat **1**(H), Cat **2**(Me), Cat **3**(Et) and Cat **4**(Ph), we selected Cat **4**(Ph) for screening due to its ease of preparation, better thermal stability having higher m.p. and yield of catalyst preparation was relatively high. In the screening process, the reaction conditions used are listed as follows: bromobenzene, 1 mmol; phenylboronic acid (1.3 mmol), base (2 mmol), Cat **4**(Ph, (1 mol%). The bases, NaOH, KOH, $\mathrm{Na_2CO_3}$, $\mathrm{K_2CO_3}$ and $\mathrm{Cs_2CO_3}$, were screened using catalyst Cat **4**(Ph) (1 mol%) with temperature kept at 100 °C and ethanol–water solvent ratio of 9:1 (v/v; 10 mL) was used (eqn (1)). Based on the less time needed for one cycle, KOH and $\mathrm{K_2CO_3}$ were selected for further screening (cycle defines completion of reaction).

$$\mathrm{Ph-Br+PhB(OH)}\xrightarrow[\mathrm{EtOH-H_2\mathit{O},\ Base}]{\mathrm{Cat\ 4(Ph),\ 100^{\circ}\mathit{C}}}\mathrm{Ph-Ph} \qquad (1)$$

The time for a cycle (completion of reaction) was 2 h for KOH and 3 h for $\mathrm{K_2CO_3}$. These two type of bases were further studied

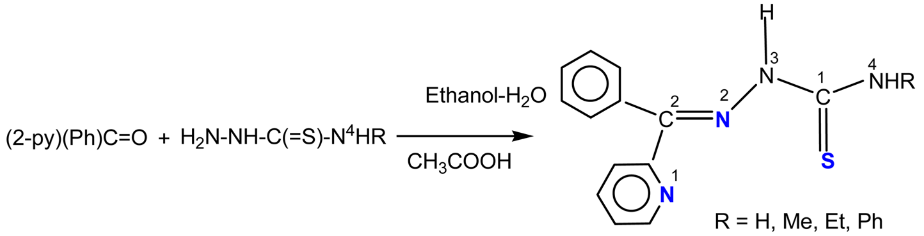


Fig. 2 Equation representing preparation of 2-benzoylpyridine *N*4(*R*)-thiosemicarbazones

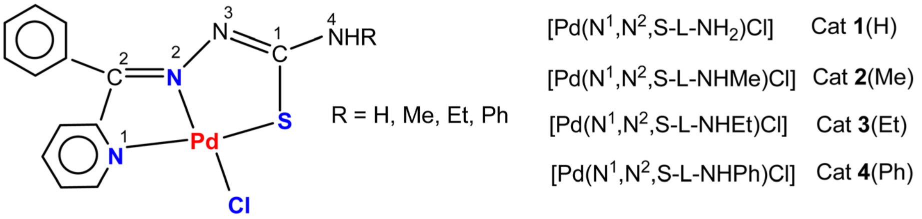


Fig. 3 Palladium complexes with pyridine based thiosemicarbazones

for different cycles at different temperatures (Table s1). In case of KOH, the time for a cycle (completion of reaction) was 4.5 h at 50 °C, for four cycles (*in situ* addition of aryl halide and phenylboronic acid), the time was 4 h at 70 °C and for 3 cycles, the time for a cycle was 2 h at 100 °C. The yields varied between 80–83% for KOH base operated between 50–100 °C. In case of K_2CO_3, it worked for eight cycles at 50 °C and the addition of reactants was *in situ* to the same reaction vessel after the completion of one cycle. In KOH after 3 cycles, the catalyst started turning black at 100 °C, suggesting its dissociation and was not pursued further. Thus, the base KOH was effective at 100 °C but less so at 50 °C, while K_2CO_3 provided more robust and recyclable conditions up to 8 cycles without loss of activity. The ethanol–water solvent ratio of 9 : 1 (v/v; 10 mL) was used up to 4 cycles and for 8 cycles, this ethanol–water solvent ratio used was 18 : 2 (v/v).

Interestingly, the catalyst under screening {1 mol%; Cat **4**(Ph)} worked smoothly in K_2CO_3 base at a low temperature of 50 °C (eqn (2)), and a total of 8 cycles (after completion of each cycle, *in situ* additions of reactants-aryl halide and phenylboronic acid) were possible and the final isolated yield was 92%. Thus we selected K_2CO_3 as a base for the cross coupling reactions in the aqueous ethanol medium at a temperature of 50 °C for all the four catalysts under study. Thus in the ethanol–water mixture (18 : 2, v/v), the Cat **4**(Ph), K_2CO_3, a base, $PhB(OH)_2$ and bromobenzene were added, and a homogeneous mixture was formed on mild heating at about 50 °C (eqn (2); Table s1).

$$\mathrm{Ph-Br} + \mathrm{PhB(OH)_2} \xrightarrow[\mathrm{K_2CO_3,EtOH-H_2O}]{\mathrm{Cat\ 4(Ph),\ 50\ ^\circ}C} \mathrm{Ph{-}Ph} \qquad (2)$$

Results and discussion

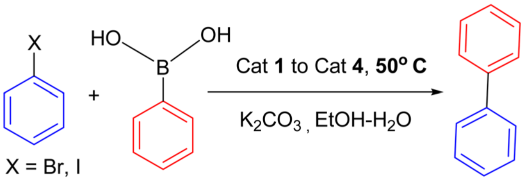
Procedure for catalytic reactions and other details

The procedure for cross coupling reactions, after the selection of K_2CO_3 base, temperature of 50 °C and aqueous ethanol medium, is described as follows. To a round bottomed flask (50 or 100 mL) fitted with a condenser was added a Pd catalyst (1 mol%; 10^{-2} mmol) {Cat. **1**(H), Cat **2**(Me), Cat **3**(Et) or Cat **4**(Ph)} in ethanol (18 mL), followed by the addition of an aryl halide (1 mmol), K_2CO_3 (2 mmol) base in water (2 mL) and phenylboronic acid (1.3 mmol). The flask fitted with the condenser was placed in an oil bath and heated at a predetermined temperature of 50 °C under atmospheric conditions. The progress of the reaction was monitored using a standard TLC method, and the reaction was considered complete when TLC spot due to aryl halide does not appear. In order to maintain the high efficiency of the catalyst, the di-aryl product was not separated after one cycle, further addition of second lot of reactants (aryl halide and phenylboronic acid) was carried out, and the process was continued until the reaction was complete. In this way six more cycles were performed, each time checking the completion of the reaction (in all total 8 cycles). This procedure has been used for the reactions involving activation of carbon-bromine/carbon-iodine bonds of: (a) bromobenzene and iodobenzene using Cat **1**(H); (b) bromobenzene using Cat **2**(Me) and Cat **3**(Et); (c) bromobenzene, *para*-cyanobormobenzene, *para*-methoxybromobenzene, *para*-methylbromobenzene, as well as, iodobenzene, para-cyano iodobenzene, *para*-methoxyiodo -benzene, *para*-methyliodobenzene using Cat **4**(Ph). Finally, the activation of carbon–iodine bond of iodobenzene with Cat **2**(Me) and Cat **3**(Et), required higher volume of aqueous ethanol (ethanol-45 mL: water-5 mL). The detailed procedure for isolation of di-aryl products and their characterization are placed as SI (see s3–s7).

After one cycle (completion of reaction), the separation of catalyst was considered unnecessary-time consuming, loss of catalyst during separation process, lower yield of coupled product, wastage of solvents. The idea of *in situ* addition was more comfortable, more economic in time and chemicals and with high yields. The catalyst could easily perform several cycles, 8 in present case. The catalyst was separated after 8 cycles. The separated catalyst studied using UV-visible spectroscopy and m.pt, which were similar to the catalyst before use. It showed robust nature of catalysts.

Carbon–carbon cross coupling reactions

The catalytic activity of each of Pd-catalysts Cat **1**(H), Cat **2**(Me), Cat **3**(Et) or Cat **4**(Ph), has been studied using Suzuki–Miyaura C–C cross-coupling reactions. In this study, cross coupling reactions of arylbromide/aryliodide with phenylboronic acid have been performed using the above mentioned Pd catalysts (1 mol% for each catalyst) with K_2CO_3 base in aqueous ethanol at 50 °C under normal atmospheric conditions. Scheme 1 depicts the coupling reactions of bromo-/iodo-benzenes with phenylboronic acid. It involves the activation of carbon-bromine and carbon-iodine bonds of bromo-/iodo-benzenes followed by their couplings with phenyl boronic acid, in the presence of a Pd catalyst (1 mol%; Cat **1**(H), Cat **2**(Me), Cat **3**(Et) and Cat **4**(Ph). The C–C cross coupling of both arylbromide and aryliodide occurred efficiently at a temperature of 50 °C in



Yield %	Cat **1**	Cat **2**	Cat **3**	Cat **4**
Br	95	88	86	93
I	92	84	85	91

Scheme 1 Coupling reactions of bromo-/iodo-benzenes with phenyl boronic acid.

aqueous ethanol. For a given catalyst, after completion of first cycle, the reactants {Ph–Br and $PhB(OH)_2$ or Ph–I and $PhB(OH)_2$} were added to the same reaction vessel without adding any more solvent, base, or catalyst. The addition of reactants for each cycle was continued, and with a given catalyst, a total of eight cycles were successfully performed (corresponding to 8 cycles, the effective catalyst loading works up to, 0.125 mol%). The coupling of bromobenzene (or iodobenzene) with phenylboronic acid using catalysts, Cat **1**, Cat **2**, Cat **3** and Cat **4**, formed the same diaryl product (entries 1–8, Table 1).

Further, the Cat **4**(Ph) was selected, among four catalysts owing to its somewhat higher activity, for studying the activation of C–X bonds of substituted bromobenzenes, namely, *para*-cyano bormobenzene, *para*-methoxy bromobenzene, *para*-methyl bromobenzene, and substituted iodobenzenes, namely, para-cyano iodobenzene, *para*-methoxy iodobenzene and para-methyl iodobenzene. The products of activation of C–Br/C–I bonds of these substituted aryl halides formed *p*-substituted di-phenyl compounds which are presented in Scheme 2 (entries 9–14). The same substituted products *p*-NC–C_6H_4–Ph, *p*-MeO–C_6H_4–Ph and *p*-H_3C–C_6H_4–Ph, were obtained from both substituted aryl bromides and aryliodides (entries 9–14) Table 1 (see s3–s7).

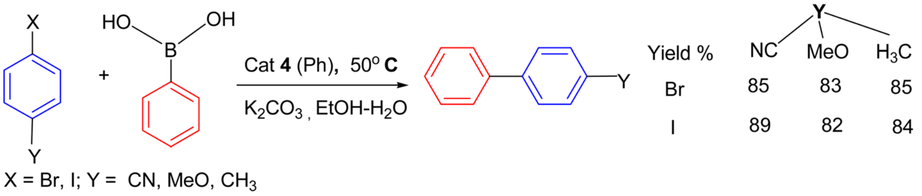
Reaction data and interpretation

The details of aryl halides used, reaction time taken for a cycle, yield and turn over number (TON) of di-aryl products isolated are placed in Table 1. The activation of C–Br bond of bromo benzene using a catalyst (Cat **1** to **4**) required time for a cycle from 3.5 to 4.0 h (entries, 1, 3, 5, 7). In contrast, for the activation of C–I bond of iodobenzene, the time for a cycle was from, 1.0–1.5 h (entries 2, 4, 6, 8). It was noted that the activity of Cat **1**(H)/Cat **4**(Ph) in the activation of C–Br/C–I bonds (bromo-/iodo-benzenes) was marginally higher than that of Cat **2**(Me)/Cat **3**(Et). As regards the substituted aryl halides, the time for activation of C–Br bond for a cycle varied from 2.0–6.0 h, while for a C–I bond activation, time was 0.75–4.0 h for a cycle. Generally speaking, the activation of C–I bond is easier than that of C–Br bond, conforming to the expected trend of labile activity of C–X bonds (I > Br). Finally, based on the use of Cat

Table 1 Details of aryl halides used, di-phenyl products, TON and TOF parameters[a,b,c]

Entry	Ar–X	Products	Cycles (time, h)	Isolated yield %[f]	Product (M)	TON[d] (TOF)[e]
Cat **1**(H)						
1[b]	Ph–Br	Ph–Ph	8 (28 h)	95%	7.6×10^{-3} M	760 (27)
2[b]	Ph–I	Ph–Ph	8 (8 h)	92%	7.4×10^{-3} M	740 (93)
Cat **2** (Me)						
3[b]	Ph–Br	Ph–Ph	8 (32 h)	88%	7.0×10^{-3} M	700 (22)
4[c]	Ph–I	Ph–Ph	8 (12 h)	84%	6.7×10^{-3} M	670 (56)
Cat **3** (Et)						
5[b]	Ph–Br	Ph–Ph	8 (32 h)	86%	6.9×10^{-3} M	690 (22)
6 [c]	Ph–I	Ph–Ph	8 (12 h)	85%	6.8×10^{-3} M	680 (57)
Cat **4** (Ph)						
7[b]	Ph–Br	Ph–Ph	8 (28 h)	93%	7.4×10^{-3} M	740 (26)
8[b]	Ph– I	Ph–Ph	8 (8 h)	91%	7.3×10^{-3} M	730 (91)
9[b]	*p*-NC–C_6H_4–Br	*p*-NC–C_6H_4–Ph	8 (16 h)	85%	6.8×10^{-3} M	680 (43)
10[b]	*p*-MeO–C_6H_4–Br	*p*-MeO–C_6H_4–Ph	8 (48 h)	83%	6.6×10^{-3} M	660 (14)
11[b]	*p*-H_3C–C_6H_4–Br	*p*-H_3C–C_6H_4–Ph	8 (48 h)	85%	6.8×10^{-3} M	680 (14)
12[b]	*p*-NC–C_6H_4–I	*p*-NC–C_6H_4 – Ph	8 (6 h)	89%	7.1×10^{-3} M	710 (118)
13[b]	*p*-MeO-C_6H_4–I	*p*-MeO–C_6H_4–Ph	8 (32 h)	82%	6.6×10^{-3} M	660 (21)
14[b]	*p*-H_3C–C_6H_4–I	*p*-H_3C–C_6H_4–Ph	8 (32 h)	84%	6.7×10^{-3} M	670 (21)

[a] Reaction conditions: aryl halide (R–X) (1 mmol), Ph-$B(OH)_2$ (1.3 mmol), K_2CO_3 (2 mmol), Cat **1**–**4**(10^{-2} mmol; 1 mol%; effective 0.125 mol% for 8 cycles. [b] Ethanol–water (in mL) (18 : 2, v/v). [c] Ethanol–water (45 : 5 in mL, v/v), temperature 50 °C. [d] TON = (no. of moles of product)/(no. of moles of catalyst), TOF = TON/reaction time. [e] TOF per hour. [f] Yields are isolated yields and correspond to cumulative 8-cycle reactions, *i.e.*; total 8 mmol of Ar–X.



Scheme 2 Coupling reactions of bromo-/iodo-benzenes (different substituents).

4(Ph), the substituents at para-position of bromo-/iodo-benzenes, affected the lability of C–X bonds (X = Br, I) in the order: Y = CN > H > MeO ~ Me (Scheme 2). In other words, the presence of methoxy (MeO–) and methyl groups in the para position, made the activation of C– Br/C– I bonds more difficult, while CN group made it easier. The percent yield of di-phenyl products varied from 84 to 95% for un-substituted aryl halides (entries 1–8), and for the substituted di-aryl products (entries 9–14), the percent yield varied from 82 to 89%. Further, the turn over number for un-substituted aryl halides varied as follows: 730–760 (Cat **1**, Cat **4**), 670–700 (Cat **2**, Cat **3**) and for substituted aryl halides, the TON varied from 660–710 (Cat **4**) The different values are attributed to the effect of the substituents effect.

Novel features of catalysts

Several novel features of the catalysts under study are summarized as follows. In the coupling reaction system, the catalysts become soluble in hot reaction mixture in ethanol-H_2O (9 : 1 ratio) at 50 °C, and thus the low boiling solvent system supports the stability of a catalyst. In performing a cross coupling reaction, there is no need to isolate the catalyst after one cycle, rather only reactants (aryl halide and phenyl boronic acid) are added *in situ* and eight cycles were efficiently achieved for a coupling reaction. The di-aryl products have been isolated in good yield with high turnover numbers (TON), and also the time of reaction is not high. It was observed that the melting points of the catalysts before catalysis (220–290 °C) and after catalysis (219–288 °C) are very similar (see: s3). Finally, the electronic absorption spectra of catalysts before catalysis and after catalysis are very similar, which supports that the catalysts remain essentially unchanged (Fig. 4). These studies suggest that the path of coupling reactions appears homogeneous, as the catalysts after reaction remain unchanged, thus ruling out the formation of nanoparticles. Also K_2CO_3 being a mild base, used in the present studies, keeps the catalyst stable unlike strong bases such as KOH, which affect a catalyst.

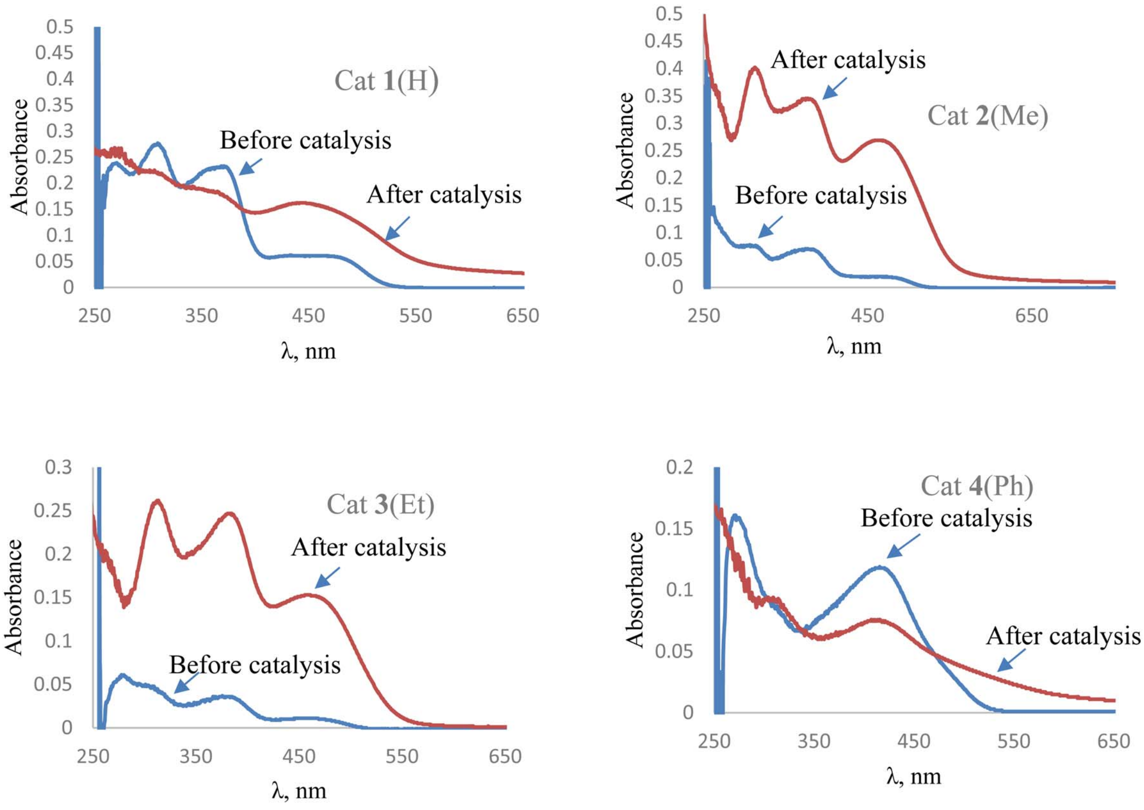


Fig. 4 UV-visible spectra of catalysts before and after catalysis.

The pyridyl nitrogen (N^1), azomethine nitrogen (N^2), and thiolato sulfur(S) atoms are bonded to Pd metal center with the fourth site of catalysts occupied by the chloride anion (Fig. 3 for numbering). The stereochemical environments of the Pd metal center do not constitute crowding which might be of relevance in the oxidative addition of aryl halides in catalysis. Further, the presence of pyridine and thiolate moieties create hemilabile properties of the catalysts involving C–C coupling. At the end, the manuscript reports a methodological study without the understanding of the catalytic cycle.

Conclusion

In conclusion, a new series of stable, easily accessible, recyclable, pyridyl bonded and phosphine free green Pd-catalysts with central core, {Pd(N,N,S-L)Cl}, have been developed for Suzuki–Miyaura cross-coupling reactions with potential for other couplings. In this study, the C–C cross-couplings of unsubstituted and substituted aryl bromides and aryl iodides with phenyl boronic acid have been efficiently carried out. The products were free from any impurity, have high isolated yield and TON. The easy preparation and stability of pyridyl bonded Pd-catalysts provide the sound background to use such catalysts in cross couplings for a variety of halogen-containing organic compounds of biochemical and industrial significance. It is added here that the activation of more inert C–Cl bonds of aryl halides as well as other challenging substrates, generally with different reaction requirements are in our future plans. Finally, it is remarked that these Pd catalysts, with Pd metal bonded to a pyridyl group, nitrogen of azomethine moiety, thiolato sulfur and chloride anion, have displayed higher stability and efficient performance, relative to those metal-thiosemicarbazone complexes reported in literature[20–28] (see s8).

Author contributions

Ridhima Aggarwal (writing of original draft, methodology, formal analysis, data curation); Ritu Bala (supervision, analysis and editing); Tarlok Singh Lobana (conceptualization, critical analysis, writing, review and editing).

Conflicts of interest

There are no conflicts of interest to declare.

Data availability

The data used to support investigations is given in supplementry information (SI). The main article contains data related to products described. Supplementary information is available. See DOI: https://doi.org/10.1039/d6ra02949c.

Acknowledgements

The authors are grateful to the Guru Nanak Dev University Amritsar and DST-FIST for the general research facilities for carrying out this research work. One of us (TSL) thanks National Academy of Sciences of India for 'NASI Honorary Scientist' position.

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