SYNTHESIS AND CHARACTERISATIONS OF NICKEL(II)–HYDRAZONE COMPLEX AS CATALYST IN SUZUKI REACTION

(Sintesis, dan Pencirian Nikel(II)– Hidrazon Kompleks Sebagai Pemangkin dalam Tindak Balas Suzuki)

Aisyah Ahmad Fauzi[1], Norul Azilah Abdul Rahman[1,2], and Nur Rahimah Said[1*]

[1]School of Chemistry and Environment,
Faculty of Applied Sciences,
Universiti Teknologi MARA,
Cawangan Negeri Sembilan, Kampus Kuala Pilah,
72000 Kuala Pilah, Negeri Sembilan, Malaysia
[2]School of Chemistry and Environment,
Faculty of Applied Sciences Universiti Teknologi MARA,
40450 Shah Alam, Selangor, Malaysia

Corresponding author: nurra1435@uitm.edu.my

Abstract

Dichloro-*N'*-(3-chlorobenzylidene) benzohydrazide nickel(II) complex was successfully synthesised using 4-chloro-*N'*-(4-chlorobenzylidene) benzohydrazide ligand with nickel(II) chloride. The synthesised ligand and complex were characterised by various instruments including FTIR, ^{1}HNMR, ^{13}CNMR, and UV-Vis spectroscopy. The preliminary complexation study between Ni^{2+} cation and ligand showed that 1:1 stoichiometric formation corresponded to the metal-ligand ratio. The catalytic performance of the complex was tested using a Suzuki reaction between phenylboronic acid and four different aryl bromides (1-bromo-4-nitrobenzene, 4-bromoanisole, 4-bromoacetophenone, and bromobenzene) at different solvents and bases. The per cent (%) conversion rate of reactant to the product was determined using GC-FID. The best catalytic performance was found in the reaction between phenylboronic acid and 1-bromo-4-nitrobenzene using 0.5% mmol catalyst loading, methanol as a solvent, and K_2CO_3 as a base at temperature of 65°C within 2 h reaction time, giving a conversion rate of 81.86%.

Keywords: hydrazone ligand, nickel (II)-hydrazone complex, Suzuki reaction

Abstrak

Kompleks dikloro-N'-(3-klorobenzilidena) benzohidrazida nikel(II) telah berjaya disintesis menggunakan ligan 4-kloro-*N'*-(4-klorobenzilidena) benzohidrazida dengan nikel(II) klorida. Ligan dan kompleks yang disintesis dicirikan oleh pelbagai alat terdiri daripada FTIR, ^{1}HNMR, ^{13}CNMR, dan spektroskopi UV-Vis. Kajian awal pembentukan kompleks antara kation Ni^{2+} dan ligan menunjukkan stoikiometri pembentukan ialah 1:1 sepadan dengan nisbah logam-ligan. Prestasi pemangkinan kompleks telah diuji menggunakan tindak balas Suzuki antara asid fenilboronik dan empat aril bromida yang berbeza (1-bromo-4-nitrobenzena, 4-bromoanisol, 4-bromoacetofinon, dan bromobenzena) pada parameter yang berbeza seperti jenis pelarut dan bes. Peratus (%) kadar

penukaran bahan tindak balas kepada produk ditentukan menggunakan GC-FID. Prestasi pemangkinan terbaik didapati dalam tindak balas antara asid fenilboronik dan 1-bromo-4-nitrobenzena dengan menggunakan pemuatan mangkin 0.5% mmol, metanol sebagai pelarut, K_2CO_3 sebagai bes pada suhu 65°C dalam masa tindak balas 2 jam memberi kadar penukaran sebanyak 81.86%.

Kata kunci: ligan hidrazon, kompleks nikel (II)-hidrazon, tindak balas Suzuki

Introduction

Suzuki reaction is one of the most used techniques for producing C-C bonds. It involves coupling an organoboron reagent with an organic halide or pseudo-halide in the presence of a palladium or nickel catalyst and a base [1]. Nickel catalyst have various advantages over palladium catalyst that are more commonly used, including the capacity to activate aliphatic electrophiles and the ability to avoid β-hydrogen elimination by alkyl-metal intermediates that help in avoiding lowering the yield [2]. In addition, nickel systems are frequently more reactive in oxidative addition or insertion reactions due to the smaller atomic radius, lower electronegativity, and greater negative redox potentials of low-valent nickel species [3]. Due to the economic aspect the selection of nickel-based catalysts is ideal for industrial-scale use more than noble metal-based catalysts due to their lower cost and high activity [4]. Many of industries use the Suzuki reaction, such as polymers, pharmaceutically active chemicals, herbicides, novel materials, liquid crystals, and chemical synthesis [5].

Improving the catalytic activity of nickel-based catalyst towards the specified reaction is important and influenced by its structure. Thus, a suitable ligand design is an essential step in the development of a catalyst that lead to higher reaction rates, improved lifetime, and stability. The ability of ligands to donate electrons is crucial in coordination chemistry because it is one of the most important factors influencing the properties and reactivities of complexes [6]. Hydrazone is a ligand that has different binding modes and lone pair electrons with the structure $R_1R_2C=NNH_2$. In such instances one donating element (iminic nitrogen, N), and its subgroups (acyl and aroylhydrazones) can function as bidentate (N, O) or tridentate (N, O, X=O, N, S) ligands [7, 8]. The exploration of ligands containing hydrazone is interesting because the diversity of it is seen in the coordination, a preference for higher coordination number stereochemistry, the capacity to operate as neutral or deprotonated ligands, and the ability to assume various conformations [9]. Due to its flexibility and versatility, the coordination chemistry of hydrazone-based ligands has proven to be highly relevant due to their strong complexation potential towards a wide range of metals ions and the possibility of catalytic application [5, 10].

Exploration of the capability of hydrazone as a ligand with nickel(II) catalyst, particularly is currently limited. The goal of this research is to design a novel nickel(II)-hydrazone complexes that can be used as Suzuki reaction catalysts. The optimum reaction conditions of a newly synthesised catalyst were studied and identified using several parameters.

Materials and Methods
Chemicals and instruments

All the chemicals and solvents obtained from commercial suppliers were used as received. The chemicals used were 4-chlorobenzyldehyde (Sigma), 4-chlorobenzhydrazide (Sigma), dimethyl sulfoxide (DMSO) (Merck), methanol (Merck), sodium acetate (NaOAc)(Merck), sodium carbonate (Na_2CO_3) (Sigma), potassium carbonate (K_2CO_3) (Merck), dimethylacetamide (DMA) (Merck), phenylboronic acid (Sigma), nickel(II) chloride (Merck), 1-bromo-4-nitrobenzene (Merck), 1-bromobenzene (Merck), 1-bromoacetophenone (Merck), 4-bromoanisole (Merck) and nitrogen gas. All solid products produced at the end of every synthesis were collected by high vacuum filtration or slow evaporation at room temperature.

The product was characterised using Fourier Transform Infrared (FTIR) spectroscopy, Nuclear Magnetic Resonance (NMR) and UV-Visible (UV-Vis) Spectroscopy. Meanwhile the catalytic performance was determined by using Gas Chromatography Flame Ionisation Detector (GC-FID). The FTIR spectrometer use is a Perkin Elmer Spectrum 400 where the FTIR spectra were determined as reduced total reflectance (ATR) in the range of 4000-200 cm⁻¹. The ¹H and

^{13}CNMR spectroscopy were analysed using a Bruker Advance 400 spectrometer model at 400 MHz with tetramethylsilane (TMS) as an internal standard. The UV-Visible spectroscopy use is a T80+ UV-Vis spectrometer in of 500-240 nm range. The % of conversion rate and turnover number (TON) were calculated using the below equation that use the data from GC-FID. The analysis used HP-5 capillary column (15 m x 0.25 mm x 0.25 mm) with Flame Ionization Detector. The samples were injected at 50°C, with a maximum temperature of 250°C. The temperature was raised at a rate of 15°C per minute and 1.9162 mL/min was utilised as the flow rate [7].

$$\% \text{ Conversion rate} = \frac{(A_{initial}) - (A_{final})}{(A_{initial})} \times 100 \qquad (1)$$

Where; $A_{initial}$ = peak area of reactant before reaction, and A_{final} = peak area of reactant after reaction

$$\text{Turnover number (TON)} = \frac{\text{Percentage of conversion rate}}{\text{Amount of catalyst loading}} \qquad (2)$$
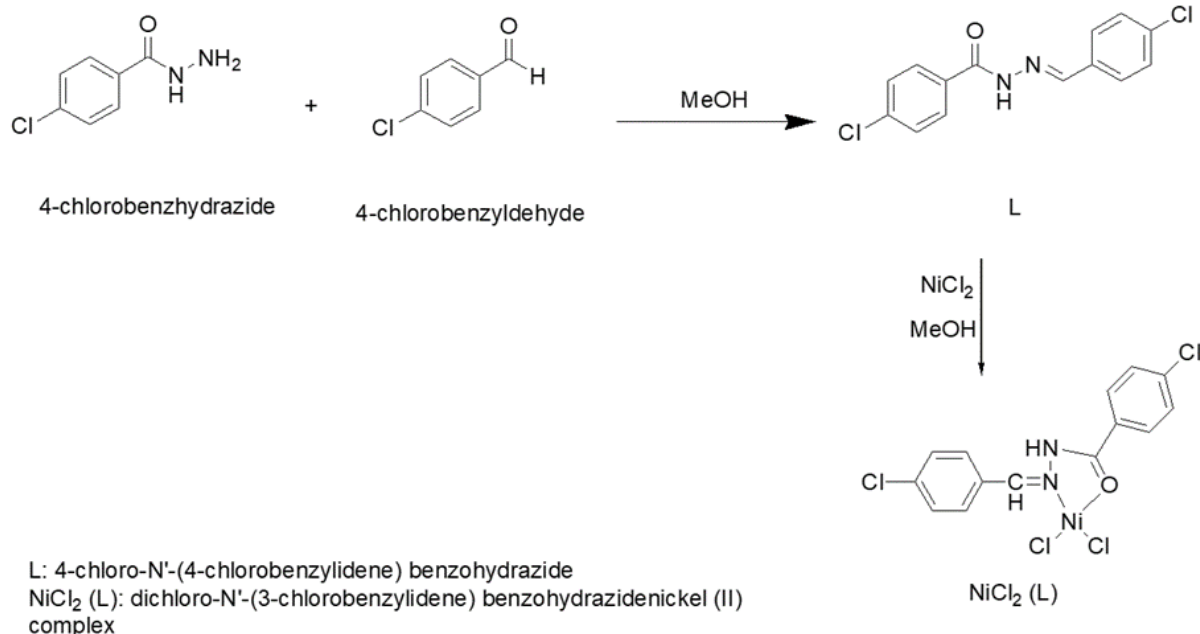
Synthesis of compounds
The outline for the preparation of nickel (II)-hydrazone complex is given in Scheme 1.

Synthesis of hydrazone ligand (L)
Hydrazone ligand prepared in the presence of nitrogen gas, an equimolar of 4-chlorobenzhydrazide (0.5 g, 2.98 mmol) and 4-chlorobenzyldehyde (0.5 g, 3.79 mmol) refluxed in 10 mL of methanol for 2 hours. The reaction mixture was then allowed to cool to room temperature before filtering using vacuum filtration to obtain a solid product. The solid was washed several times before being recrystallized from methanol forming white crystals.

L: 4-chloro-N'-(4-chlorobenzylidene) benzohydrazide
NiCl₂ (L): dichloro-N'-(3-chlorobenzylidene) benzohydrazidenickel (II) complex

Scheme 1. Synthesis steps of nickel (II)-hydrazone complexes

Synthesis of nickel(II)-hydrazone complex (NiCl₂(L))

After combining stoichiometric amounts of ligand (0.1 mmol) and nickel chloride (0.1 mmol) dissolved in methanol (15 mL), the reaction mixture was refluxed for 2 h. Filtering off the precipitates was then performed before washing the mixture with methanol and drying it in a vacuum desiccator over anhydrous $CaCl_2$.

Preliminary complexation study

A preliminary complexation study was conducted to determine the stoichiometry ratio between ligand and metal using the UV-Vis spectroscopy titration method. Solutions of hydrazone ligand and Ni^{2+} cation were prepared in DMF with concentration of 2.3×10^{-6} mmol and 1×10^{-4} mmol, respectively. The source of Ni^{2+} cation was nickel chloride. The quartz cuvette was filled with 3 mL of ligand solutions and titrated with Ni^{2+} cation solution. At each titration the solution mixture was left about 5 min before run at the UV-Vis in the 270-300 nm range [11,7].

Catalytic testing

The investigation into the catalytic activity of the complex (0.5% mmol) in the Suzuki reaction was tested by the reaction of phenylboronic acid (0.182 g, 1 mmol) with 1-bromo-4-nitrobenzene (0.20 g, 1 mmol) in 5 mL methanol under 65°C with the presence of K_2CO_3 as a base (0.276 g, 2 mmol). All chemicals were mixed in a three-neck round bottom flask and refluxed for 2 h in the presence of nitrogen gas. The mixture was then poured into a separatory funnel, followed by the addition of water (30 ml) and dichloromethane (3 x 10 ml). After allowing the mixture to settle for 30 minutes, the organic layer was collected and discarded into a beaker, and then dried over $MgSO_4$. The mixture was subsequently filtered using vacuum filtration to obtain the product. The product was evaporated using a rotary evaporator and dried in an oven. Meanwhile, the catalytic performance was analyzed using GC-FID spectroscopy. The steps were repeated with using 4-bromoacetophenone, bromobenzene and 4-bromoanisole as an aryl bromide as substituted of 1-bromo-4-nitrobenzene. Different types of solvents and bases were also tested. The reaction is shown in Scheme 2, where R is referred to as $-NO_2$, $-OCH_3$, $-COCH_3$, and H.
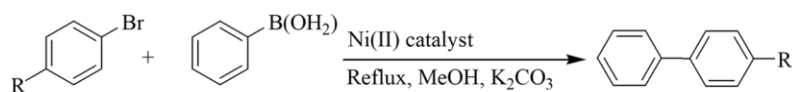
Scheme 2. Catalytic reaction of 1-bromo-4-nitrobenzene with phenylboronic acid

Results and Discussion
Characterization of synthesized compounds

This study successfully synthesised 4-chloro-*N*'-(4-chlorobenzylidene) benzhydrazide ligand and dichloro-*N*'-(3-chlorobenzylidene) benzohydrazide nickel(II) complex. The physical properties of the synthesised ligand and complex are listed in Table 1. According to the observations, the colour of the ligand changed because of the complexation process, from white to pale green. Meanwhile, the melting points of the complex was greater than the respective ligand due to the interaction of nickel(II) with the ligand's structures. These metal-ligand bonding in the structure of the complexes required more energy to break, which caused an increase in the melting point [7].

Table 1. Physical properties of synthesized compounds

Sample	Colour	Melting Point (°C)	Yield (%)
Ligand	White, powder	168-169	82.41
Complex	Pale green, powder	220-221	41.87

The formation of ligand and complex were confirmed using FTIR, ^{1}HNMR, ^{13}CNMR, and UV-Vis spectroscopies. The significant FTIR absorption bands a re summarised in Table 2. The successfully synthesised ligand is indicated by the presence of a strong absorption band at the range of the carbonyl group but at an unusually low value (1650 cm^{-1}), signified by the C=O amide. New medium absorption bands of C=N imine at 1600 cm^{-1} is also an important signal to confirm the formation. The C=N bond was formed by the reaction between the C=O aldehyde of 4-chlorobenzaldehyde and primary amine (-NH$_2$) of 4-chlorobenzhydrazide via the removal of H$_2$O molecules. However, the presence of a resonance effect in the structure led to the absorption band of C=N observed at a lower frequency when compared to the normal range, which is around 1650 cm^{-1}. Other absorption peaks were observed at 3218 cm^{-1} and 1090 cm^{-1}, which were attributed to the N-H and C-H stretching, respectively [7, 12]. The coordination of nickel(II) to the ligand in the FTIR spectrum could be observed by the shift of C=O and C=N stretching absorption bands to the low frequency at 1620 cm^{-1} and 1567 cm^{-1}, respectively. This observation indicated that the C=O oxygen and the C=N nitrogen were probably involved in coordinating to the central nickel (II) ion via contributing the lone pair [13].

Table 2. Significant FTIR absorption bands of synthesized compounds

Assignment	Wavenumber (cm^{-1})	
	Ligand	Complex
N-H	3218	3214
C=O amide	1650	1620
C=N imine	1600	1567
C-N	1090	1095
C-Cl	819	819

The spectra of ^{1}HNMR and ^{13}CNMR (Figure 1) were recorded for synthesised ligand, and the significant attributes are tabulated in Tables 3 and 4. A singlet appeared at 8.44 ppm and was assigned to the proton of azomethine (CH=N) proton. Another important peak at 12.00 ppm was assigned to the proton of N-H adjacent to C=O, which was observed as an enolic form [13]. The structures of the ligand were further supported by ^{13}CNMR data. The carbonyl carbon signal appeared at 162 ppm (C=O), whereas signals that appeared at 147 ppm were assigned to the carbon of the azomethine group (CH=N). The other five signals at 129-137 ppm were due to the substituted benzene ring carbon. Unfortunately, the reading of signals for the complex was unreadable due to the paramagnetic effect of nickel in the compound [14].
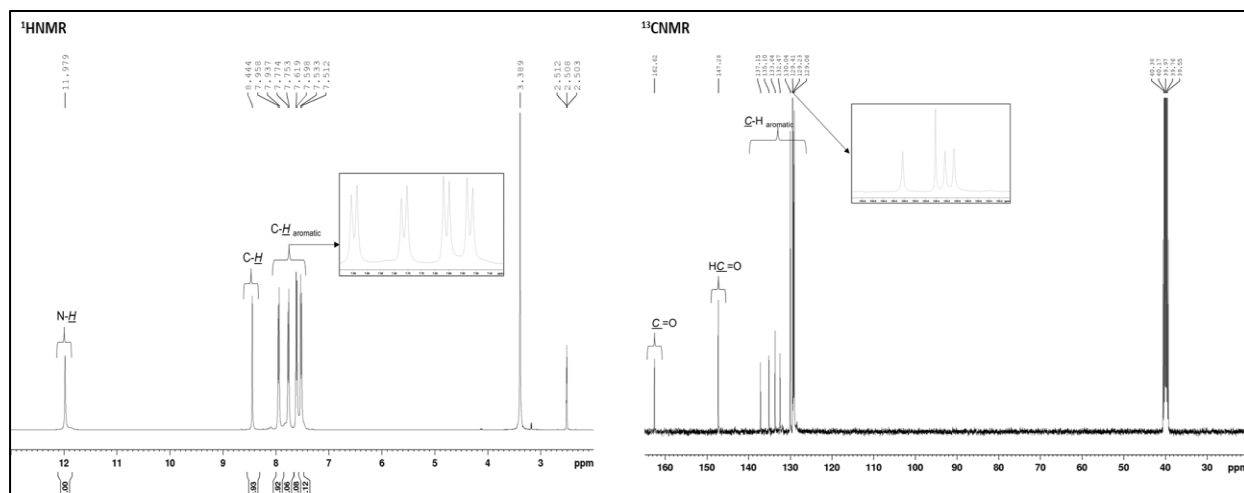
Figure 1. ¹HNMR and ¹³CNMR spectra of hydrazone ligand

Table 3. Significant attributes of ¹HNMR data of ligand

Attributions	Chemical Shift, δ (ppm)
	Ligand
-CH aromatic	7.51 [2H]
	7.60 [2H]
	7.75 [2H]
	7.94 [2H]
-CH	8.44 [1H]
-NH	11.98 [1H]

Table 4. Significant attributes of ¹³CNMR data of ligand

Attributions	Chemical Shift, δ (ppm)
	Ligand
C=O	162
HC=N	147
CH	129-137

Figure 2 shows the UV-Vis spectra of the ligand and complex. The ligand showed absorption bands at 257 nm and 298 nm. These wavelengths were assigned to the π – π* transition in the structure of the ligands. The spectrum of the complex also showed two absorption bands at 258 nm and 312 nm, signifying a similar pattern of the ligand in the region. These absorption bands were also presented in the spectrum of the nickel(II) complex, although they underwent red shift. The coordination of the ligand to the nickel(II) ion was supported by this shift in the spectra of the produced complex [15]. The region for nickel metal is 480 nm but it could not be observed in this study because nickel contained unpaired electrons exhibited d-d transition and paramagnetic causing weak absorption [16].
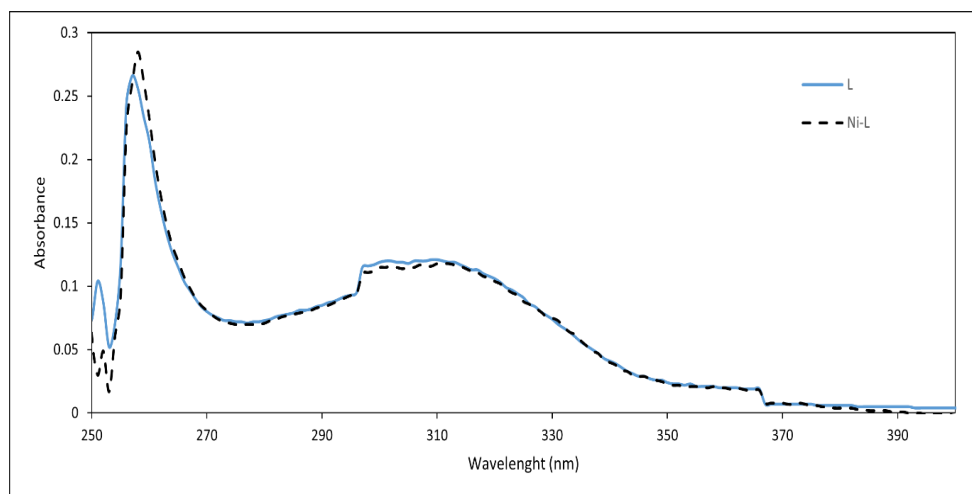
Figure 2. UV-Vis spectrum for ligand and complex

Preliminary complexation study

The preliminary complexation study using the titration method between ligand and nickel(II) was analysed via UV-Vis spectrum in the range of 270 nm to 300 nm. As seen in Figure 3, the absorption spectra of the ligand steadily increased as the mole fraction of Ni^{2+} ion increased. A graph of absorbance versus molar ratios of $[Ni^{2+}]/[L]$ was plotted. It showed that the stoichiometry was 1:1, consequently supporting the structure of the nickel complex [17].
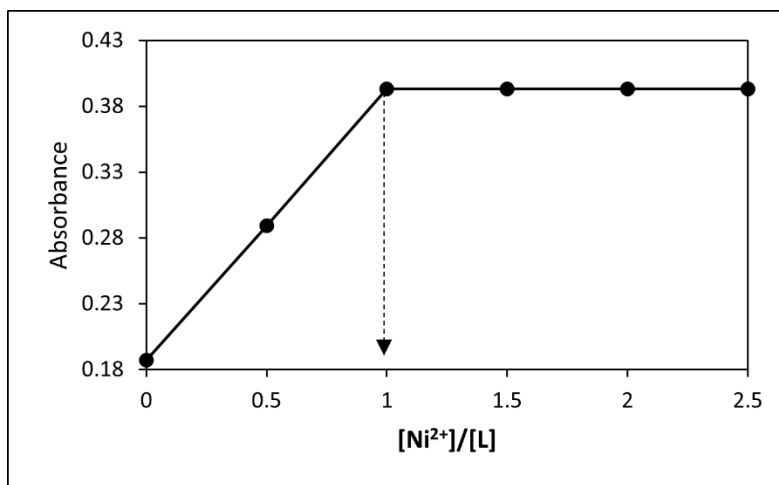

Figure 3. Graph plotted based on absorbance versus $[Ni^{2+}]/[L]$

Catalytic testing

By using 0.5% mmol of catalyst loading, the catalytic activity of Ni-L complex was investigated in a reflux system with different aryl bromides, types of solvent, and bases within a 2 h reaction time. Catalytic performance was measured using data from GC-FID spectra. The conversion rate (%) and turnover number (TON) of arylbromides were computed by using equations 1 and 2 and presented in Table 5.

Table 5. The catalytic performance of Ni-L catalyst in Suzuki Reaction

Entry	R	Solvent	Base	Conversion Rate (%)	Turnover Number (TON)
1	NO_2	MeOH	K_2CO_3	81.86	163.72
2	OCH_3	MeOH	K_2CO_3	0	0
3	$COCH_3$	MeOH	K_2CO_3	69.86	139.72
4	H	MeOH	K_2CO_3	0	0
5	NO_2	MeOH	Na_2CO_3	29.76	59.52
6	NO_2	MeOH	NaOAc	41.7	83.40
7	NO_2	DMA	K_2CO_3	37.06	74.12

Reaction condition; Catalyst loading= 0.5 mmol%, Reaction time= 2h

In the presence of K_2CO_3 base, the complex catalytic performance of a Suzuki reaction was tested in the reaction of different types of arylbromide where R is –NO_2, -H, -OCH_3 and –$COCH_3$ (Entry 1-4) with phenylboronic acid. Based on the result in Table 5, the complex showed good catalytic activities in the reaction of 1-bromo-4-nitrobenzene (Entry 1), giving the highest conversion rate of 81.86%. The presence of NO_2 as a substituent aryl bromide caused resonance and inductive effects on electronic charge stabilisation. Meanwhile, arylbromide that contains electron donating group (EDG), such as –OCH_3, showed less reactive reaction (Entry 2). This finding is because slower rate of transmetallation occurs in EDG compared to electron-withdrawing groups (EWG) [16].

Considering the results obtained, 1-bromo-4-nitrobenzene showed relatively better catalytic activity than the other arylbromides. Therefore, 1-bromo-4-nitrobenzene was selected as the model for the study of different bases (Entries 1, 5 and 6). Three types of bases were selected, namely K_2CO_3, Na_2CO_3, and NaOAc. Meanwhile, the catalyst loading and reaction time remained constant. The reaction that used K_2CO_3 produced the highest conversion rate of 81.86% (Entry 1) as compared to other bases Na_2CO_3 and NaOAc, which showed only 29.76% (Entry 5) and 41.73% (Entry 6), respectively. K_2CO_3 is the strongest inorganic base and has a high capability of neutralising protons generated in the oxidative addition mechanism [7, 12]. On other hand, the lowest conversion rate was observed in Entry 5 by using Na_2CO_3 as a base. It has a slower rate of dissolution into a polar protic solvent that causes low yield [18].

The reaction was repeated in a different solvent, i.e., DMA (Entry 7). A similar reaction condition was used as the reaction conducted in Entry 1. The results of the catalytic reaction that used methanol as a solvent showed a higher conversion rate of 81.86% (Entry 1) compared to DMA, which only released 37.06% (Entry 7). This result concluded that the most suitable solvent for this reaction was methanol due to the solubility of starting material and K_2CO_3 in a protic solvent, which promoted rapid reaction and at the same time, pointed to hydrogen bonding as an important contribution to better coupling reactions [19].

A plausible reaction mechanism of the reaction between 1-bromo-4-nitrobenzene and phenylboronic acid is portrayed in Scheme 3. The reaction was started with the reduction of the catalyst, complex $NiCl_2(L)$ to the catalytic active species Ni(L) with the presence of K_2CO_3 and phenylboronic acid, where L was the bidentate hydrazone ligand as shown in Scheme 1. The active species was Ni(0)-catalysed coupling reaction in three steps; (I) oxidative addition of 1-bromo-4-nitrobenzene to generate **(a)**, (II) transmetalation of phenylboronic acid in the formation of the complex **(b)**, and (III) reductive elimination of **(b)** to produce the product 1-nitro-4-phenylbenzene **(c)** and regeneration of active species [20].
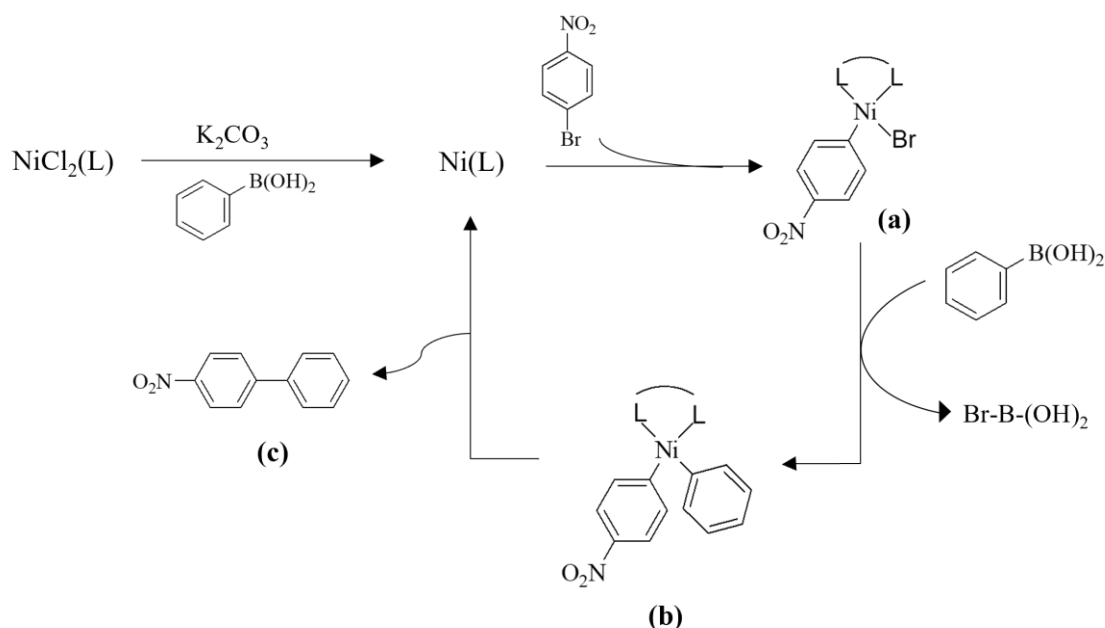
Scheme 3. The proposed mechanism of the Suzuki reaction in the presence of a $NiCl_2(L)$ as a catalyst

Conclusion

This study successfully demonstrated the synthesis and characterisation of hydrazone ligand and nickel(II)-hydrazone complex. The synthesised nickel(II) complex can be used as a catalyst for the Suzuki reaction in MeOH as the solvent, K_2CO_3 as a base, and the reaction temperature of 65°C. The proposed complex exhibited the best catalytic performance with the highest conversion rate (%) and TON. The reaction was conducted in the presence of a small amount of catalyst loading (0.5 mmol%) at a 2h reaction time.

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