

## Synthesis, Characterization and Preliminary Catalytic Activity of Five-membered Chelate Salen-Palladium(II) Complexes Toward Mizoroki-Heck Reaction

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**Abstract:** Two reliable and economical Salen-palladium(II) complexes, *N,N'*-bis(4-methoxy-salicylidene)propane-1,2-diaminepalladium (II) ( $M_{SB-1}$ ), and *N,N'*-bis(4-methyl- $\alpha$ -salicylidene)propane-1,2-diaminepalladium(II) ( $M_{SB-2}$ ) have been successfully synthesized via complexation reaction between Schiff base ligands ( $L_{SB-1}$  and  $L_{SB-2}$ ) with palladium(II) acetate, respectively. The synthesized compounds were successfully characterized using several types of analytical and spectroscopic methods such as CHN elemental analyses, FTIR spectroscopy, and NMR spectroscopy. Previously, most of researchers highlighted the used of metal phosphine complex as an efficient catalyst for carbon-carbon bond formation of Mizoroki-Heck reaction. However, due to the air, moisture-labile and the high cost of phosphine ligand compared to palladium metal itself, there is an urge in the search of alternative cheap and relatively stable phosphine-free catalysts that could offered comparable activity. The synthesized catalysts were introduced and subjected to the Mizoroki-Heck. The performances of catalytic activity were monitored by GC-FID at 3 hours reaction period. Preliminary results showed that the percentage conversion of 4-bromonitrobenene to the coupled products were 100% indicated that  $M_{SB-1}$  and  $M_{SB-2}$  can act ideal potential catalysts in the Mizoroki-Heck reaction.

**Key words:** Schiff bases • Salen-palladium(II) complexes • Homogeneous catalyst • Mizoroki-Heck reaction

### INTRODUCTION

The palladium catalysed Mizoroki-Heck reaction is one of the most popular C-C bond forming reaction and most employed in organic transformation [1, 2]. Previously, most of chemists have been focused on using phosphine-based palladium complexes as potential catalysts for carbon-carbon coupling reaction [3]. Notwithstanding the fact that phosphine-based complexes had many advantages in catalysed C-C bond reaction, a major drawback of this catalyst has been considered due to the cost of phosphine itself, air and moisture-labile as well as readily to undergo oxidation [3, 4]. In addition, phosphine-based catalysts with the disadvantages of difficult to handle and recover making

it is less useful for industrial scale reactions [5]. Therefore, most of the efforts today emphasize in the search of more promising, economical and relatively stable phosphine-free catalysts that could offer comparable activity [6].

Nowadays, there is another type of ligand that receiving attention from all the researches, as possible replacement of phosphines in Heck coupling reactions is nitrogen containing ligand [7]. Schiff base ligand is the condensation product of primary amines and carbonyl compounds in which the carbonyl group (C=O) has been replaced by an imine group (C=N) [8]. Schiff base ligands are easily synthesized and likely to undergo complexation with almost all metal ions to form Schiff base metal complexes [9]. Most of the Schiff base metal complexes show excellent catalytic activity and played an important

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role in various reactions to increase their yield and product selectivity [10]. Furthermore, many studies focus on tetradentate  $N_2O_2$  Schiff base ligands to synthesize metal complexes due to the outstanding characteristics such as comparatively tolerance, facile approach, and highly stable to air and moisture [11].

In this research paper, we wish to report the synthesis and characterization of two Salen-palladium(II) complexes with tetradentate  $N_2O_2$  chelate Schiff base ligands derived from 2-hydroxy-4-methoxyacetophenone and 2-hydroxy-4-methylacetophenone with 1,2-diaminopropane. The synthesized Salen-palladium(II) complexes were then subjected to the homogeneous Mizoroki-Heck cross-coupling reaction of 4-bromonitrobenzene with methyl acrylate in order to evaluate the performance of the catalysts.

## Experimental

**Material, Methods, and Instruments:** All reagents were obtained commercially from various suppliers and were used as received without further purification: palladium(II) acetate (Aldrich), 2-hydroxy-4-methoxyacetophenone (Aldrich), 2-hydroxy-4-methylacetophenone (Aldrich), 1,2-diamino propane (Aldrich), 4-bromonitrobenzene (Aldrich) and methyl acrylate (Thermo fisher). The synthesizing works for Schiff base ligands and Salen-palladium(II) complexes were carried out without taking any precaution steps to exclude moisture and air unless specifically stated.

The melting points of synthesized compounds were determined by using Stuart Scientific Melting Point Apparatus SMP3 and were not corrected. Carbon-Hydrogen-Nitrogen (CHN) elemental analysis was carried out using CHNS-O Analyzer FlashEA 1112 series. The FTIR spectra were recorded on Perkin Elmer Spectrum 100 spectrometer using KBr pellet within the range 4000 - 400  $cm^{-1}$ . Bruker Avance III 400 MHz NMR spectrometer was used to record the  $^1H$  (400.11 MHz) and  $^{13}C$  (100.61 MHz) spectra with TMS as an internal standard using deuterated chloroform ( $CDCl_3$ ) as the solvent at room temperature in the range between  $^H$  0-15 ppm and  $^C$  0-200 ppm respectively.

Gas Chromatography (GC) analyses were carried out on an Agilent Technologies 6890N Gas Chromatograph Series equipped with a non-polar capillary column (HP-5, (5%-Phenyl)-methylpolysiloxane) using Flame Ionic Detector (FID). The injection mode was set to be splitless, 1  $\mu$ L of sample was injected with inlet temperature of 300  $^{\circ}C$ , the oven temperature increment was set at 15  $^{\circ}C$  per minute and final temperature was 320  $^{\circ}C$ .

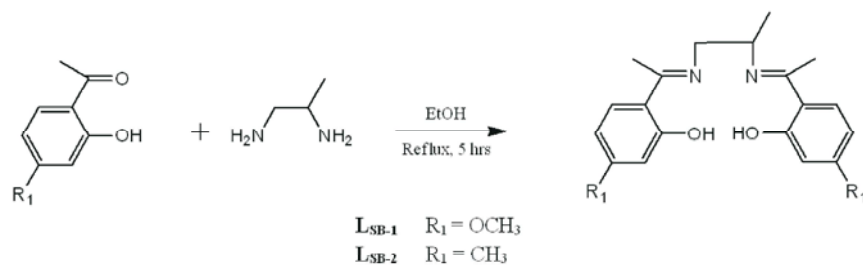
**Preparation of Schiff Base Ligands:** The desired  $N_2O_2$  Schiff base ligands  $L_{SB-1}$  and  $L_{SB-2}$  were synthesized according to the literature methods [6]. The ligand  $L_{SB-1}$  was synthesized by condensing 2-hydroxy-4-methoxyacetophenone (2 mmol, 0.3342 g) with 1,2-diaminopropane (1 mmol, 0.0741 g) with molar ratio of 2:1 in 10 mL absolute ethanol respectively. Then both solutions were transferred to the three-neck round bottom flask. The resulting mixture was stirred and refluxed at 65  $^{\circ}C$  for 5 hours until the yellow precipitate formed (Scheme 1). Then, the Schiff base ligand was filtered, washed with cold ethanol and dried in a vacuum desiccator with blue silica gel. After that, the product was recrystallized using mixed solvents of chloroform and hexane in order to remove any impurity. Yield: 76%. Melting point: 224.2  $^{\circ}C$ .

Ligand  $L_{SB-2}$  was synthesized using the same method as stated above. 2-hydroxy-4-methylacetophenone (10 mmol, 1.5071 g) with 1,2-diaminopropane (5 mmol, 0.3707 g) were dissolved in 10 mL of absolute ethanol respectively. Yellow precipitate was obtained in the reaction and mixed solvents of acetone and hexane were used to recrystallize the product. Yield: 72%. Melting point: 241.7  $^{\circ}C$ .

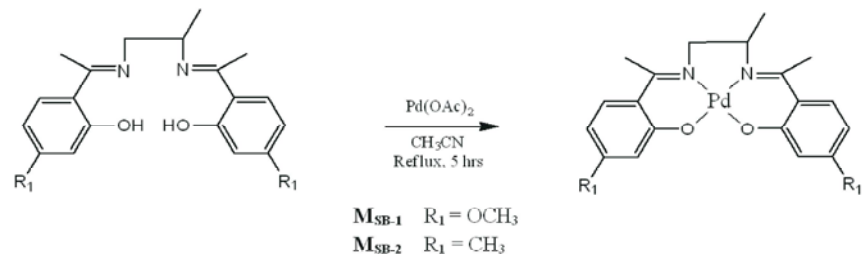
**Preparation of Salen-palladium(II) Complexes:** The corresponding Salen-palladium(II) complexes  $M_{SB-1}$  and  $M_{SB-2}$  (Scheme 2) were synthesized according to the literature methods [6].  $M_{SB-1}$  was prepared through complexation reaction of palladium(II) acetate (1 mmol, 0.2245 g) with the synthesized Schiff base ligand  $L_{SB-1}$  (1 mmol, 0.3707 g) in the molar ratio of 1:1. Both reagents were dissolved in 10 mL of acetonitrile and transferred to three-neck round bottom flask. The mixture was stirred and refluxed for 5 hours until yellow precipitate formed. The metal complex formed was separated by vacuum filtration, washed with cold acetonitrile and dried in a vacuum desiccator over blue silica gel. The solid product was recrystallized using methanol to yield a purer compound. Yield: 69%. Melting point: > 350  $^{\circ}C$ .

Salen-palladium(II) complex  $M_{SB-2}$  was synthesized followed the previous method. Schiff base ligand  $L_{SB-2}$  (5 mmol, 0.6445 g) with palladium(II) acetate (5 mmol, 1.1226 g) were dissolved in 10 mL of acetonitrile respectively. Yellow precipitate was obtained in the reaction and methanol was used to recrystallize the product. Yield: 42%. Melting point: > 350  $^{\circ}C$ .

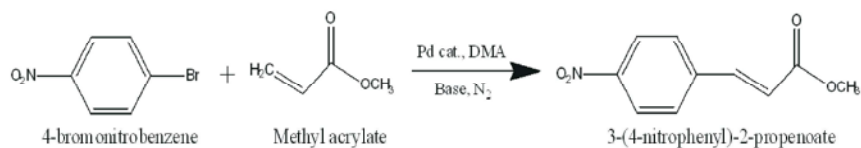
**Homogeneous Catalytic Testing in Mizoroki-Heck Reaction:** 4-bromonitrobenzene (1 mmol), methyl acrylate (3 mmol), Salen-palladium(II) complexes (1 mmol%), base



Scheme 1: Synthesis of Schiff base ligands



Scheme 2: Synthesis of Salen-palladium(II) complexes



Scheme 3: Heck coupling reaction of 1-bromo-4-nitrobenzene with methyl acrylate

NaHCO<sub>3</sub> (2.4 molar equiv.) and *N,N*-dimethylacetamide (5 mL) were mixed together in a Radley's 12-placed reaction carousel whilst purging with nitrogen gas and heated to synthesize 3-(4-nitrophenyl)-2-propenoate (Scheme 3). The reaction carousel was then heated to 120 °C with the temperature carefully controlled by a contact thermometer ( $\pm 1$  °C) for 3 hours. The conversion of reactants was monitored by GC-FID. After that, the catalyst was separated from the reaction mixture by simple filtration to remove the homogeneous catalyst when the reaction was completed. 2% of HCl was added to the filtrate and the mixture was allowed to cool to 0 °C for precipitation. The precipitate was filtered, washed with distilled water and was dried in a vacuum desiccator over blue silica gel. The identity of the isolated product was checked by FTIR spectroscopy and <sup>1</sup>H, <sup>13</sup>C NMR spectroscopy.

## RESULT AND DISCUSSION

Two inexpensive and moisture stable Salen-Palladium(II) complexes were successfully synthesized and obtained in high yield through condensation reaction between 1,2-diaminopropane with 2-hydroxy-4-

methoxyacetophenone and the 4-methyl derivative, respectively. The synthesized compounds were characterized via several spectroscopic techniques such as CHN elemental analysis, FTIR spectroscopy, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. As expected, the preliminary results of Mizoroki-Heck reaction monitored by GC-FID exhibited excellent conversion for this process and gave the desired products.

**CHN Elemental Analyzer Analysis:** The values of elemental analyses of prepared ligands and complexes were good in agreement with the calculated molecular formula values (Table 1) and support their proposed composition.

Table 1: Comparison of theoretical and calculated value of C, H, and N.

Element		Ligand		Pd(II) complexes	
		L <sub>SB-1</sub>	L <sub>SB-2</sub>	M <sub>SB-1</sub>	M <sub>SB-2</sub>
Carbon, C (%)	Theoretical	68.09	58.41	53.12	74.52
	Calculated	67.82	62.96	53.76	74.61
Hydrogen, H (%)	Theoretical	7.07	6.39	5.09	7.74
	Calculated	7.27	6.78	5.03	7.62
Nitrogen, N (%)	Theoretical	7.56	5.92	5.90	8.28
	Calculated	7.52	7.44	6.04	9.10

Table 2: Important IR bands of ligands and its palladium(II) complexes.

Compound	$\mu(\text{O-H})$	$\mu(\text{C=N})$	$\mu(\text{C=C aromatic})$	$\mu(\text{C-O})$	$\mu(\text{C-N})$
$L_{\text{SB-1}}$	3444	1606	1449	1143	1378
$L_{\text{SB-2}}$	3387	1611	1570	1151	1377
$M_{\text{SB-1}}$	-	1609	1415	1213	1354
$M_{\text{SB-2}}$	-	1591	1412	1161	1374

**FTIR Spectroscopy:** The important stretching vibrations of the ligands and its metal complexes are listed in the Table 2. Infrared spectra of the synthesized compounds ( $L_{\text{SB-1}}$  and  $L_{\text{SB-2}}$ ) and the metal complexes ( $M_{\text{SB-1}}$  and  $M_{\text{SB-2}}$ ) have been analysed in the expected frequency region of the  $\mu(\text{O-H})$ ,  $\mu(\text{C=N})$ ,  $\mu(\text{C=C aromatic})$ ,  $\mu(\text{C-N})$ , and  $\mu(\text{C-O})$ . The comparison between the ligands and the palladium(II) complexes spectra provided an evidences for the coordinating mode of the ligands in the complexes. According to the IR spectra for the ligands, the broad OH vibrations are assigned at  $3444 \text{ cm}^{-1}$  ( $L_{\text{SB-1}}$ ) and  $3387 \text{ cm}^{-1}$  ( $L_{\text{SB-2}}$ ), respectively. However, for the IR spectra of palladium(II) complexes ( $M_{\text{SB-1}}$  and  $M_{\text{SB-2}}$ ), O-H bands have disappeared suggesting that the strong participation of hydroxyl group in the chelate formation to Pd ion via the deprotonation of the phenolic hydrogen [12]. The value for  $\mu(\text{C=N})$  stretching vibration of the free ligands at about  $1606 \text{ cm}^{-1}$  ( $L_{\text{SB-1}}$ ) and  $1611 \text{ cm}^{-1}$  ( $L_{\text{SB-2}}$ ) get considerably shifted after complexation, implying that the coordination of imine nitrogen with palladium owing to the donation of electron from nitrogen atom to the empty *d*-orbital of the metal [13].

**Nuclear Magnetic Resonance (NMR) Spectroscopy:**  $^1\text{H}$  and  $^{13}\text{C}$  NMR were used to indicate the chemical structure of the synthesized ligands and its metal complexes. The chemical shifts of the different types of protons in the  $^1\text{H}$  NMR spectra of the ligands ( $L_{\text{SB-1}}$  and  $L_{\text{SB-2}}$ ) and its Pd(II) complexes are presented in Table 3. As observed in the  $^1\text{H}$  NMR spectra of free ligands, the chemical shift of phenolic proton (Ar-OH) was observed at very downfield region  $\delta_{\text{H}}$  12.28-12.74 ppm due to hydrogen-bonded phenolic protons. Upon comparison, the proton signals are completely disappeared in case of Pd(II) complexes further proved that -OH groups had participated in chelation with proton displacement. This confirms the

bonding of the oxygen atoms to the metal ions (C-O-M) [14]. Meanwhile, in the region of  $\delta_{\text{H}}$  6.29-6.59 ppm were assigned for hydrogen of the aromatic ring. The alkyl protons =N-CH<sub>2</sub> were observed as multiplet peaks at  $\delta_{\text{H}}$  3.60-3.75 ppm. Then, the other doublet at  $\delta_{\text{H}}$  1.42 ppm and  $\delta_{\text{H}}$  1.40 ppm is due to the -CH<sub>3</sub> methyl protons resonances in ligands  $L_{\text{SB-1}}$  and  $L_{\text{SB-2}}$ , respectively.

The  $^{13}\text{C}$  NMR spectra (Table 3) showed the presence of expected number of signals corresponding to different types of carbon atom present in the compounds. The Schiff base ligand ( $L_{\text{SB-1}}$  and  $L_{\text{SB-2}}$ ) shows the signal at  $\delta_{\text{C}}$  20.05 ppm and 14.35 due to carbon atoms methyl groups. After the complexation occurred, the chemical shift were shifted downfield at  $\delta_{\text{C}}$  20.88 ppm and 16.87 ppm, respectively. Furthermore, the aromatic carbon resonance can be found in between  $\delta_{\text{C}}$  102.07-103.73 ppm. The spectra of Schiff base ligands ( $L_{\text{SB-1}}$  and  $L_{\text{SB-2}}$ ) exhibit strong band at  $\delta_{\text{C}}$  168.94 ppm and 163.73 ppm due to azomethine group. Once the coordination of metal formed ( $M_{\text{SB-1}}$  and  $M_{\text{SB-2}}$ ), the resonances were shifted upfield at  $\delta_{\text{C}}$  165.31 ppm and 163.49 ppm. This indicates that palladium is involved in coordination of the metal complexes [15].

**Catalytic Studies:** The Salen-palladium(II) complexes  $M_{\text{SB-1}}$  and  $M_{\text{SB-2}}$  have been prepared in this study were tested as homogeneous catalysts in the Mizoroki-Heck reaction between 4-bromonitrobenzene with methyl acrylate in the presence of sodium bicarbonate (NaHCO<sub>3</sub>) as base, *N,N*-dimethylacetamide (DMA) as solvent, at 120 °C for 3 hours. The reactions were carried out in a Radleys 12-placed carousel reactor vessel whilst continuously purged with nitrogen gas. The temperature was carefully controlled using a contact thermometer ( $\pm 1$  °C). The reaction was monitored by Gas Chromatography Flame Ionization Detector (GC-FID) by determining the percentage conversion of starting material which is 4-bromonitrobenzene to the coupled product. A control experiment was also performed for comparison with catalytic study. The catalyst loading was kept to 1.0 mmol% so as to give an expected turnover number (TON) of 100 if 100% conversion was achieved.

Table 3: NMR spectral data ( $\delta$  ppm) of Schiff base ligands and its Palladium(II) complexes

Compound	$^1\text{H}$ NMR					$^{13}\text{C}$ NMR	
	$\delta(\text{Ar-OH})$	$\delta(\text{Ar-H})$	$\delta(\text{=N-CH}_2)$	$\delta(\text{CH}_3)$	$\delta(\text{Ar-H})$	$\delta(\text{CH}_3)$	$\delta(\text{C=N})$
$L_{\text{SB-1}}$	12.74	6.29	3.60	1.42	102.07	20.05	168.94
$L_{\text{SB-2}}$	12.28	6.56	3.75	1.40	118.79	14.35	163.73
$M_{\text{SB-1}}$	-	6.21	3.42	1.30	103.65	20.88	163.70
$M_{\text{SB-2}}$	-	6.34	3.45	1.40	116.51	16.87	163.49

Table 4: The catalytic activity and performance of  $M_{SB-1}$  and  $M_{SB-2}$ .

Complex	Without		
	catalyst	$M_{SB-1}$	$M_{SB-2}$
Catalyst loading (mmol%)	0.00	1.00	1.00
Retention time (hours)	3	3	3
Temperature (°C)	120	120	120
Conversion of 4-bromonitrobenzene (%)	11	100 (100)	100 (100)

\*The parenthesis indicated the turnover number (TON); moles of substrate converted per mole of metal in the catalyst.

The reactions of 4-bromonitrobenzene using  $M_{SB-1}$  and  $M_{SB-2}$  as homogeneous catalysts exhibited excellent yield with 100% conversion of starting materials into the desired product after 3 hours reaction period. However, optimization techniques for catalytic activity should be considered in using variety of reaction conditions such as different of bases, temperature, catalyst loading and solvent used in order to get the maximum of product conversion using optimum condition.

As a conclusion, these preliminary findings indicated that the synthesized complexes  $M_{SB-1}$  and  $M_{SB-2}$  can act as potential catalysts in the Mizoroki-heck reaction. As shown in Table 4, the catalytic data indicated that  $M_{SB-1}$  and  $M_{SB-2}$  complexes can be used as phosphine-free catalysts in the Mizoroki-Heck reaction involving 4-bromonitrobenzene with methyl acrylate which gave 100% conversion after just *ca.* 3 hours of reaction time.

## CONCLUSION

In conclusion, two novel salen-palladium(II) complexes ( $M_{SB-1}$  and  $M_{SB-2}$ ) were successfully synthesized and characterized via CHN elemental analysis, FTIR spectroscopy, and NMR spectroscopy. These catalysts were found efficiently catalyzed Mizoroki-Heck reaction of 4-bromonitrobenzene with methyl acrylate.

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