

# Catalytic Activity Study of Synthesized Palladium(II)-Hydrazone Complexes in the Heck Reaction: Optimization of the Amount of Catalyst Loading and Reaction Time

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Palladium offers various applications in the field of fine chemicals, especially as a catalyst in carbon-carbon coupling reactions. Pd<sup>2+</sup> ions which are attached to a suitable ligand, such as a hydrazone derivative, improve the catalytic performance of palladium (Pd(II)) as a catalyst. This study focused on the catalytic performance of two synthesized Pd(II)-hydrazone complexes (Pd-L<sub>1</sub> and Pd-L<sub>2</sub>) as catalysts in the Heck reaction. The reaction of synthesized hydrazone ligands L<sub>1</sub> and L<sub>2</sub> in methanol with Pd(II) chloride produced Pd-L<sub>1</sub> and Pd-L<sub>2</sub> complexes, respectively. Structures of the synthesized compounds were confirmed by using Fourier transform infrared (FT-IR), <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR), and UV-Vis spectroscopies. The preliminary complexation study between Pd<sup>2+</sup> cations and hydrazone ligands (L<sub>1</sub> and L<sub>2</sub>) which showed stoichiometric of 1:1 and 1:2 formation corresponded to the metal-ligand ratio. Catalytic activity study of both complexes in the Heck reaction between 1-bromo-4-nitrobenzene and styrene at different catalyst loadings and reaction times was conducted and analyzed by using gas chromatography-flame ionisation detector (GC-FID) spectroscopy. The best catalytic activity was by using 0.5 mmol% Pd-L<sub>1</sub> catalyst loading at 60 min of reaction time, in DMA solvent, and Na<sub>2</sub>CO<sub>3</sub> as a base.

**Key words:** Hydrazone ligand; palladium(II)-hydrazone complex; Heck reaction

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The preparation of ligand is feasibly the most important step in the development of metal complexes which exhibit unique properties and novel reactivity. Suitable ligand designs have led to catalysts which exhibit higher reaction rates, improved lifetime, and stability. Hydrazone is an organic compound which contains the structure R<sub>1</sub>R<sub>2</sub>C=NNH<sub>2</sub> that has various binding modes and lone pair electrons [1,2]. This compound is used as a ligand in the formation of Pd(II) complexes to enhance the catalytic activity in the Heck reaction. Due to its versatility, this ligand is also used in other research areas, such as anti-tumour, anti-tubercular, and anti-microbial activities [3].

Reactions in which Pd(II) complexes catalyze carbon-carbon cross-coupling of an aryl or a vinyl halide and an alkene are referred to as the Heck reactions. The presence of Pd(II) in the Heck reaction is established as an excellent method for the creation of new C-C bonds [4, 5]. However, a suitable ligand in the complex formation and optimum conditions for the Heck reaction need to be discovered. This study focused on synthesized hydrazone ligands in the formation of Pd(II)-hydrazone complexes (Pd-L<sub>1</sub> and Pd-L<sub>2</sub>) that are suitable as catalysts in the Heck

reaction. The catalytic activity of the complexes was evaluated by optimising the amount of catalyst loading and reaction time.

## MATERIALS AND METHODS

### 1. Materials & Instruments

The chemicals and solvents were used without further purification. The chemicals were palladium(II) chloride, 3-nitrobenzaldehyde, 4-chlorobenzaldehyde, 4-methoxybenzohydrazide, 1-bromo-4-nitrobenzene, styrene, sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>), and magnesium sulphate (MgSO<sub>4</sub>). Meanwhile, the solvents used were *N,N*-dimethylacetamide (DMA), dimethyl sulphoxide (DMSO), and methanol (MeOH). All solid products produced at the end of every synthesis were collected by high vacuum filtration, rotary evaporation or slow evaporation technique at room temperature.

The melting points of the products were measured by using Stuart SMP10. The FT-IR spectra were recorded between 4000 – 400 cm<sup>-1</sup> as attenuated total reflectance (ATR) on Perkin Elmer Spectrum 400 FTIR spectrometer. <sup>1</sup>H and <sup>13</sup>C-NMR spectra of the samples were recorded on Bruker Avance 400

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spectrometer at 400 MHz by using tetramethylsilane (TMS) as the internal standard and DMSO-<sub>d6</sub> as a solvent. Electronic spectra were recorded in DMSO with Systronics double beam UV-Vis spectrophotometer in the range of 200 – 800 nm.

The catalytic activities of the synthesized complexes were determined by using gas chromatography (GC) – by calculating the conversion rate of the reactants. The products were analyzed with a 30 m × 250 μm × 0.25 μm nominal capillary column (ULTRA-1.0.05, 100% dimethylpolysiloxane) by using Flame Ionisation Detection (FID) (Agilent 7820A). 0.5 μL samples were injected at 50°C. The increment of temperature was set at 15°C per min and the final temperature was 300°C. Meanwhile, the flow rate used was 1.9162 mL/min. Percentage conversion of the reaction was calculated by using the equation below:

$$\text{Percentage \% conversion} = \frac{(A_{\text{initial}}) - (A_{\text{final}})}{(A_{\text{initial}})} \times 100$$

Where;

$A_{\text{initial}}$  = peak area of reactant before reaction

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

## 2. Methods

### 2.1 Synthesis of ligands and complexes

Hydrazone ligand  $L_1$  was prepared by refluxing an equimolar of 4-methoxybenzohydrazide (0.1 mmol) and 3-nitrobenzaldehyde (0.1 mmol) in 10 mL of

methanol for 2 h in the presence of nitrogen gas. The reaction mixture was allowed to cool down at room temperature and then filtered by using vacuum filtration to gain a solid product. The solid was washed several times and recrystallized from methanol, which was obtained as white crystals [6]. The expected product, 4-methoxy- $N'$ -(3-nitrobenzylidene) benzohydrazide ( $L_1$ ) was confirmed by using FT-IR, NMR, and UV-Vis spectroscopies. The melting point of the compound was determined from the melting point apparatus. The procedure was repeated by replacing 3-nitrobenzaldehyde with 4-chlorobenzaldehyde to form 4-methoxy- $N'$ -(4-chlorobenzylidene) benzohydrazide ( $L_2$ ). The structures of the synthesized ligands are shown in Figure 1.

The structures of the synthesized Pd- $L_1$  and Pd- $L_2$  complexes are shown in Figure 2. The complexes were prepared directly from the ligands as in the following procedure. Ligand  $L_1$  (0.1 mmol) was dissolved in 15 mL of methanol and then followed by the addition of palladium(II) chloride (0.1 mmol). The mixture was refluxed for 90 min with the presence of nitrogen gas. The synthesized product was filtered by using vacuum filtration and washed with methanol. The product was stored over anhydrous CaCl<sub>2</sub>. The melting point of the product was determined and the structure obtained was characterized by using FT-IR, NMR, and UV-Vis spectroscopies. The procedure was repeated by replacing ligand  $L_1$  with ligand  $L_2$ . The products obtained were dichloro-4-methoxy- $N'$ -(3-nitrobenzylidene) benzohydrazidepalladium(II) complex (Pd- $L_1$ ) and di-4-methoxy- $N'$ -(4-chlorobenzylidene) benzohydrazidepalladium(II) complex (Pd- $L_2$ ).

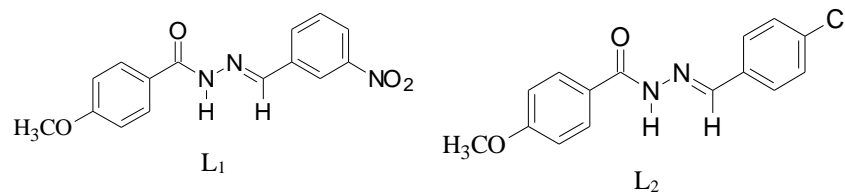


Figure 1. The structures of hydrazone ligands

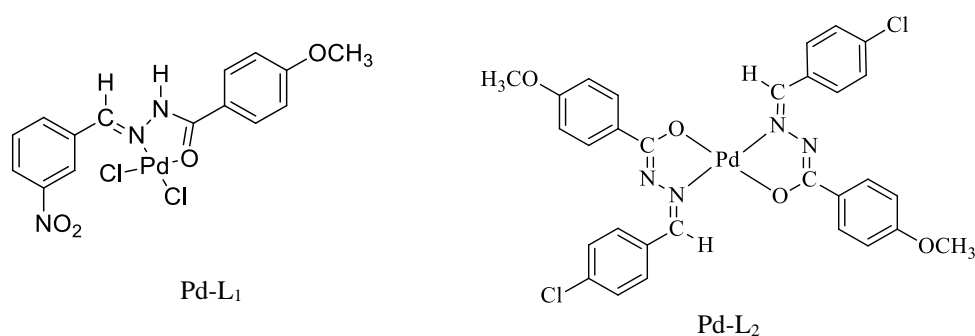
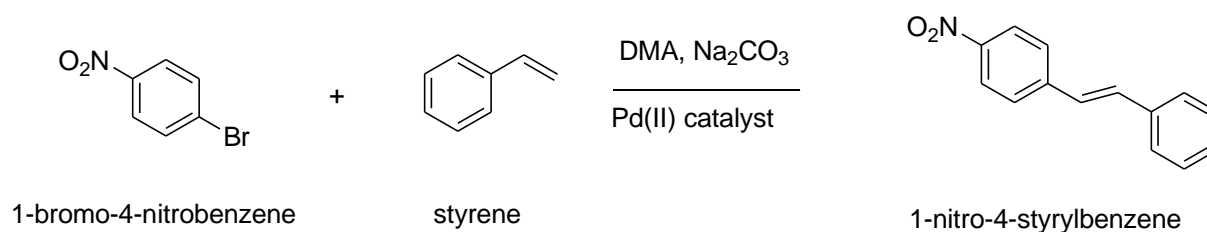


Figure 2. The structures of palladium(II)-hydrazone complexes



**Figure 3.** The Heck reaction between 1-bromo-4-nitrobenzene and styrene

## 2.2. Preliminary Complexation Study

Preliminary complexation study is to determine the stoichiometry between ligand and metal. The study was conducted by using UV-Vis spectroscopy titration method. Individual solutions of  $2.5 \times 10^{-5}$  M ligand and  $1.0 \times 10^{-4}$  M  $\text{Pd}^{2+}$  cation were prepared in DMSO. The cuvette was placed with 2.5 mL of ligand solution and titrated with  $\text{Pd}^{2+}$  cation solution. The UV-Vis spectra were recorded after each titration in the range of 270 nm – 300 nm about 5 min after each titration [7].

## 2.3. Catalytic Activity Study

The investigation into the catalytic activity of the complexes in the Heck reaction was done through the reaction of 1-bromo-4-nitrobenzene with styrene to produce 1-nitro-4-styrylbenzene as shown in Figure 3. 1-bromo-4-nitrobenzene (0.20 g; 1 mmol), styrene (0.17 g; 2 mmol), sodium carbonate  $\text{Na}_2\text{CO}_3$  (0.25 g; 2.4 mmol), and DMA (10 mL) were added into a round-bottom flask. The mixture was heated at  $70^\circ\text{C}$  in the presence of nitrogen gas for 1 h. The reaction mixture was allowed to cool at room temperature and extraction was carried out by using water (30 mL) and dichloromethane ( $3 \times 10$  mL). The organic layer was dried over  $\text{MgSO}_4$  and left to evaporate by using rotary evaporator to get the final product in a powder form [8]. The product was confirmed by using FT-IR spectroscopy.

The steps were repeated with 1.0 mmol% and 0.5 mmol% catalyst loadings. The reaction mixture solution was collected at 15 min, 30 min, 45 min, and 60 min during the reflux process and was analyzed by using GC-FID. The conversion rate and turnover number (TON) of the reactions were calculated from GC-FID spectra.

## RESULTS AND DISCUSSION

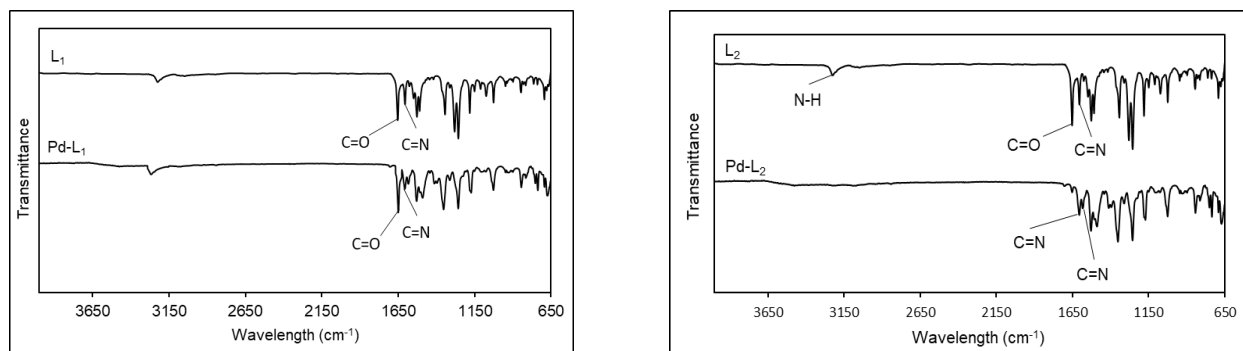
### 1. Characterization

The physical properties of the synthesized ligands and complexes are listed in Table 1. From the observation, the complexation process changed the color of both ligands. Meanwhile, the melting points of both complexes were higher than the respective ligands due to the coordination of Pd(II) with the ligands' structures. The presence of metal-ligand bonding in the complexes' structures needed higher energy to break and consequently increased the melting point.

The structures of all the synthesized compounds were confirmed by using FT-IR,  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ , and UV-Vis spectroscopies. The FT-IR spectra of the ligands and complexes are shown in Figure 4. The synthesized ligands  $\text{L}_1$  and  $\text{L}_2$  were confirmed by the presence of new absorption bands of  $\text{C}=\text{N}$  at  $1604\text{ cm}^{-1}$  ( $\text{L}_1$ ) and  $1610\text{ cm}^{-1}$  ( $\text{L}_2$ ) due to the formation of azomethine linkage between  $\text{C}=\text{O}$  aldehyde of 3-nitrobenzaldehyde for  $\text{L}_1$  or 4-chlorobenzaldehyde for  $\text{L}_2$  and  $\text{N-H}_2$  of 4-methoxybezohydrazide by removal of  $\text{H}_2\text{O}$  molecules. This was supported by the absence of  $\text{C}=\text{O}$  aldehyde ( $1702\text{ cm}^{-1}$  or  $1690\text{ cm}^{-1}$ ) and  $\text{N-H}_2$  ( $3323\text{ cm}^{-1}$ ) absorption bands in the spectra of the ligands [9]. After complexation with  $\text{PdCl}_2$ , the spectrum of  $\text{Pd-L}_1$  showed that the absorption bands of  $\text{C}=\text{O}$  amide and  $\text{C}=\text{N}$  shifted from  $1652\text{ cm}^{-1}$  to  $1649\text{ cm}^{-1}$  and  $1604\text{ cm}^{-1}$  to  $1609\text{ cm}^{-1}$ , respectively. These indicated that Pd(II) was coordinated with the ligands through the O and N atoms by a contribution of the lone pair to Pd(II) known as a dative bond. Meanwhile, in the spectrum of  $\text{Pd-L}_2$ , the absorption band of  $\text{C}=\text{N}$  shifted from  $1610\text{ cm}^{-1}$  to  $1604\text{ cm}^{-1}$  and the disappearance of the absorption bands of  $\text{C}=\text{O}$  amide ( $1649\text{ cm}^{-1}$ ) and  $\text{N-H}$  ( $3254\text{ cm}^{-1}$ ) was observed.

**Table 1.** Physical properties of synthesized compounds

Compound	Color	Melting point ( $^\circ\text{C}$ )	% Yield
$\text{L}_1$	Yellowish	188 – 189	78.06
$\text{Pd-L}_1$	Dark brown	220 – 221	79.00
$\text{L}_2$	White	197 – 198	79.00
$\text{Pd-L}_2$	Golden-yellow	300 – 310	71.94

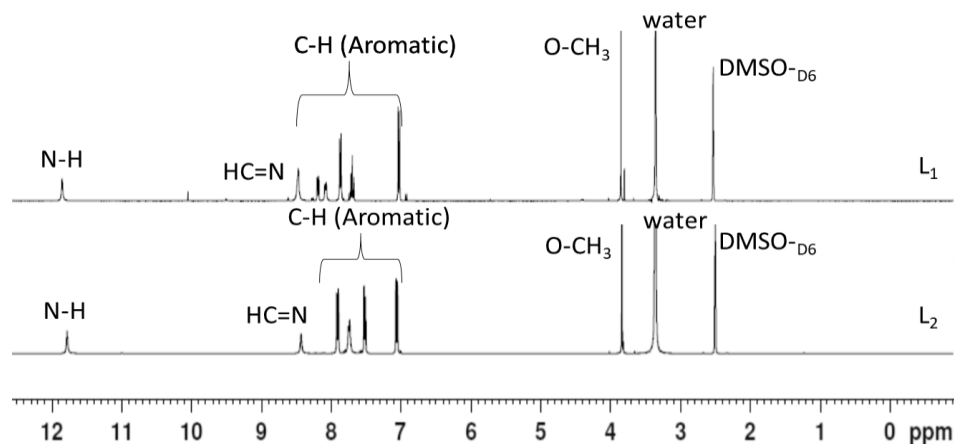


**Figure 4.** FT-IR spectra of the synthesized compounds

The N atom was coordinated with palladium by the dative bond, while the O atom was coordinated by enolization and deprotonation of N-H amide. This was proven by the appearance of a new absorption band of C=N at  $1590\text{ cm}^{-1}$  after complexation [10-12].

The  $^1\text{H-NMR}$  spectra are shown in Figure 5 and its significant attributions are listed in Table 2. The sharp singlet peaks of  $-\text{CH}_3$  proton can be clearly observed at chemical shift of 3.84 ppm for both ligands. Meanwhile, broad singlet peaks appeared at

the most deshielded chemical shifts of 11.98 ppm ( $L_1$ ) and 11.78 ppm ( $L_2$ ), which belonged to N-H protons in the ligands. This was due to the high partially negative charge of N atom that would attract a partially positive charge of H atom, and consequently reduced the electron density of H [13]. Other important peaks observed were singlet peaks that appeared at chemical shifts of 8.56 ppm ( $L_1$ ) and 8.43 ppm ( $L_2$ ). It indicated the successful formation of the azomethine linkage (HC=N) in the ligand formation [14].



**Figure 5.**  $^1\text{H-NMR}$  spectra of hydrazone ligands

**Table 2.** Significant attributions of  $^1\text{H-NMR}$  data of hydrazone ligands

Attributions	Chemical Shift, $\delta$ (ppm)	
	$L_1$	$L_2$
$-\text{OCH}_3$	3.84 [3H, s]	3.84 [3H, s]
$-\text{CH}_{\text{aromatic}}$	7.07 [2H, d] 7.74 [1H, t] 7.93 [2H, d] 8.13 [1H, d] 8.24 [1H, d] 8.53 [1H, s]	7.07 [2H, d] 7.53 [2H, d] 7.76 [2H, d] 7.92 [2H, d]
$-\text{CH}$	8.56 [1H, s]	8.43 [1H, s]
$-\text{NH}$	11.98 [1H, s]	11.78 [1H, s]

The  $^{13}\text{C}$ -NMR spectra of both ligands are shown in Figure 6. The spectrum of  $L_1$  showed that  $-\text{OCH}_3$  resonated at 55.94 ppm, which was a higher chemical shift as compared to the normal chemical shift of  $-\text{CH}_3$  around 30 ppm. This shift was due to the inductive effect of the electronegative oxygen atom attached to the methyl group [13]. The ligand also showed signals at 162.65 ppm and 148.78 ppm for  $\text{NC}=\text{O}$  amide and  $\text{HC}=\text{N}$  azomethine carbons, respectively. This proved the formation of  $\text{C}=\text{N}$  group from the reaction between aldehyde and amine group in the formation of hydrazone ligands [15]. Similar assignments of chemical shifts can also be observed for  $L_2$ . Unfortunately, the  $^1\text{H}$  and  $^{13}\text{C}$ -NMR spectra for

both complexes were not available owing to their poor solubility.

Figure 7 shows the UV-Vis spectra of the ligands and their complexes. Ligands  $L_1$  and  $L_2$  showed absorption bands at 306 nm and 312 nm, respectively. These wavelengths were assigned to the  $\pi - \pi^*$  transition in the structure of the ligands [16]. The spectrum of  $\text{Pd-}L_2$  complex showed absorption bands at 295 nm, 386 nm, and 408 nm, but  $\text{Pd-}L_1$  complex only had two absorption bands at 296 nm and 347 nm. The different absorption bands indicated the differences in their coordination structures were consistent with the result obtained from FT-IR [12].

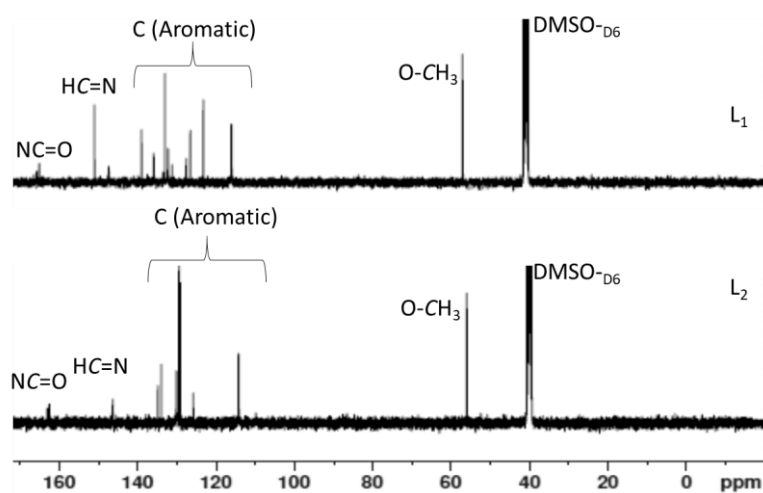


Figure 6.  $^{13}\text{C}$ -NMR spectra of hydrazone ligands

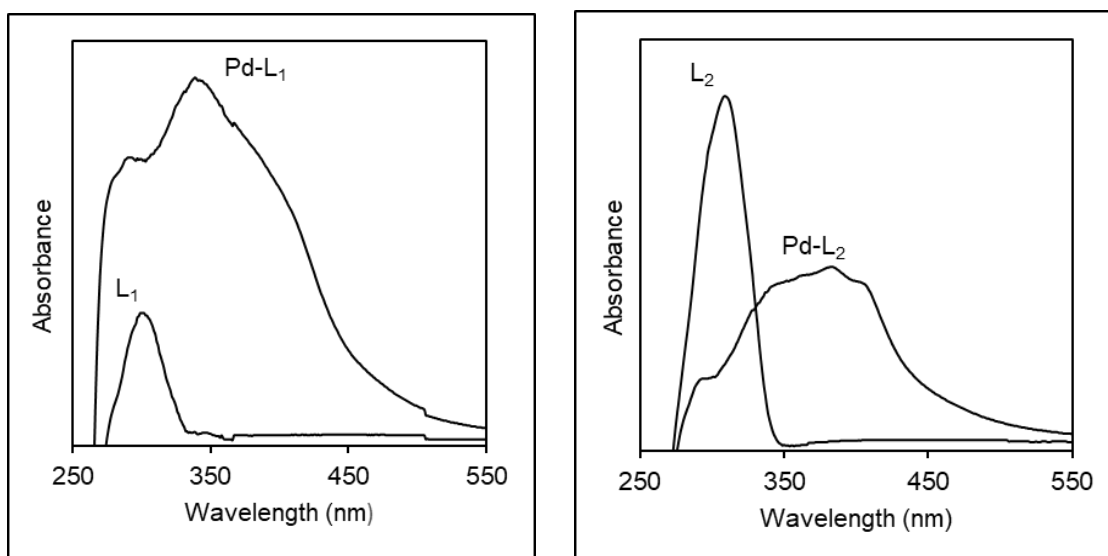
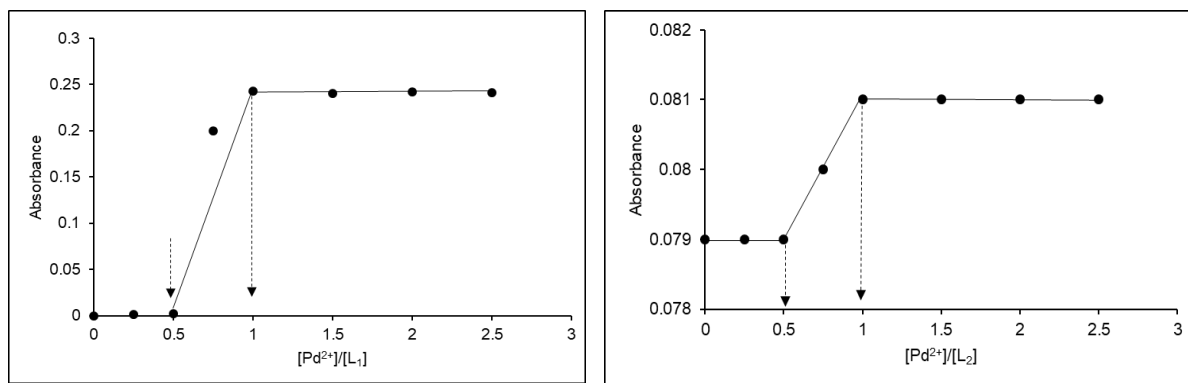


Figure 7. UV-Vis absorption spectra of hydrazone ligands and complexes



**Figure 8.** Graphs of absorbance versus  $[Pd^{2+}]/[L_1]$  and absorbance versus  $[Pd^{2+}]/[L_2]$

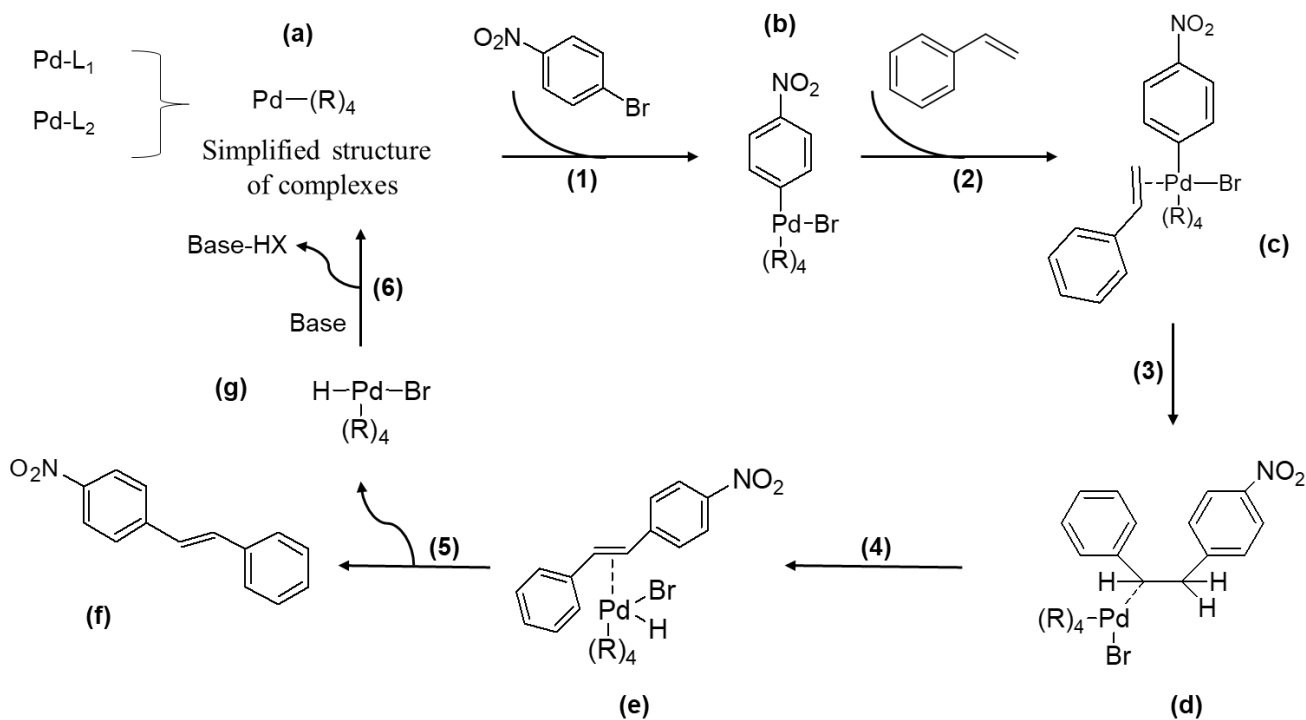
## 2. Preliminary Complexation Study

The preliminary complexation study by using titration technique between ligands and Pd(II) was analyzed by using UV-Vis absorption spectra in the range of 270 nm to 300 nm. This study gave a clue that the metal-ligand coordination probability occurred in the structure of complexes [7]. It was observed that the absorption spectra of both ligands had gradually risen with the rise in the molar fraction of  $Pd^{2+}$  cation, as shown in Figure 8. Graphs of absorbance versus molar ratios of  $[Pd^{2+}]/[L]$  were plotted and showed that the stoichiometry were 1:1 or 1:2 for both ligands. This result supported the data that were gained from the FT-IR spectra and it was observed that  $L_2$  was more preferable to 1:2 metal-ligand coordination structure even though 1

to 1 mol ratio of starting material was used.

## 3. Catalytic Activity Study

Catalytic performances of Pd- $L_1$  and Pd- $L_2$  as Heck reaction catalysts were tested in the reaction of 1-bromo-4-nitrobenzene and styrene in the presence of  $Na_2CO_3$  base and DMA. FT-IR spectroscopy was used to confirm the structures of the targeted products produced. The formation of a C=C bond was observed with the appearance of a strong adsorption band at  $1638\text{ cm}^{-1}$ . The absorption band was recorded at a higher position as compared to the C=C of styrene ( $1629\text{ cm}^{-1}$ ) due to increase in structure stability, whereby the structure changed from the monosubstituted double bond to the disubstituted double bond [17].



**Figure 9.** The mechanism of the Heck reaction in the presence of a synthesized catalyst

**Table 3.** Effects of catalyst loading and reaction time on the Heck reaction of 1-bromo-4-nitrobenzene

Entry	Catalyst loading (mmol %)	Reaction time (minute)	Conversion of 1-bromo-4-nitrobenzene, (%) (TON)	
			Pd-L <sub>1</sub>	Pd-L <sub>2</sub>
1	0.0	15	9.80(0)	2.79(0)
2		30	15.47(0)	-4.17(0)
3		45	15.83(0)	2.38(0)
4		60	25.14(0)	13.54(0)
5	0.5	15	0 (0)	3.78(7.56)
6		30	52.15(104.30)	5.70(11.41)
7		45	55.84(111.68)	17.53(35.06)
8		60	57.50(115.00)	21.57(43.14)
9	1.0	15	0 (0)	0 (0)
10		30	3.02(3.02)	17.02(17.02)
11		45	14.11(14.11)	19.54(19.54)
12		60	18.17(18.17)	4.80(4.80)

A plausible mechanism for the synthesis of 1-nitro-4-styrylbenzene in the presence of a catalyst is illustrated in Figure 9. The mechanism in the Heck reaction involves: (1) oxidative addition of 1-bromo-4-nitrobenzene on the coordinative unsaturated (a) species; (2) Styrene insertion to Pd(II) intermediate (b) and  $\pi$ -alkene complex is formed (c); (3) Migratory insertion, insert the aryl moiety in (c) into double bond forms a  $\sigma$ -alkyl palladium complex (d); (4) Internal rotation formed Pd and  $\beta$ -hydrogen in syn-coplanar geometry (e) by rearrangement of  $\sigma$ -alkyl palladium; (5)  $\beta$ -hydride elimination releases targeted product (f) and Pd(II) species (g); (6) The addition of base regenerates the catalyst by the removal of HX from the structure of (g) [18, 19].

The catalytic activities of Pd-L<sub>1</sub> and Pd-L<sub>2</sub> complexes were studied at every 15 min reaction time within 1 h by using 0.5% and 1.0% mmol of the amount of catalyst loading. The data from GC-FID spectra were used to measure catalytic performance. The conversion rate (%) of 1-bromo-4-nitrobenzene formation and turnover number (TON) were calculated and are tabulated in Table 3. Both complexes showed good catalytic activities at 60 min reaction time with 0.5 mmol% of catalyst loading (Entry 8). However, Pd-L<sub>1</sub> showed a double conversion rate at similar reaction conditions due to the presence of activation group  $-\text{NO}_2$  which increased the stability of the complex's structure and enhanced the catalytic activity [20]. Entries 9-12 show the catalytic activity data with increase in the amount of catalyst loading. These conditions caused the reduction in conversion rate because of the formation of inactive palladium black that would restrain the catalytic cycles [9].

## CONCLUSION

This study revealed the synthesis of Pd-L<sub>1</sub> and Pd-L<sub>2</sub> complexes which could be used as catalysts in the Heck reaction. From the catalytic activity results, 0.5 mmol% of Pd-L<sub>1</sub> catalyst loading at 60 min reaction time showed the best catalytic performance with the highest TON. However, further study is needed to investigate the optimum conditions in terms of temperature, solvent system, and base to improve the catalytic activity.

## ACKNOWLEDGEMENTS

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