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Research paper

Tetradentate Palladium(II) Salophen Complexes: Synthesis, Characterization and Catalytic Activities in Copper-Free Sonogashira Coupling Reaction

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Abstract

This paper reports the synthesis and characterization of three salophen ligands; *2,2'-((1E,1'E)-(1,2 phenylenebis(azanylylidene))bis(methanylylidene))diphenol* [L1H], *2,2'-((1E,1'E)-(1,2-phenylenebis(azanylylidene))bis (methanylylidene))bis(4-chlorophenol)* [L1C] and *2,2'-((1E,1'E)-(1,2-phenylenebis(azanylylidene))bis(methanylylidene))bis(4-methoxylphenol)* [L1OME]. The compounds were prepared from condensation reaction between salicylaldehyde, and its derivatives, with *ortho*-phenylenediamine. Their palladium(II) complexes, namely PdL1H, PdL1C and PdL1OME were synthesized through insertion reaction between the ligands with palladium(II) acetate. All compounds were characterized through melting point, elemental analysis, infrared spectroscopy, ^{1}H and ^{13}C NMR spectroscopy. Palladium(II) complexes were tested as homogenous catalysts in copper-free Sonogashira coupling reaction between iodobenzene and phenylacetylene in DMSO using triethylamine as base with 1.0 mmol% catalyst loading. The most performing catalyst was PdL1OME with 91% conversion followed by PdL1H (83%) and PdL1C (27%).

Keywords: *Schiff bases; palladium(II) complexes; copper-free; Sonogashira; catalysis*

1. Introduction

Palladium-catalysed sp^2–sp Sonogashira coupling reaction of terminal alkynes with aryl halides is one of the most promising methods for the formation of phenylated alkynes [1]. These products have wide applications in synthesis of natural products, biologically active molecules, heterocycles, molecular electronics, dendrimers and conjugated polymers or nanostructures [2]. Coupling reaction has remarkably evolved over the years since it was first introduced by Sonogashira in 1975 [3]. The evolution of the reaction encompasses the elimination of the co-catalyst, copper salts, from the reaction due to the undesirable side occurrence of homocoupling and possible contamination of the end product [4].

Palladium, the main catalyst, has been used widely and a plethora of research activities had been performed to tune its catalytic activity by varying the ligand environment. This includes the gradual replacement of phosphine-based ligands to nitrogen-based ligands such as Schiff bases as the former are unstable towards air, moisture and temperature, highly toxic and cost-ineffective [5]. The sensitivity of phosphine complexes may contribute to P–C bond degradation especially when the reaction is carried out at elevated temperatures lead to decomposition of the catalyst which could intensely affect conversion and selectivity [6].

Other than their facile preparation, Schiff base complexes have been reported to be stable in ambient conditions and are able to withstand at high temperatures [7]. Salophen ligands, a general name commonly used for Schiff bases synthesised from derivatives of salicylaldehyde and *ortho*-phenylinediamine, offer tetradentate (*ONNO*) chelating system, enabling the formation of stable complexes with strong $\pi \rightarrow \pi^*$ intramolecular electronic interactions [8].

Palladium complexes containing salophen ligands have been investigated quite extensively in other coupling reactions i.e. Heck and Suzuki [9,10] but their employment in copper-free Sonogashira coupling reaction is still scarce, especially as homogenous catalysts. Hence, this paper reports the synthesis of salophen ligands and their corresponding palladium(II) complexes to test their catalytic activities in copper-free Sonogashira coupling reaction.

2. Method

All chemicals and Analar grade solvents purchased from commercial suppliers were used without further purification. The microanalytical 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. Perkin-Elmer Spectrum One FTIR spectrometer using KBr pellets was employed to record infrared (IR) spectra of ligands and complexes between 450–4000 cm^{-1}. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Varian 600MHz spectrometer as $CDCl_3$ or DMSO-d_6 solutions and expressed in parts per million (δ, ppm). The percent conversion of iodobenzene was monitored using Gas Chromatography-Flame Ionization Detection model Agilent 6890N.

2.1. General Synthesis of Salophen Ligands

About 10 mL of hot ethanolic solution of *ortho*-phenylenediamine $C_6H_8N_2$ (1 mmol) was added to a stirred solution of salicylaldehyde derivatives (2 mmol) in absolute ethanol (5 mL) (Figure 1). The solution was refluxed over a period of 4 h, subsequently cooled and chilled in the chiller at about 4°C overnight. The coloured solid obtained was filtered off, washed with cold ethanol and air-dried.

(a) L1H
M.p. (°C) 168-170; Yield: 56.0; IR (KBr Pellets) cm^{-1} 1612 (C=N), 1237 (C-OH); ^1H NMR ($CDCl_3$) δ; 6.93-7.41 (6H, m, ArH), 13.24 (1H, s, OH); Anal. **Found** (Calc.) for $C_{20}H_{16}N_2O_2$; C: **73.85** (75.93), H: **4.87** (5.10), N: **8.54** (8.86)

(b) L1C
M.p. (°C) 209-215; Yield – 78.7; IR (KBr Pellets) cm^{-1} 1615 (C=N), 1275 (C-OH); ^1H NMR ($CDCl_3$) δ; 7.00-7.38 (5H, m, ArH), 13.00 (1H, s, OH); Anal. **Found** (Calc.) for $C_{22}H_{14}Cl_2N_2O_2$; C: **62.10** (62.36), H: **3.59** (3.66), N: **7.25** (7.27)

(c) L1OME
M.p. (°C) 165-168; Yield – 79.2; IR (KBr Pellets) cm^{-1} 1616 (C=N), 1273 (C-OH); ^1H NMR ($CDCl_3$) δ; 6.91-7.37(5H, m, ArH), 12.62 (1H, s, OH); Anal. **Found** (Calc.) for $C_{22}H_{20}N_2O_4$; C: **67.49** (66.99), H: **5.14** (5.62), N: **7.41** (7.10)
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2.2. General Synthesis of Palladium (II) Salophen Complexes

About 1 mmol palladium(II) acetate was dissolved in 10 mL of acetonitrile in a round-bottomed flask. The 1 mmol of salophen ligand was dissolved separately in 10 mL of acetonitrile (Fig.1). The ligand solution was added dropwise into the flask containing the metal solution before being refluxed for 6 h. Then, the coloured solid formed was filtered off, washed with a small amount of cold acetonitrile and dried in air.

(a) PdL1H
M.p. (°C) 320-327; Yield – 86.0; IR (KBr Pellets) cm^{-1} 1607 (C=N), 1247 (C-O); ^1H NMR ($CDCl_3$) δ; 6.67-8.49 (6H, m, ArH); Anal. Found (Calc.) for $C_{20}H_{14}N_2O_2Pd$; C: 55.23 (54.38), H: 3.06 (3.17), N: 7.38 (6.76)

(b) PdL1C
M.p. (°C) >300; Yield – 83.3; IR (KBr Pellets) cm^{-1} 1607 (C=N), 1286 (C-O); Anal. Found (Calc.) for $C_{20}H_{12}Cl_2N_2O_2Pd$; C: 50.53 (49.06), H: 2.59 (2.47), N: 6.05 (5.72)

(c) PdL1OME
M.p. (°C) >300; Yield – 85.1; IR (KBr Pellets) cm^{-1} 1607 (C=N), 1287 (C-O); Anal. Found (Calc.) for $C_{22}H_{18}N_2O_4Pd$. H_2O; C: 51.90 (52.97), H: 3.54 (4.04), N: 5.71 (5.62)

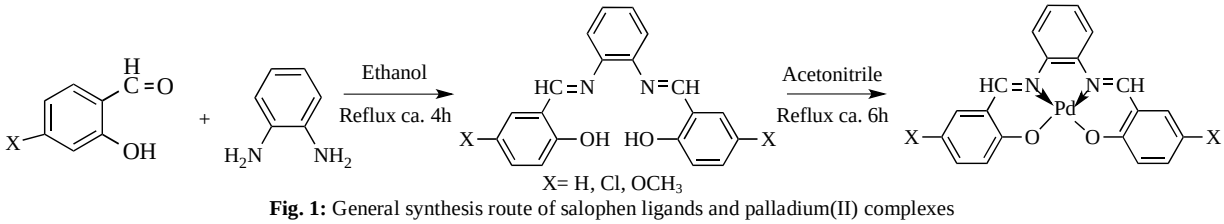

Fig. 1: General synthesis route of salophen ligands and palladium(II) complexes

2.3 Catalytic Activity of Nickel(II) Schiff-BaseComplexes for Sonogashira Reaction

A Radley tube was charged with iodobenzene (1.0 mmol), phenylacetylene (1.5 mmol), palladium(II) Schiff base complex (1 mmol%) and triethylamine (Et_3N) (2.0 mmol) (Fig. 2). The mixture was heated at 100 °C for 12 hours in a 12-place Radley carousel with stirring under aerobic condition in 7 mL of DMSO. A 0.5-1.0 mL of the solution was collected in GC vial upon completion of the reaction. The % conversion was monitored by GC-FID, calculated as follows:

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

A_{int} = peak area of iodobenzene before reaction
A_{final} = peak area of iodobenzene after reaction

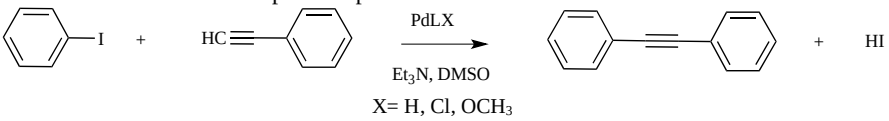

Fig. 2: The procedure for copper-free Sonogashira reaction

3. Results and Discussion

3.1. Elemental Analysis and Melting Points

The elemental analysis data of the compounds are presented in **Error! Reference source not found.** As can be seen that the elemental analysis are in close agreement with the theoretical values, indicating that the structures of the ligands and palladium(II) complexes. The melting points of the complexes are higher than that of their respective parent ligands, most likely because of the increase of the molecular mass of the former and the presence of ionic and dative covalent bonds between the metal center and the donor atoms of the ligand. The two temperatures presented in **Error! Reference source not found.** represent the points at which the compounds started to melt and completely melted.

3.2. Infrared Spectroscopy

The infrared data of all compounds are tabulated in **Error! Reference source not found.** and representative spectra of L1H and PdL1H are shown in . The weak and broad band for hydroxyl was detected in the range of 3200-3226 cm^{-1} in all free ligands. The intensity of the peak was relatively weak, likely due to intermolecular hydrogen bonding between phenolic proton and azomethine nitrogen [11] owing to the presence of moisture in the compounds. The hydroxyl functional group was detected in the vicinity of 2400-3200 in the spectra as the compound likely to have a molecule of water as indicated in Table 1. The peak of hydroxyl, however, was absent in all spectra of palladium(II) complexes, suggesting the occurrence of complexation between metal centers and phenolic oxygen. On the other hand, the up-frequency shift of C-O stretching bands from 1237-1275 cm^{-1} in free ligands to

1247-1287 cm^{-1} in complexes, indicating the coordination that took place between metal centre and phenolic oxygen [12].

The ν(C=N) stretching frequencies of all ligands were observed in the range of 1612-1616 cm^{-1}. The great shifting of these peaks to lower frequencies of 1607 cm^{-1} in all palladium(II) complexes indicates that complexation between metal centres and ligands has been successfully achieved through imine nitrogen. The lower frequencies of C=N in complexes signifies the reduction in the strength of the bond as a lone pair of electrons from imine nitrogen has been donated for sharing with the Pd(II) centre, forming a dative bond [12]. This was further evidenced by the shifting of C-N stretching bands from lower, 1317-1351 cm^{-1} in free ligands, to higher frequencies, 1365-1375 cm^{-1} in complexes.

Table 1: Physicochemical properties of L1OME, L1C, L1OME and their respective palladium(II) complexes

Compounds	Color	Percent Yield (%)	Chemical Formula	Melting Point (°C)	Elemental Analysis % Found (Calculated)		
					C	H	N
L1H	Yellow	56.0	$C_{20}H_{16}N_2O_2$	168-170	73.85 (75.93)	4.87 (5.10)	8.54 (8.86)
PdL1H	Yellow	86.0	$C_{20}H_{14}N_2O_2Pd$	>300	55.23 (54.38)	3.06 (3.17)	7.38 (6.76)
L1C	Yellow	78.7	$C_{20}H_{14}Cl_2N_2O_2$	209-215	62.10 (62.36)	3.59 (3.66)	7.25 (7.27)
PdL1C	Orange	83.3	$C_{20}H_{12}Cl_2N_2O_2Pd$	>300	50.53 (49.06)	2.59 (2.47)	6.05 (5.72)
L1OME	Orange	79.2	$C_{22}H_{20}N_2O_4$	165-168	67.49 (66.99)	5.14 (5.62)	7.41 (7.10)
PdL1OME	Dark Red	85.1	$C_{22}H_{18}N_2O_4Pd$	>300	51.90 (52.97)	3.54 (4.04)	5.71 (5.62)

Table 2: Infrared Data for Ligands and Palladium(II) Complexes

Compounds	Frequency, cm^{-1}					
	OH	C=N	C-N	C-O	Pd-N	Pd-O
L1H	3225	1612	1317	1237	-	-
PdL1H	-	1607	1375	1247	534	461
L1C	3226	1615	1351	1275	-	-
PdL1C	-	1607	1376	1286	523	484
L1OME	3200	1616	1330	1273	-	-
PdL1OME	-	1607	1365	1287	533	478

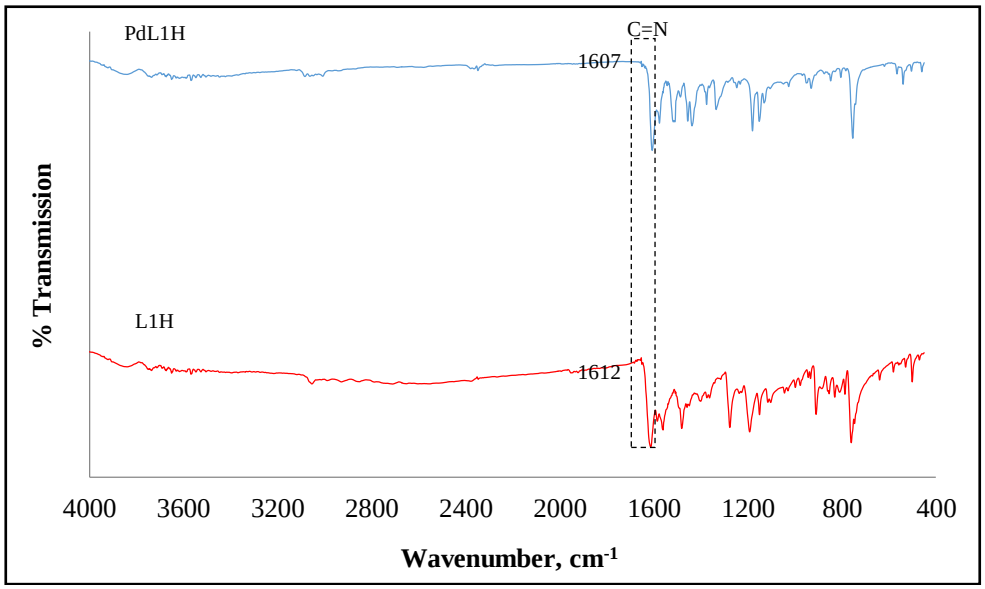

Fig. 3: Representative Infrared Spectra of L1H and PdL1H

The appearance of new weak peaks in palladium(II) complexes in the range of 461-484 cm^{-1} and 523-534 cm^{-1}, assignable to Pd-O and Pd-N, respectively, indicating that the coordination between metal centers and ligands was established through phenolic oxygen and azomethine nitrogen. These peaks were observed to be absent in the spectra of free ligands and are in concordance with the values reported by [13]. The peaks of metal-oxygen and metal-nitrogen stretching frequencies, in some cases, can be very difficult to observe [14, 15].

3.3. NMR Spectroscopy

A broad singlet peak in the region 12.62-13.09 ppm was detected in the spectra of all free ligands, assignable to OH protons which were observed downfield likely due to the formation of hydrogen bonding between the phenolic protons with azomethine nitrogen [11]. These phenolic protons were not seen in the spectra of complex of PdL1H, suggesting the coordination between phenolic oxygen with the metal centers through deprotonation of the phenolic protons.

As tabulated in Table 3, azomethine proton, HC=N appears as singlet at region of 8.57-8.65 ppm for all free ligands. The peak was shifted upfield at 8.49 ppm in PdL1H which indicates that in complexes, the protons are being less shielded due to reduction in electron density of the imine bond as a lone pair of electrons from nitrogen has been shared with metal center through a dative bond.

The chemical shifts of aromatic protons in free ligands were observed as multiplets in the range of 6.93-7.38 ppm. These hydrogens experienced the shielding effect of diamagnetic anisotropy caused by circulating π-electrons in the aromatic rings. The values of coupling constants of 2-3 Hz and 6-9 Hz suggest the presence of *meta* and *ortho* hydrogens in the chemical structures, respectively. The number of hydrogens obtained from the integration is in good agreement with the proposed chemical structures.

^{13}C NMR data of all compounds are tabulated in Table 4. The azomethine carbon, HC=N was discovered at 161.79 ppm in L1H and it was observed at 152.50 ppm in PdL1H. The downshifting of azomethine proton signal validates that coordination of metal centres to the ligands was successfully established through azomethine nitrogen. Complexation can also be discerned from the shift-

ing of aromatic carbons from 117.96-133.39 ppm in L1H to the region of 115.67-136.36 ppm in PdL1H. The displacement of C-OH peak by about 9 ppm in PdL1H is also another evidence of the metal-phenolic oxygen coordination. Owing to limitations of solubility in all common solvents, no NMR spectra of PdL1OME and PdL1C could be obtained.

Table 3: ^{1}H NMR chemical shifts δ(ppm) of compounds

Compounds	Chemical shifts, δ (ppm)			
	δ(O-H)	δ(HC=N)	δ(Ar-H)	δ (CH_3)
L1H	13.09(*s*)	8.65(*s*)	6.93-7.41(*m*)	-
PdL1H	-	8.49(*s*)	6.67-7.43(*m*)	-
L1C	13.00(*s*)	8.57(*s*)	7.00-7.38(*m*)	-
L1OME	12.62(*s*)	8.63(*s*)	6.91-7.37(*m*)	2.28(*s*)

Note: (s) = singlet; *(m)* = multiplet; Ar = aromatic

Table 4: ^{13}C NMR chemical shifts (δ/ppm) of compounds

Compounds	Chemical shifts, δ (ppm)				
	C-OH/C-O	HC=N	Ar-H	Ar-OCH_3	Ar-Cl
L1H	163.74	161.79	117.96-133.39	-	-
PdL1H	167.67	152.50	115.67-136.36	-	-
L1C	162.53	159.92	119.21-142.22	-	123.71
L1OME	163.42	152.20	115.33-142.60	155.70	-

3.3. Catalytic Activities of Palladium (II) Salophen Complexes

The catalytic activities of palladium(II) salophen complexes and their respective percent conversions of iodobenzene after 12 hours of reaction are presented in Table 5. The catalyst loading of palladium complexes was 1.0 mmol% and the base used was triethylamine (Et_3N). There was no conversion of iodobenzene observed in the negative control, when there was no catalyst used in the reaction and the opposite was true for the positive control with 100% conversion in the presence of $Pd(OAc)_2$.

The best performing catalyst was PdL1OME with 91% conversion, followed by PdL1H (83%) and PdL1C (27%). Based on these results, it is apparent that the electron donating substituent, -OCH_3, enhances the catalytic activities of the complexes. On the other hand, electron withdrawing substituent, -Cl, seemed to be less effective in enhancing the catalytic performance of the complexes. There was no black palladium seen after the completion of the reaction, indicating that the catalytic site of the complexes was still active and was able to withstand high temperature of 100 ^{o}C.

Table 5: The percent conversion of iodobenzene after 12 hours of reaction

Catalyst	% Conversion*
PdL1H	83
PdL1C	27
PdL1OMe	91
$Pd(OAc)_2$	100
Control	0

*GC Yield

4. Conclusion

Three salophen ligands and their new palladium(II) complexes were successfully synthesized and characterized. Through infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy, the ligands were indicated to bond to Pd(II) centre through phenolic oxygen and imine nitrogen, in tetradentate manner. The order of catalytic activity for copper-free Sonogashira reaction was PdL1OME (91%) > PdL1H (83%) > PdL1C (27%) suggesting the influence of electron withdrawing substituent on the catalytic activity of the complex. This paper reports the first application of new palladium(II) Schiff base complexes (PdL1OMe and PdL1C) as homogenous catalyst in copper-free Sonogashira reaction.

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