## Accepted Manuscript

Accepted Date:

Dinuclear Pd(II) complexes containing bis-O,N-bidentate Schiff base ligands: Synthesis, characterization, DFT study and application as Suzuki-Miyaura coupling catalysts

Raja Nandhini, Galmari Venkatachalam, Madhu Deepan Kumar, Madhavan Jaccob

PII: DOI: Reference:	S0277-5387(18)30694-6 https://doi.org/10.1016/j.poly.2018.10.058 POLY 13532
To appear in:	Polyhedron
Received Date:	9 August 2018
Revised Date:	10 October 2018

13 October 2018



Please cite this article as: R. Nandhini, G. Venkatachalam, M. Deepan Kumar, M. Jaccob, Dinuclear Pd(II) complexes containing bis-O,N-bidentate Schiff base ligands: Synthesis, characterization, DFT study and application as Suzuki-Miyaura coupling catalysts, *Polyhedron* (2018), doi: https://doi.org/10.1016/j.poly.2018.10.058

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.

# Dinuclear Pd(II) complexes containing bis-O,N-bidentate Schiff base ligands: Synthesis, characterization, DFT study and application as Suzuki-Miyaura coupling catalysts

Raja Nandhini<sup>a</sup>, Galmari Venkatachalam<sup>a,\*</sup>, Madhu Deepan Kumar<sup>b</sup>, Madhavan Jaccob <sup>b,\*</sup>

<sup>a</sup>PG & Research Department of Chemistry, Government Arts College, Dharmapuri- 636 705, Tamilnadu, India.

<sup>b</sup>Computational Chemistry Laboratory, Loyola Institute of Frontier Energy (LIFE) & Department of Chemistry, Loyola College, Nungambakkam, Chennai -600 034, Tamil Nadu, India.

Corresponding Author: \*E-mail address: gvchem@gmail.com [Dr. G. Venkatachalam]

#### Abstract

The reaction of binucleating Schiff base ligands with  $[PdCl_2(PPh_3)_2]$  and  $[Pd(OAc)_2]$  afforded a new family of binuclear palladium(II) Schiff base complexes of the type  $[Pd_2(L)_2]$  and  $[Pd_2Cl_2(PPh_3)_2(L)]$ . All the palladium complexes are air stable and fully characterized by elemental analysis, FT-IR, UV-Vis and <sup>1</sup>H NMR spectral methods. These palladium(II) Schiff base complexes exhibit characteristic metal to ligand charge transfer (MLCT) transitions. Quantum mechanical calculations were also performed to investigate the electronic structure, assign the vibrational spectra and to determine the nature of the frontier molecular orbitals and absorption spectra of the above complexes. These palladium(II) Schiff base complexes exhibited good catalytic activity in the carbon-carbon Suzuki coupling reaction of different aryl halides using phenyl boronic acid.

Keywords: Pd(II), Schiff base ligands, Characterization, Coupling reaction, DFT study

#### 1. Introduction

Palladium-catalyzed reactions have become a powerful tool in chemical synthesis. Amongst them, the palladium-catalyzed Suzuki-Miyaura cross-coupling reaction has become an important protocol for the synthesis of biaryls [1-4]. In particular, the Suzuki-Miyaura reaction, employing organoboron compounds, represents an effective method for the construction of C-C bonds and has potential applications in pharmaceutical, material and agricultural chemistry [5-11]. Moreover, the palladium assisted method offers many advantages over other transitionmetal catalyzed reactions, such as the commercial availability of a large panel of boronic acid derivatives, easy handling, easy removal of boron residues and high functional group tolerance, explaining the increasing interest not only in academic research but also in the industrial scientific community. Even though significant progress has been made, there is a continuous demand for alternative protocols to achieve new, easy preparations, stable ligands and efficient catalytic systems. When two metal centres are incorporated in close proximity, the complexes have the potential of catalyzing either more efficiently or with different chemo, regio or stereoselectivity than those of corresponding mono nuclear complexes due to the co-operation of the two metals in the transition state of the catalytic reactions [12]. For these reasons we have been targeting inexpensive approaches to self-assembled dinuclear molecular structures and have selected imine based ligands. The stability of the imine bond towards hydrolysis is greatly enhanced by conjugation with an aryl ring and the coordination chemistry of such donor units is well established [13].

Usually catalytic systems for these transformations composed of Pd(0) or Pd(II) derivatives associated with the appropriate ligands and efficiency for the catalytic system have been achieved by changing the ligand environment around palladium center. Among the

commonly used phosphine based ligands, such as tertiary phosphines, hemilabile-type phosphines, for example sterically congested biphenyl-type phosphines, show excellent activity as a ligand in this transformation. Recently, different nitrogen containing ligands, such as N-heterocyclic carbenes, amines, oxime-based pallada cycles [14–20] etc, have attracted considerable attention as competent ligands for the Suzuki–Miyaura reaction [21–23]. In the past few years, great advances have been made in developing active and efficient catalysts by modifying traditional ligands and discovering new systems [24, 25].

We have used a novel inexpensive Schiff base ligand system which allows a cage-like complex molecular architecture to be generated. Herein, we describe the synthesis and characterization of a new type of dinuclear palladium(II) complex containing bis-bidentate Schiff base ligands. The catalytic performance of these palladium(II) Schiff base complexes for the carbon-carbon Suzuki coupling reaction of arylhalides has been investigated.



Fig 1. Schiff base ligands.

#### 2. Experimental Section

#### 2.1. Materials

All the used reagents were chemically pure and analytical reagent grade. Solvents were purified and dried according to standard procedures. The alcohols and their corresponding ketones or aldehydes used in the catalytic studies were purchased from Merck and Aldrich. The analysis of carbon, hydrogen and nitrogen content were performed in a Carlo Erba 1106–model 240 Perkin Elmer analyzer at the Sophisticated Test and Instrumentation Centre (STIC), Cochin University, Kochi, India. The infrared spectra FT–IR spectra of the complexes were recorded in an Agilent resolution pro spectrophotometer. A JASCO V–630 UV–Visible Varian spectrophotometer was used to record the electronic spectra.<sup>1</sup>H NMR spectra were recorded on a Bruker 400 MHz instrument using tetramethylsilane (TMS) as an internal reference.

#### 2.2. Synthesis and characterization of the Schiff base ligands

The Schiff base ligand  $H_2L_4$  was prepared by the reaction of 4,4'-diaminodiphenyl ether (1.00 g, 5.00 mmol) and o-vanillin (1.52 g, 10.00 mmol) in methanol (40 mL). The obtained reaction mixture was stirred at room temperature for one hour to give an orange precipitate, which was then filtered and washed with methanol [26].

The other three ligands  $(H_2L_1, H_2L_2 \text{ and } H_2L_3)$  were prepared using an analogous procedure as for the ligand  $H_2L_4$ .

**H**<sub>2</sub>**L**<sub>1</sub>: IR (cm<sup>-1</sup>): 1611 (HC=N), 3037 (OH), <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ (ppm): 6.8-8.2 (m, Ar), 9.4 (2H, s, -HC=N), 3.4 (s, 2H), 15.5 (2H, s, OH).

H<sub>2</sub>L<sub>2</sub>: IR (cm<sup>-1</sup>): 1616 (HC=N), 3220 (OH), <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ (ppm): 6.8-8.2 (m, Ar), 9.3

(2H, s, -HC=N), 15.5 (2H, s, OH).

H<sub>2</sub>L<sub>3</sub>: IR (cm<sup>-1</sup>): 1615 (HC=N), 2921 (OH), <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ (ppm): 6.8-8.2 (m, Ar), 9.4

(2H, s, -HC=N), 3.8 (6H, s, 2OCH<sub>3</sub>), 3.2 (s, 2H), 15.5 (2H, s, OH).

2.3. Synthesis of the binuclear palladium (II) Schiff base complexes  $[Pd_2(L_{1-4})_2]$  (1-4)

An equimolar ratio of the Schiff base ligands  $(H_2L_1-H_2L_4)$  (1 mmol, 0.508 g), Pd(OAc)<sub>2</sub> (1 mmol, 0.224 g) and triethylamine (0.2 mL) were mixed in acetonitrile with constant stirring for 3h. The precipitate of the resulting product was filtered and dried in vacuo.

[Pd<sub>2</sub>(L<sub>1</sub>)<sub>2</sub>] (1) Yellow solid, M.p. 230 °C. Anal calcd. for C<sub>70</sub>H<sub>48</sub>O<sub>4</sub>N<sub>4</sub>Pd<sub>2</sub>: C, 68.85; H, 3.93; N, 4.59. Found: C, 54.26; H, 3.35; N, 3.77. IR (cm<sup>-1</sup>): 1598, 1534, 1498, 1359, 1183, 744. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ (ppm): 6.9–8.5 (m, Ar), 3.81 (2H, CH<sub>2</sub>), 9.1 (–HC=N). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ (ppm): 47.0 (CH<sub>2</sub>), 118-136 (m, Ar), 163 (–HC=N).

[Pd<sub>2</sub>(L<sub>2</sub>)<sub>2</sub>] (**2**): Orange solid. M.p. 240 °C. Anal calcd. for C<sub>68</sub>H<sub>44</sub>O<sub>6</sub>N<sub>4</sub>Pd<sub>2</sub>: C, 66.66; H, 3.59; N, 4.57. Found: C, 56.15; H, 3.30; N, 3.60. FT–IR (cm<sup>-1</sup>): 1600, 1534, 1488, 1357, 1181, 742. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ (ppm): 6.9–8.2 (m, Ar), 9.2 (–HC=N).

[Pd<sub>2</sub>(L<sub>3</sub>)<sub>2</sub>] (**3**): Yellow solid. M.p. 210 °C. Anal calcd. for C<sub>58</sub>H<sub>48</sub>O<sub>8</sub>N<sub>4</sub>Pd<sub>2</sub>: C, 64.44; H, 4.44; N, 5.18. Found: C, 53.21; H, 3.02; N, 3.46. IR (cm<sup>-1</sup>): 1591, 1560, 1320, 1187, 735. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ (ppm): 6.2–7.8 (m, Ar), 3.81 (2H, CH<sub>2</sub>), 3.2 (3H, OCH<sub>3</sub>), 9.4 (–HC=N). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ (ppm): 46.03 (CH<sub>2</sub>), 57.04 (OCH<sub>3</sub>), 117–140 (m, Ar), 165 (–HC=N).

[Pd<sub>2</sub>(L<sub>4</sub>)<sub>2</sub>] (**4**): Yellow solid. M.p. 200 °C. Anal calcd. for C<sub>56</sub>H<sub>44</sub>O<sub>10</sub>N<sub>4</sub>Pd<sub>2</sub>: C, 58.53; H, 3.83; N, 4.87. Found: C, 50.12; H, 3.13; N, 3.42. IR (cm<sup>-1</sup>): 1602, 1541, 1491, 1319, 1182, 692. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ (ppm): 6.5–7.9 (m, Ar), 3.5 (3H, OCH<sub>3</sub>), 8.8 (–HC=N).

2.4. Synthesis of the binuclear palladium (II) Schiff base complexes  $[Pd_2Cl_2(PPh_3)_2(L_{1-4})]$  (5–8)

A 1:2 ratio of the Schiff base ligands  $(H_2L_1-H_2L_4)$  (1 mmol; 0.508 g), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (2 mmol; 1.402 g) and triethylamine (0.2 mL) were mixed in ethanol and refluxed for 5h. The precipitate of the resulting product was filtered and dried in vacuo.

 $[Pd_2Cl_2(PPh_3)_2(L_1)]$  (5) Yellow-brown solid. M.p. 230 °C. Anal calcd. for  $C_{71}H_{69}O_2N_2Pd_2$ : C, 65.03; H, 5.26; N, 2.13. Found: C, 64.50; H, 4.62; N, 2.50. IR (cm<sup>-1</sup>): 1596, 1531, 1425, 1358, 1181, 818, 709. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  (ppm): 7–7.8 (m, Ar), 5.3 (2H, CH<sub>2</sub>), 8.7 (–HC=N).

[Pd<sub>2</sub>Cl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(L<sub>2</sub>)] (**6**): Orange solid, M.p. 240 °C. Anal calcd. for C<sub>70</sub>H<sub>67</sub>O<sub>3</sub>N<sub>2</sub>Pd<sub>2</sub>: C, 54.06; H, 5.10; N, 2.13. Found: C, 50.15; H, 4.90; N, 2.10. IR (cm<sup>-1</sup>): 1599, 1532, 1487, 1426, 1238, 821, 743. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ (ppm): 7.1–8.3 (m, Ar), 8.6 (–HC=N). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ (ppm): 119–136 (m, Ar), 168 (–HC=N).

[Pd<sub>2</sub>Cl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(L<sub>3</sub>)] (7): Yellow solid. M.p. 210 °C. Anal calcd. for C<sub>65</sub>H<sub>54</sub>O<sub>4</sub>N<sub>2</sub>Pd<sub>2</sub>: C, 51.06; H, 4.24; N, 2.19. Found: C, 50.01; H, 3.02; N, 1.98. IR (cm<sup>-1</sup>): 1589, 1433, 1311, 1235, 1186, 733. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ (ppm): 6.8–7.4 (m, Ar), 5.3 (2H, CH<sub>2</sub>), 3.5 (3H, OCH<sub>3</sub>), 7.7 (–HC=N).

[Pd<sub>2</sub>Cl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(L<sub>4</sub>)] (**8**): Yellow solid. M.p. 200 °C. Anal calcd. for C<sub>64</sub>H<sub>52</sub>O<sub>5</sub>N<sub>2</sub>Pd<sub>2</sub>: C, 50.63; H, 4.11; N, 2.21. Found: C, 49.12; H, 3.50; N, 2.11. IR (cm<sup>-1</sup>): 1599, 1480, 1237, 1180, 822. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ (ppm): 6.5–7.7 (m, Ar), 3.5 (3H, OCH<sub>3</sub>), 7.8 (–HC=N). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ (ppm): 56.0 (OCH<sub>3</sub>), 120–145 (m, Ar), 169 (–HC=N).

### 3. Result and discussion

Complexes of the types  $[Pd_2(L)_2]$  and  $[Pd_2Cl_2(PPh_3)_2(L)]$  (L = binucleating Schiff base ligands) were synthesized with the aim of highlighting the influence of the ligands and the catalytic properties. The reactions leading to metal complexes are shown in Schemes 1 and 2.



Scheme 1. Synthesis of dinuclear Pd(II) Schiff base complexes.



Scheme 2. Synthesis of dinuclear Pd(II) Schiff base complexes.

The ligand provides two O, N-donor binding sites separated by spacers. The chosen spacer incorporates phenyl groups that sterically prevent the two palladium binding sites from coordinating to a single metal centre. The central ether and methylene units introduce enhanced flexibility into the ligand backbone, as suggested by Hannon *et al.*, [27] and this enhanced flexibility permits the ligand to support cage-like ligand arrays. The palladium metal ion requires two bidentate Schiff base units to satisfy their coordination requirements, forming a cage-like structure. The elemental analysis of all the complexes (1–8) are consistent with the corresponding proposed molecular formula of the dinuclear palladium(II) complexes. Attempts to grow single-crystals suitable for X-ray diffraction were unsuccessful.

#### 3.1. Characterization of the complexes

The IR spectra of the Schiff bases (H<sub>2</sub>L<sub>1</sub>–H<sub>2</sub>L<sub>4</sub>) showed strong bands at 1619–1612 cm<sup>-1</sup> and they are assigned based on the (CH=N) stretching frequency. The C=N stretching frequencies displayed by the palladium(II) Schiff base complexes are lower than those for the uncomplexed ligands. This lowering of the C=N stretching frequency, observed at 1589–1602 cm<sup>-1</sup> for these palladium complexes, is attributed to coordination of the C=N bond in the chelate ring to the metal center [28]. The broad stretching frequency of the OH band around 3400 cm<sup>-1</sup> in the ligands H<sub>2</sub>L<sub>1</sub>–H<sub>2</sub>L<sub>4</sub> is absent in these complexes, suggesting the deprotonation of the OH groups and subsequent coordination of the phenolic oxygen atoms to the metal centre. Representative FT–IR spectra of complexes **1–8** are given in Figs. S1–S15 (see supporting information). In addition to these, strong bands observed around 1425–1433 cm<sup>-1</sup>in all the complexes (**5–8**) are attributed to coordinated PPh<sub>3</sub> ligands in the Pd(II) complexes.

The UV–Vis spectra of all the complexes in chloroform solutions exhibit characteristic absorptions in the region 200–800 nm. Representative UV-Vis spectra of complexes **1–8** are given in Figs. S16–S23 (see supporting information). Strong absorption bands observed at 230–250 nm are assigned to the  $\pi \rightarrow \pi^*$  transition in the Schiff base ligands, whereas the medium absorption bands, appearing at 270–290 nm, are assigned to the  $n\rightarrow\pi^*$  transition. The  $\pi\rightarrow\pi^*$  and  $n\rightarrow\pi^*$  transitions for the free ligands were shifted to higher wavelengths as a consequence of the coordination to the metal ions, indicating the formation of Schiff base metal complexes. In addition, these spectra showed a band around 415–442 nm, assigned to an MLCT transition, which strongly favours the square-planar geometry around the central metal ion [29–31].

The <sup>1</sup>H NMR data of the synthesized complexes shows that aromatic OH peaks in these dipalladium(II) complexes, expected to appear in the downfield region around  $\delta$  12.0-13.0ppm for H<sub>2</sub>L<sub>1</sub>-H<sub>2</sub>L<sub>4</sub>, are not observed and it this due to the coordination of the phenolic oxygen atom

to the metal atom by deprotonation. The presence of the azomethine proton (CH=N) attached to the phenyl ring was confirmed by the singlet around  $\delta$  9.1–7.8 ppm. Further, the aromatic protons of all these complexes are observed as multiplets around  $\delta$  6.2–8.2 ppm. The methylene (CH<sub>2</sub>) proton bridging the two phenyl rings in the complexes **1**, **3** and **5**, 7 was observed around  $\delta$ 3.81 and 5.3 ppm as a singlet. The signals for the methoxy proton (OCH<sub>3</sub>) in the complexes **3**, **4** and **7**, **8** appeared as a singlet around  $\delta$  3.2 and 3.5 ppm respectively. The <sup>13</sup>C NMR spectra of complexes **1**, **3**, **6** and **8** were recorded and showed peaks around  $\delta$  169-162 ppm for the azomethine carbon (CH=N) atom. The –CH<sub>2</sub> carbon peak appeared at  $\delta$  46.11 and 47.03 ppm for complexes **1** and **3**, respectively. The methoxy carbon signal (OCH<sub>3</sub>) was observed for complex **3** at  $\delta$  57.04 ppm. The <sup>1</sup>H and <sup>13</sup>C NMR spectra are shown in Figs. S24–S35 (Supporting information).

### 3.2. Electronic structures of the complexes

To gain a molecular-level understanding of the electronic structures and absorption properties of the studied complexes, we carried out a computational characterization using density functional theory (DFT) calculations. The B3LYP functional along with the LANL2DZ basis set for Pd and 6-31G(d) [32] for other atoms were used throughout this work. Considering the possibility of low-spin (S=0) and high-spin states (S=1) for these complexes, the molecular structure of **5** was fully optimized in both spin states and spin density plots were generated, which are shown in Fig 2.



Fig 2. Computed spin density plots along with the MESP map of the low-spin and high-spin complexes of 5.

From the plot, it is apparent that a significant quantity of electron spin density is localized on the Pd atoms and slightly on the coordinated O atoms in high-spin species, whereas no spin density was observed in the low-spin complex, confirming the presence of unpaired electrons in the high-spin species. Furthermore, the molecular electrostatic potential (MESP) map was drawn for **5** to investigate the electrostatic regions around the complex. From Fig. 2, it can be seen that the region in the vicinity of the chloride atoms intercedes with red, indicating that they are nucleophilic in nature. Especially, this observation is conspicuous in the case of the high-spin complex. Comparing the relative energies of both spin-states, the low-spin state was found to be 48.6 kcal/mol lower than the high-spin complex. This substantiates that the low-spin species, with the fundamental electronic configuration of  $(d_{xz})^2(d_{yz})^2(d_{zz})^2(d_{xy})^2(d_{xy2}-v^2)^0$ , is the ground

state for this kind of complex. Therefore, all the other titled binuclear palladium(II) Schiff base complexes were optimized in their low-spin state and the geometries are provided in Fig. 3.



Fig 3. B3LYP/LANL2DZ(6-31G(d)) optimized geometries of all the titled complexes.

In the absence of X-ray crystallographic characterization of the synthesized complexes, to gain insight into the molecular geometrical parameters a detailed examination of the DFT optimized structures was performed and important bond distances are collected in Table 1.

Bond Lengths	1	2	Bond Lengths	5	6
Pd1-N1	2.051	2.061	Pd1-N	2.107	2.108
Pd1-N2	2.051	2.056	Pd1-O	2.026	2.027
Pd1-O1	2.027	2.020	Pd1-Cl	2.368	2.367
Pd1-O2	2.027	2.030	Pd1-PPh <sub>3</sub>	2.357	2.356
Pd2-N1	2.066	2.070	Pd2-N	2.083	2.084
Pd2-N2	2.066	2.073	Pd2-O	2.062	2.064

Table 1. Calculated selected bond lengths (Å) of complexes 1, 2 and 5, 6.

Pd2-O1	2.052	2.043	Pd2-Cl	2.363	2.363
Pd2-O2	2.052	2.037	Pd2-PPh <sub>3</sub>	2.341	2.339

In all the four complexes, the Pd–N and Pd–O bond lengths range from 2.08 to 2.1 Å and 2.02 to 2.06 Å respectively, while the Pd–Cl and Pd–PPh<sub>3</sub> bond lengths in **5** and **6** fall in the range from 2.33 to 2.36 Å. The accuracy of the computed bond parameters and other geometrical features are corroborated by the close agreement observed between the DFT and experimental vibrational stretching frequencies, as shown in Table 2.

ID	DFT	(cm <sup>-1</sup> )	Experiment (cm <sup>-1</sup> )		
IK	1	2	1	2	
v <sub>C=N</sub>	1585	1625	1598	1600	
υ <sub>C-0</sub>	1347	1379	1359	1357	
	5	6	5	6	
v <sub>C=N</sub>	1588	1588	1596	1599	
$v_{C-O}$	1444	1292	1358	1238	
V <sub>Pd-PPh3</sub>	719	720	740	743	

Table 2. Computed vibrational stretching frequencies of all the four investigated complexes.

The computed C=N stretching frequencies for **5**, **6** and **1** are in the range 1585–1588 cm<sup>-1</sup> which is closer to the experimental range of 1596–1599 cm<sup>-1</sup>. For **2**, the computed C=N stretching frequency appears at 1625 cm<sup>-1</sup> and the experimental frequency for the same occurs at 1600 cm<sup>-1</sup>. Similarly, the DFT calculated Pd–PPh<sub>3</sub> stretching frequencies for **5** and **6** were found to occur at ~720 cm<sup>-1</sup>, while experimentally it was observed at around 740 cm<sup>-1</sup>. The computed C-O bond stretching frequency was also found to be closer to the experimental results (see Table 2). These observations demonstrate that our computed results are authentic and reliable.

#### 3.3. Absorption spectral behaviour

Using time dependent-density functional theory (TD-DFT), the UV/Visible absorption spectra were simulated for all the titled complexes. The experimental chloroform solvent

condition was set up computationally by employing a self-consistent reaction field-polarizable continuum model (SCRF-PCM) [33, 34].



Fig 4. Simulated absorption spectra of complexes 5, 6 and 1, 2.

In the present work, the absorption spectra of all the four complexes (Fig 4) under investigation show similar absorption characteristics. All the four complexes show three major absorption bands in both the ultraviolet and visible regions. In order to gain more insight into the electronic spectra of these complexes, we have computed the absorption parameters and the results are summarized in Table 3 along with experimental absorption maxima.

**Table 3.** TD–DFT calculated electronic transitions assignment, nature of the transitions, absorption maxima and oscillator strengths.

DFT λ/nm	Expt. λ/nm	f	Transitions assignment	Nature of Transition	
	1	1	1		
445.74	430	0.20	HOMO ( $\alpha$ ) $\rightarrow$ LUMO+2 ( $\alpha$ ) (89%) HOMO ( $\beta$ ) $\rightarrow$ LUMO+2 ( $\beta$ ) (89%)	MLCT	
363.31	302	0.21	HOMO-3 ( $\alpha$ ) $\rightarrow$ LUMO+4 ( $\alpha$ ) (64%) HOMO-3 ( $\beta$ ) $\rightarrow$ LUMO+4 ( $\beta$ ) (64%)	n-π*	
332.36	250	0.37	HOMO-8 ( $\alpha$ ) $\rightarrow$ LUMO+1 ( $\alpha$ ) (35%) HOMO-8 ( $\beta$ ) $\rightarrow$ LUMO+1 ( $\beta$ ) (35%)	ππ*	
	·	·	2		
447.68	420	0.22	HOMO ( $\alpha$ ) $\rightarrow$ LUMO ( $\alpha$ ) (32%) HOMO ( $\beta$ ) $\rightarrow$ LUMO ( $\beta$ ) (32%)	ICT	
401.98	315	0.21	HOMO-2 ( $\alpha$ ) $\rightarrow$ LUMO+1 ( $\alpha$ ) (28%) HOMO-2 ( $\beta$ ) $\rightarrow$ LUMO+1 ( $\beta$ ) (28%)	n-π*	
340.31	245	0.30	HOMO-4 ( $\alpha$ ) $\rightarrow$ LUMO+2 ( $\alpha$ ) (14%) HOMO-4 ( $\beta$ ) $\rightarrow$ LUMO+2 ( $\beta$ ) (14%)	ππ*	
		1	5		
393.61	430	0.17	HOMO ( $\alpha$ ) $\rightarrow$ LUMO+2 ( $\alpha$ ) (60%) HOMO ( $\beta$ ) $\rightarrow$ LUMO+2 ( $\beta$ ) (60%)	MLCT	
347.82	330	0.27	HOMO-4 ( $\alpha$ ) $\rightarrow$ LUMO+1 ( $\alpha$ ) (42%) HOMO-4 ( $\beta$ ) $\rightarrow$ LUMO+1 ( $\beta$ ) (42%)	n-π*	
322.74	280	0.30	HOMO-2 ( $\alpha$ ) $\rightarrow$ LUMO+3 ( $\alpha$ ) (72%) HOMO-2 ( $\beta$ ) $\rightarrow$ LUMO+3 ( $\beta$ ) (72%)	ππ*	
6					
395.67	440	0.23	HOMO ( $\alpha$ ) $\rightarrow$ LUMO+2 ( $\alpha$ ) (48%) HOMO ( $\beta$ ) $\rightarrow$ LUMO+2 ( $\beta$ ) (48%)	MLCT	
368.13	315	0.22	HOMO-1 ( $\alpha$ ) $\rightarrow$ LUMO+1 ( $\alpha$ ) (35%) HOMO-1 ( $\beta$ ) $\rightarrow$ LUMO+1 ( $\beta$ ) (35%)	n-π*	
319.00	270	0.28	HOMO-2 ( $\alpha$ ) $\rightarrow$ LUMO+3 ( $\alpha$ ) (35%) HOMO-2 ( $\beta$ ) $\rightarrow$ LUMO+3 ( $\beta$ ) (35%)	ππ*	

From the table it is clear that all our computed absorption maxima are in excellent agreement with the experimental values. Investigation of the corresponding frontier molecular orbitals (FMO) responsible for the origin of the three intense absorptions bands (Figs. 5–8) reveals that all these transitions resemble MLCT,  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  natures and appear in the

ranges 393 to 447 nm, 347 to 401 nm and 319 to 340 nm, respectively. In the case of **5**, **6** and **1**, the longer wavelength bands mainly arise due to the transition occurring between the HOMO and LUMO+2, which manifest MLCT character, while for **2** it is between the HOMO and LUMO, with intramolecular charge transfer (ICT) nature. The oscillator strength of the  $\pi \rightarrow \pi^*$  band is relatively higher for all four complexes, being in the range 0.28 to 0.37 nm, while the MLCT bands, which appear in at longer wavelengths, exhibit relatively lower oscillator strengths in the range 0.17 to 0.23 nm.



Fig 5. Frontier molecular orbitals of three major absorption bands of 1.



Fig 6. Frontier molecular orbitals of three major absorption bands of 2.



Fig 7. Frontier molecular orbitals of three major absorption bands of 5.



Fig 8. Frontier molecular orbitals of three major absorption bands of 6.

#### 3.4. Suzuki reaction of aryl halides with phenylboronic acid

To optimize the catalyst loading, it is preferable to use a small amount of catalyst and to achieve a high yield in the Suzuki cross coupling reactions. Recently, it has been reported that high catalyst loading leads to palladium inactive black formation and also inhibits the catalytic cycles. To our pleasure, the reaction worked well with different catalyst ratios and the reaction of bromobenzene with phenylboronic acid furnished good yields when 1mol% of catalysts were loaded. We have chosen (1 mol%) catalyst [Pd<sub>2</sub>(L)<sub>2</sub>] and [Pd<sub>2</sub>Cl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(L)] loading as the best conditions for further coupling reactions.

The catalytic activity of the synthesized Pd(II) Schiff base complexes  $[Pd_2(L)_2]$  and complexes containing triphenylphosphine ligands,  $[Pd_2Cl_2(PPh_3)_2(L)]$ , were investigated under the same reaction conditions and the results are summarized in Tables 4 and 5. Aryl bromides with various functional groups efficiently reacted with boronic acids using K<sub>2</sub>CO<sub>3</sub> and (5 mL) methanol at reflux temperature in the presence of the palladium(II) complexes as a catalyst for

2h to yield Suzuki coupling products in moderate to good conversions. The conversions are good in all the case of bromobenzenes (entry 1) and *p*-bromomethoxybenzene (entry 4).

**Table 4**. Catalytic Suzuki carbon-carbon coupling reactions of arylhalides by  $[Pd_2(L)_2]$  (1-4)<sup>a</sup>

	-Br +	$\succ B(OH)_2  \frac{Pd_2(L)_2(1-4) / (1 \text{ mol})}{K_2CO_3/MeOH}$	%) ►			8
Entry	Substrate	Substrate Product			6) <sup>b</sup> ces	
1	Br		66	58	<u> </u>	<b>4</b> 54
2	Cl-NO <sub>2</sub>	0 <sub>2</sub> N-	73	59	57	30
3	Br-CH3	H <sub>3</sub> C-	70	75	62	73
4	Br-OCH3	H <sub>3</sub> CO	83	60	56	67
5	CI-CN	NC	42	37	59	46
6	СІ—ОН	но	60	50	48	35
7	Br		63	69	55	65
8	Br CHO	онс	56	60	50	30
9	Cl		30	32	39	35

<sup>a</sup>Reaction condition: aryl halides (1 mmol), phenylboronic acid (1.2 mmol), K<sub>2</sub>CO<sub>3</sub> (1 mmol), catalyst (1 mol%), temperature 80 °C.

<sup>b</sup>Isolated yield after column chromatography.

In addition, compared to the complexes of the type  $[Pd_2(L)_2]$ , the complexes of the type  $[Pd_2Cl_2(PPh_3)_2(L)]$ , containing Schiff base and triphenylphosphine ligands, showed enhanced catalytic efficiency by adjusting the steric crowding around the palladium(II) metal center. Further, the  $\pi$ -acceptor and  $\sigma$ -donor ability of the PPh<sub>3</sub> and Schiff base ligands make the metal center more susceptible for this catalytic reaction.

It is not easy to compare the catalytic results with literature reports due to the variety of different reaction conditions, but a tentative comparison with the Suzuki-Miyaura reaction of the catalytic system reported by Kunz, *et al* [35, 36] implies that the present complexes lead to catalysts of similar reactivity, even with three times lesser catalyst loading at low temperature.

MA

### Table 5.

Catalytic Suzuki carbon-carbon coupling reaction of arylhalides by  $[Pd_2Cl_2(PPh_3)_2(L)_2]$  (5–8)<sup>a</sup>

$ \begin{array}{ c c c c } \hline & & & & & & & & & & & & & & & & & & $						
Entry Oliver Diale			Yield (%) <sup>b</sup>			
	Substrate	Floduct	5	<u>6</u>	7	8
1	Br		71	75	60	60
2		O2N	73	59	57	58
3	Br-CH3	H <sub>3</sub> C	83	65	59	68
4	Br-OCH3	H <sub>3</sub> CO	68	62	56	67
5	CI-CN		70	67	62	60
6	СІ-ОН	но	86	89	86	92
7	Br		78	60	54	61
8	Вг СНО	онс	80	75	60	85
9	Cl		30	35	41	37

<sup>a</sup>Reaction condition: aryl halides (1 mmol), phenylboronic acid (1.2 mmol), K<sub>2</sub>CO<sub>3</sub> (1 mmol), catalyst (1 mol%), temperature 80 °C. <sup>b</sup>Isolated yield after column chromatography.

*p*-Bromotoluene reacts with aryl boronic acid, producing the corresponding biphenyl with moderate to excellent conversions (entry 3, 83%). Good conversion was noticed for all the substrates in 2h. As expected, very satisfactory results were obtained for all the electron-deficient substrates in the boronic acid (entries 6), having conversions of 83, 86, 89 and 92%. 2-Bromotoluene (entry 7), gave the corresponding product in a slightly lower yield (54–78%), which may be due to steric effects compare with *p*-bromotoluene (entry 3). Further, 4-bromotoluene and chlorobenzonitrile can also react with phenylboronic acid with good conversions. The catalytic activity of the present complexes is good and although several catalytic systems have been reported, a catalyst of this type is new for its bis-bidentate O, N-donor environment with the palladium center.

#### 4. Conclusion

We have synthesized a new family of dinuclear palladium(II) Schiff base complexes of the types  $[Pd_2(L)_2]$  and  $[Pd_2Cl_2(PPh_3)_2(L)]$ , using bis-bidentate Schiff base ligands with metal precursors. All the complexes were characterized by elemental analysis, IR, UV–Vis and <sup>1</sup>H NMR spectral methods. The electronic structures and spectroscopic properties were thoroughly investigated by DFT calculations as well. Furthermore, the computed IR frequencies and electronic spectra are in close agreement with the experimental results. The catalytic performance of these complexes towards the carbon-carbon Suzuki coupling reaction of aryl halides was studied and shows moderate to good conversions. Comparing the complexes, the advantage of using a triphenylphosphine ligand with the Schiff base ligand in  $[Pd_2Cl_2(PPh_3)_2(L)]$ is modulation of the steric environment around the palladium center, which is the appropriate choice of ligands for catalytic reactions. Thus, the presence of triphenylphosphine and Schiff base ligands seems to play an important role in the catalytic activity of these complexes.

#### Acknowledgements

G.V gratefully acknowledges the University Grants Commission (UGC), New Delhi, India, for providing financial support to undertake this work.

#### References

- [1] (a) L. Yin, J. Liebscher, Chem. Rev. 107 (2007) 133–173;
  - (b) N. E. Leadbeater, M. Marco, J. Org. Chem. 68 (2003) 888-892;
  - (c) Y. Gong, W. He, Org. Lett. 4 (2002) 3803–3805;
  - (d) B. Basu, P. Das, M. M. H. Bhuiyan, S. Jha, Tetrahedron Lett. 44 (2003) 3817-3820;
  - (e) T. R. Hoye, M. Chen, J. Org. Chem. 61 (1996) 7940-7942;
  - (f) S. M. S. Hussain, M. B. Ibrahim, A. Fazal, R. Suleiman, M. Fettouhi, B. E. Ali, Polyhedron 70 (2014) 39–49;
  - (g) V. Hensel, K. Lutzow, J. Jocob, K. Gessler, A. -D. Schluter, Angew. Chem., Int. Ed. 36 (1997) 2654–2656;
  - (h) E. B. Schwartz, C. B. Knobler, D. J. Cram, J. Am. Chem. Soc. 114 (1992) 10775– 10784;
  - (i) S. -I. Mohri, M. Stefinovic, V. Snieckus, J. Org. Chem. 62 (1997) 7072–7073.
- [2] (a) E. C. Constable, Prog, Inorg. Chem. 42 (1994) 67–138;
  - (b) E. C. Constable, A. J. Edwards, M. J. Hannon, P. R. Raithby, J. Chem. Soc., Chem Commun. (1994) 1991–1992;
  - (c) E. C. Constable, S. M. Elder, M. J. Hannon, A. Martin, P. R. Raithby, D. A. Tocher, J. Chem. Soc., Dalton Trans. (1996) 2423–2433;
  - (d) E. C. Constable, S. M. Elder, M. J. Hannon, A. J. Edwards, P. R. Raithby, J. Chem. Soc.,

Dalton Trans. (1994) 2669–2677.

- (e) J. L. Pratihar, P. Pattanayak, D. Patra, C-H. Lin, S. Chattopadhyay, Polyhedron 33 (2012) 67–73.
- [3] (a) A. F. Littke, G.C. Fu, Angew. Chem. 41 (2002) 4176–4211;
  - (b) D. A. Albisson, R. B. Bedford, S. E. Lawrence, P. N. Scully, Chem. Commun. (1998) 2095–2096;
  - (c) G. T. Crisp, Chem. Soc. Rev. 27 (1998) 427-436;
  - (d) M. Casey, J. Lawless, C. Shirran, Polyhedron 19 (2000) 517-520.
  - (e) J. L. Pratihar, N. Maiti, P. Pattanayak, S. Chattopadhyay, Polyhedron 24 (2005) 1953.
  - (f) S. Mohanty, B. Punji, M. S. Balakrishna, Polyhedron 25 (2006) 815-820.
- [4] (a) M. Raja, R. Ramesh, Y. Liu, Tetrahedron Lett. 52 (2011) 5427–5430;
  - (b) A. Ghorbani-Choghamarani, A. Naghipour, H. Babaee, B. Notash, Polyhedron 119 (2016) 517–524;
  - (c) A. F. Littke, L. Schwarz and G. C. Fu, J. Am. Chem. Soc., 124 (2002) 6343-6348;
  - (d) D. W. Old, J. P. Wolfe and S. L. Buchwald, J. Am. Chem. Soc., 120 (1998) 9722–9723;
  - (e) M. G. Andreu, A. Zapf and M. Beller, Chem. Commun., (2000) 2475–2476;
  - (f) N. Kataoka, Q. Shelby, J. P. Stambuli, J. F. Hartwig, J. Org. Chem., 67 (2002) 5553– 5566;
  - (g) R. B. Bedford, S. J. C. Cazin, S. J. Coles, T. Gelbrich, M. B. Hursthouse, V. J. M. Scordia, Dalton Trans., (2003) 3350–3356.
- [5] (a) J. Hassan, M. Sevignon, C. Gozzi, E. Schulz, M. Lemaire, Chem. Rev. 102 (2002) 1359– 1369;
  - (b) I. Nakamura, Y. Yamamoto, Chem. Rev. 104 (2004) 2127–2198;

- (c) N. Liu, C. Liu, Z. L. Jin, J. Catal. 31 (2010) 1316–1320;
- (d) Y. Kitamura, A. Sakurai, T. Udzu, T. Maegawa, Y. Monguchi, H. Sajik, Tetrahedron 63 (2007) 10596–1060.
- (e) P.O. Lumme, H. Knuuttila, Polyhedron 14 (1995) 1553–1563.
- [6] (a) N. Miyaura, T. Yanagi, A. Suzuki, Synth. Commun.11 (1981) 513–519;
  - (b) T. Watanabe, N. Miyaura, A. Suzuki, Synlett, (1992) 207–210;
  - (c) G. W. Kabalka, L. Wang, V. Namboodiri, Synthesis (2003) 217–222;
  - (d) D. Zim, A. L. Monteiro, Tetrahedron Lett. 43 (2002) 4009-4011.
- [7] N. Miyaura, A. Suzuki, Chem. Rev. 95 (1995) 2457–2483.
- [8] A. Suzuki, J. Organomet. Chem. 576 (1999) 147-168.
- [9] S. Kotha, K. Lahiri, D. Kashinath, Tetrahedron. 58 (2002) 9633–9695.
- [10] S. Darses, J. P. Genet, Chem. Rev. 108 (2008) 288-325.
- [11] D. Pandiarajan, R. Ramesh, Y. Liu, R. Suresh, Inorg. Chem. Commun. 33 (2013) 33–37.
- [12] (a) C. J. McKenzie, R. Robson, J. Chem. Soc., Chem. Commun. (1988) 112–114.
  - (b) R. W. Cruse, S. Kaderli, C. J. Meyer, A. D. Zuberbühler, K. D. Karlin, J. Am. Chem. Soc. 110 (1988) 5020–5024;
  - (c) K. D. Karlin, P. Ghosh, R. W. Cruse, A. Farooq, Y. Gultneh, R. R. Jacobson, N. J. Blackburn, R. W. Strange, J. Zubieta, J. Am. Chem. Soc. 110 (1988) 6769–6780;
    (d) P. Kalck, Polyhedron 7 (1988) 2441–2450;
  - (e) J. Jenck, P. Kalck, E. Pinelli, M. Siani, A. Thorez, J. Chem. Soc., Chem. Commun. (1988) 1428–1430;
  - (f) A. M. Joshi, K. S. MacFarlane, B. R. James, J. Organomet. Chem. 448 (1995) 161–167;
    (g) V. K. Jain, G. S. Rao, Inorg. Chim. Acta. 127 (1987) 161–167;

- (h) H. Steinhagen, G. Helmchen, Angew. Chem. Int. Ed. Engl. 35 (1996) 2339-2342;
- (i) M. E. Broussard, B. Juma, S. G. Train, W. -J. Peng, S. A. Laneman, G. G. Stanley, Science. 260 (1993) 1784–1788;
- (j) R. C. Matthews, D. K. Howell, W. -J. Peng, S. G. Train, W. D. Treleaven, G. G. Stanley, Angew. Chem., Int. Ed. Engl. 35 (1996) 2253–2256;
- (k) W. -J. Peng, S. G. Train, D. K. Howell, F. R. Fronczek, G. G. Stanley, Chem. Commun. (1996) 2607–2608;
- (1) G. Süss-Fink, Angew. Chem., Int. Ed. Engl. 33 (1994) 67-69.
- [13] (a) T. Koizumi, T. Teratani, K. Okamoto, Inorg. Chim. Acta. 363 (2010) 2474–2480;
  (b) K. Gholivand, R. Salami, K. Farshadfar, R. J. Butcher, Polyhedron 119 (2016) 267–276.
- [14] (a) W. A. Herrmann, V. P.W. Bohm, C. P. Reisinger, J. Organomet. Chem. 576 (1999) 23–41;
  - (b) M. Sebastian, V. Arun, P. P. Robinson, A. A. Varghese, R. Abraham, E. Suresh,K. K. M. Yusuff, Polyhedron 29 (2010) 3014–3020;
  - (c) M. Ulusoy, Birel Ö, O. Şahin, O. Büyükgüngör, B. Cetinkaya, Polyhedron 38 (2012) 141–148.
- [15] (a) J. Dupont, M. Pfeffer, J. Spencer, Eur. J. Inorg. Chem. (2001) 1917–1927;
  (b) S. Kim, E. Kim, H. -J. Lee, H. Lee, Polyhedron 69 (2014) 149;
  - (c) S. Dehghanpour, A. Mahmoudi, S. Rostami, Polyhedron 29 (2010) 2190–2195.
- [16] (a) M. Beller, H. Fischer, W.A. Hermann, K. Ofele, C. Brossmer, Angew. Chem. Int. Ed. 34 (1995) 1844–1848;
  - (b) S. J. Scales, H. Zhang, P. A. Chapman, C. P. McRory, E. J. Derrah, C. M. Vogels, M.

T. Saleh, A. Decken, S. A. Westcott, Polyhedron 23 (2004) 2169–2176;

(c) W. M. Motswainyana, S. O. Ojwach, M. O. Onani, E. I. Iwuoha, J. Darkwa, Polyhedron 30 (2011) 2574–2580;

(d) J. Manzur, A. M. García, A. Vega, A. Ibañez, Polyhedron 26 (2007) 115.

- [17] S. Gibson, D. F. Foster, G. R. Eastham, R. P. Tooze, D. Cole-Hamilton, J. Chem. Commun.(2001) 779–780.
- [18] R. B. Bedford, S. L. Welch, Chem. Commun. (2001) 129–130.
- [19] C. M. Zhang, M. L. Trudell, Tetrahedron Lett. 41 (2000) 595–598.
- [20] D. S. McGuinness, K. J. Cavell, Organometallics 19 (2000) 741-748.
- [21] G. R. Rosa, G. Ebeling, J. Dupont, A. L. Monteiro, Synthesis 18 (2003) 2894–2897.
- [22] J. L. Bolliger, O. Blacque, C. M. Frech, Angew. Chem. Int. Ed. 46 (2007) 6514–6517.
- [23] A. M. Sheloumov, P. Tundo, F. M. Dolgushin, A. A. Koridze, Eur.J. Inorg. Chem. (2008) 572–576.
- [24] (a) M. Catellani, E. Motti, N. Della Ca, R. Ferraccioli, Eur. J. Org. Chem. (2007) 4153–4165;
  - (b) D. Alberico, M. E. Scott, M. Lautens, Chem. Rev. 107 (2007) 174-238;
  - (c) A. Suzuki, Angew. Chem. Int. Ed. 50 (2011) 6722–6737;
  - (d) N. Miyaura, A. Suzuki, Chem. Rev. 95 (1995) 2457–2483;
  - (e) J. Hassan, M. Sevignon, C. Gozzi, E. Schulz, M. Lemaire, Chem. Rev. 102 (2002) 1359–1469.
- [25] (a) R. Franzen and Y. Xu, Can. J. chem. 83 (2005) 266–272;
  - (b) K. Shaughnessy, D. Vasher, Curr. Org. Chem. 9 (2005) 585-604;
- [26] A. A. Jarrahpour, M. Zarei, Molbank (2004) M352.

- [27] M. J. Hannon, C. L. Painting, A. Jackson, J. Hamblin, W. Errington, Chem. Commun. (1999) 2023–2024.
- [28] S. K. Che Soh, M. Shamsuddin, J. Chem. (2013) 1-8.
- [29] D. Wang, M. Wang, X. Wang, Y. Chen, A. Gao, L. Sun, J. Catal. 237 (2006) 248-254.
- [30] R. Ferreira, H. Garcia, B. de Castro, C. Freire, Eur. J. Inorg. Chem. (2005) 4272-4279.
- [31] R. Borhade, B. Waghmode. Tetrahedron Lett. 49 (2008) 3423-3429.
- [32] D. Becke, J. Chem. Phys. 98 (1993) 5648–5652.
- [33] V. Barone, M. Cossi and J. Tomasi, J. Comput. Chem. 19 (1998) 404-417.
- [34] J. Tomasi, B. Mennucci, R. Cammi, Chem. Rev. 105 (2005) 2999-3094.
- [35] (a) M. Nonnenmacher, D. Kunz, F. Rominger, T. Oeser, J. Organomet. Chem. 692 (2007) 2554–2563;
  - (b) S. K. Shneider, P. Roembke, G. R. Julius, C. Loschen, H. G. Raubenheimer, G. Frenking, W. A. Herrmann, Eur. J. Inorg. Chem. (2005) 2973–2977;
  - (c) L. Ray, M. M. Shaikh, P. Ghosh, Dalton Trans. (2007) 4546-4555;
  - (d) H. Tomioka, T. Itoh, K. Hirai, J. Am. Chem. Soc. 126 (2004) 1130-1140;
  - (e) P. Meier, S. Legraverant, S. Muller, J. Schaub, Synthesis (2003) 551–554.
- [36] L. You, W. Zhu, S. Wang, G. Xiong, F. Ding, B. Ren, I. Dragutan, V. Dragutan, Y. Sun, Polyhedron 115 (2016) 47–53.

# Dinuclear Pd(II) complexes containing bis-O,N-bidentate Schiff base ligands: Synthesis, characterization, DFT study and application as Suzuki-Miyaura coupling catalysts

Raja Nandhini<sup>a</sup>, Galmari Venkatachalam<sup>a,\*</sup>, Madhu Deepan Kumar<sup>b</sup>, Madhavan Jaccob <sup>b,\*</sup>

<sup>a</sup>PG & Research Department of Chemistry, Government Arts College, Dharmapuri- 636 705, Tamilnadu, India.

<sup>b</sup>Computational Chemistry Laboratory, Loyola Institute of Frontier Energy (LIFE) & Department of Chemistry, Loyola College, Nungambakkam, Chennai -600 034, Tamil Nadu, India.



# Dinuclear Pd(II) complexes containing bis-O,N-bidentate Schiff base ligands: Synthesis, characterization, DFT study and application as Suzuki-Miyaura coupling catalysts

Raja Nandhini<sup>a</sup>, Galmari Venkatachalam<sup>a,\*</sup>, Madhu Deepan Kumar<sup>b</sup>, Madhavan Jaccob <sup>b,\*</sup>

<sup>a</sup>PG & Research Department of Chemistry, Government Arts College, Dharmapuri- 636 705, Tamilnadu, India.

<sup>b</sup>Computational Chemistry Laboratory, Loyola Institute of Frontier Energy (LIFE) & Department of Chemistry, Loyola College, Nungambakkam, Chennai -600 034, Tamil Nadu, India.



The reaction of binucleating Schiff base ligands with  $[PdCl_2(PPh_3)_2]$  and  $[Pd(OAc)_2]$ afforded a new family of binuclear palladium(II) Schiff base complexes of the type  $[Pd_2(L)_2]$  and  $[Pd_2Cl_2(PPh_3)_2(L)]$ . These palladium(II) Schiff base complexes exhibited good catalytic activity in the carbon-carbon Suzuki coupling reaction of different aryl halides using phenyl boronic acid.