



## Substituent Effect on Catalytic Activity of Palladium(II) Schiff Base Complexes for Sonogashira Reaction

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### ABSTRACT

Chemical industries are greatly assisted by catalysts; and commonly used catalysts for C-C formation reactions are mainly phosphine-based complexes which are air and moisture sensitive. New air stable Schiff base Pd(II) complexes have been synthesised, characterised and screened for their catalytic potential. This paper reports three ONNO Schiff bases, namely, L2C [2,2'-((1E,1'E)-((2,2-dimethylpropane-1,3-diyl) bis (azanylylidene)) bis (methanylylidene))- bis (4-chlorophenol)], L2M [2,2'-((1E,1'E)-((2,2-dimethylpropane-1,3-diyl)bis(azanylyli-dene)) bis (methanylylidene)) bis (4-methylphenol)] and L2H [2,2'-((1E,1'E) - ((2,2-dimethyl-propane-1,3-diyl) bis (azanylylidene)) bis (methanylylidene)) diphenol]. These were synthesised from 2,2-dimethyl-1,3-propanediamine and salicylaldehyde derivatives with Cl, CH<sub>3</sub> and H at the *meta* position, respectively. The compounds were reacted with palladium(II) acetate yielding three palladium(II) complexes denoted as PdL2C, PdL2M and PdL2H. The structures of all compounds were elucidated through elemental analysis, <sup>1</sup>H and <sup>13</sup>C NMR, FTIR and melting point. The complexes were screened for catalytic activities in Sonogashira coupling reaction between iodobenzene and phenylacetylene in DMSO. PdL2H was found to be the most active catalyst with 87% iodobenzene conversion after 12 hours of reaction.

**Keywords:** Catalysis, palladium(II) complexes, Schiff bases, Sonogashira, substituent

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### INTRODUCTION

Schiff bases have become trendy in the study of coordination compounds due to several interesting chemical and physical properties, as well as applicability in various fields. Schiff bases are able to coordinate many different metals especially transition metals and

stabilise them in multiple oxidation numbers. Schiff bases bearing O and N donors are very popular due to diverse chelating ability. The outstanding chelating ability is mainly assisted by the lone pair of electrons located in  $sp^2$  hybrid orbitals of the azomethine nitrogen. The metal complexes of Schiff bases can be air-stable and possess the ability to tolerate high temperatures which are among the key criteria of good catalysts (Keypour, Salehzadeh, & Parish, 2002).

Palladium has become an active part of coordination and organometallic chemistry related to all types of catalysis including homogeneous, heterogeneous, heterogenised and nanocatalysis. Palladium complexes are excellent and versatile catalysts in many important chemical reactions such as carbon-carbon coupling, alkylation, carbonylation and oxidation (Barder et al., 2005). They are widely employed as catalysts because Pd catalysed reactions can proceed under mild conditions, producing high yields, and bearing outstanding level of stereo-, regio-, and chemoselectivity (Ghammamy & Sedaghat, 2012).

It has been reported that in Sonogashira-Hagihara coupling reactions, palladium compounds such as  $Pd(PPh_3)_4$ ,  $PdCl_2(PPh_3)_2$ ,  $PdCl_2(CH_3CN)_2$  and  $Pd(OAc)_2$  have been commonly used as catalysts (Chinchilla & Nájera, 2011). However, phosphines have some drawbacks in that they are very sensitive to aerial oxidation and moisture and consequently demanding inert conditions which cause difficulty in handling and synthesis applications (Suzuka et al., 2010). In addition, phosphine ligands are expensive and therefore, the search for phosphine-free ligands is imperative.

Thus, this paper aims at reporting the synthesis, physicochemical and spectral characterisation of tetradentate Schiff bases and their palladium(II) complexes, as well as their catalytic activities in Sonogashira coupling reaction.

## METHOD

All chemicals and solvents purchased from commercial suppliers were used without further purification. The micro-analytical data (C, H and N) of all ligands and complexes were obtained from Thermo Scientific Flash 2000 Elemental Analyser. Melting points were determined using Stuart SMP10 and were uncorrected. Perkin-Elmer Spectrum One FTIR spectrometer using KBr pellets were employed to record Infrared (IR) spectra of ligands and complexes between  $4000 - 450\text{ cm}^{-1}$ . Meanwhile,  $^1H$  and  $^{13}C$  NMR spectra were recorded on a Bruker Varian-600MHz spectrometer using deuterated  $CDCl_3$  and expressed in a unit of parts per million ( $\delta$ , ppm). The percent conversion of iodobenzene was monitored using Gas Chromatography-Flame Ionization Detection model Agilent 6890N.

## Synthesis of L2C

A hot solution of 2,2-dimethyl-1,3-propanediamine  $C_5H_{14}N_2$  (1 mmol, 0.1022g) in absolute EtOH (10 ml) was added to a stirred solution of chlorosalicylaldehyde  $C_7H_5ClO_2$  (2 mmol, 0.3132 g) in absolute EtOH (10 ml). The solution was refluxed for 5 h, and then cooled. The yellow solid obtained was filtered off, washed with cold ethanol, and dried.

### Synthesis of L2M

A hot solution of 2,2-dimethyl-1,3-propanediamine  $C_5H_{14}N_2$  (1 mmol, 0.1022g) in absolute EtOH (10 ml) was added to a stirring solution of methylsalicylaldehyde  $C_8H_8O_2$  (2 mmol, 0.2724 g) in absolute EtOH (10 ml). The solution was refluxed for 4 h, and then cooled. The light yellow solid obtained was filtered off, washed with cold ethanol and dried.

### Synthesis of L2H

A hot solution of  $C_5H_{14}N_2$  (1 mmol, 0.1022 g) in absolute EtOH (10 ml) was added into a stirring solution of  $C_7H_6O_2$  (2 mmol, 0.2442 g) in absolute EtOH (10 ml). The solution was refluxed for 5 h before it was cooled. The yellow solid obtained was filtered off, washed with cold ethanol, and dried.

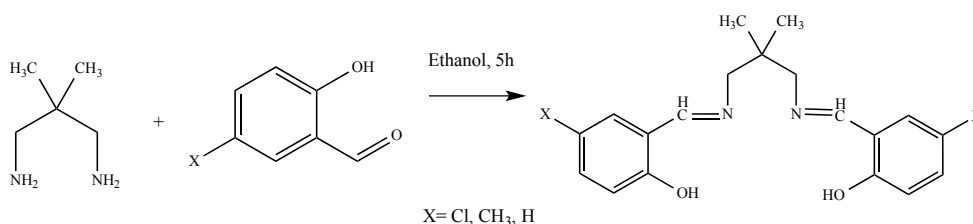


Figure 1. General synthesis of Schiff base ligands

### Synthesis of PdL2C

Palladium(II) acetate (1 mmol, 0.2248 g) was dissolved in 20 mL of acetonitrile. 1 mmol (0.3793 g) of  $C_{19}H_{20}Cl_2N_2O_2$  was dissolved separately in 20 mL of acetonitrile. The ligand solution was added dropwise into the metal salt solution, refluxed for 6 h, and cooled to room temperature. The yellow solid obtained was filtered off, washed with cold acetonitrile, and dried in air.

### Synthesis of PdL2M

The palladium(II) acetate (1 mmol, 0.2248 g) was dissolved in 20 mL of acetonitrile. 1 mmol (0.3385 g) of  $C_{21}H_{26}N_2O_2$  was dissolved separately in 20 mL of acetonitrile. The ligand solution was added dropwise into the metal salt solution, refluxed for 6 h, and cooled to room temperature. The orange solid obtained was filtered off, washed with cold acetonitrile, and dried in air.

### Synthesis of PdL2H

The palladium(II) acetate (1 mmol, 0.2248 g) was dissolved in 20 mL of acetonitrile. 1 mmol (0.3104 g) of  $C_{19}H_{22}N_2O_2$  was dissolved separately in 20 mL of acetonitrile. The ligand solution was added dropwise into the metal salt solution, refluxed for 6 h and cooled to room temperature. The dark grey solid obtained was filtered off, washed with cold acetonitrile, and dried in air.

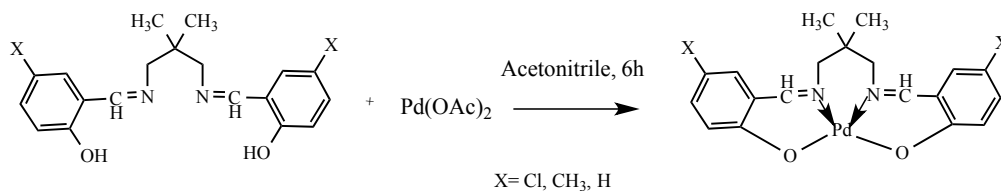


Figure 2. General synthesis of Pd(II) complexes

### Catalytic Activity Screening for Sonogashira reaction

A round-bottomed flask was charged with iodobenzene (1.0 mmol), phenylacetylene (1.5 mmol), palladium(II) Schiff base complex (0.01 mmol) and triethylamine (2.0 mmol), with stirring under aerobic condition in 7 mL of DMSO. The mixture was heated at 100°C for 12 h, monitored every 3 hours by Gas Chromatography-Flame Ionisation Detection (GC-FID) to determine the percentage conversion of iodobenzene, and calculated as follows:

$$\% \text{ Conversion} = (A_{\text{int}} - A_{\text{final}})/A_{\text{int}} \quad [1]$$

$A_{\text{int}}$  = peak area of iodobenzene before reaction

$A_{\text{final}}$  = peak area of iodobenzene after reaction

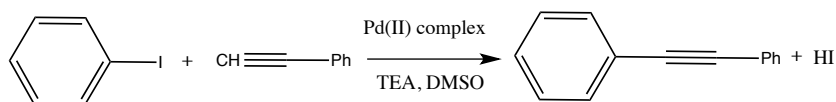


Figure 3. General procedure of Sonogashira reaction

## RESULTS AND DISCUSSION

### Elemental Analysis

The analytical data of the compounds are presented in Table 1. The experimental C, H, N percentages are in concordance with the theoretical values, indicating that the intended compounds (Figure 1 and Figure 2) have been obtained. As expected, the melting points of the parent ligands were lower than those of the complexes due to the presence of strong ionic and dative bonds in the complexes.

Table 1  
*Physicochemical data of ligands and palladium(II) complexes*

Compd.	Color	Percent Yield (%)	Chemical Formula	Melting Point (°C)	Elemental Analysis % found (calculated)		
					C	H	N
L2H	Yellow	96.6	C <sub>19</sub> H <sub>22</sub> N <sub>2</sub> O <sub>2</sub>	116	72.78 (73.52)	7.12 (7.14)	9.60 (9.03)
PdL2H	Brown	64.8	C <sub>19</sub> H <sub>20</sub> N <sub>2</sub> O <sub>2</sub> Pd	292	53.62 (55.02)	4.66 (4.86)	7.50 (6.75)
L2C	Yellow	90.9	C <sub>19</sub> H <sub>20</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>2</sub>	136	60.17 (60.17)	5.94 (5.32)	7.30 (7.39)
PdL2C	Yellow	87.8	C <sub>19</sub> H <sub>18</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>2</sub> Pd	278	47.23 (46.18)	4.10 (3.75)	5.87 (5.79)
L2M	Light Yellow	89.2	C <sub>21</sub> H <sub>26</sub> N <sub>2</sub> O <sub>2</sub>	110	74.31 (74.53)	8.70 (7.74)	8.35 (8.28)
PdL2M	Orange	85.4	C <sub>21</sub> H <sub>24</sub> N <sub>2</sub> O <sub>2</sub> Pd	254	57.55 (56.96)	5.57 (5.46)	6.81 (6.33)

### Infrared Spectroscopy

The  $\nu(\text{C}=\text{N})$  peaks of all ligands appeared in the range of 1630 to 1631  $\text{cm}^{-1}$  (Table 2 and Figure 4). These peaks shifted by about approximately 10 to 20  $\text{cm}^{-1}$  to lower frequencies of 1610 to 1620  $\text{cm}^{-1}$  in all Pd(II) complexes indicating that the  $\text{C}=\text{N}$  was experiencing a lowering in bond strength upon complexation. A possible explanation for the lowering of the  $\text{C}=\text{N}$  bond strength is the inductive effect of donation of imine lone pair of electrons to metal centres in the formation of the dative covalent bond with palladium. The lone pair of electrons on N is donated to the metal centre in the Lewis acid-base interaction, resulting in an inductive reduction of the electron density on the  $\text{C}=\text{N}$ , and making it weaker.

The peak of OH in free ligands was detected as a broad peak in the area of 3200  $\text{cm}^{-1}$ , and slightly displaced from the expected region (3300 - 3800  $\text{cm}^{-1}$ ), probably due to the formation of hydrogen bond between OH and  $\text{N}=\text{C}$ . The coordination between palladium and oxygen can be glimpsed through the disappearance of OH signal in palladium(II) complexes indicating deprotonation of the hydroxyl. The great displacement of the C-O band from 1229  $\text{cm}^{-1}$  in L2H to 1199  $\text{cm}^{-1}$ , a lower frequency in PdL2H, is also a useful evidence for the coordination of O to palladium. This is further corroborated by the shifting trend of C-N peaks, from lower to higher frequencies, indicating of a bond formation between nitrogen and metal.

There are new bands found in the range of 501 to 509  $\text{cm}^{-1}$  and 573 to 589  $\text{cm}^{-1}$  for palladium(II) complexes assignable to Pd-O and Pd-N, respectively, assenting with the values reported by Mohd Tajuddin et al. (2012). This indicates that the coordination between metal with phenolic oxygen and metal with imine nitrogen has been efficaciously attained.

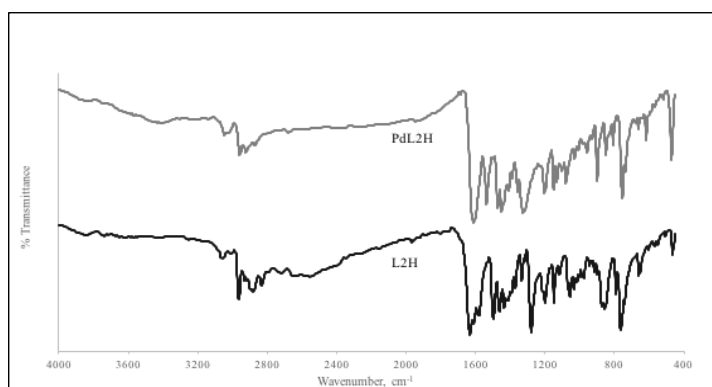


Figure 4. Representative IR spectra (L2H and PdL2H)

Table 2  
Main FTIR spectral data of ligands and their palladium(II) complexes

Compd.	Frequency, $\nu(\text{cm}^{-1})$						
	OH	C=N	C-N	C-O (phenol)	Pd-N	Pd-O	C-H $sp^3$
L2C	3249	1631	1308	1229	-	-	2971
PdL2C	-	1611	1319	1204	581	509	2963
L2M	3253	1631	1371	1228	-	-	2963
PdL2M	-	1620	1318	1207	573	518	2962
L2H	3246	1630	1333	1229	-	-	2964
PdL2H	-	1610	1328	1199	589	501	2956

### NMR Spectroscopy

From  $^1\text{H}$  NMR spectra (Table 3 and Table 4), OH signal appears as broad peak at the downfield region of 13.35 -13.60 ppm in all ligands. The phenolic protons are highly deshielded due to the presence of O and formation of hydrogen bonding (Aranha et al., 2006). The electronegativity of oxygen withdraws the density of electrons from acidic proton and causes the chemical shift to appear at the downfield region. The chemical shifts of aromatic protons appear as multiplets at 6.80-7.30 ppm. The coupling constants tabulated in Table 3 are in the range of 1 to 3 Hz and 6 to 9 Hz, suggesting the existence of *meta* and *ortho* aromatic protons, respectively. This is in agreement with the chemical shifts reported by Mohd Tajuddin et al. (2012). The protons are deshielded due to diamagnetic anisotropy that is contributed by circulating p electrons in the aromatic rings. The number of protons obtained is in concordance with the structure.

The chemical shifts for azomethine proton, H-C=N, appear as a singlet around the vicinity of 8.30 ppm for all ligands, implying that there is no pronounced effect of both electron-withdrawing and electron-donating substituents. The methyl group on the aromatic ring was detected as a singlet at 2.32 ppm in L2M, slightly downfield in comparison with the aliphatic methyl groups, owing to the resonance of electron in the aromatic environment.

Table 3  
<sup>1</sup>H NMR chemical shifts (d/ppm) of ligands

Compd.	Chemical shifts, d/ppm					
	d(O-H)	d(HC=N)	d(Ar-H)	d(Ar-CH <sub>3</sub> )	d(CH <sub>3</sub> ) aliphatic	d(CH)
L2C	13.51( <i>b</i> )	8.30( <i>s</i> )	6.91-7.35( <i>m</i> )	-	0.97( <i>s</i> )	3.50( <i>s</i> )
L2M	13.35( <i>b</i> )	8.31( <i>s</i> )	6.91-7.35( <i>m</i> )	2.32( <i>s</i> )	0.92( <i>s</i> )	3.50( <i>s</i> )
L2H	13.60( <i>b</i> )	8.37( <i>s</i> )	6.91-7.35( <i>m</i> )	-	1.11( <i>s</i> )	3.52( <i>s</i> )

Note: (*s*) = singlet; (*d*) = doublet; (*t*) = triplet; (*m*) = multiplet; (*b*) = broad; Ar = aromatic

Table 4  
<sup>1</sup>H NMR chemical shifts (d/ppm) of aromatic protons of L2H

d(Ar-H)	Multiplicity	Coupling constants, J (Hz)	Number of hydrogen
6.91	<i>td</i>	7.5, 1.1	1
7.00	<i>dd</i>	8.3, 1.1	1
7.29	<i>dd</i>	7.7, 1.7	1
7.35	<i>ddd</i>	8.6, 7.2, 1.7	1

Note: (*td*) = triplet of doublet; (*dd*) = doublet of doublet; (*ddd*) = doublet of doublet of doublet; Ar = aromatic

In the <sup>13</sup>C NMR spectra (Table 5), the peaks of carbon bonded to oxygen of the phenolic group, d(C-OH) appear in the vicinity of 165 ppm, slightly farther downfield than the azomethine carbon. This can be explained by the presence of oxygen and delocalisation of p electrons in benzene rings. The azomethine carbon appears consistently around 160 ppm with no significant influence of the substituent groups.

The presence of Cl in L2C, however, has increased the shifting of aromatic carbons by about ~2 ppm, slightly downfield as compared to the other two ligands. The electronegativity of Cl in L2C has effect on reducing the valence electron density, deshielding the carbon from the applied magnetic field. The signals of Ar-CH<sub>3</sub> and Ar-Cl were discovered at 20.33 and 123.86 ppm, respectively.

Table 5  
<sup>13</sup>C NMR chemical shifts (d/ppm) of ligands

Comp.	Chemical shifts, d (ppm)							
	C-OH	HC=N	Ar-H	Ar-CH <sub>3</sub>	Ar-Cl	CH <sub>3</sub>	CH	C(CH <sub>3</sub> ) <sub>2</sub>
L2C	164.69	160.13	118.21- 132.25	-	123.86	22.87	68.13	36.30
L2M	165.72	159.03	116.68- 133.10	20.33	-	23.47	68.01	36.26
L2H	165.75	161.22	116.97- 132.33	-	-	24.40	68.16	36.27

All palladium(II) complexes have poor solubility in all deuterated solvents, hence, no <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained.

## Sonogashira Coupling Reaction

All palladium complexes were screened as a catalyst in Sonogashira cross-coupling reaction of iodobenzene with phenylacetylene in the presence of KOH as a base in dimethylsulfoxide (DMSO) at 100°C with 1 mmol% catalyst loading.

The percentage conversion of iodobenzene was monitored using GC-FID, where sampling was done every 3 hours. Table 6 shows that the PdL2H catalysed the highest conversion of iodobenzene (87%), followed by PdL2M (73%), and PdL2C (57%). Meanwhile, control reaction was done with the absence of catalyst, where no conversion of iodobenzene after 12 h of reaction was detected.

Table 6  
*Percentage of iodobenzene conversion*

Catalyst	% Conversion of Iodobenzene			
	3h	6h	9h	12h
PdL2C	37	45	50	57
PdL2M	37	48	72	73
PdL2H	34	43	52	87

The results showed that the highest conversion of iodobenzene was attained at 12 hours, the highest reaction time. It appears that the catalytic property of these compounds was mainly controlled by the steric factor where the unsubstituted PdL2H exhibited the highest activity at 87%. With no bulky substituents at the aromatic ring, the catalytic activity was enhanced.

Comparing the catalytic activities of the substituted compounds PdL2C (57%) and PdL2M (73%), the electronic factor was also found to play an important role, albeit less significantly. The electron donating substituent, namely methyl in PdL2M, was shown to enhance the catalytic activity in comparison with the electron withdrawing Cl in PdL2C.

## CONCLUSION

Three tetradentate Schiff bases and their respective palladium(II) complexes were successfully synthesised and characterised via elemental analysis, IR spectroscopy, as well as <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy.

Through infrared spectroscopy, the Schiff base ligands were observed to coordinate to palladium(II) centre through phenolic oxygen and azomethine nitrogen. PdL2H showed the highest catalytic activity in Sonogashira coupling reaction, with 87% conversion of iodobenzene after 12 h of reaction time at 100°C at 1 mmol % catalyst loading under aerobic condition.

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