Synthesis and Characterization of Pd(II) and Ni(II) Complexes of Schiff Bases and Catalytic Activity of Pd(II) Complexes

Amalina Mohd Tajuddin[1], Hadariah Bahron
and Shahrul Nizam Ahmad

Faculty of Applied Sciences,
Universiti Teknologi MARA,
40450 Shah Alam, Selangor, Malaysia
[1]E-mail: amalina9487@salam.uitm.edu.my

ABSTRACT

Six new Pd(II) and Ni(II) metal complexes of N, O-bidentate (L1, L2) and ONNO-tetradentate (L3) Schiff base ligands have been synthesized. The compounds were characterized via various physicochemical and spectroscopic techniques namely elemental analysis (CHN), FT-IR, 1H and 13C NMR as well as magnetic susceptibility measurement. All complexes showed diamagnetism indicating that they are square planar complexes. Catalytic performance of Pd(L1)2 and Pd(L2)2 were investigated for Heck cross-coupling reaction under optimum operating parameters, monitored using GC-FID for 6 h of reaction time in inert conditions. High catalytic activities of up to 90% were observed in the presence of triethylamine as base and DMA as solvent at 100°C with 1 mmol% catalyst loading. The mechanism of catalyzed Heck reaction is proposed to go through a series of conversion of Pd(0)/Pd(II).

Keywords: *Schiff base, palladium(II), nickel(II), Heck reaction, catalysis*

INTRODUCTION

Schiff bases have been often used as chelating ligands in the area of coordination chemistry and their metal complexes have been of great attention, mainly because of their wide application in the field of synthesis and catalysis. It is well known that N and O atoms play a key role in the coordination of metals, which exert two opposite electronic effects: the

phenolate oxygen is a hard donor known to stabilize the higher oxidation state of the metal atom whereas the imine nitrogen is a softer donor that will stabilize the lower oxidation state of metal atom [1-2].

Catalyst works by changing the activation energy of a reaction, providing an alternative pathway for a reaction that requires less energy. Activation energy is the minimum energy required for the reaction to occur without which the molecules of reactants will not undergo collision that causes a reaction to proceed.

Heck reaction is important for industrial and pharmaceutical applications. Pd(II) Schiff base complexes have been actively investigated for catalysis in Heck reaction. The catalytic cycle involves a series of transformations around the palladium centre. The palladium(0) compound required in the cycle was commonly generated *in situ* from the reaction of a palladium(II) precursor [3] with a reducing agent such as a base.

The work discussed herein describes the synthesis and characterization of bidentate and tetradentate Schiff bases and their Pd(II) and Ni(II) complexes. The catalytic activities for the $Pd(L1)_2$ and $Pd(L2)_2$ for Heck reaction are also reported.

EXPERIMENTAL

All the chemicals and solvents received from commercial suppliers were used as received. Carbon, hydrogen, and nitrogen analyses were carried out on Thermo Finnigan Flash EA 2000 Elemental Analyser. Melting points were determined using Buchii-B454 and were uncorrected. Infrared (IR) spectra were recorded on Perkin-Elmer model 1750X FTIR spectrophotometer using KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Varian-300MHz spectrometer using deuterated $CDCl_3$ and expresses in parts per million (δ, ppm). Magnetic measurements were carried out using the Guoy method with $Hg[(Co(SCN)_4]$ as calibrant on Sherwood Auto Magnetic Susceptibility Balance.

Synthesis of (E)-2-methoxy-6-((phenylimino)methyl)phenol (L1)

The synthesis of L1 was carried out using the established protocol [4]. Yellow solid; yield, 37%; m.p. 62-65°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.82 (s, 2H, CH_2), 3.90 (s, 3H, Ar-OCH_3), 6.84-7.32 (phenylic hydrogen groups), 8.42 (s, 1H, =CH), 13.85 (b, 1H, OH). ^{13}C NMR (300MHz, $CDCl_3$): δ 56.0 (Ar-OCH_3), 62.6 (CH_2), 113.9, 117.9, 122.9, 127.6, 128.7 (ArC), 151.7 (C1), 127.3 (C13), 165.7 (N=CH). Anal. Calcd for $C_{15}H_{15}NO_2$: C, 74.67; H, 6.27; N, 5.81%; Found: C, 74.77; H, 6.31; N, 5.91%. IR (KBr, cm^{-1}): 3471 υ(OH), 1634 υ(C=N), 1344 υ(C-N), 1254 υ(C-O), 1054 υ(OCH_3).

Synthesis of (E)-2-methoxy-6-((4-methoxy-phenylimino) methyl)phenol (L2)

L2 was synthesized by the same procedure as for L1 except benzylamine was replaced with 4-methoxybenzylamine. Yellow liquid at room temperature. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.79 (s, H, OCH_3), 4.74 (s, 2H, CH_2), 3.88 (s, 3H, Ar-OCH_3), 6.76-7.24 (phenylic hydrogen groups), 8.38 (s, 1H, =CH). ^{13}C NMR (300MHz, $CDCl_3$): δ 56.03 (OCH_3), 56.04 (Ar-OCH_3), 61.9 (CH_2), 114.0, 114.3, 117.9, 122.9, 129.9, 129.9 (ArC), 151.9 (C1), 158.8 (C13), 165.2 (N=CH). Anal. Calcd for $C_{16}H_{17}NO_3$: C, 70.83; H, 6.32; N, 5.23%; Found: C, 71.08; H, 6.32; N, 5.23%. IR (KBr, cm^{-1}): 3467 υ(OH), 1630 υ(C=N), 1344 υ(C-N), 1251 υ(C-O), 1033 υ(OCH_3).

Synthesis of 6,6'-(1E,1'E)-(1,2-phenylenebis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)bis(2-methoxyphenol) (L3)

L3 was synthesized using the same procedure as for L1 except benzylamine was replaced with *ortho*-phenylenediamine. Orange solid; yield 81%; m.p. 174-176 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.86 (s, 6H, OCH_3), 6.81-7.29 (m, 10H, phenylic hydrogen groups), 8.58 (s, 1H, =CH), 13.24 (s, 1H, OH), ^{13}C NMR (300MHz, $CDCl_3$): δ 56.10 (OCH_3), 115.1, 118.5, 119.2, 120.2, 124.0, (ArC), 142.4 (C-CH), 148.5 (C-OCH_3), 151.6 (C-OH), 164.2 (N=CH). Anal. Calcd for $C_{22}H_{20}N_2O_2$: C, 70.20; H, 5.36; N, 7.44%; Found: C, 69.71; H, 5.30; N, 7.12%. IR (KBr, cm^{-1}): 1613 υ(C=N), 1257 υ(C-O), 972 υ(OCH_3).

Synthesis of Complexes

The synthesis of Pd(II) and Ni(II) complexes of the bidentate ligands L1 and L2 were carried out by refluxing for 4 hours 1:2 molar ratio of M(OAc):Ligand in acetonitrile (Pd)/ethanol (Ni), as shown in Figure 1.

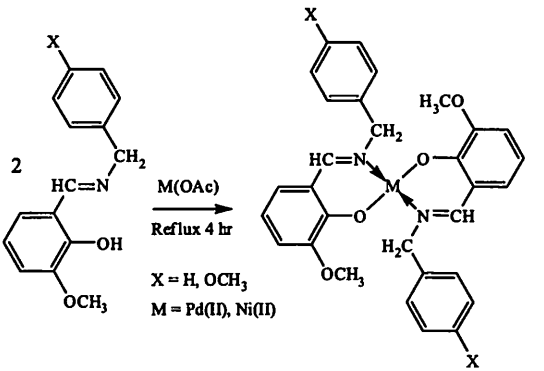

Figure 1: Formation of ML1 and ML2

The synthesis of Pd(II) and Ni(II) complexes of the tetradentate ligands L3 were carried out by refluxing for 6 hours 1:1 molar ratio of M(OAc):Ligand in acetonitrile (Pd)/ethanol (Ni), as shown in Figure 2.

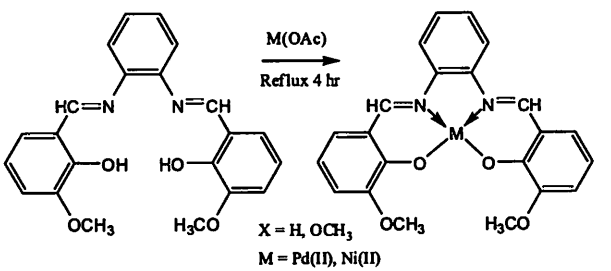

Figure 2: Formation of ML3

[Pd(L1)$_2$] Brown solid; yield, 91%; m.p. 256-259°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.12 (s, 2H, CH_2), 3.75 (s, 3H, Ar-OCH_3), 6.46-7.46 (phenylic hydrogen groups), 7.72 (s, 1H, =CH). ^{13}C NMR (300MHz, $CDCl_3$): δ 55.9 (Ar-OCH_3), 68.9 (CH_2), 114.0, 120.2, 125.4, 127.4, 128.4 (ArC), 127.2 (C13), 162.9 (N=CH). Anal. Calcd for $C_{30}H_{28}N_2O_4Pd$: C, 69.70; H, 5.48; N, 5.41%; Found: C, 61.47; H, 4.79; N, 4.72%. IR (KBr, cm$^-$

^{1}): 1622 υ(C=N), 1316 υ(C-N), 1241 υ(C-O), 1095 υ(OCH_3), 657 υ(Pd-N), 416 υ(Pd-O). μ_{eff} (B.M.) (298 K): diamagnetic.

[Ni(L1)$_2$] Green solid; yield, 82%; m.p. 207-213°C. Anal. Calcd for $C_{30}H_{28}N_2O_4Ni$: C, 66.82; H, 5.23; N, 5.19%; Found: C, 66.83; H, 5.88; N, 5.18%. IR (KBr, cm^{-1}): 1615 υ(C=N), 1341 υ(C-N), 1249 υ(C-O), 1080 υ(OCH_3), 602 υ(Ni-N), 544 υ(Ni-O). μ_{eff} (B.M.) (298 K): diamagnetic.

[Pd(L2)$_2$] Brown solid; yield, 81%; m.p. 204-205°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.77 (s, H, OCH_3), 5.04 (s, 2H, CH2), 3.76 (s, 3H, Ar-OCH_3), 6.47-7.39 (phenylic hydrogen groups), 7.69 (s, 1H, =CH). ^{13}C NMR (300MHz, $CDCl_3$): 55.2 (OCH_3), 55.9 (Ar-OCH_3), 58.3 (CH_2), 113.9, 114.0, 125.5, 129.8 (ArC), 158.8 (C13), 162.4 (N=CH). Anal. Calcd for $C_{32}H_{32}N_2O_6Pd$: C, 59.4; H, 4.98; N, 4.33%; Found: C, 59.12; H, 4.99; N, 4.35%. IR (KBr, cm^{-1}): 1620 υ(C=N), 1320 υ(C-N), 1239 υ(C-O), 1032 υ(OCH_3), 567 υ(Pd-N), 515 υ(Pd-O). μ_{eff} (B.M.) (298 K): diamagnetic.

[Ni(L2)$_2$] Brown solid; yield, 82.2%; m.p. 180-182°C. Anal. Calcd for $C_{32}H_{32}N_2O_6Ni$: C, 64.13; H, 5.38; N, 4.67%; Found: C, 63.91; H, 6.28; N, 4.64%. IR (KBr, cm^{-1}): 1611 υ(C=N), 1330 υ(C-N), 1239 υ(C-O), 1081 υ(OCH_3), 649 υ(Ni-N), 566 υ(Ni-O). μ_{eff} (B.M.) (298 K): diamagnetic.

[PdL3] Brown solid; yield, 95%; m.p. 258 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.84 (s, H, OCH_3), 6.52-6.94 (phenylic hydrogen groups), 7.70 (s, 1H, =CH). ^{13}C NMR (300MHz, $CDCl_3$): 55.4 (OCH_3), 152 (N=CH). Anal. Calcd for $C_{22}H_{18}N_2O_2Pd(H_2O)_3$: C, 49.40; H, 4.52; N, 5.24%; Found: C, 47.38; H, 4.17; N, 5.96%. IR (KBr, cm^{-1}): 1603 υ(C=N), 1247 υ(C-O), 981 υ(OCH_3), 649 υ(Pd-N), 566 υ(Pd-O). μ_{eff} (B.M.) (298 K): diamagnetic.

[NiL3] Brown solid; yield, 93%; m.p. 249 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.86 (s, H, OCH_3), 6.56-6.94 (m, phenylic hydrogen groups), 7.70 (s, 1H, =CH). ^{13}C NMR (300MHz, $CDCl_3$): 55.3 (OCH_3), 151.3 (N=CH). Anal. Calcd for $C_{22}H_{18}N_2O_2Pd(H_2O)$: C, 58.58; H, 4.47; N, 6.21%; Found: C, 57.40; H, 4.44; N, 6.07%. IR (KBr, cm^{-1}): 1608 υ(C=N), 1244 υ(C-O), 988 υ(OCH_3), 589 υ(Ni-N), 440 υ(Ni-O). μ_{eff} (B.M.) (298 K): diamagnetic.

General Procedure for Heck Coupling Reaction

Two catalytic reactions were performed by a similar procedure using $Pd(L1)_2$ and $Pd(L2)_2$ complexes. The complexes were tested as homogeneous catalysts in a series of Heck coupling reactions between iodobenzene and methyl acrylate to produce methyl cinnamate. The mixture of iodobenzene (1 mmol), methyl acrylate (2 mmol), triethylamine, Et_3N (2.4 mmol), palladium(II) Schiff base complex (0.01 mmol) and solvent *N,N*-dimethylacetamide, DMA (7 mL) were mixed in a Radley's 12-place reaction carousel and refluxed whilst being purged with nitrogen (Figure 3). The reaction was stirred for 6, 12 and 24 h at 100°C and monitored using gas chromatography.

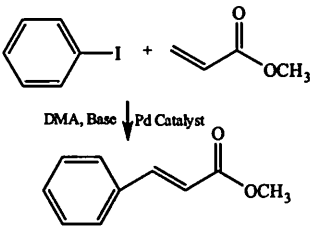

Figure 3: Heck Reaction of Lodobenzene with Methyl Acrylate Catalyzed with Pd(II) Complexes

RESULTS AND DISCUSSION

Infrared Spectroscopy

All spectra of ligands exhibit the peak for n(C=N) in the range 1613-1636 cm^{-1}, indicating the formation of Schiff bases. The broad bands at 3600-2400 cm^{-1} could be attributed to the intramolecular hydrogen-bonded O-H group [5].

The azomethine C=N bands shifted to lower frequencies, 1608-1623 cm-1 in all complexes due to the withdrawal of electron density from the nitrogen atom owing to coordination [3]. A similar effect was observed in the stretching vibration of the Schiff base phenolic C-O, with respect to the same group in the complexes where it was shifted to lower frequencies, suggesting oxygen coordination to the metal as per reported by Gupta *et al.* [6].

The appearance of new peaks at 462-544 cm^{-1} and 581-660 cm^{-1} in the spectra of complexes that ascribed M-O and M-N vibrations supporting the participation of the nitrogen atom of the azomethine group and oxygen atom of the of OH group of the ligand in the complexation with metal ions [7]. Representative IR spectra of L2 and its metal complexes are shown in Figure 4.

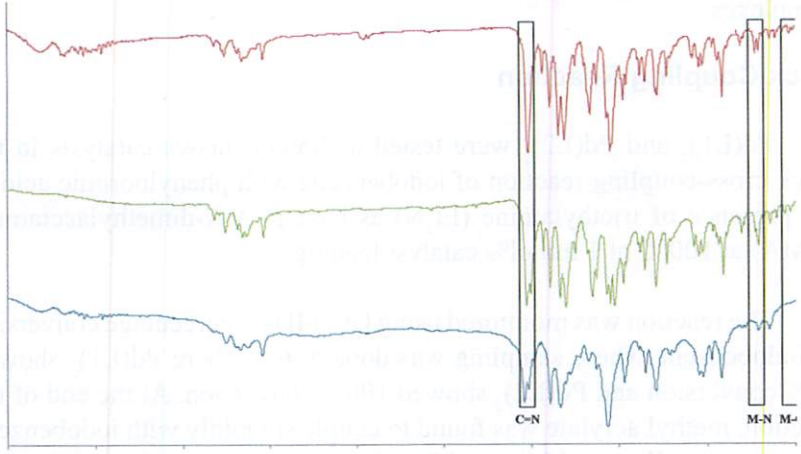

Figure 4: Representative IR Spectra of L2 and its Metal Complexes

NMR Spectroscopy

^1H NMR spectra of the ligands clearly show the presence of $-OCH_3$ groups through singlets that appear in the region 3.79-3.90 ppm. These peaks only shifted very slightly upfield to 3.75-3.76 ppm in the spectra of the metal complexes, indicating that the $-OCH_3$ moieties are not involved in the complexation. The –OH chemical shifts in the ligands observed in the region of 13.24-13-85 disappeared in the spectra of the complexes, clearly indicating deprotonation upon complexation.

In the ^{13}C NMR spectra, the imine carbons (C=N) in the ligands are found as singlets in the region of 164-165 ppm, agreeing with data reported by Senol *et al.* [8]. They were shifted upfield to the region of 162.4-162.9 in the spectra of the Pd(II) complexes. This shifting supports the suggestion of the coordination of the imine nitrogen to the metal centre. In the free ligands, C-OH signals appear at 151.5-151.9 ppm and disappeared upon

complexation, as similarly reported by Senol *et al.* [8] indicating that the complexations were successfully achieved through deprotonation of phenol.

Magnetic Susceptibility

All complexes displayed diamagnetic behavior. This clearly indicates the absence of unpaired electrons, characteristic of square planar d^8 complexes.

Heck Coupling Reaction

$Pd(L1)_2$ and $Pd(L2)_2$ were tested as homogeneous catalysts in the Heck cross-coupling reaction of iodobenzene with phenylboronic acid in the presence of triethylamine (Et_3N) as base in *N,N*-dimethylacetamide (DMA) at 100°C at 1 mmol% catalyst loading.

The reaction was monitored using GC-FID by percentage conversion of iodobenzene where sampling was done at 6 h where $Pd(L1)_2$ showed 93% conversion and $Pd(L2)_2$ showed 100% conversion. At the end of the reaction, methyl acrylate was found to couple smoothly with iodobenzene providing excellent yields up to 90% after 6 h for both catalysts. A control reaction without catalyst had been set up and there was no indication of iodobenzene conversion after 24 h.

Proposed Mechanism of Homogeneous Heck Reaction

In the traditional mechanism of the Heck reaction (Figure 5) the process starts from reduction of $Pd(II)L_2$ precursor to Pd(0)L2 (Step 1). Since typical strong reducing agents are, in most cases, not present in the reaction mixture, the palladium reduction is assumed but not explained in detail [9].

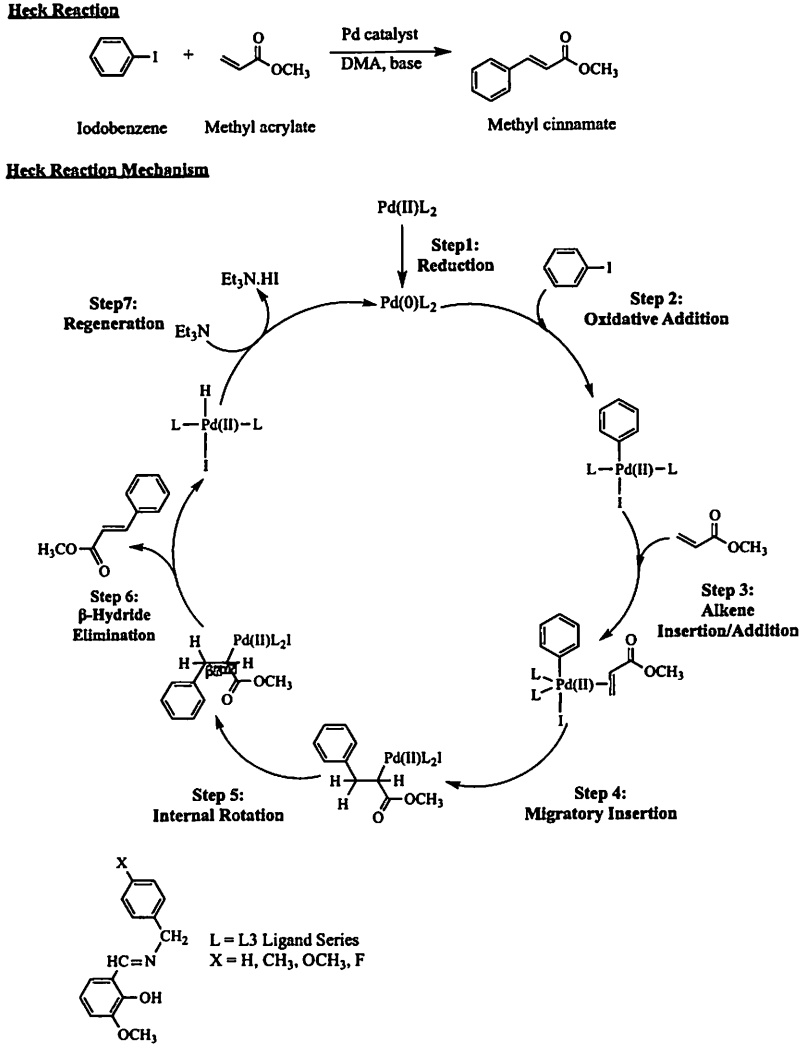

Figure 5: Proposed Mechanism of the Catalyzed Heck Reaction

However, in a phosphine-free system such as the current work, triethylamine that was used as a base can participate in the reduction of Pd(II) to Pd(0) as described by Beletskaya and Cheprakov (2000) [10]. In phosphine containing systems, hard nucleophiles such as hydroxide or alkoxide anions, water or acetate ion and amines are considered as reducing agents.

The oxidative addition of aryl halide to a Pd(0) complex (Step 2) is a key step in Heck reaction as well as other reactions with aryl halides used as substrates. Activation of ArX (iodobenzene) through oxidative addition produces a Pd(II) complex with aryl and halide ligands coordinated to the metal which next reacted with olefin forming an π-olefin complex (Step 3).

The olefin (methyl acrylate) bonded to palladium underwent a migratory insertion (Step 4) forming a new C-C bond with the neighbouring aryl moiety, followed by an internal rotation (Step 5) to align the aryl with the olefin to become co-planar and *cis* to one another. β-hydride elimination (Step 6) followed subsequently to remove the final product, arylated olefin (methyl cinnamate), from the coordination sphere of palladium. Palladium remained after this stage in the form of a hydrido complex and was converted back to the initial form by reaction with a base (Et3N) (Step 7) acting as HX acceptor [9].

CONCLUSION

A tetradentate, two bidentate ligands and their Pd(II) and Ni(II) complexes were successfully synthesized as confirmed by the characterization via elemental analysis, IR spectroscopy, NMR spectroscopy and magnetic susceptibility. The Schiff base ligands coordinated through phenolic oxygen and azomethine nitrogen atoms as bidentate and tetradentate chelates as indicated by the spectral data. Magnetic moment reading suggested a square planar geometry for all complexes. It was observed that $Pd(L1)_2$ and $Pd(L2)_2$ complexes displayed properties of good catalysts for the Heck reaction, with up to 100% conversion of iodobenzene after 6 h of reaction time at 100°C in inert conditions.

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