

N,N'-bis-(5-METHYL-METHYLSALICYLIDENE)-2,2-DIMETHYLPROPANE-1,3-DIAMINE PALLADIUM(II) : CATALYST FOR HECK REACTION

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Abstract

A new palladium(II) complex of a Schiff base ligand, "N,N'-bis-(5-methyl-methylsalicylidene)-2,2-dimethylpropane-1,3-diamine" has been synthesized and characterized by analytical and spectroscopic data such as FTIR, ¹H and ¹³C NMR spectroscopy, X-ray crystallography and CHN elemental analysis. The ligand acted as a N,N,O,O tetradentate ligand in which the metal is coordinated to the azomethine nitrogen and phenolic oxygen. The palladium complex was tested as a catalyst in the Heck reaction of iodobenzene with methyl acrylate in the presence of sodium hydrogen carbonate as base in N,N-dimethylacetamide at reflux temperature (120°C). The activity of the catalyst was monitored by ¹H NMR.

Abstrak

Kompleks palladium(II) dengan ligan bes Schiff, "N,N'-bis-(5-metil-metilsalisiliden)-2,2-dimetilpropan-1,3-diamina" yang baru telah berjaya disintesis dan dicari melalui data analisis dan data spektroskopi seperti FTIR, RMN ¹H dan ¹³C spektroskopi, Kristalografi sinar-X dan analisis unsur CHN. Ligan ini berfungsi sebagai ligan tetradentat N,N,O,O dan terkoordinat kepada logam pusat melalui kedua-dua atom nitrogen azometina dan kedua-dua atom oksigen fenolik. Kompleks palladium ini telah diuji sebagai mangkin dalam tindakbalas Heck antara iodobenzena dan metil akrilat dalam N,N-dimetilasetamida dengan kehadiran bes natrium hidrogen karbonat pada suhu refluks (120°C). Aktiviti pemangkinan ini dipantau menggunakan RMN ¹H.

Introduction

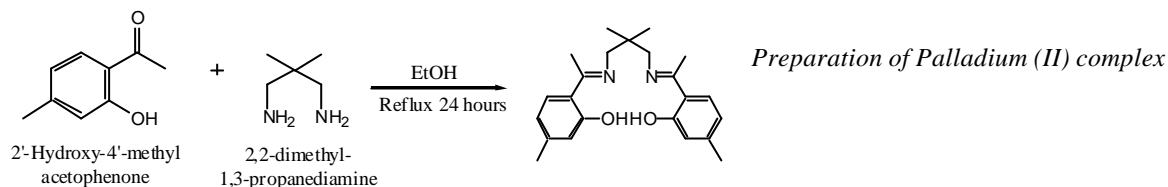
Active and well designed Schiff base ligands are considered as 'privileged ligands' because they are easily prepared by the condensation between aldehydes or ketones and amines and are able to stabilize different metals in various oxidation states. Metal complexes of Schiff bases have been widely studied due to the versatility of their steric and electronic properties, which can be fine-tuned by choosing the appropriate amine precursors and ring substituents [1]. N,O- bidentate and N₂O₂ -tetradentate ligands (soft and hard donor) possess many advantages such as facile approach, relative tolerance, readily adjusted ancillary ligands, and tunable steric and electronic coordination environments on the metal center [2]. Because of these values, tetradentate N₂O₂ ligands and their transition metal complexes, act as catalyst. Thus, this group of compounds have attracted significant attention being relevant to their application in agrochemical and pharmaceutical industries.

Palladium compounds are well known as very important reagent and catalyst in many organic reactions because of their stability and easy handling. Palladium(II) complexes with Schiff base ligands were found to be efficient homogeneous catalyst for the hydrogenation of functional groups like -NO₂, -NH₂OH, >C=C<, >C=N-, and >C=O under mild reaction conditions in moderate coordinating solvents [3-4]. However, the ability of palladium Schiff base complexes to act as catalysts in Heck reactions has not been thoroughly investigated. In this paper, we report the preparation of the new palladium(II) Schiff base complex along and their catalytic activity in Heck reaction.

Experimental

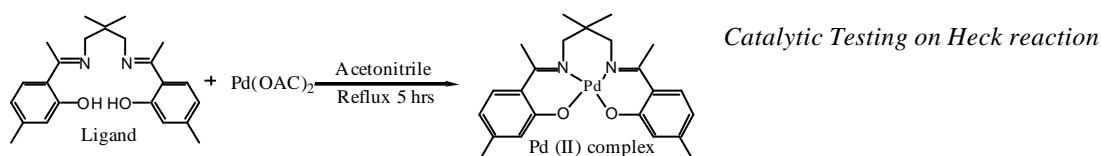
Preparation of *N,N'*-bis-(5-methyl-methylsalicylidene)-2,2-dimethylpropane-1,3-diamine ligand

The stoichiometric amount of 2'-hydroxy-4'-methylacetophenone (10 mmol, 1.50 g) is added dropwise to 2,2-dimethyl-1,3-propanediamine solution (5 mmol, 0.51g) in 10 ml dry ethanol (Scheme 1). The contents were refluxed in a three necked round bottom flask under N_2 atmosphere overnight, which afforded yellow precipitate then was separated by vacuum filtration, washed and dried in a vacuum desiccator. It was then recrystallized from a mixture of solvents (chloroform and hexane) with ration 1:1 and suitable crystal for X-ray crystallography was collected by slow evaporation of the solvent at below room temperature (4°C).



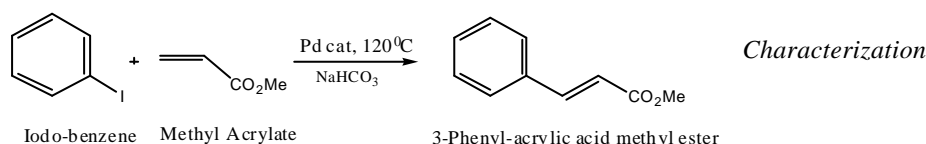
Scheme 1: Preparation of Schiff-base Ligand

Scheme 2 shows the preparation of palladium(II) complex. The ligand *N,N'*-bis-(5-methyl-methylsalicylidene)-2,2-dimethylpropane-1,3-diamine (0.5 mmol, 0.18g) was dissolved in 10 ml of dry acetonitrile in a three necked round bottom flask. At the same time, palladium(II) acetate (0.5 mmol, 0.11g) was dissolved separately in 10 ml of dry acetonitrile. Then, the metal solution was added dropwise into the flask containing the ligand solution. The contents were refluxed under N_2 atmosphere for 5 hours. The excess solvent was evaporated at reduced pressure utilising a rotary evaporator and kept in a vacuum desiccators.



Scheme 2: Preparation of palladium(II) complex

Iodobenzene (1 mmol, 0.20g), methyl acrylate (3 mmol: 0.3 ml), sodium hydrogen carbonate (2.4 molar equiv.), palladium catalyst (1 mol %) and solvent *N,N*-dimethylacetamide (15 ml) were mixed together in Radley's 12-placed reaction carousel whilst purged with nitrogen and heated to 120°C for 48 hours. The reaction was monitored at regularly intervals by ^1H NMR (Scheme 3).



Scheme 3: Heck reaction catalyzed by Pd catalyst

All glass wares were dried overnight in an oven. Commercial grade solvents were distilled according to normal procedures and dried over molecular sieves (4\AA) before use. All other chemicals were purchased from Aldrich, Merck or Fluka and were used without further purification and all reactions were conducted under nitrogen atmosphere.

The melting point of the solid products was measured using Electrothermal Digital Melting Point Apparatus and were uncorrected. FTIR spectra of the synthesized samples were recorded on a Shimadzu FTIR spectrometer in the range of $4000\text{--}400\text{ cm}^{-1}$ as potassium bromide (KBr) disc. The proton (^1H) and carbon (^{13}C) NMR spectra were recorded in CDCl_3 on a Bruker Avance 300MHz spectrometer. The chemical shifts are reported in ppm and trimethylsilane (TMS) is used as reference compound. The elemental analysis was carried out using Thermo Finnigan CE 125 CHN analyzer. The structure of the compound was determined using single crystal X-ray diffraction techniques utilising a Bruker SMART APEX CCD.

Results and Discussion

Physical Measurements

The new schiff-base ligand *N,N'*-bis-(5-methyl-methylsalicylidene)-2,2-dimethylpropane-1,3-diamine was obtained as a yellow solid form, yield: 1.1 g (60%), melting point 111-112°C, CHN elemental analysis: $C_{23}H_{30}N_2O_2$; Experiment: C 76.07%, H 8.46%, N 7.39 (Calculated: C 75.37%, H 8.25%, N 7.64%). The palladium complex of this ligand was obtained as a green solid, yield 0.21g (90%), melting point 341-343°C, CHN elemental analysis: $C_{23}H_{28}N_2O_2Pd$; Experiment: C 59.29%, H 6.16%, N 5.11% (Calculated: C 58.66%, H 5.99%, N 5.95%).

Fourier Transform Infra Red (FTIR) analysis

Figure 1 shows the FTIR spectra of ligand and complex. The FTIR spectrum of a starting material; 2,2-dimethyl-1,3-propanediamine shows two bands at 3377 cm^{-1} and 3303 cm^{-1} , which are characteristic of the NH_2 stretching mode while the 2'-hydroxy-4'-methylacetophenone shows a strong absorption band at 1637 cm^{-1} which is assigned to the C=O stretching band. From FTIR spectrum of Schiff base ligand, new strong and sharp absorption band can be observed at 1613 cm^{-1} which is assigned to azomethine group (C=N) stretching mode. Besides, the absorption bands for NH_2 stretching mode and C=O stretching mode have totally disappeared confirming the formation of azomethine compound.

The FTIR spectrum of palladium(II) complex shows that the absorption band for C=N stretching mode was shifted from 1612 cm^{-1} in free ligand to the strong and sharp absorption band at 1599 cm^{-1} in the complex indicating that the nitrogen atom is involved in bond formation with the metal ion. Besides, the broad O-H band at 3428 cm^{-1} in the ligand has disappeared in the complex, suggesting the strong participation of phenolic proton to the metal centre. Table 1 lists significant FTIR bands of starting materials, ligands and complex.

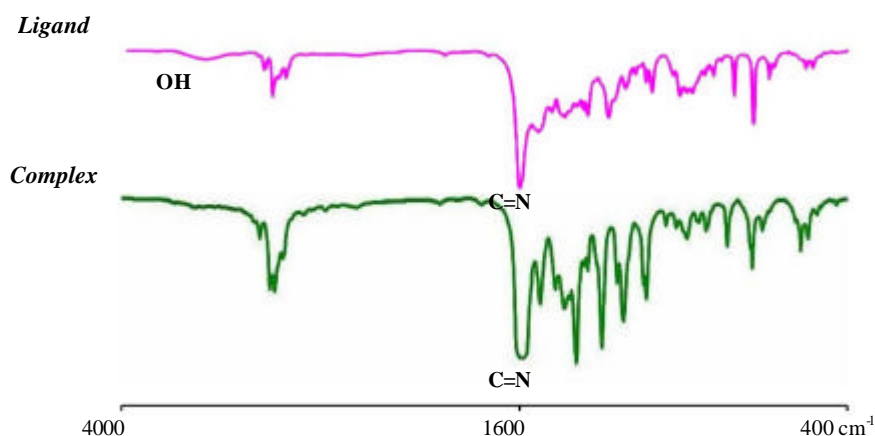


Figure 1: FTIR spectrum of ligand and complex

Table 1: Significant FTIR bands of starting materials, ligand and complex

Assign.	Starting materials (cm^{-1})		Ligand (cm^{-1})	Pd complex (cm^{-1})
	2,2-dimethyl-1,3-propanediamine	2'-hydroxy-4'-methylacetophenone		
NH_2	3377 and 3303	-	-	-
C=O	-	1637	-	-
C=N	-	-	1613	1599
O-H	-	3421	3428	-

Nuclear Magnetic Resonance (NMR) Spectroscopy

According to the 1H -NMR spectrum (Figure 2) for the ligand, the proton signal of the phenolic proton (Ar-OH) in $CDCl_3$ appeared at very downfield δ 12.30 as a singlet. However, it disappeared in the 1H -NMR spectrum for the complex due to the participation of Oh group in chelating to metal ion through proton displacement [5].

Besides, the displacement of chemical shifts of aromatic proton to upper field, from δ 6.60-7.40 in free ligand to δ 6.42-7.26 in the complex confirming the coordination of azomethine nitrogen and oxygen atom to the palladium atom.

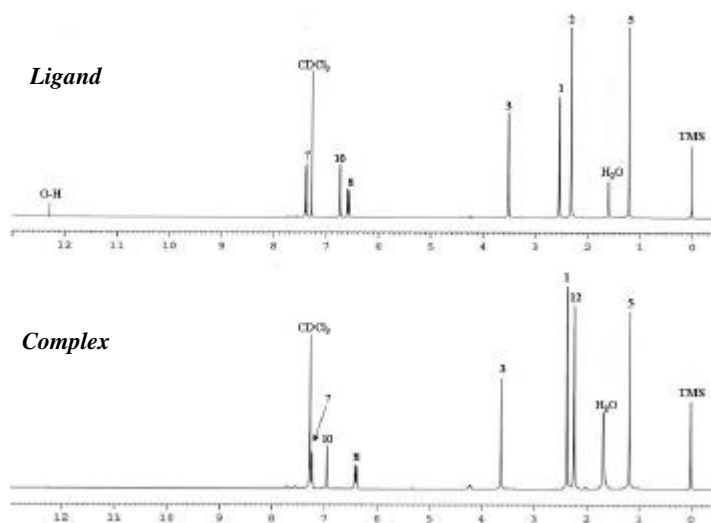


Figure 2: ^1H NMR spectrum of ligand and complex

From the ^{13}C NMR spectrum (Figure 3), showed the displacement of azomethine carbon (C=N) from δ 171.83 in the non-coordinated ligand to the down field δ 218.15 in the complex due to the coordination of azomethine nitrogen atom to the palladium metal.

This supported the FTIR data in which the ligand is coordinated to the palladium atom through the nitrogen atom of C=N and the oxygen atom of the phenolic proton. The rest of carbon signal for both ligand and complex are shown in Table 2.

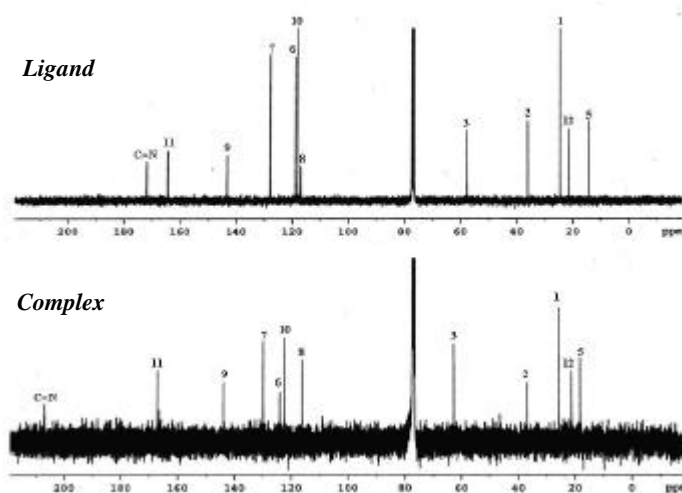


Figure 3: ^{13}C NMR spectrum of ligand and complex

Table 2: Significant ^1H and ^{13}C spectral data of ligand and complex

Assignments	Chemical shift, δ ppm			
	Ligand		Pd complex	
	^1H	^{13}C	^1H	^{13}C
-CH ₃ (5)	1.27 (s)	14.26	1.19 (s)	18.26
-CH ₃ (12)	2.31 (s)	21.37	2.16 (s)	21.14
-CH ₃ (1)	2.52 (s)	24.61	2.37 (s)	25.82
-C(2)	-	35.97	-	36.80
-CH ₃ (3)	3.51 (s)	57.62	3.63 (s)	62.69
-C(6)	-	116.99	-	124.14
-CH(Ar)(8)	6.57-6.60 (d)	118.15	6.39-6.42 (d)	116.28
-CH(Ar)(10)	6.74 (s)	118.91	6.95 (s)	122.35
-CH(Ar)(7)	7.37-7.40 (s)	127.84	7.23-7.26 (d)	129.81
-C(9)	-	143.23	-	143.92
Ar-OH	12.30 (s)	164.31	-	167.09
C=N	-	171.83	-	218.15

Single-crystal X-ray Crystallography

Suitable crystals for ligand were grown by slow evaporation from solution of dichloromethane and *n*-hexane at 4°C. The Ortep plot for *N,N'*-bis-(5-methyl-methylsalicylidene)-2,2-dimethylpropane-1,3-diamine is shown in Figure 4 and the selected bond and angle is listed in Table 3.

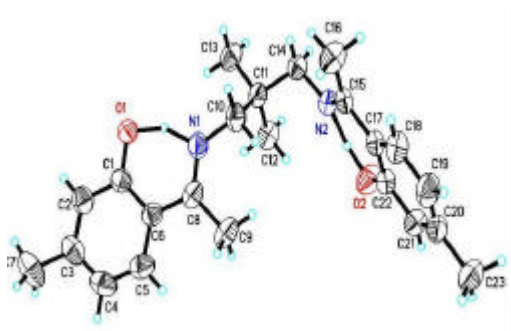


Figure 4: Perspective view of *N,N'*-bis-(5-methyl-methylsalicylidene)-2,2-dimethylpropane-1,3-diamine

Table 3: Selected bond distance (\AA) and angles ($^\circ$) for *N,N'*-bis-(5-methyl-methylsalicylidene)-2,2-dimethylpropane-1,3-diamine

Assignments	Bond distance, \AA
N(1)-C(8)	1.295(2)
N(2)-C(15)	1.286(2)
N(1)-H(1A)	1.27(3)
N(2)-H(2A)	1.42(3)

From analysis showed that bond lengths of azomethine C8=N1, 1.295 (2) \AA and C15=N2, 1.286 (2) \AA in the molecule are consistent with normal C=N bond lengths [6]. There are exist two intramolecular strong hydrogen bonding, N1-H1A and N2-H2A which contribute to the stability of the molecule.

Based on FT IR, ^1H NMR, ^{13}C NMR spectroscopic studies and the structure of the single crystal X-ray crystallography new Schiff base ligand (Figure 5) and the palladium complex (Figure 6) are shown below.

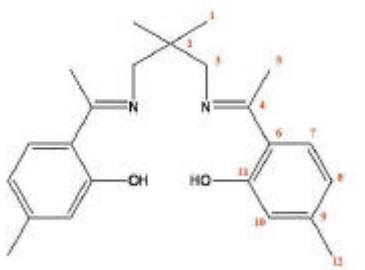


Figure 5: Structure of N,N'-bis-(5-methyl-methylsalicylidene)-2,2-dimethylpropane-1,3-diamine ligand

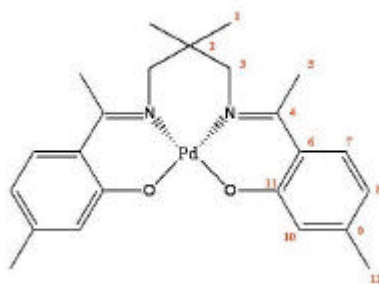


Figure 6: Structure of palladium(II) complex of N,N'-bis-(5-methyl-methylsalicylidene)-2,2-dimethylpropane-1,3-diamine ligand

Catalytic Studies

The palladium complex that has been prepared in this research was tested as a catalyst in the Heck reactions of iodobenzene with methyl acrylate in the presence of sodium hydrogen carbonate as base in N,N-dimethylacetamide at reflux temperature (120°C). Sodium hydrogen carbonate was chosen as a base due to the capability of this base to give highest conversion compare to other bases [7]. Catalytic loading was kept to 1.0 mol%, so as to give an expected turnover number of 100 if 100% conversion was achieved. The reaction was monitored by % conversion of the aryl iodide starting material from ^1H NMR [8]. The result has been summarized in the Table 4. All these data indicate that the palladium complex may be utilised as a catalyst in the Heck reaction.

Table 4: Activities of palladium catalyst on the Heck reaction between Iodobenzene and methyl acrylate

Catalyst	% Conversion	
	After 24 hours	After 48 hours
Palladium complex	83	100
Without catalyst	0	0

Conclusion

New Schiff-base N_2O_2 tetradentate ligand, "N,N'-bis-(5-methyl-methylsalicylidene)-2,2-dimethylpropane-1,3-diamine" has been successfully synthesized by condensation reaction between 2'-hydroxy-4'-methylacetophenone and 2,2-dimethyl-1,3-propanediamine. The complex was prepared by heating an equimolar amount of Schiff base ligand and palladium(II) acetate. The coordination of palladium metal ion is through the azomethine nitrogen and phenolic oxygen. This complex has been tested in Heck reaction and showed % 100 conversion after 48 hours and achieved TON = 100 mmol products/ mmol Pd.

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