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# Highly efficient palladium(II) hydrazone based catalysts for the Suzuki coupling reaction in aqueous medium<sup>†</sup>

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Synthesis of a new family of air stable palladium(II)benzhydrazone complexes of the general formula [PdCl(PPh<sub>3</sub>)(L)] (where HL = thiophene aldehyde benzhydrazones) incorporating PPh<sub>3</sub> and chloride as co-ligands has been described through a single and convenient step with good yields. All the new complexes have been fully characterized by means of elemental analysis, IR, UV-vis, and NMR spectral methods. The molecular structures of three of the complexes were determined by single crystal X-ray crystallography, which confirm the coordination mode of benzhydrazone and reveal the presence of a distorted square planar geometry around the Pd ion. The complexes 1-5 (0.05 mol%) have been found to be a highly active catalytic system in the mono and double Suzuki–Miyaura cross coupling reaction of deactivated aryl and heteroaryl bromides with different types of aryl boronic acids in neat water and the maximum yield was up to >99%. Notably, these catalysts work well with ultra-low loading of the catalysts and show high turnover numbers in a short time towards different substrates. Moreover, the catalysts could be simply recovered and reused five times without significant loss of efficiency.

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## Introduction

Suzuki-Miyaura cross coupling reaction<sup>1</sup> is a powerful method for carbon-carbon bond formation that has been applied in a variety of settings such as natural product synthesis, polymers, many pharmaceutically active compounds, herbicides, new materials, liquid crystals and fine chemical synthesis.<sup>2</sup> Further, the attractive features of the Suzuki coupling reactions are the wide availability, stability to air and moisture, and low toxicity of boronic acid as well as the facile removal of boron containing side products of the coupling process. In the past few years, great advances have been made in developing active and efficient catalysts by modifying traditional ligands and discovering new systems.<sup>3-5</sup> Sterically demanding, electron rich phosphines, such as tri-tert-butylphosphine, have shown high catalytic activity for a variety of substrates.<sup>6</sup> Further, new types of ligands, such as heterocyclic carbenes,<sup>7</sup> imine and amine palladacycles (1a),8 oximepalladacycles (1b),9 diazabutadiene (1c),10 and simple amines (1d)11 have also emerged for the use in the Suzuki-Miyaura cross coupling reaction.



Though palladium complexes exhibit excellent results in Suzuki cross coupling reactions, most of them were conducted in some organic solvents. Because, reaction solvents are one of the most important constituents in any chemical process and play a key role in deciding its environmental impact as well its cost, safety and health issues. The ideal solution is to use green solvent which does not pollute the environment. Thus, naturally abundant water appears to be a superior choice as a 'green solvent' because of its non-toxic, non-corrosive and nonflammable nature. In particular case of Suzuki–Miyaura cross coupling reaction, the choice of water as the medium is

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particularly suitable due to the excellent stability of boronic acids in aqueous media. Though the Suzuki coupling reaction has strongly benefited from aqueous chemistry,<sup>12</sup> most of halogenated substrates are insoluble in water, resulting in poor reactivity. To solve this problem, numerous efforts have been made, such as synthesizing water-soluble ligands,<sup>13</sup> adding surfactants and/or phase-transfer agents, using co-solvents<sup>14</sup> or using microwave or ultrasound<sup>15</sup> even utilizing an inorganic salt as a promoter.<sup>16</sup> Yet, most aqueous protocols for cross coupling reactions have some drawbacks such as high catalyst loading, elevated temperature, complex workup procedure including column chromatography or require the addition of organic cosolvents.<sup>17</sup>

Generally, the coordination chemistry of hydrazone based ligands proved to be very interesting, because of their excellent complexation ability towards transition metals and the possibility of analytical applications. The chemical interest arises from the ability of benzoylhydrazone to adopt various coordination modes, leading to enormous structural diversity of their complexes. These chelating ligands can exhibit amido-imidol tautomerism and coordinate in either neutral, monoanionic, dianionic or tetra anionic form bearing unusual coordination numbers. However, coordination modes are depended on the reaction conditions, such as metal ion, its concentration, the pH of the medium and the nature of the hydrazone ligand.<sup>18</sup> The most predominant coordination mode is bidentate, achieved through hydrazine nitrogen and carbonyl oxygen atoms.19 Though several hydrazone metal complexes are known for their biological activities,<sup>20</sup> catalytic applications of these complexes in carbon-carbon coupling reactions are not much explored.

In continuation of our research on synthesis and catalytic applications of Ru and Pd complexes,<sup>21</sup> herein, we describe the synthesis and characterization of new air stable palladium(II) benzhydrazone complexes incorporated with chloride and triphenylphosphine as ancillary ligands. Further, we have developed the complexes as excellent catalysts for the Suzuki cross-coupling reactions. The assessment of palladium catalysts and optimization of the reaction for the coupling of a number of substrates including deactivated and sterically hindered aryl and hetero aryl bromides with different boronic acids in water have been carried out (Scheme 1).

## Result and discussions

The benzhydrazone ligands HL1–HL5 were prepared according to the literature procedure,<sup>22</sup> in which to a stirred ethanolic solution of *p*-substituted benzhydrazide, a solution of thiophene-2-aldehyde or 3-methylthiophene-2-aldehyde in equimolar ratio in ethanol was added drop wise and the reaction mixture was refluxed for 3 h. The cream or pale brown solid was obtained in 83–88% yield after filtered and dried in air. The new palladium catalyst precursors of the type  $[Pd(Cl)(PPh_3)(L)]$ were synthesized by reacting one equivalent of benzhydrazone ligands HL1–L5 with one equivalent of  $PdCl_2(PPh_3)_2$  in DMF/ ethanol under refluxed for 2 h (Scheme 2). All the complexes are obtained as orange solids in high yields 80–83%. The addition of triethylamine to the reaction mixture was used to abstract a proton from the imidol oxygen and to facilitate the coordination of the imidolate oxygen to the palladium. All the complexes are soluble in basic water, CH<sub>3</sub>OH, DMF, DMSO, and CH<sub>3</sub>CN. The analytical data of all the palladium( $\pi$ ) complexes are in good agreement with the molecular structures proposed.

#### Characterization of the complexes

The FT-IR spectra of the free ligands showed a medium to strong band in the region 3191–3280 cm<sup>-1</sup> which is characteristic of the N–H functional group. The ligands also display  $\nu_{C=N}$ and  $\nu_{\rm C=0}$  absorptions in the region 1590–1649 cm<sup>-1</sup>. The disappearance of the C=O band observed in the free ligand correlates with the loss of double-bond character upon deprotonation of the N-H group. This supports the lengthening of the C-O bond which we observe in representative molecular structures. These observations may be attributed to the enolisation of -NH-C=O and subsequent coordination through the deprotonated imidolate oxygen  $v_{(C-O)}$  is appeared around 1290-1254 cm<sup>-1</sup>. A strong sharp absorption band around 1648–1660 cm<sup>-1</sup> in the spectrum of the ligand may be assigned for the imine stretching frequency. This band is shifted to the lower wave numbers upon complexation with the metal by 15-20 cm<sup>-1</sup>. In addition, other characteristic bands due to triphenylphosphine are also present around 1436–1486  $\text{cm}^{-1}$  in the spectra of all the complexes. The absorption spectrum of the complexes in chloroform at room temperature showed three bands in the region 240-397 nm. The high intensity bands in the region 240-339 nm were assignable to ligand-centered (LC) transitions and have been designated as  $\pi - \pi^*$  and  $n - \pi^*$  transitions. In the complexes the lowest energy bands observed in the region 389–397 nm were attributed to the  $Pd(d\pi) \rightarrow L(\pi^*)$ metal to ligand charge transfer (MLCT) transitions.

The <sup>1</sup>H NMR spectra of all the complexes were recorded in CDCl<sub>3</sub> to confirm the bonding of the benzoylhydrazone ligand to the palladium(II) ion. Multiplets observed in the region  $\delta$  8.40–6.45 ppm in the complexes have been assigned to the



Scheme 2 The formation of palladium catalyst precursors of the type  $[PdCl(PPh_3)(L)]$ .

#### Paper

aromatic protons of PPh3 and benzhydrazone ligands. The signal due to the azomethine proton appears in the region  $\delta$  8.93–8.31 ppm. The position of the azomethine signal in the complexes is slightly downfield in comparison with that of the free ligand, suggesting deshielding of the azomethine proton due to its coordination to palladium. The singlet due to the -NH proton of the free ligand in the region  $\delta$  11.61–11.92 ppm is absent in the complex, further supporting enolisation and coordination of the imidolate oxygen to the Pd(II) ion. Therefore, the <sup>1</sup>H NMR spectra of the complexes confirm the bidentate coordination mode of the benzhydrazone ligands to Pd(n)ion and also indicates the presence of PPh3 group. For the complexes 4 and 5, additional methyl signals of the thiophene ring are observed as a singlet at  $\delta$  2.49–2.50 ppm, whereas for complexes 2 and 4, the methoxy signals of the benzhydrazone ring are observed as a singlet at  $\delta$  3.82 ppm. The <sup>1</sup>H NMR spectra of all the complexes further support the coordination mode of the benzhydrazone ligand to the palladium(II) ion via the azomethine nitrogen and the imidolate oxygen along with the presence of triphenylphosphine group (Fig. S2-S7, ESI<sup>+</sup>).

#### X-ray crystallographic studies

The solid state structures of the complexes 1, 4 and 5 were determined by single crystal X-ray diffraction to confirm the coordination mode of the benzhydrazone ligand in the complexes and the geometry of the palladium complexes. Crystals of 1, 4 and 5 grew from slow evaporation of DMF/ ethanol solvent at room temperature and the complexes crystallized in  $P2_1/n$  space group. The ORTEP view of complexes 1, 4 and 5 has shown in Fig. 1-3. The selected bond lengths and bond angles are given in Table 1 and the crystallographic data and structural refinement parameters are given in Table 8. The ligand coordinates with Pd(II) ion *via* the azomethine nitrogen and the imidolate oxygen forming five membered chelate ring. One triphenylphosphine group (trans to the azomethine nitrogen) and one chloride ion (trans to imidolate oxygen) also coordinate to the palladium(II) ion to form a ONClP square plane. The complex is having a distorted square planar geometry as reflected in all the bond parameters around Pd(II) ion. The bond angles around palladium(II) ion are O(1)-Pd(1)-N(1) = $79.30(11)^{\circ}$ ,  $O(1)-Pd(1)-P(1) = 94.02(8)^{\circ}$ ,  $N(1)-Pd(1)-Cl(1) = 94.02(8)^{\circ}$ 



**Fig. 1** Molecular structure of **1**; thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms were omitted for clarity.



**Fig. 2** Molecular structure of **4**; thermal ellipsoids are drawn at the 30% probability level. All hydrogen atoms were omitted for clarity.

94.52(8)° and P(1)–Pd(1)–Cl(1) = 92.03(4)°, and bond lengths of 1.992(3) Å for Pd(1)–O(1), Pd(1)–P(1) 1.992(3) Å for Pd(1)–P(1), 2.054(3) Å for Pd(1)–N(1) and 2.2913(10) Å for Pd(1)–C(1). The bond lengths and bond angles of the present complexes are in good agreement with the reported data on related square planar palladium benzhydrazone complexes.<sup>23</sup> Further, the Pd(1)–P(1) bond length of 2.2631(9) Å is in agreement with other structurally characterized palladium–phosphine complexes.<sup>24</sup> Further, it was observed that the complexes 4 and 5 adopts a similar geometry as in the complex 1, with slight changes in bond angles and bond distances.

#### Coupling reaction of aryl halides

The Suzuki coupling reaction of deactivated aryl halides with aryl boronic acids catalyzed by palladium complexes are enlarged due to their unique properties and variable oxidation states. Our study commenced with the coupling of a wide range of deactivated aryl or hetero aryls bromides and different aryl boronic acids using all five palladium(n) hydrazone complexes as catalysts for the synthesis of biaryls. Literature studies reveal that there is not a set of rule that a specific solvent and a certain base are used to attain the highest efficiency of catalysis in Suzuki–Miyaura cross coupling reactions. Aryl bromides are cheaper and readily available substrates than the corresponding iodides but more reluctant to undergo the catalytic Suzuki

> P1 Pd1 N1 S1 O1 C25 O1 C25

Fig. 3 Molecular structure of 5; thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms were omitted for clarity.

Table 1 Selected bond lengths (Å) and bond angles (°) of complexes 1, 4 and 5

Complex	1	4	5
Pd(1)-O(1)	1.992	2.005	2.0153
Pd(1)-Cl(1)	2.2913	2.2749	2.2667
Pd(1)-P(1)	2.2631	2.2565	2.2773
Pd(1)-N(1)	2.054	2.057	2.0566
C(1)-S(1)	1.702	1.702	1.7125
C(4)-S(1)	1.726	1.738	1.7320
C(6)-O(1)	1.313	1.302	1.3024
C(5)-N(1)	1.279	1.289	1.3063
C(6)-N(2)	1.304	1.303	1.2824
N(1)-N(2)	1.387	1.396	1.3921
O(1)-Pd(1)-N(1)	79.30	78.88	78.66
O(1)-Pd(1)-P(1)	94.02	93.22	96.17
N(1)-Pd(1)-P(1)	172.79	169.89	174.64
O(1)-Pd(1)-Cl(1)	173.31	174.42	172.07
N(1)-Pd(1)-Cl(1)	94.52	95.65	94.44
P(1)-Pd(1)-Cl(1)	92.03	92.33	90.62
C(5)-N(1)-Pd(1)	130.3	130.1	129.24
N(2)-N(1)-Pd(1)	113.1	113.1	113.19
C(6)-O(1)-Pd(1)	110.5	110.9	110.77
C(5)-N(1)-N(2)	116.6	116.8	111.23
C(1)-S(1)-C(4)	91.1	90.7	91.61

reaction. Therefore, we have checked the catalytic efficacy of palladium benzhydrazone catalysts in Suzuki reaction using aryl bromide as the substrate. We initially investigated the reaction of 4-bromoacetophenone with phenylboronic acid using complex 1 (1 mol%) as a test catalyst to establish the

Table 2	Optimization	of	reaction	conditions <sup>a</sup>
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$$\underset{H_3C}{\overset{O}{\longrightarrow}} \underset{H_3C}{\overset{O}{\longrightarrow}} \underset{H_3C}{\overset{H_3C}{\longrightarrow}} \underset{H_3C}{\overset{O}{\longrightarrow}} \underset{H_3C}{\overset{O}{\overset{O}{\longrightarrow}} \underset{H_3C}{\overset{O}{\overset}} \underset{H_3C}{\overset{O}$$

Entry	Solvent	Base	Yield <sup><math>b</math></sup> (%)	TON
1	H <sub>2</sub> O	K <sub>2</sub> CO <sub>2</sub>	99	99
2	H <sub>2</sub> O	K <sub>2</sub> CO <sub>3</sub>	$63^d$	63
3	Dioxane-H <sub>2</sub> O	K <sub>2</sub> CO <sub>2</sub>	87	89
4	DMF-H <sub>2</sub> O	K <sub>2</sub> CO <sub>3</sub>	95	95
5	Toluene-H <sub>2</sub> O	K <sub>2</sub> CO <sub>3</sub>	97	97
6	Toluene	K <sub>2</sub> CO <sub>3</sub>	89	89
7	Dioxane	K <sub>2</sub> CO <sub>3</sub>	86	86
8	THF	K <sub>2</sub> CO <sub>3</sub>	54	54
9	DMF	K <sub>2</sub> CO <sub>3</sub>	94	94
10	$H_2O$	_ 0	_	_
11	H <sub>2</sub> O	Na <sub>2</sub> CO <sub>3</sub>	96	96
12	H <sub>2</sub> O	кон	93	93
13	H <sub>2</sub> O	NaOH	92	92
14	H <sub>2</sub> O	K <sub>3</sub> PO <sub>4</sub>	90	90
15	H <sub>2</sub> O	Et <sub>2</sub> N	73	73
16	$\tilde{H_2O}$	Pyridine	51	51

<sup>*a*</sup> Reaction condition: 4-bromoaceophenone (1 mmol), phenylboronic acid (1.5 mmol), base (2 mmol) catalyst 1 (1 mol%) and solvent (2 mL) at 100 °C for 3 h under air. <sup>*b*</sup> Isolated yield after column chromatography based on 4-bromoacetophenone (average of two runs). <sup>*c*</sup> TON mol of product/mol of catalyst. <sup>*d*</sup> Reaction in open air at r.t. for 32 h.

 Table 3
 Effect of catalyst loading<sup>a</sup>

H <sub>3</sub> C	$Br + B(OH)_2 - H_2OH_2$	D, 100° C, 3 h	CH3
Entry	Catalyst (mol%)	$\mathbf{Yield}^{b}\left(\%\right)$	TON <sup>c</sup>
1	1.0	99	99
2	0.5	99	198
3	0.2	99	495
4	0.1	95	950
5	0.05	93	1860
6	0.01	71	7100
7	0.001	60	60 000
8	0.0001	Traces	_

 $^a$  Reaction condition: 4-bromoacetophenone (1 mmol), phenylboronic acid (1.5 mmol), base (2 mmol) and solvent (2 mL) at 100 °C for 3 h.  $^b$  Isolated yield after column chromatography based on 4-bromoacetophenone (average of two runs).  $^c$  TON mol of product/mol of catalyst.

feasibility of our study and to optimize the reaction condition including solvents, bases (Table 2) and catalyst loading (Table 3). The initial study was begun in water as a solvent with 2.0 equiv. of K<sub>2</sub>CO<sub>3</sub> as base at 100 °C in the reaction and the desired coupling product was obtained in 99% isolated yield (Table 2, entry 1) and yield was decreased to 63% at r.t. (entry 2). Although cross-coupling reactions were carried out in an open vessel under an atmosphere of air, less than 1% of homo coupling was observed. Correspondingly, washing the residue twice with desalinated water was sufficient to obtain pure products. However, we have also examined to increase the yield of the reaction by optimize the different solvents and co-solvent. The dioxane-H<sub>2</sub>O solvent system with K<sub>2</sub>CO<sub>3</sub>, however, gave lesser yield of 87% than water as a solvent (entry 3). The yield was gradually increase to 94% and 97% with traces of byproduct when DMF-H<sub>2</sub>O and toluene-H<sub>2</sub>O were the solvent of choice (entry 4 and 5). The reaction was more efficient in toluene (89%) but still significant amounts of biphenyl as a byproduct prompted us to study in various solvents (entry 6). When, the etheral solvent dioxane was used in the reaction the





Entry	Complex	$\operatorname{Yield}^{b}(\%)$	
1	$(1) [Pd(Cl)(PPh_3)(L1)]$	93	
2	(2) [Pd(Cl)(PPh <sub>3</sub> )(L2)]	91	
3	(3) [Pd(Cl)(PPh <sub>3</sub> )(L3)]	88	
4	(4) [Pd(Cl)(PPh <sub>3</sub> )(L4)]	92	
5	(5) [Pd(Cl)(PPh <sub>3</sub> )(L5)]	90	

 $^a$  Conditions: 4-bromoacetophene (1.0 mmol), phenylboronic acid (1.5 mmol), catalyst 0.05 mol%, K<sub>2</sub>CO<sub>3</sub> (2.0 mmol), water (3 mL), 100 °C, 3 h.  $^b$  Isolated yields.







<sup>*a*</sup> Reaction condition: aryl bromide (1 mmol), substituted phenylboronic acid (1.5 mmol), base (2 mmol), solvent (2 mL) at 100 °C for 3 h. <sup>*b*</sup> Isolated yield after column chromatography based on aryl bromide (average of two runs). <sup>*c*</sup> Double Suzuki cross coupling (aryl bromide (1.0 mmol), arylboronic acid (3 mmol), 0.05 mol% complex **1**,  $K_2CO_3$  (4.0 mmol) were used). <sup>*d*</sup> Aryl chloride (1 mmol), substituted phenylboronic acid (1.5 mmol), base (2 mmol), solvent (2 mL) at 100 °C for 8 h.

yield was decreased to 86% (entry 7) while in THF the yield was drastically decreased to 54% (entry 8). The reaction rate and yield was significantly enhanced when polar solvent like DMF used in the reaction (entry 9) but still with traces of biphenyl was obtained as a by-product. Hence, water is used as a choice of solvent for further studies due to its high yield, non-toxic, environmental benefits and safety. In the absence of base no reaction was occurred, indicates base is necessary for the reaction (entry 10). Since base plays a major role in Suzuki cross coupling reaction, a series of bases such as K2CO3, Na2CO3, KOH, NaOH, K<sub>3</sub>PO<sub>4</sub>, NEt<sub>3</sub>, and pyridine were tested and highest yield was obtained with K<sub>2</sub>CO<sub>3</sub> base (entries 11-16). Among all the bases, inorganic bases gave better result than organic bases. The bases such as carbonates or phosphate allow us to obtain much higher reaction rates. Based on this we chose K<sub>2</sub>CO<sub>3</sub> as base and H<sub>2</sub>O as solvent for further studies.

Further to optimize the catalyst loading, it is preferred to use small amount of catalyst and still achieve high TON in the Suzuki-Miyaura cross coupling reactions. Recently, it has been reported high catalyst loading leading to palladium inactive black formation and also inhibit the catalytic cycles.25 To our pleasure the reaction worked well with different catalyst: substrate (C/S) ratio and the results are summarized in Table 3. The reaction of 4-bromoacetophenone with phenylboronic acid furnished excellent yields (99%) when 1.0, 0.5 or 0.2 mol% of catalysts were loaded (entries 1 to 3). Even when 0.05 mol% of the catalyst used, excellent isolated yield of the cross coupling product is obtained (entry 5). Further, it was observed that even under very low catalyst loading of 0.01 mol% the reaction proceeds smoothly accompanied by a drop in isolated yields with high turnover number (entry 6). Notably, the reaction can also be conducted with an ultra-low catalyst loading of 0.001 mol% which resulting the highest turnover value of 60 000 (entry 7). Since the isolated yield are good with appreciable TON when 0.05 mol% of catalyst is used, it was concluded that 0.05 mol% catalyst loading is the best condition for further coupling reactions.

Since the importance of catalyst stability and longevity has major applications for industrial processes, next we examined the efficiency of performance of changing the *R* substituents on the benzhydrazone ligand coordinated to palladium (Table 4). To this purpose, we have studied the catalytic activities of all complexes 1–5 in the coupling reaction using C : S ratio of 1 : 2000 (0.05 mol%) and it was observed that all the complexes displayed more or less similar catalytic activity, suggesting that there is no significant effect on the catalysis despite the change in the substituent on the aromatic fragment of the benzhydrazone ligand in the complexes. Substitution of methyl and methoxy group of the coordinated ligand in complex 4 and 5 does not make any changes in yield. So we have chosen complex 1 for further studies for its excellent catalytic activity over the other four complexes.

Under the above optimal condition for a cross-coupling reaction (0.05 mol% of catalyst 1, 2 equiv. of  $K_2CO_3$ , water, 100 °C) different aryl and heteroaryl bromides and various functional boronic acids were studied. It should be pointed out that, in contrast with other catalytic systems that require specific bases/additives or relative amounts of starting materials, the use of complex 1 in water proved to be quite insensible to such variables/variations, a clear advantage from a practical point of view.<sup>26</sup>

Among all possible combinations 2,6-biphenylic coupling products were synthesized in good to excellent isolated yields (Tables 5 and 6, entries 1-30). A variety of functionalities are well tolerated for the aryl bromide containing ketone, methyl and methoxy groups. Furthermore, a diverse choice of aryl boronic acids bearing methyl, chloride and methoxy substituents were successfully coupled in the cross coupling reactions. The coupling of 4-bromoacetophenone with phenylboronic acid, 4-methyl phenylboronic acid, 4-methoxy phenylboronic acid and 4-chlorophenylboronic acid gave the desired products in high yields from 90-98% showing high efficiency and good selectivity (Table 5, entries 1-4). Among these, coupling of 4methoxy phenylboronic acid gave excellent conversion of biaryls (entry 3), which takes place at a faster rate than that of phenylboronic acid. The presence of electron withdrawing substituent (chloro) on boronic acids reduces the conversion considerably. Additionally, 4-bromotoluene could also couple with various arylboronic acids in high yields (entries 6-9). 4-

#### Table 6 Suzuki coupling of heteroaryl bromides with aryl boronic acids<sup>a</sup>



<sup>*a*</sup> Reaction condition: heteroaryl bromides (1 mmol), substituted phenylboronic acids (1.5 mmol), base (2 mmol), solvent (2 mL) at 100 °C for 3 h. <sup>*b*</sup> Isolated yield after column chromatography based on heteroaryl bromides (average of two runs). <sup>*c*</sup> Double Suzuki cross coupling (heteroaryl bromide (1.0 mmol), arylboronic acid (3 mmol), 0.05 mol% complex **1**,  $K_2CO_3$  (4.0 mmol) were used).

 Table 7
 Recycling of catalyst<sup>a</sup>





Methoxybromobenzene underwent smooth reaction with various arylboronic acids and gave the coupled products in high yields (entries 10–13). Among all *p*-bromoacetophenone gave high yield compared to other aryl bromides. An increase in the amount of phenyl boronic acid and the prolongation of the reaction time have a slight impact upon the selectivity toward terphenyl (entries 14–16). Under present optimal condition, we have attempted for coupling of aryl chloride with arylboronic acid and the catalyst was found to stable and active enough to handle deactivated aryl chloride. However the coupled product was obtained albeit with low yield even prolonging reaction time (entry 5).

The Suzuki–Miyaura cross coupling reactions of heteroarylhalides is of more interest in the pharmaceutical industry for the preparation of biologically active compounds. Practically, pyridine and thiophene based compounds are the most common heterocyclic pharmaceutically active compounds.<sup>27</sup> Despite efforts by numerous groups, pyridine based bromides have been proved to be a particularly difficult class of substrates for Suzuki reactions. The Suzuki-Miyaura cross coupling reaction of hetero aryl bromides with boronic acids using the same complex 1 was performed and the results are summarized in Table 6. Interestingly, the reactions could also be conducted with catalyst loading of 0.05 mol%. The reactions of 2-bromopyridine with boronic acids bearing electron withdrawing and electron donating substituents were efficient and afforded the desired products in high yields (entries 17-20). Further, double Suzuki coupling of 2,6-dibromo pyridine with various aryl boronic acid have been performed and gave the expected triaryls product in 78-81% isolated yield (entries 21-23). Electronically activating group in heteroaryl ring provided the corresponding coupling product in 70-76% yield (entry 24-26). The reaction of 2-bromothiophene with different aryl boronic acids proceeded well and corresponding products were obtained in good yields (Table 6, entries 27-30) and the electronically activated boronic acid gave best yield then electronically deactivated and nonactivated boronic acids. All these indicated that the electron donating substituents on the boronic acids had great influence on the cross coupling reactions. The loss of yields in these reactions compared to aryl halides indicate that the hetero element in the *a*-substituted hetero aryl bromides would have a possible interaction with palladium which has a deactivation effect on the rate of the reaction.28

At this point, a comparison in terms of catalytic efficiency and scope of application can be established between our complex **1** and other structurally related palladium catalysts. Zeng and his co workers have reported a pyridyl-supported pyrazolyl-N-heterocyclic carbene complex for Suzuki–Miyaura reaction of aryl halides in air and water with 2 mol% catalyst loading.<sup>29</sup> A palladium chelating complex with nitrogen ligands have proven to be efficient catalyst for Suzuki reaction of aryl bromides in the presence of TBAB–water mixture at higher temperature.<sup>30</sup> Moreover, an efficient palladium-catalyzed ligand-free Suzuki–Miyaura coupling in water has been

#### Table 8 Crystal data and structure refinement for complexes

	Complex 1	Complex 4	Complex 5
Empirical formula	C <sub>30</sub> H <sub>24</sub> CN <sub>2</sub> OPPdS	C <sub>31</sub> H <sub>26</sub> ClN <sub>2</sub> OPPdS	C <sub>32</sub> H <sub>28</sub> ClN <sub>2</sub> O <sub>2</sub> PPdS
Formula weight	633.39	647.42	677.44
Wavelength (Å)	0.71073	0.71073	0.71073
Temperature (K)	296(2)	293	296(2)
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	P2(1)/c	P2(1)/n	$P\bar{1}$
a (Å)	14.4356(4)	9.4677(5)	9.605(2)
b (Å)	11.5647(3)	31.1867(15)	18.386(5)
c (Å)	17.7528(4)	10.2754(5)	19.197(5)
$\alpha(\circ)$	90	90	112.769(12)
$\beta$ (°)	107.8100(10)	107.706(2)	101.774(12)
$\gamma$ (°)	90	90	97.141(13)
Volume (Å <sup>3</sup> )	2821.68(12)	2890.3(3)	2981.6(13)
F(000)	1280	1312.0	1376
Crystal size (mm <sup>3</sup> )	0.35 imes 0.30 imes 0.30	0.30 imes 0.20 imes 0.20	0.16 imes 0.14 imes 0.12
Goodness-of-fit on $F^2$	1.143	1.313	0.846
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0347, wR_2 = 0.0959$	$R_1 = 0.0339, wR_2 = 0.0774$	$R_1 = 0.0380, wR_2 = 0.0693$
R indices (all data)	$R_1 = 0.0605, WR_2 = 0.1292$	$R_1 = 0.0774, wR_2 = 1.313$	$R_1 = 0.0693, wR_2 = 0.1168$

developed with good yields using 2 mol% of catalyst and 8 mol% of additives.<sup>31</sup> Suzuki-Miyaura coupling of heterocyclic substrates using palladium complexes containing in expensive phosphine ligands with lower substrate scope has been described by Aziz Fihri et al.32 Recently, Yuhong Zhang and co-workers have developed a phosphine free catalyst system for the Suzuki reaction of aryl halides with high catalyst loading and aid of poly(ethylene glycol) (PEG).<sup>33</sup> Our complex 1, bearing the key hydrazone ligand and phosphine moiety, has proven to be an excellent, much more efficient, and general catalyst in Suzuki coupling reactions, with the crucial advantage of the use of aqueous environments. It can be tentatively proposed that the relatively distorted square planar geometry due to a higher ring strain and the phosphine function have a beneficial effect not only in the activity of palladium complex 1 but also in its solubility in aqueous media and stability under the reaction conditions.

Further, to show the recycling ability of our new catalyst, the reaction of phenylboronic acid with 4-bromoacetophenone was conducted under optimal reaction condition (Table 7). A flask was charged with 4-bromoacetophenone, phenylboronic acid, catalyst 1, K<sub>2</sub>CO<sub>3</sub>, and water (3 mL). The mixture was stirred at 100 °C for 3 h in open air. After the mixture was cooled, the aqueous layer was extracted with diethyl ether ( $3 \times 3$  mL), and the flask was charged again with 4-bromoacetophenone (1 mmol) and phenylboronic acid and K<sub>2</sub>CO<sub>3</sub>. Every time after cooling and extraction with diethyl ether, the reagents and base were added and the reaction was repeated. The combined organic layer was dried over sodium sulfate and evacuated in vacuo and the residue was analyzed by <sup>1</sup>H and <sup>13</sup>C NMR. The recovered catalyst was successfully reused in the subsequent three cycles with consistent activity with 93%, 90%, and 82% isolated yields (entries 1-3). The coupled product was significantly dropped in fourth and fifth cycles (entries 4 and 5). A drastic decrease was observed after fifth run (entries 6 and 7), probably due to a gradual decomposition of catalyst 1 under the reaction conditions.34

# Conclusion

In conclusion, we have successfully demonstrated the synthesis and characterization of a new series of simple and efficient air stable Pd(II) complexes bearing bidentate benzhydrazone ligands. Analytical, spectral and single crystal X-ray diffraction studies of the complexes evidenced azomethine nitrogen and the imidolate oxygen co-ordination mode of the ligand to palladium and reveals the presence of a distorted square planar geometry around Pd(II) ion. The catalysts were found to be active for the Suzuki-Miyaura coupling reaction of challenging substrates like deactivated aryl and heteroaryl bromides in good to excellent yields in water. The catalysts work well with 0.05 mol% and exhibit appreciable TON in relatively short time. The catalyst can be recyclable for at least five times with excellent yields. The coupling reaction can be readily carried out under in open atmosphere and the reaction conditions were optimized for a simple, green and support free procedure, without using any phase transfer agents/additives. Detailed studies of the reaction mechanism will be undertaken in our future work.

# Experimental section

#### General

All reactions were carried out under an atmosphere of air. C, H, N and S analyses were carried out with a Vario EL III CHNS elemental analyzer. IR spectra were recorded on a Perkin-Elmer 597 spectrophotometer, using KBr pellets. <sup>1</sup>H NMR and <sup>13</sup>C NMR were conducted on a high resolution Bruker Avance 400 spectrometer, in CDCl<sub>3</sub> as solvent. All chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane. Abbreviations used in the NMR follow-up experiments: br, broad; s, singlet; d, doublet; t, triplet; m, multiplet. Electronic spectra of the complexes in chloroform solution were recorded with a Cary 300 Bio UV-vis Varian spectrophotometer in the range 800-200 nm using cuvettes of 1 cm path length. Melting points were performed with an electrical instrument and are uncorrected. The ligands HL1-HL5, were prepared according to literature methods. All other chemicals were used as received. Solvents were dried and freshly distilled prior to use. Ethanol was dried over Na/ diethylphthalate, distilled under argon and deoxygenated prior to use. NEt3 was purchased from Merck and dried over CaH<sub>2</sub>, distilled under argon and deoxygenated prior to use. Column chromatography was performed on neutral silica gel.

#### Synthesis of the palladium complexes

All the new palladium complexes were prepared by the following general procedure: ethanolic solution (20 mL) of  $[PdCl_2(PPh_3)_2]$  (50 mg, 1 equiv.) was slowly added the appropriate hydrazone ligand (16.4–19.5 mg, 1 equiv.) and triethylamine (0.5 equiv.) in DMF (5 mL). The reaction mixture was allowed to reflux for 2 hours. Orange color solid was filtered, washed with diethyl ether (5 mL) and recrystallized from ethanol–dimethylformamide. The purity of the complexes was checked by TLC. All the complexes were highly soluble in basic water, MeOH,  $CH_2Cl_2$ ,  $CHCl_3$  and acetone.

 $[Pd(Cl)(PPh_3)(L1)]$  (1). A solution of  $[PdCl_2(PPh_3)]$  (50 mg, 0.071 mmol) in ethanol (20 mL) was added drop wise to the DMF solution (5 mL) of ligand HL1 (16.4 mg, 0.071 mmol) and triethylamine (0.69 mL, 0.5 equiv.) were added. The reaction mixture was refluxed for 2 h and thereafter kept for crystallization. Brown crystals of the product were obtained on slow evaporation of the reaction mixture over the period of 2 weeks. The crystals obtained were suitable for X-ray diffraction. Yield: 82% (45.4 mg), mp 220 °C (with decomposition). Found: C, 56.88; H, 3.82; N, 4.42; S, 5.06. Calc. for C<sub>30</sub>H<sub>24</sub>ClN<sub>2</sub>OPPdS: C, 56.81; H, 3.99; N, 4.44; S, 5.07. IR (KBr, cm<sup>-1</sup>): 1597 s  $\nu_{(C=N-N=C)}$ , 1281 (m)  $\nu_{(C-O)}$ , 425 (s)  $\nu_{(M-N)}$ . <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) ( $\delta$ (ppm)): 8.34 (s, 1H, CH=N), 7.13–7.84 (m, 23H, aromatic).  $\delta_{\rm C}$ (100 MHz) 144.97, 136.20, 137.41, 131.47, 129.36, 126.86. UV-vis (CHCl<sub>3</sub>,  $\lambda_{\text{max}}$  (nm));  $\varepsilon$  (dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>): 389(2614), 368(4219) and 282(4004).

 $[Pd(Cl)(PPh_3)(L2)]$  (2). The complex 2 was prepared by the same procedure as that described for complex 1 with HL2 (18.5 mg, 0.071 mmol) and  $[PdCl_2(PPh_3)]$  (50 mg, 0.071 mmol). Yield: 81% (42.9 mg), mp 218 °C (with decomposition). Found: C,

56.12; H, 3.95; N, 4.22; S, 4.83. Calc. for  $C_{31}H_{26}ClN_2O_2PPdS$ : C, 56.11; H, 3.96; N, 4.21; S, 4.82. IR (KBr, cm<sup>-1</sup>): 1557 s  $\nu_{(C=N-N=C)}$ , 1255 (m)  $\nu_{(C-O)}$ , 434 (s)  $\nu_{(M-N)}$ . <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) ( $\delta$  (ppm)): 8.31 (s, 1H, CH=N), 6.79–8.30 (m, 24H, aromatic), 3.82 (s, 3H, methoxy).  $\delta_{C}$  (100 MHz) 135.07, 135.00, 132.06, 130.53, 128.54, 128.02, 113.22. UV-vis (CHCl<sub>3</sub>,  $\lambda_{max}$  (nm));  $\varepsilon$  (dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>): 390(1081), 369(7689) and 288(5534).

[Pd(Cl)(PPh<sub>3</sub>)(L3)] (3). The complex 3 was prepared by the same procedure as that described for complex 1 with HL3 (18.8 mg, 0.071 mmol) and [PdCl<sub>2</sub>(PPh<sub>3</sub>)] (50 mg, 0.071 mmol). Yield: 83% (43.7 mg), mp 226 °C (with decomposition). Found: C, 53.95; H, 3.47; N, 4.19; S, 4.80. Calc. for C<sub>30</sub>H<sub>24</sub>Cl<sub>2</sub>N<sub>2</sub>OPPdS: C, 53.94; H, 3.48; N, 4.18; S, 4.79. IR (KBr, cm<sup>-1</sup>): 1595 s  $\nu_{(C=N-N=C)}$ , 1290 (m)  $\nu_{(C-O)}$ , 423 (s)  $\nu_{(M-N)}$ . <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) ( $\delta$  (ppm)): 8.82 (s, 1H, CH=N), 6.45–7.79 (m, 24H, aromatic).  $\delta_{\rm C}$ (100 MHz) 135.11, 135.05, 134.51, 134.46, 130.21, 128.81, 128.20, 126.37, 125.64. UV-vis (CHCl<sub>3</sub>,  $\lambda_{\rm max}$  (nm));  $\varepsilon$  (dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>): 394(0948), 339(97 416) and 242(8926).

[Pd(Cl)(PPh<sub>3</sub>)(L4)] (4). The complex 4 was prepared by the same procedure as that described for complex 1 with HL4 (17.3 mg, 0.071 mmol) and [PdCl<sub>2</sub>(PPh<sub>3</sub>)] (50 mg, 0.071 mmol). Yield: 80% (43.4 mg), mp 223 °C (with decomposition). Found: C, 57.51; H, 4.05; N, 4.33; S, 4.95. Calc. for C<sub>31</sub>H<sub>26</sub>ClN<sub>2</sub>OPPdS: C, 57.50; H, 4.07; N, 4.30; S, 4.96. IR (KBr, cm<sup>-1</sup>): 1588 s  $v_{(C=N-N=C)}$ , 1288 (m)  $v_{(C-O)}$ , 430 (s)  $v_{(M-N)}$ . <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) ( $\delta$  (ppm)): 8.44 (s, 1H, CH=N), 6.94–7.84 (m, 27H, aromatic), 2.49 (s, 3H, methyl).  $\delta_{\rm C}$  (100 MHz) 135.11, 135.05, 134.99, 134.70, 134.62, 132.02, 131.24, 130.55, 129.86, 128.44, 127.93, 127.35, 14.08. UV-vis (CHCl<sub>3</sub>,  $\lambda_{\rm max}$  (nm));  $\varepsilon$  (dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>): 396(1186), 348(6205) and 242(1599).

[Pd(Cl)(PPh<sub>3</sub>)(L4)] (5). The complex 5 was prepared by the same procedure as that described for complex 1 with HL5 (19.5 mg, 0.071 mmol) and [PdCl<sub>2</sub>(PPh<sub>3</sub>)] (50 mg, 0.071 mmol). Yield: 82% (42.4 mg), mp 224 °C (with decomposition). Found: C, 56.73; H, 4.31; N, 4.17; S, 4.73. Calc. for C<sub>32</sub>H<sub>28</sub>ClN<sub>2</sub>O<sub>2</sub>PPdS: C, 56.72; H, 4.18; N, 4.15; S, 4.75. IR (KBr, cm<sup>-1</sup>): 1599 s  $\nu_{(C=N-N=C)}$ , 1284 (m)  $\nu_{(C-O)}$ , 428 (s)  $\nu_{(M-N)}$ . <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) ( $\delta$  (ppm)): 8.41 (s, 1H, CH=N), 6.79–8.40 m, 25H, aromatic). 2.50 (s, 3H, methyl). 3.81 (s, 3H, methoxy).  $\delta_{\rm C}$  (100 MHz) 135.12, 135.06, 134.82, 134.63, 131.05, 130.54, 129.38, 127.92, 113.22, 55.42, 14.08. UV-vis (CHCl<sub>3</sub>,  $\lambda_{\rm max}$  (nm);  $\varepsilon$  (dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>): 396(2686), 348(6205) and 240(7573).

#### General procedure for the Suzuki-Miyaura reaction

A mixture of aryl halide (1 mmol), arylboronic acid (1.5 mmol),  $K_2CO_3$  (2.0 mmol), catalyst (0.05 mol%) and deoxygenated  $H_2O$  (3 mL) was loaded into a 5 mL round bottom flask. The mixture was stirred at 80 °C for 3 h in open air. After the mixture was cooled, the aqueous layer was extracted with diethyl ether (3 × 3 mL). The combined organic layers were concentrated *in vacuo* and the remaining residue was purified by Column chromatography (*n*-hexane–ethyl acetate: 200 : 1) to yield a colorless product.

#### Recycling of the catalyst

A 25 mL of round-bottom flask was charged with 4-bromoacetophenone (1.0 mmol) and phenylboronic acid (1.5 mmol) was added catalyst (0.05 mol%) in water (3 mL) at 100 °C in the presence of  $K_2CO_3$  (2.0 mmol). The mixture was stirred at 100 °C for 3 h in air. After the mixture was cooled, the aqueous layer was extracted with diethyl ether (3 × 3 mL) and the flask was charged again with 4-bromoacetophenone (1.0 mmol), phenylboronic acid (1.5 mmol) and  $K_2CO_3$  (2.0 mmol) was added and the reaction was repeated. The identity of the recovered catalyst is further confirmed by TLC and <sup>1</sup>H NMR spectrum before next cycle.

#### X-ray crystallography

Single crystals of all the complexes were grown by slow evaporation of DMF-ethanol mixture at room temperature. A single crystal of suitable size was covered with Paratone oil, mounted on the top of a glass fiber, and transferred to a Stoe IPDS diffractometer using monochromated Mo-K $\alpha$  radiation (kI = 0.71073). Data were collected at 293 K. Corrections were made for Lorentz and polarization effects as well as for absorption (none). The structure was solved with direct method using SIR-97 (ref. 1) and was refined by full matrix least-squares method<sup>2</sup> on  $F^2$  with SHELXL-97. Non-hydrogen atoms were refined with anisotropy thermal parameters. All hydrogen atoms were geometrically fixed and allowed to refine using a riding model. Frame integration and data reduction were performed using the Bruker SAINT-Plus (Version 7.06a) software. The multiscan absorption correction was applied to the data using SADABS software. Crystal data for the structure are given in ESI (Table 1<sup>+</sup>). CCDC reference numbers 1403396, 1434719 and 1435108 contain the supplementary crystallographic data for 1,4&5.†

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