



# A simple and facile to prepare Pd(II) complex containing the pyridyl imine ligand [C<sub>5</sub>H<sub>4</sub>N-2-CH<sub>3</sub>C=N-(CH<sub>2</sub>)<sub>3</sub>NH<sub>2</sub>]. Structural characterization and catalytic evaluation in Suzuki–Miyaura C–C couplings



J. Roberto Pioquinto-Mendoza <sup>a, \*\*</sup>, Patricia Conelly-Espinosa <sup>a</sup>, Reyna Reyes-Martínez <sup>a</sup>, Rubén A. Toscano <sup>a</sup>, Juan M. Germán-Acacio <sup>b</sup>, Alcives Avila-Sorrosa <sup>c</sup>, Oscar Baldovino-Pantaleón <sup>d</sup>, David Morales-Morales <sup>a, \*</sup>

<sup>a</sup> Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior S/N, Ciudad Universitaria, C.P. 04510 Mexico

<sup>b</sup> Research Support Network, Instituto Nacional de Ciencias Médicas y Nutrición SZ, Universidad Nacional Autónoma de México (CIC-UNAM), México D.F., Mexico

<sup>c</sup> Departamento de Química Orgánica, Escuela Nacional de Ciencias Biológicas, Instituto Politécnico Nacional, Carpio y Plan de Ayala S/N, Colonia Santo Tomás, México D.F., 11340 Mexico

<sup>d</sup> UAM Reynosa Rodhe, Universidad Autónoma de Tamaulipas, Carr. Reynosa-San Fernando S/N, Reynosa, Tamaulipas 88779, Mexico

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Dedicated with great admiration to my friend Prof. F. Ekkehardt Hahn on the Occasion of His 60th Birthday. Happy Birthday Ekke!

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## ABSTRACT

The facile and simple synthesis and structural characterization of a Pd(II) complex derived from the ligand *N*<sub>7</sub>-(1-(pyridin-2-yl)ethylidene)propane-1,3-diamine (**L1**) is described. The Pd(II) species [Pd(**L1**)Cl][BF<sub>4</sub>] (**PdL1**) has been fully characterized and its structure unequivocally determined by single crystal X-ray diffraction techniques. The molecular structure of **PdL1** shows the ligand **L1** coordinated in a κ<sup>3</sup>-*N,N,N*-tridentate fashion thus affording a slightly distorted square planar compound. This species was employed as catalyst in Suzuki–Miyaura couplings affording good to excellent yields. Furthermore, in the solid state this compound exhibited extended hydrogen-bond networks.

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## 1. Introduction

Studies on metallic complexes based on pyridyl imine ligands have been carried out related to cytotoxicity [1,2] antimicrobial [3] and catalytic properties in either ethylene or alkenes polymerization [4–8]. On the other hand, there are reports where pyridyl imine ligands have been used in supramolecular chemistry to

promote the formation of helicates [9] and mesocates [10]. In addition, group 10 transition metal complexes based on pyridyl imine ligands have also been synthesized, thus nickel derivatives have been important for the mimicking of active centers of metalloproteins and as catalysts on industrially relevant transformations [9,11–13]. On the other hand, the Suzuki–Miyaura cross coupling reaction [14] has been recognized as a truly powerful tool in organic synthesis, in this context palladium complexes with imine ligands have been successfully used as catalyst or catalyst precursors in this transformation [15–26], some of which have been employed successfully under aqueous conditions or using neat water as solvent, being thus relevant in the context of green

\* Corresponding author.

\*\* Corresponding author.

E-mail address: [damor@unam.mx](mailto:damor@unam.mx) (D. Morales-Morales).

chemistry [16,17,19–21,24,25]. Some other imine ligands have been employed in metal-assisted catalytic couplings using  $[\text{Pd}(\text{CH}_3\text{COO})_2]$  [27] and some complexes have been supported in either microporous or silica materials providing excellent, recoverable heterogeneous catalysts [28–30]. Recently, significant progress has been made in the Suzuki–Miyaura coupling reaction through the use of phosphine-free ligands, such as N-heterocyclic carbenes, N,N,O-tridentate, N,N,N-tridentate, N,O-bidentate, N,S-bidentate, and N,N-bidentate ligands (including diimine and diamino) [31]. The latter-mentioned heteroatoms acting as chelating sites towards a metal center providing a proper chemical environment. Thus, in this paper we report the synthesis, characterization, catalytic evaluation and supramolecular studies in the solid state of a simple, facile to synthesize yet highly active Pd(II) complex derived from a N,N,N tridentate pyridyl imine ligand.

## 2. Experimental section

All manipulations of air and moisture sensitive materials were carried out under dinitrogen atmosphere using Schlenk techniques. Solvents were dried according to standard methods and distilled immediately before their use.  $\text{PdCl}_2$ , 2-acetylpyridine and 1,3-diaminopropane were purchased from Aldrich Chemical Co. and used as received without further purification. The non-symmetric ligand  $N_7$ -(1-(pyridin-2-yl)ethylidene)propane-1,3-diamine (**L1**) was prepared by slight modification of the procedure previously described [32]. Melting points were recorded on a Mel–Temp II apparatus and are reported without correction. Elemental analyses were performed on a Perkin Elmer 240. CHNS analyses were performed in Thermo Scientific Flash 2000 elemental analyzer, using a Mettler Toledo XP6 Automated-S Microbalance and sulfanilamide as standard (Thermo Scientific BN 217826, attained values N = 16.40%, C = 41.91%, H = 4.65%, y S = 18.63%; certified values N = 16.26%, C = 41.81%, H = 4.71%, y S = 18.62%). Infrared spectra were recorded on a FT–IR 200 Perkin–Elmer spectrophotometer in the 4000–400  $\text{cm}^{-1}$  range using KBr pellets. NMR spectra were recorded on a JEOL GX300 spectrometer;  $^1\text{H}$  (300 MHz),  $^{13}\text{C}\{^1\text{H}\}$  (75 MHz) and  $^{19}\text{F}\{^1\text{H}\}$  (282.2 MHz) spectra were obtained in  $\text{DMSO}-d_6$ . Chemical shifts (ppm) of  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  spectra are relative to the frequency of  $\text{Si}(\text{CH}_3)_4$ .

### 2.1. Synthesis of complex $[\text{Pd}(\text{L1})\text{Cl}][\text{BF}_4]$ (**PdL1**)

To a hot acetonitrile solution (15 mL) of  $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$  (0.1 g, 0.39 mmol) a solution of ligand **L1** (0.069 g, 0.39 mmol) and  $\text{NaBF}_4$  (0.051 g 0.47 mmol) in 10 mL of dichloromethane was slowly added. The resulting reaction mixture was then set to reflux under stirring for 24 h. After this time, the mixture was allowed to reach room temperature and the produced solid then filtered from the mixture under vacuum to afford a yellow solid of **PdL1**. Yield 95% (0.15 g). m.p.: 223 °C (dec). Anal. Calcd for  $\text{C}_{10}\text{H}_{15}\text{B}_1\text{Cl}_1\text{F}_1\text{N}_3\text{Pd}_1 \cdot 3\text{H}_2\text{O}$  (%): C, 26.11; H, 4.60; N, 9.14. Found (%): C, 25.95; H, 4.71; N, 9.17. IR data ( $\text{KBr}$ ,  $\nu$  in  $\text{cm}^{-1}$ ): 3238 ( $\text{NH}_2$ ); 3116 ( $\text{CH}_{\text{arom}}$ ); 2947 ( $\text{CH}_3$ ,  $\text{CH}_2$ ); 2929 ( $\text{CH}_2\text{N}$ ); 1635 ( $\text{C}=\text{N}$ ); 1592 ( $\text{C}=\text{N}$ ,  $\text{C}=\text{C}$ ).  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO}-d_6$ ,  $\delta$  in ppm): 8.95 (d, 1H,  $J = 7.65$  Hz,  $\text{H}_6$ ); 8.39 (t, 1H,  $J = 7.65$  Hz,  $\text{H}_3$ ); 8.31 (d, 1H,  $J = 7.65$  Hz,  $\text{H}_2$ ); 7.95 (t, 1H,  $J = 7.65$  Hz,  $\text{H}_4$ ); 5.13 (s, 2H,  $\text{NH}_2$ ); 3.63 (br, 2H,  $\text{H}_7$ ); 2.59 (s, 3H,  $\text{CH}_3$ ); 2.34 (br, 2H,  $\text{H}_9$ ); 1.85 (s, 2H,  $\text{H}_8$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{DMSO}-d_6$ ,  $\delta$  in ppm): 180 ( $\text{C}_6$ ); 157 ( $\text{C}_1$ ); 151 ( $\text{C}_5$ ); 143 ( $\text{C}_3$ ); 130 ( $\text{C}_4$ ); 128 ( $\text{C}_2$ ); 55 ( $\text{C}_7$ ); 51 ( $\text{C}_9$ ); 29 ( $\text{C}_8$ ); 17 ( $\text{CH}_3$ ).  $^{19}\text{F}\{^1\text{H}\}$  NMR (282.2 MHz,  $\text{DMSO}-d_6$ ,  $\delta$  in ppm): –149.13.

### 2.2. General procedure for the Suzuki–Miyaura cross coupling

All Suzuki–Miyaura couplings were performed in glass tubes suitable for use in a microwave reactor. Bromobenzene (2.4 mmol),

phenyl boronic acid (2.95 mmol),  $\text{Na}_2\text{CO}_3$  (4.9 mmol), 0.1 mol% of **PdL1** ( $2.4 \times 10^{-3}$  mol) in 5 mL of a mixture  $\text{H}_2\text{O}:\text{DMF}$  (2:1). The mixtures were stirred until homogeneous and heated at 100 °C under microwave irradiation during 5 min with a ramp of 1 min in a CEM Discover reactor coupled to a CEM Explorer robotic system. Subsequently, the reaction mixture was cooled to room temperature and the mixture extracted with  $\text{CH}_2\text{Cl}_2$  (3 X 4 mL), the organic phase was treated with anhydrous  $\text{Na}_2\text{SO}_4$  after filter over celite and analyzed by Gas Chromatography (GC–MS) on an Agilent 6890N GC with a 30.0 m DB-1MS capillary column coupled to an Agilent 5973 Inert Mass Selective detector. Supplementary experiments of catalysis were carried out under the same reactions conditions using different bases  $\text{Na}_3\text{PO}_4$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{Li}_2\text{CO}_3$ ,  $\text{Cs}_2\text{CO}_3$ ,  $\text{Rb}_2\text{CO}_3$ ,  $\text{NaOH}$ ,  $\text{KOH}$ ,  $\text{Et}_3\text{N}$ ,  $\text{DBU}$  and  $\text{DMAP}$  and using different *p*-substituted bromobenzenes, namely, 4-bromoaniline, 4-bromophenol, 4-bromoanisole, 4-bromotoluene, 4-bromobenzaldehyde, 4-bromoacetophenone, 4-bromobenzonitrile. Results presented are the average of two runs.

### 2.3. Mercury drop experiments [33].

Following the above described procedures; additionally adding two drops of elemental Hg to the reaction mixture. After the prescribed reaction times, the solution was filtered and analyzed by GC–MS: no significant difference in conversion between these experiments and those in the absence of mercury was observed, indicating that heterogeneous Pd(0) is not involved. This experiment was performed under the optimized conditions for entry 6 (*i.e.* with bromobenzene).

### 2.4. Data collection and refinement for compounds $[\text{Pd}(\text{L1})\text{Cl}][\text{BF}_4]$ (**PdL1**)

The diffraction data of **PdL1** were collected at room temperature on a Bruker Smart Apex CCD diffractometer, which was equipped with graphite monochromated  $\text{Mo K}\alpha$  ( $\lambda = 0.71073$  Å) radiation. Data refinement was carried by standard methods with use of well-established computational procedures [34]. The structure factors were obtained after Lorentz and polarization and absorption corrections. The positions of the atoms, including the metal atoms, were located by the direct method [35]. The F atoms of the  $\text{BF}_4$  anion and the solvent water molecule were found disordered over two positions (the ratio of 0.784:0.216 and 0.50:0.50 occupancy), attempt to refine anisotropically the O atoms of the disordered water molecule resulted in non-positive-definite and were included isotropically refined. The remaining atoms were found in a series of alternating difference Fourier maps and least-square refinements [36]. The details of the structure determinations are given in Table 1.

## 3. Results and discussion

Complex  $[\text{Pd}(\text{L1})\text{Cl}][\text{BF}_4]$  (**PdL1**) was obtained from the stoichiometric reaction between **L1**,  $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$  and a slight excess of  $\text{NaBF}_4$  (Scheme 1).

Analysis by  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR techniques afforded spectra for **L1** and its palladium complex  $[\text{Pd}(\text{L1})\text{Cl}][\text{BF}_4]$  (**PdL1**). Thus, the  $^1\text{H}$  NMR spectra of the free ligand showed signals due to the pyridinic protons exhibiting an ABCD pattern. A clear difference is observed when these data are compared with the resonances observed for the same protons in complex  $[\text{Pd}(\text{L1})\text{Cl}][\text{BF}_4]$  (**PdL1**) that shift to higher frequencies. The differences in chemical shift ( $\Delta\delta$ ) observed are in the range of  $\delta$  0.34–0.54 ppm. Similar trends have been reported for other Pd(II) complexes [12,37], behavior that has been attributed to deshielding of the nuclei due to coordination with the

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