Symmetrical Palladium (II) N,N,O,O-Schiff Base Complex: Efficient Catalyst for Heck and Suzuki Reactions

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ABSTRACT

Palladium is arguably the most versatile and most widely applied catalytic metal in the field of fine chemicals due to its high selectivity and activity. Palladium catalyst offers an abundance of possibilities of carbon-carbon bond formation in organic synthesis. In this research, three different Schiff base ligands have been prepared by condensation reaction between appropriate aldehyde or ketone with amine namely 2,2-dimethyl-1,3-propanediamine in the molar ratio of 2:1. The corresponding palladium (II) Schiff base complexes were prepared through the reaction between the Schiff base ligand with palladium (II) acetate in a molar ratio 1:1. FTIR, ¹H-NMR and ¹³C-NMR spectroscopic data revealed that the ligands are N,N,O,O-tetradentate coordinated to the Pd atom through both the azomethine N atoms and phenolic O atoms. From X-ray Crystallographic analysis, it showed that the complex exists as square planar geometry. The synthesized palladium (II) Schiff base complexes were then subjected in catalytic Heck and Suzuki reaction of iodo benzene.

Keywords: Palladium (II) Schiff Base Complex; Heck Reaction; Suzuki Reaction

1. Introduction

Tetradentate Schiff base is one of the most extensively studied ligands in coordination chemistry. They can coordinate with a large number of transition metals, as well as possessing numerous interesting properties to related catalysis and electrochemistry. One type of tetrade ntate Schiff base ligand is N,N,O,O-tetradentate donor set which possesses many advantages such as facile approach, relative tolerance, readily adjusted ancillary ligands, and tunable steric and electronic coordination environments on the metal center [1,2]. Furthermore, they can be synthesized both simply and cheaply in a bulk amount which properties that become very important when industrial applications are being sought. Based on these unique properties, N,N,O,O-tetradentate Schiff base ligands and their transition metal complexes, as catalyst, have attracted significant attention being relevant for their application in agrochemical and radionuclide industries for cancer targeting, as model system for biological macromolecule [3]. In this research, we had prepared palladium (II) complexes coordinated with various types of Schiff base ligands. The synthesized palladium (II) Schiff base complexes were then subjected to Heck and Suzuki reactions in order to evaluate the activity of the catalyst.

2. Experimental

2.1. Chemicals and Instrumentation

All glass wares were dried overnight in oven. Commercial grade solvents were distilled according to normal procedures and dried over molecular sieves (4 Å) before used. All other chemicals were purchased from Aldrich, Merck and Fluka and were used without further purification and all reactions were conducted under inert condition. The melting point of the solid products was measured using Electrothermal Digital Melting Point Apparatus and was uncorrected. The CHN elemental analysis was determined using a Thermo Finnigan CE 125 CHN analyzer. Fourier Transform Infrared (FTIR) spectra of the synthesized samples were recorded on Shimadzu FTIR spectrometer in the range of 4000 - 400 cm⁻¹ as potassium bromide (KBr) disc. The proton ¹H and carbon ¹³C Nuclear Magnetic Resonance (NMR) spectra were recorded in CDCl₃ or DMSO on a Bruker Avance 300 MHz and 400 MHz spectrometer. The chemical shifts are reported in ppm relative to trimethylsilane (TMS). Single-crystal X-ray Crystallography was performed by using a Bruker SMART APEX2 CCD area detector diffractometer. Determination of products from the catalytic testing was carried out using gas chromatographic (GC) technique. Reaction mixture was analyzed by Agilent
Technologies GC equipped with a 30 m × 250 µm × 0.25 µm nominal capillary column (ULTRA-1.0.05, 100% dimethylpolysiloxane) using Flame Ionization Detection (FID).

2.2. Catalyst Preparation and Characterization

The stoichiometric amount of appropriate aldehyde or ketone derivatives (10 mmol) was added dropwise to a 2.2-dimethyl-1,3-propanediamine solution (0.51 g; ρ = 0.851; 5 mmol; 0.6 mL) in 10 mL dry ethanol. The mixture was refluxed (78°C) under nitrogen gas atmosphere after which the solid product had formed. The solid products of Schiff base ligands were then separated by vacuum filtration, washed with cold ethanol and dried in vacuum desiccator (25°C) for overnight. In order of complexation method, Schiff base ligand (5 mmol) was dissolved in a 10 mL of dry acetonitrile. Palladium (II) acetate (1.10 g; 5 mmol) which was dissolved separately in a 10 mL of dry acetonitrile was then added dropwise into the flask containing the ligand solution. The mixture was stirred and refluxed (90°C) under N_2 gas atmosphere after which the solid product had formed. The product was then separated by vacuum filtration, washed with cold acetonitrile and dried in a vacuum desiccator (25°C).

2.3. Physical Properties Elemental Carbon, Hydrogen and Nitrogen Analysis (CHN)

Schiff base Ligand 1: yellow needles solid (80%); m.p 111°C - 112°C; C (76.07) H (8.46) N (7.39); Schiff base Ligand 2: yellow needles solid (85%); m.p 95°C - 96°C; C (74.60) H (7.27) N (9.17); Schiff base Ligand 3: yellow solid (86%); m.p 132°C - 133°C; C (47.92) H (4.40) N (6.02); Complex 1: green solid (90%); m.p 132°C - 133°C; C (47.92) H (4.40) N (6.02); Complex 1: green solid (90%); m.p 341°C - 353°C; C (59.29) H (6.16) N (5.41); Complex 2: orange solid (80%); m.p 335°C - 336°C; C (55.46) H (5.02) N (6.18); Complex 3: orange solid (87%); m.p 305°C - 306°C; C (40.12) H (3.45) N (5.21).  

2.4. Fourier Transform Infrared (FTIR)

Analysis of FTIR shows that some significant changes of the important bands can be observed from FTIR spectra of free Schiff base ligands and their complexes. The displacement of C = N stretching frequencies from 1615 - 1631 cm⁻¹ in the free Schiff base ligands to lower values of 1606 - 1611 cm⁻¹ in the complexes indicating the coordination of azomethine nitrogen to the palladium metal. This result shows that the contribution of C = N stretching mode has been reduced as the electron pairs on a nitrogen atom is involved in bond formation with the palladium ion [4]. Besides, the broad OH band at >3400 cm⁻¹ in the free Schiff base ligands spectrum has totally disappeared in complexes spectrum, suggesting the strong participation of the OH group in chelate formation to the palladium atom via the deprotonation of phenolic hydrogen [5].

Schiff base ligand 1: 3434 (OH) 1615 (C = N) 1544, 1455 (C = C ar.) cm⁻¹; Schiff base ligand 2: 3440 (OH) 1631 (C = N) 1579, 1428 (C = C ar.) cm⁻¹; Schiff base ligand 3: 3446 (OH) 1631 (C = N) 1570, 1478 (C = C ar.) cm⁻¹; Complex 1: 1606 (C = N) 1528, 1478 (C = C ar.) cm⁻¹; Complex 2: 1611 (C = N) 1539, 1428 (C = C ar.) cm⁻¹; Complex 3: 1608 (C = N) 1526, 1461 (C = C ar.) cm⁻¹.

2.5. Nuclear Magnetic Resonance (NMR)

From ¹H-NMR data, the strong participation of the OH group in chelation through the deprotonation of phenolic hydrogen is indicated by the disappearance of the OH singlet signal at very downfield chemical shift in the free Schiff base ligand spectrum [5]. Meanwhile, based on ¹³C-NMR analysis, displacement of phenolic carbon (C-OH) and azomethine carbon (C = N) from upfield in non-coordinated ligands to the downfield in the complexes suggest the deprotonation and coordination of azomethine nitrogen atom and phenolic oxygen atom to the palladium atom. Besides that, the signals from aromatic carbons in the complexes have shifted from upfield to the downfield after complexation, which further supported the FTIR data in which the ligand is coordinated to the palladium atom through the azomethine nitrogen atom and the phenolic oxygen atom.

Schiff base ligand 1: ¹H-NMR 12.30 (C-OH) 6.57 - 7.40 (C-H ar.) ppm ¹³C-NMR 171.83 (C = N) 164.31 (C-OH) ppm; Schiff base ligand 2: ¹H-NMR 13.60 (C-OH) 6.88 - 7.37 (C-H ar.) ppm ¹³C-NMR 165.71 (C = N) 161.29 (C-OH) ppm; Schiff base ligand 3: ¹H-NMR 13.53 (C-OH) 6.87 - 7.43 (C-H ar.) ppm ¹³C-NMR 164.59 (C = N) 160.26 (C-OH) ppm; Complex 1: ¹H-NMR 6.39 - 7.26 (C-H ar.) ppm ¹³C-NMR 218.15 (C = N) 167.09 (C-OH) ppm; Complex 2: ¹H-NMR 6.49 - 7.25 (C-H ar.) ppm ¹³C-NMR 162.96 (C = N) 165.34 (C-OH) ppm; Complex 3: ¹H-NMR 6.72 - 7.48 (C-H ar.) ppm ¹³C-NMR 163.61 (C = N) 204.45 (C-OH) ppm.

2.6. X-Ray Crystallography Analysis

Suitable crystal of Schiff base ligand 1 for X-ray analysis was obtained by slow evaporation of the ligand solution in dichloromethane and n-hexane (1:1) mixture at low temperature (4°C). From analysis, the bond lengths of azomethine C8-N1, 1.295(2) Å and C15-N2, 1.286(2) Å in the molecule are consistent with normal C = N bond lengths as observed in other similar azomethine compound [6]. Besides, there are two intramolecular strong hydrogen bonding, N1-H1A and N2-H2A which contribute to the stability of the molecule (Figure 1).

Suitable crystal of palladium (II) complex 2 for X-ray analysis...
analysis was obtained by slow evaporation of a mixture solution of chloroform and n-hexane (1:1) at low temperature (4°C). As shown in Figure 2, the PdII metal centre has a cis-planar coordination by the two phenolic oxygen atoms and two imine nitrogen atoms. The Pd-O distances are in the range 1.979(3) - 2.008(4) Å with Pd-N distances 1.981(3) - 2.014(3) Å, which are typical of the square-planar PdII complex of Schiff base ligand [7]. The bond angles around PdII ions suggested that the complex has a distorted square-planar geometry as indicated by the angles O-Pd-O in the range 79.66(11) - 80.54(16), O-Pd-N in the range 92.14(13) - 92.95(11) and N-Pd-N in the range 94.92(12) - 94.95(15), deviating substantially from that expected for a regular square-planar geometry.

2.7. Catalytic Testing

2.7.1. Heck Reaction

Palladium (II) complexes were tested in Heck reaction between iodobenzene and methyl acrylate to produce methyl cinnamate. The general procedure is as follow: iodobenzene (0.20 g; $\rho = 1.830$; 0.11 mL; 1 mmol), methyl acrylate (0.17 g; $\rho = 0.955$; 0.18 mL; 2 mmol), base (2.4 mmol), palladium (II) Schiff base complex (1.0 mmol %; 0.01 mmol) and solvent N,N-dimethylacetamide, DMA (5 mL) were mixed together in a Radley’s 12-placed reaction carousel and was reflux for 24 hours whilst being purged with nitrogen. (Bases: Et3N, KF, K2CO3 and K3PO4; Temperature: 100°C, 120°C and 140°C).

2.7.2. Suzuki Reaction

Palladium (II) complexes were tested in Suzuki reaction between iodobenzene and phenylboronic acid to produce biphenyl. The general procedure is as follow: iodobenzene (0.20 g; $\rho = 1.830$; 0.11 mL; 1 mmol), phenylboronic acid (0.24 g; 2 mmol), base (2.4 mmol), palladium (II) Schiff base complex (1.0 mmol %; 0.01 mmol) and solvent DMA (5 mL) were mixed together in Radley’s 12-placed reaction carousel and was reflux for 24 hours whilst being purged with nitrogen. (Bases: Et3N, KF, K2CO3 and K3PO4; Temperature: 100°C, 120°C and 140°C).

3. Results and Discussion

3.1. Catalytic Heck Reaction Studies

The synthesized palladium (II) complexes were subjected in the catalytic Heck reaction of iodobenzene and methyl acrylate by using DMA solve + nt. Catalyst loading was kept to 1.0 mmol%, so as to give an expected TON of 100 if 100% conversion of iodobenzene was achieved.

3.1.1. Effect of Bases

The function of base in Heck reaction is to neutralize the acidic condition product by hydrogen halide in reductive elimination step and regeneration of catalyst to continue the catalytic cycles. In this study, four types of bases have been used; Et3N, NaHCO3, Na2CO3 and NaOAc, in order to study the effect of bases towards the percentage conversion of iodobenzene. Some organic bases act as a source of hydride and promote the hydrogenation of aromatic compounds. Due to this property or effect, there is usually a competition between vinylation and hydrogenation in the Heck reaction and the selectivity pattern will be influenced by the type of base used. As reported by Kiviaho [8], selectivity for a vinylation product like methyl cinnamate is high when Et3N is the base used in the reactions which correspond to our studies in which Et3N gives 100% conversion of iodobenzene with complex 1 and more than 90% conversion with the other two complexes. In contrast, the low conversion achieved for NaHCO3 is probably due to the insolubility of NaHCO3 in the organic solvent used.

3.1.2. Effect of Temperature

Reaction temperature assists in the activation of the iodobenzene which usually occurs at reaction temperature more than 100°C. However, the reaction temperature must be carefully controlled to avoid the formation of palladium black which will inhibit the catalytic cycle if the temperature is too high. In order to study the effect of temperature on the conversion of iodobenzene, the catalytic reaction temperatures were varied at 100°C, 120°C and 140°C using Et3N as base. From the results, it
showed that the best reaction temperature was found to be 140°C, which all the complexes gave 100% conversion. Among all of the three complexes, complex 1 still maintained with the highest conversion even at lower temperature than 120°C. The higher activities of this complex may be explained in terms of ligand effect. The bulkier and more electron-rich ligand is thought to accelerate the oxidative addition of aryl halides and reductive elimination steps, so that the catalyst regeneration in catalytic cycles is faster [9]. However from our observation, the Heck reaction using temperature greater than 140°C was avoided due to the formation of palladium black, which therefore terminated the catalytic cycle.

3.2. Catalytic Suzuki Reaction Studies

The synthesized palladium (II) complexes were subjected in the catalytic Suzuki reaction of iodobenzene and phenylboronic acid by using DMA solvent. Catalyst loading was kept to 1.0 mmol%, so as to give an expected TON of 100 if 100% conversion of iodobenzene was achieved.

3.2.1. Effect of Bases

In this study, four types of bases have been used; Et₃N, KF, K₂CO₃, and K₃PO₄, in order to study the effect of bases towards the percentage conversion of iodobenzene. The type of bases was chosen based on their performance in Suzuki reaction to form similar biphenyl products [10, 11]. In Suzuki reaction, the presence of base is needed since the cross coupling via transmetallation step is difficult due to the low nucleophilicity of organic groups (R) on the boron atom. The role of the base is explained by activation of palladium (II) complex or boranes. According to Kotha [12], the base is involved in the coordination sphere of the palladium to activate the palladium catalyst by formation of intermediate (alkoxo) palladium species which is known to accelerate the transmetallation step. Besides, the nucleophilicity of organic groups is enhanced by quaternization of the boron with bases which facilitates transmetallation. From our observation, the Et₃N is the most favourable one compared to other bases. Most probably, the Et₃N mixed well with the reaction mixture since it exists in liquid form and easily interferes in coordination sphere of palladium complex.

3.2.2. Effect of Temperature

In order to study the effect of temperature on the conversion of iodobenzene, the catalytic reaction temperatures were varied at 100°C, 120°C, and 140°C with Et₃N as base. From the results, it showed that the best reaction temperature was found to be 140°C, where 100% conversion was achieved after 24 hours reaction by using complex 1. Among three complexes, the complex 2 was the worst performer with only giving 5% conversion compared to 46% conversion with complex 1 at 100°C reaction temperature. This can be explained by the presence of the methyl group on the carbon of the azomethine group of complex 1 which dramatically increases the rate of reaction. This may be due to the electronic effect of a methyl group, which ultimately increases the electronic environment around the palladium centre [13]. The electronic properties on palladium centre facilitate the interruption of palladium catalyst in aryl or vinyl halides bonding in the oxidative addition steps on the catalytic cycles and ultimately increasing the rate of reaction.

4. Conclusion

In this research, three palladium (II) Schiff base complexes have been successfully synthesized and characterized. Based on the elemental CHN analysis, FTIR, 1H, 13C-NMR spectral studies and X-ray crystallographic analysis, we suggest that the Schiff base ligands acted as N,N,O,O-tetradeinate ligand and have bonded to the palladium atom through the azomethine nitrogen atom (C = N) and the phenolic oxygen atom. These complexes were then subjected in catalytic Heck and Suzuki reaction of iodobenzene. The results showed that the complex 1 gives conversion up to 100% using triethylamine as base at temperature 120°C - 140°C for both Heck and Suzuki reaction of iodobenzene. The higher activities of the complex 1 may be explained in term of ligand effect. The oxidative addition is known as the rate determining step in cross coupling reaction, thus, electron-rich ligands are usually needed to make the palladium metal easily oxidized. The presence of the methyl group on the carbon azomethine (C = N) increased the electronic environment around the palladium centre which ultimately, accelerates the oxidative addition of aryl halides and reductive elimination steps.

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REFERENCES


