### Accepted Manuscript

A simple and efficient tetradentate Schiff base derived palladium complex for Suzuki-Miyaura reaction in water

Anindita Dewan, Utpal Bora, Geetika Borah

PII:	S0040-4039(14)00065-3
DOI:	http://dx.doi.org/10.1016/j.tetlet.2014.01.041
Reference:	TETL 44073
To appear in:	Tetrahedron Letters
Received Date:	6 December 2013
Revised Date:	7 January 2014
Accepted Date:	10 January 2014



Please cite this article as: Dewan, A., Bora, U., Borah, G., A simple and efficient tetradentate Schiff base derived palladium complex for Suzuki-Miyaura reaction in water, *Tetrahedron Letters* (2014), doi: http://dx.doi.org/ 10.1016/j.tetlet.2014.01.041

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

# ACCEPTED MANUSCRIPT

### **Graphical Abstract**

To create your abstract, type over the instructions in the template box below. Fonts or abstract dimensions should not be changed or altered.





Tetrahedron Letters journal homepage: www.elsevier.com

### A simple and efficient tetradentate Schiff base derived palladium complex for Suzuki-Miyaura reaction in water

Anindita Dewan<sup>a\*</sup> Utpal Bora<sup>a,b</sup> and Geetika Borah<sup>a</sup>

<sup>a</sup>Department of Chemistry, Dibrugarh University, Dibrugarh 786004, Assam, India <sup>b</sup>Department of Chemical Sciences, Tezpur University, Tezpur 784028, Assam, India

\* Corresponding author e-mail: ani\_dewan@yahoo.co.in (A. Dewan). Tel.: +91-373-2370210; fax: +91-373-2370323

Article history:	
Received	A simple and efficient catalytic system based on Pd complex of tetradentate Schiff
Received in revised form	base ligands is found to be highly active (up to 99% isolated yield) for Suzuki–Miyaura reaction
Accepted	of aryl bromides with arylboronic acids in water at room temperature. Further the scope of this
Available online	protocol has been extended to the Suzuki-Miyaura cross coupling reaction of aryl chlorides with
	arylbronic acids in isopropanol.
Keywords:	2009 Elsevier Ltd. All rights reserved.
Suzuki Miyaura	
Aryl halides	
Tetradentate Schiff base	
Water	
Isopropanol	

The Suzuki-Miyaura cross-coupling reaction of aryl halides with arylboronic acids has been considered as one of the most powerful, versatile and popular tool for selective preparation of biaryl compounds which are important structural moieties in numerous polymers, agrochemicals, natural products and pharmaceutical intermediates.<sup>1</sup> Usually catalytic system for these transformations composed of Pd(0) or Pd(II) derivatives associated with appropriate ligands and the efficiency of catalytic system has been achieved by changing the ligand environment around palladium center.<sup>2</sup> Among the assortment ligands used, phosphine based ligands such as tertiaryphosphines, hemilabile-type phosphines, sterically congested biphenyl-type phosphines show excellent activity as ligand in this transformation.<sup>3</sup> Recently different nitrogen containing ligands such as N-heterocyclic carbenes<sup>4</sup> amines,<sup>5</sup> oxime-based palladacycles<sup>6</sup> etc have attracted considerable attention as competent ligand for Suzuki-Miyaura reaction. Among the various N-based ligands, Schiff bases are well known as chelating multidentate ligands in coordination chemistry as well as in catalysis because of their simple and convenient synthetic route with commercially available and economical starting material and high stability under a wide range of redox conditions.<sup>7</sup> Additionally, electronic and steric properties of Schiff bases could be easily manipulated by appropriately selecting the precursor. Tetradentate Schiff bases are unique class of Schiff base ligand which form coordination complex with the metal ion in a tetradentate manner.8 These types of Schiff base complexes with various active metals exhibit excellent performance as catalyst in different organic transformations and recently we were able to use Cu salen complex of tetradentate Schiff base ligands for Chan Lam cross coupling reaction in water.9 From environmental and economic points of view, the use of water as an environmentally benign and economically favorable alternative to organic solvents in chemical transformation has gained notable interest, because water is an inexpensive, readily available, non-toxic and nonflammable solvent.<sup>10</sup> Therefore with an aim to develop novel catalytic systems for Suzuki-Miyaura cross coupling reactions in water with improved yield under simple reaction protocol we herein wish to report a facile and efficient room temperature

Suzuki-Miyaura reaction strategy using a unique palladium tetradentate Schiff base complex as catalyst in water. These tetradentate ligands, due to the existence of multiple bonding sites is expected to increase the steric congestion around the metal centre which is considered to be vital for facilitating the reductive elimination step in the Suzuki-Miyaura cross-coupling reaction pathway.

Initially, we have synthesized and characterized four new palladium complexes C1, C2, C3 and C4 with tetradentate Schiff base ligands N, N'-bis(salicylidene)-phenylmethanediamine (L1), *N*,*N*-bis(salicylidene)-2-chloro-phnylmethanediamine(L2), N, N'-bis(salicylidene)-2-methoxy-phnylmethanediamine (L3) and N, N'-bis(salicylidene)-2-nitro-phnylmethanediamine (L4) derived salicylaldehyde and corresponding from substituted benzaldehyde as reported in the literature.8 The new palladium complexes C1, C2, C3 and C4 (Figure 1) were prepared by refluxing methanolic solution of the corresponding tetradentate ligands L1, L2, L3 and L4 with equimolar amount of palladium acetate. It is noteworthy to mention that we have followed the green chemistry protocol to synthesize the ligands under solventfree conditions.<sup>8</sup> The newly synthesized complexes C1, C2, C3, and C4 were characterized by elemental analysis, IR, <sup>1</sup>H- and <sup>13</sup>C-NMR and mass spectral data.<sup>11</sup>



Figure 1: Screened Ligands and Complex.

1

## ACCEPTED MANUSCRIPT

#### Tetrahedron

The spectral analysis of the prepared complexes corroborates with the reported one. The value of elemental analyses and the appearances of molecular ion peaks in ESI-mass spectra of complexes C1, C2, C3 and C4 support their proposed structure. In the FTIR spectra of complexes, the value for  $\nu$  (C=N) stretching vibration of the free ligand at about 1620 cm<sup>-1</sup> gets considerably shifted to lower frequency at about 1600 cm<sup>-1</sup> after complexation, implying the coordination of imine nitrogen with palladium owing to the donation of electrons from nitrogen atom to the empty *d*-orbitals of the metal. The  $\nu$  (O-H) signal pertaining to free ligands ( 3425 cm<sup>-1</sup> in FTIR and 13.5 ppm in <sup>1</sup>H NMR) was found to be absent in all the four complexes, supporting the deprotonation of phenolic moiety and its subsequent coordination to palladium.

Table:1 Optimization of catalyst for Suzuki-Miyaura reaction

for arylbromides

$O_2N + O_2N + O_2 O_2N + O_2 O_2 O_3 O_2 O_2 O_2 O_2 O_2 O_2 O_2 O_2 O_2 O_2$					
Entry	Pd source (mol%)	Х	Solvent	Time	Yield <sup>a</sup>
				(h)	(%)
1	$Pd(OAc)_2(0.5)$	Br	i-PrOH	15	40
2	Pd(OAc) <sub>2</sub> /L1(0.5)	Br	i-PrOH	15	70
3	Pd(OAc) <sub>2</sub> /L2 (0.5)	Br	i-PrOH	15	75
4	Pd(OAc) <sub>2</sub> /L3 (0.5)	Br	i-PrOH	15	65
5	Pd(OAc) <sub>2</sub> /L4 (0.5)	Br	i-PrOH	15	70
6	C1 (0.5)	Br	i-PrOH	3	90
7	C2 (0.5)	Br	i-PrOH	2	95
8	C3 (0.5)	Br	i-PrOH	3	80
9	C4 (0.5)	Br	i-PrOH	3	85
10	C2 (0.2)	Br	i-PrOH	2	95
11	C2 (0.1)	Br	i-PrOH	15	50
12	C2 (0.2)	Br	H <sub>2</sub> O	2	94

Reaction conditions: aryl halide (0.5 mol), phenylboronic acid (0.55 mmol), Base (1.5 mmol), Solvent (2 mL), 25  $^{\circ}$ C, in air. <sup>a</sup>Isolated yield.

Initially, to examine the efficiency of the tetradentate Schiff base ligands L1-L4 in Suzuki-Miyaura reaction, 4bromonitrobenzene (0.5 mmol) and phenylboronic acid (0.55 mmol) was chosen as model substrates and the reactions were carried out using isopropanol (2 mL) as a solvent, K<sub>2</sub>CO<sub>3</sub> (1.5 mmol) as a base, and at room temperature in the presence of palladium(II) complexes as catalysts, generated in situ from Pd(OAc)<sub>2</sub> (0.5 mol%) and ligands L1-L4 (0.5 mol%) in 1:1 molar ratio.<sup>12</sup> The results are summarized in Table 1. It has been observed from Table 1 that, even in the absence of any ligand, the coupling reaction of 4-bromonitrobenzene and phenylboronic acid proceeded. However the yield of the desired cross coupling product was very low and the reaction proceeded along with the formation of significant amount of biphenyl as a by-product (Table 1, entry 1). However, in presence of the Schiff-based ligand L1 under the present reaction conditions, the reaction proceeded with improved yield of the desired product (Table 1, entry 2) along with the significant reduction of the side product formation. Similar trend was observed with other Schiff base ligands L2-L4 (Table 1, entries 3-5). Among the four ligands used, L2 demonstrates the highest activity (Table 1, entry 3) whereas ligand L3 shows the lowest activity (Table 1, entry 4). It

has been well documented that in Suzuki-Miyaura reaction, the in situ generated catalytic species and pre-formed catalyst often show different catalytic activities.<sup>13</sup>Therefore to compare the activities of the in situ catalyst with pre-formed catalyst we have synthesized Pd-complexes using L1-L4 as ligand.<sup>11</sup> It is observed that the use of the pre-formed Pd complexes C1-C4 as a catalyst resulted in improved yields of the desired cross coupling product compared to that of the in situ catalyst (Table 1, entries 6-9). The best result was obtained with the palladium complex C2 derived bis(salicylidene)-2-chloro-phenylmethanediamine(L2), from (Table 1, entry 7). To optimize the amount of catalyst, we have carried out the reaction using different amount of the Pd complex and we found that 0.2 mol% of the C2 is sufficient to obtain 95% yield of the product (Table 1, entry 10). However the yield of the product was decreased to 50% when we carried the reaction with 0.1 mol% of the catalyst (Table 1, entry 11). Considering the advantage of water as green solvent, we examine the effectiveness of the C2 complex in water and interestingly excellent yield of the product was obtained in water at room temperature (Table 1, entry 12).

It is a well-known fact that the choice of solvent and base is very important in the Suzuki-Miyaura reaction. To study the effect of various solvents and bases in our system, we examined the reaction between 4-bromonitrobenzene with phenylboronic using palladium complex C2 as a catalyst and the results are summarized in Table 2. It is seen from the Table 2 that the reaction proceeded in both protic and aprotic solvents although significant variations in yields were noticed. The reaction seemed to be more facile in polar alcoholic solvent rather than in other solvent like THF, DMF etc. (Table 2). On the other hand the effect of the base was studied by carrying out the reaction in water with various bases, which showed that the reaction proceeded smoothly in presence of K<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub> and Na<sub>3</sub>PO<sub>4</sub> 12H<sub>2</sub>O with equal ease. However the yield significantly diminished in case of strong bases and organic bases. Surprisingly, there was an abrupt change in the rate of the reaction and yield when the reaction was carried out at 50 °C in water (Table 2, entry 15). We chose the optimized reaction conditions, aryl halides (0.5 mmol) phenylboronic acid (0.55 mmol) K<sub>2</sub>CO<sub>3</sub> (1.5 mmol) Pd complex C2 (0.2 mol %) using water as solvent at 50 °C for further studies. The results are listed in Table 3. In general, aryl bromides with electron-withdrawing and electron donating substituent underwent the coupling reactions with phenylboronic acid in nearly quantitative yields. No significant differences were observed in the yield when phenyl boronic acid was replaced by p-chlorobenzene boronic acid (Table 3, entry 4, 8, 13, 18) and p-methoxybenzene boronic acid (Table 3, entry 2, 6, 11, 16). In general ortho substituted aryl bromides required more reaction time as compared to the para substituted counterparts owing to steric hindrance afforded by ortho substituents (Table 3, entry 9, 14).

## ACCEPTED MANUSCRIPT

Table:2Solvent and base effect for Suzuki-Miyaurareaction



Entry	Solvent	Base	Time (h)	Yield (%) <sup>a</sup>
1	i-PrOH	$K_2CO_3$	2	95
2	$H_2O$	$K_2CO_3$	2	94
3	Ethanol	$K_2CO_3$	3	90
4	MeCN	$K_2CO_3$	3	45
5	EtOAc	$K_2CO_3$	3	30
6	Acetone	$K_2CO_3$	3	35
7	CHCl <sub>3</sub>	$K_2CO_3$	3	50
8	THF	$K_2CO_3$	3	80
9	DMF	$K_2CO_3$	3	70
10	$H_2O$	Na <sub>2</sub> CO <sub>3</sub>	2	98
11	$H_2O$	Na <sub>3</sub> PO <sub>4.</sub> 12H <sub>2</sub> O	2	98
12	$H_2O$	NaOH	2	20
13	$H_2O$	КОН	2	20
14	$H_2O$	Et <sub>3</sub> N	2	25
15 <sup>b</sup>	$H_2O$	$K_2CO_3$	0.5	99

Reaction conditions: 4-bromonitrobenzene (0.5 mmol), phenylboronic acid (0.55 mmol), Pd-complex C2 (0.2 mol %), Base (1.5 mmol), Solvent (2 mL), 25 °C, in air. <sup>a</sup>Isolated yield.

<sup>b</sup>Reaction is done at 50 °C

To extend the effectiveness of the current catalyst system to aryl chlorides we have carried out the cross coupling reaction using 4-methoxychlorobenzene as substrate under the same experimental conditions. The reaction between 4-methoxychlorobenzene with phenylboronic acid gave only 20% yield of the desired cross-coupling product at room temperature in water (Table 4, entry 1). Increase of catalyst loading up to 1.0 mol% showed only slight increase in the yield of the product (Table 4, entry 2). However, we were able to isolate 75% yield of the cross coupling product by using *i*-PrOH as solvent (Table 4, entry 3). Similar to the aryl bromide, in this case also the Pd-Schiff base complex C2 showed better results compared to C1, C3 and C4 (Table 4, entries 5-7). However a longer reaction time and reduced yields of the products were obtained for aryl chlorides compared to those of aryl bromides.

To evaluate the scope and limitations of the current procedure, reactions of a wide array of electronically diverse aryl chlorides with arylboronic acids were examined using the palladium complex C2 (Table 5). The aryl chlorides with electron donating substituents such as 4-methoxychlorobenzene, 4methylchlorobenzene underwent coupling reactions with arylboronic acids effectively to afford the desired biaryls in good yields (70-80%) in isoproponol (Table 5, entries 1-8). Similarly chlorobenzene also gave superior product formation with different arylboronic acids (Table 5, entries 10-12). However the reaction of aryl chlorides containing electron withdrawing substituents such as *p*-chloronitrobenzene and pchloroacetophenone with phenylboronic acid did not proceed well and gave only 40-55% (Table 5, entry 13 & 14). However,

aryl chlorides with sterically bulky electron donating substituent at ortho-position are reluctant to react with phenyl boronic acid and very poor yield was obtained (Table 5, entry 9). In general, due to strong C-Cl bond, aryl chlorides are difficult substrates for coupling reaction. It is to be mentioned that our catalyst can produce relatively less yields of coupling products with aryl chlorides compared to aryl bromides as substrates. For aryl chlorides these results are quite significant due to the use of environmentally-benign reaction media and reasonably low catalyst loading (1mol %).

**Table 3:** Suzuki-Miyaura cross-coupling reactions of various aryl bromides with arylboronic acids in water

E	Br B(OH	${}$ C2-Complex K <sub>2</sub> CO <sub>3</sub> , Water,	50°C pl	$ R^2$
R	K ·		ĸ	
Entry	$\mathbf{R}^1$	$\mathbb{R}^2$	Time (min)	Yield (%)
1	4-NO <sub>2</sub>	Н	25	98
2	4-NO <sub>2</sub>	OMe	25	95
3	4-NO <sub>2</sub>	<i>t</i> -Butyl	25	95
4	4-NO <sub>2</sub>	Cl	25	95
5	4-OMe	Н	15	95
6	4-OMe	OMe	20	95
7	4-OMe	t-Butyl	20	96
8	4-OMe	Cl	60	92
9	2-OMe	Н	60	80
10	4-CH <sub>3</sub>	Н	5	90
11	4-CH <sub>3</sub>	OMe	5	95
12	4-CH <sub>3</sub>	t-Butyl	5	98
13	4-CH <sub>3</sub>	Cl	5	95
14	2-CH <sub>3</sub>	Н	60	85
15	4-OCH	Н	25	98
16	4-OCH	OMe	25	98
17	4-OCCH <sub>3</sub>	Н	25	95
18	4-OCCH <sub>3</sub>	Cl	60	90

Reaction conditions: Arylbromide (0.5 mmol), arylboronic acid (0.55 mmol), Pd-complex C2 (0.2 mol %), Base (1.5 mmol), water (2 mL), in air.

**Table 4** Optimization of catalyst for Suzuki-Miyaura reaction

 for aryl chlorides



Entry	Catalyst (mol%)	Solvent	Time	Yield	
			(h)	(%)	
1	C2 (0.5)	$H_2O$	6h	20	
2	C2 (1.0)	$H_2O$	6h	35	
3	C2 (1.0)	<sup>i</sup> PrOH	2h	75	
4	C2(1.0)	<sup>i</sup> PrOH:H <sub>2</sub> O	6h	40	
5	C1 (1.0)	iPrOH	6	65	
6	C3 (1.0)	iPrOH	6	40	
7	C4 (1.0)	iPrOH	6	50	

Reaction conditions: 4-methoxychlorobenzene (0.5 mmol), arylboronic acid (0.55 mmol), Pd-complex, Base (1.5 mmol), water (2 mL), in air.

#### Tetrahedron

**Table 5**: Suzuki-Miyaura cross-coupling reactions of variousaryl chlorides with arylboronic acids in isopropanol

$$\mathbb{R}^{1} \xrightarrow{\text{Cl}} \mathbb{R}^{2} \xrightarrow{\text{B(OH)}_{2}} \mathbb{C2\text{-Complex}}_{K_{2}CO_{3}, i\text{-PrOH}, 50^{\circ}\text{C}} \mathbb{R}^{1} \xrightarrow{\text{Cl}} \mathbb{R}^{2}$$

Entry	$\mathbf{R}^1$	$R^2$	Time (h)	Yield (%)
1	4-OMe	Н	2	75
2	4-OMe	OMe	2	72
3	4-OMe	t-Butyl	2	75
4	4-OMe	Cl	2	70
5	4-Me	Н	2	80
6	4-Me	OMe	2	78
7	4-Me	t-Butyl	2	80
8	4-Me	Cl	2	80
9	2-Me	Н	6	40
10	Н	Н	2	85
11	Н	OMe	3	80
12	Н	t-Butyl	3	82
13	4-COMe	Н	6	40
14	$4-NO_2$	Н	6	55

Reaction conditions: arylchloride (0.5 mmol), arylboronic acid (0.55 mmol), Pd-complex C2 (1 mol %), K<sub>2</sub>CO<sub>3</sub> (1.5 mmol), *i*-PrOH (2 mL), in air.

In conclusion, we have developed a simple and efficient catalytic system based on Pd complex of tetradentate Schiff base ligands for Suzuki–Miyaura reaction of aryl bromides with arylboronic acids in water. Electronically diversified aryl bromides underwent the coupling reaction with electronically diversified arylboronic acids in excellent yields. The same catalytic system is also effective for Suzuki Miyaura reaction of less reactive aryl chlorides with arylbronic acids in isopropanol.

#### Acknowledgments

The authors acknowledge the Department of Science and Technology, New Delhi for financial support for this work under DST Woman Scientist Scheme (No SR/WOS-A/CS-78/2011(G).

#### **References and notes**

- (a) Suzuki, A. Angew. Chem., Int. Ed., 2011, 50, 6722; (b) Suzuki
   A., Yamamoto, Y., Chem. Lett., 2011, 40, 894; (c) Fihri, A.; Bouhrara, M.; Nekoueishahraki, B; Basset, J.-M.; Polshettiwar,
   V., Chem. Soc. Rev., 2011, 40, 5181; (d) Balanta, A.; Godard C.
   Claver, C.; Chem. Soc. Rev., 2011, 40, 4973.; (e) Miyaura N.;
   Suzuki, A., Chem. Rev., 1995, 95, 2457; (f) Littke F. A.; Fu, G.
   C., Angew. Chem., Int. Ed., 2002, 41, 4176; (g) Dupont, J.:
   Consorti C. S, Spencer, J., Chem. Rev., 2005, 105, 2527; (h)
   Gaikwad, A. V. Holuigue, A. Thathagar, M. B. Elshof J. E.
   Rothenberg, G., Chem.-Eur. J., 2007, 13, 6908; (i) Sellars J. D.;
   Steel, P. G.; Chem. Soc. Rev., 2011, 40, 5170.
- (a) Kranenburg, M.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. Eur. J. Inorg. Chem. 1998, 155; (b) Martin, R.; Buchwald S. L., Acc. Chem. Res. 2008, 41, 1461; (b) Bhattacharyya, P.; Woollins, J. D. Polyhedron 1995, 14, 3367.
- (a) Schareina, T.; Kepme, R. Angew. Chem. Int. Ed. 2002, 41, 1521; (b) Urgaonkar, S.; Nagarajan, M.; Verkade, J. G.

*Tetrahedron Lett.* **2002**, *43*, 8921; (c) Biricik, N.; Durap, F.; Kayan, C.; Gumgum, B.; Gurbuz, N.; Ozdemir, I.; Ang, W. H.; Fei, Z.; Scopelliti, R. *J. Organomet. Chem.* **2008**, *693*, 2693; (d) Molander, G. A.; Canturk, B. *Angew. Chem. Int. Ed.* **2009**, *48*, 9240; (e) Milde, B.; Schaarschmidt, D.; Rüffer, T.; Lang, H. *Dalton Trans.* **2012**, *41*, 5377; (f) Das, P.; Bora, U.; Tairai, A.; Sarmah, C. *Tetrahedron Lett.* **2010**, *51*, 1479, (g) Borah, G.; Boruah, D.; Sarmah, G.; Bharadwaj, S.; Bora, U. *Appl. Organometal. Chem.* **2013**, *27*, 688

- 4. Fortman, G. C.; Nolan, S. P. Chem. Soc. Rev. 2011, 40, 5151.
- (a) Das, P.; Sarmah, C.; Tairai, A.; Bora, U. Appl. Organometal. Chem. 2011, 25, 283; (b) Chahen, L.; Therrien, B.; Suss-Fink, G. Eur. J. Inorg. Chem., 2007, 32, 5045.
- (a) Botella, L.; Najera, C. Angew. Chem. Int. Ed. 2002, 41, 179;
   (b) Botella, L.; Najera, C. J. Organomet. Chem. 2002, 663, 46; (c) Beletskaya, I. P.; Cheprakov, A. V. J. Organomet. Chem, 2004, 689, 4055; (d) Alonso, D. A.; Najera, C. Chem. Soc. Rev, 2010, 39, 2891.
- (a) Shahnaz, N.; Banik, B.; Das, P., *Tetrahedron Lett.* 2013, 54, 2886; (b) Banik, B.; Tairai, A.; Shahnaz, N.; Das, P., *Tetrahedron Lett.* 2012, 53, 5627; (c) Kostas, I. D.; Steele, B. R.; Terzis, A.; Amosova, S. V.; Martynov, A. V.; Makhaeva, N. A., *Eur. J. Inorg. Chem.* 2006, 2642.
- (a) Pasini, A.; Ferrari, R.P.; Lanfranconi, S.; Pozzi, A.; Laurenti, E.; Moroni, M. *Inorganica Chimica Acta* **1997**, *266*, 1-3; (b) Naeimi, H.; Rabiei, K.; Salimi, F. Bull. Korean Chem. Soc. **2008**, *29*, 2445-2448.
- Gogoi, A.; Sarmah, G.; Dewan, A.; Bora, U.; *Tetrahedron Lett.* 2014, 55, 31 and references cited there in.
- a) Lindstrom, U. M., *Chem. Rev.*, **2002**, *102*, 2751;(b) Herrerias,
   C. I.; Yao, C. X.; Li Z.; Li, C. J., *Chem. Rev.*, **2007**, *107*,2546;
   (c). Minakata S.; Komatsu, M., Chem. *Rev.*, **2009**, *109*, 711.
- Synthesis of complex C1: A methanolic solution of ligand L1 (330 mg, 1 mmol) was mixed with Pd(OAc)<sub>2</sub> (224 mg, 1 mmol). After refluxing the reaction mixture for 3 h with stirring, the brown colour precipitate was filtered. The residue was washed with hexane and recrystalized from chloroform. Yield: 85%. Anal. Calcd (in %) for C<sub>21</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>Pd; C: 58.01; H: 3.71; N: 6.44%. Found, C: 58.18; H: 3.93; N: 6.13%. MS-ESI(CHCl<sub>3</sub>): m/z: 435[M+]; Selected IR frequency (cm<sup>-1</sup>, KBr): 1606 cm<sup>-1</sup>(ν<sub>C=N</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ/ppm: 6.72(s, 1H, CH), 8.71(s, 2H, CH=N), 7.01-7.09(m, 13H, Ph+Ph+Ph).
- 12. General procedure for Suzuki Miyaura reaction: A 25 mL synthesizer tube had taken with a mixture of aryl halide (0.5 mmol), aryl boronic acid (0.55 mmol), base (1.5 mmol), Pd-complex C1 (0.2 mol%) and the mixture was stirred in 2 mL of water at 50 °C for the required time. After completion, the reaction mixture was extracted with ether ( $3 \times 20$  mL). The combined extract was washed with brine ( $2 \times 20$  mL) and dried over Na<sub>2</sub>SO<sub>4</sub>. After evaporation of the solvent under reduced pressure, the residue was chromatographed (silica gel, ethyl acetate–hexane: 1: 9) to obtain the desired products. The products were confirmed by comparing the <sup>1</sup>H and <sup>13</sup>C NMR and mass spectral data with authentic samples.
- Bohm, V. P. W.; Gstottmayr, C. W. K.; Weskamp, T.; Hermann,
   W. H., *J.Organomet. Chem.* **2000**, *595*, 186; (b) Shi, J.-C.; Yang,
   P.-Y.; Tong, Q.; Wu, Y.; Peng, Y., *J. Mol. Catal. A: Chem.* **2006**, 259, 7.

4