

SYNTHESIS AND CHARACTERISATION OF PALLADIUM(II) SCHIFF BASE COMPLEXES AND THEIR CATALYTIC ACTIVITIES FOR SUZUKI COUPLING REACTION

(Sintesis dan Pencirian Palladium(II) Bes-Schiff Kompleks dan Aktiviti Sebagai Pemangkin untuk Tindak Balas Suzuki)

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Abstract

The syntheses, physico-chemical and spectroscopic characterization of salicylaldehyde-type Schiff-base ligands (Hapbam, HapFbam) and their novel mononuclear Pd(II) complexes (HapbamPd, HapFbamPd) are reported herein. The compounds were characterized by elemental analysis, FT-IR, ¹H NMR as well as magnetic susceptibility measurements. X-ray crystallography investigation of HapbamPd revealed that the Schiff bases behave as singly charged bidentate ligands, coordinating to the palladium centre in the ratio of ligand:metal of 2:1. The geometry of the palladium centre was a perfect square planar. The catalytic potential of the Pd(II) complexes for Suzuki coupling reaction were investigated and monitored using GC. It was observed that both Pd(II) complexes displayed properties of good catalysts for the reaction, indicated by more than 90% conversion of the starting materials to the biphenyl product after 12 hours of reaction time at 100°C in inert conditions. The catalytic activity was compared with that of commercially available palladium(II) acetate.

Keywords: Schiff base, Palladium(II), Suzuki reaction

Abstrak

Sintesis, fizik-kimia dan pencirian spektroskopi ligands-bes Schiff salicylaldehyde jenis (Hapbam, HapFbam) dan novel mononuklear mereka Pd(II) kompleks (HapbamPd, HapFbamPd) dilaporkan di sini. Sebatian dicirikan oleh unsur analisis, FT-IR, ¹H NMR serta ukuran kerentanan magnet. Potensi sebagai pemangkin Pd(II) kompleks bagi tindak balas gandingan Suzuki disiasat dan dipantau menggunakan GC. Diperhatikan bahawa kedua-dua Pd(II) kompleks dipaparkan hartanah pemangkin yang baik untuk tindak balas yang ditunjukkan oleh lebih daripada 90%. Penukaran bahan permulaan untuk produk terpoliklorin selepas 12 jam masa tindak balas pada 100°C dalam keadaan lengai. Aktiviti pemangkin dibandingkan dengan palladium(II) asetat yang boleh didapati secara komersial.

Kata kunci: bes-Schiff, Palladium(II), tindak balas Suzuki

Introduction

Schiff bases are an important class of ligands in coordination chemistry and have studied extensively [1] as they are selective and sensitive toward various metal ions. Metal complexes of Schiff bases have found diverse applications in addition to interesting structural chemistry. Metal complexes containing Schiff-base ligands also have shown attractive properties such as antibacterial behaviour, exhibit interesting magnetic properties and catalytic oxidation [2].

Palladium is a versatile metal for homogeneous and heterogeneous catalysis [3,4]. A large number of carbon-carbon bond forming reactions such as the Heck and Suzuki coupling are facilitated by catalysis with palladium compounds. During the past 10 years, there has been considerable interest in the development of new phosphorus free palladium catalysts for higher activity, stability and substrate tolerance that allow reactions to be carried out under milder reaction conditions.

This paper aims to report the synthesis and characterization bidentate Schiff base ligands and their novel palladium(II) complexes and also their catalytic activities for Suzuki coupling reaction, as shown in Figure 1.

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. The melting points were determined using Buchii-B454. IR spectra were obtained as potassium bromide (KBr) pellets using a Perkin-Elmer model 1750X FTIR spectrophotometer. ^1H NMR spectra were recorded on a Bruker Varian-300MHz spectrometer with chemical shifts given in ppm from the internal TMS or centre line of CDCl_3 . Magnetic measurements were carried out using the Guoy method with $\text{Hg}[(\text{Co}(\text{SCN})_4]$ as calibrant on Sherwood Auto Magnetic Susceptibility Balance. Molar conductance of the palladium(II) complexes were determined in CHCl_3 ($\sim 10^{-3}$ M) at room temperature using a Mettler Toledo Inlab 730 conductivity meter. A single-crystal x-ray diffraction investigation was carried out on Bruker SMART APEX CCD area-detector diffractometer.

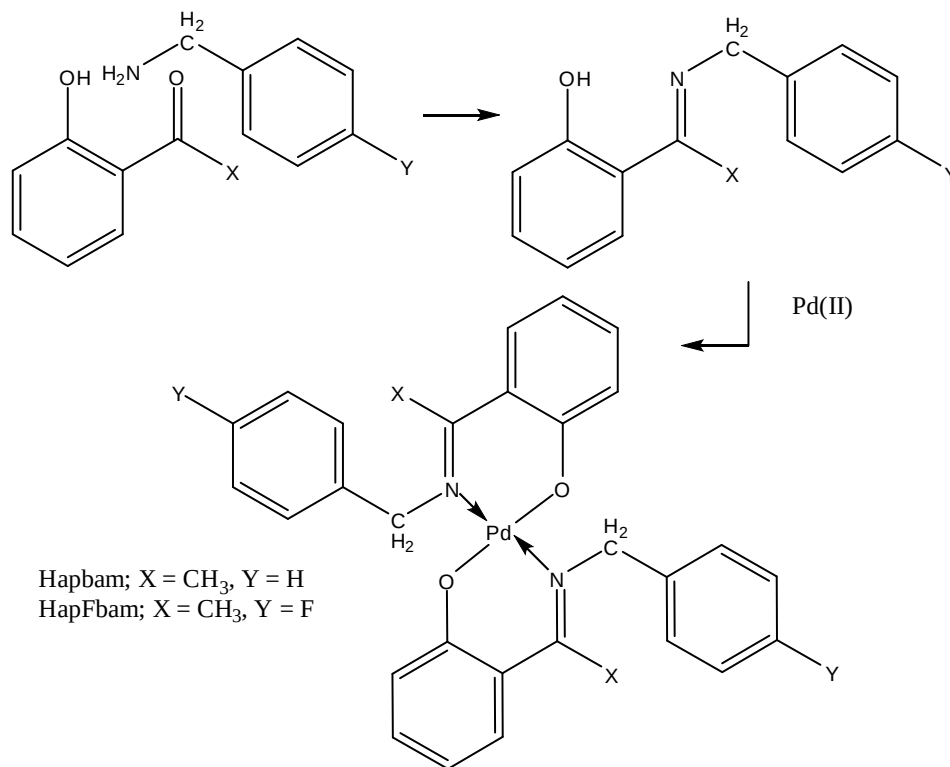


Figure 1: Synthesis scheme of the Schiff base ligands and their Pd(II) complexes

Synthesis of Ligands

(a) Synthesis of Hapbam

An ethanoic solution of 2-hydroxyacetophenone (50 mmol, 6.8126 g) was heated to boiling. Benzylamine (50 mmol, 5.3662 g) was also boiled in ethanol (10 mL). The two hot solutions were mixed in a round-bottomed flask to give a bright yellow solution. The mixture was heated under reflux for one hour. More yellow solid was appeared when the solution was allowed to cool slowly to room temperature. The solid was filtered off, washed with ice-cold ethanol and and air-dried at room temperature with 76.3% yield.

(b) Synthesis of HapFbam

An ethanoic solution of 2-hydroxyacetophenone (50 mmol, 6.8112 g) was heated to boiling. 4-fluorobenzylamine (50 mmol, 6.2647 g) was also boiled in ethanol (10 mL). The two hot solutions were mixed in a round-bottomed flask to give a bright yellow solution. Upon cooling, bright yellow solid was appeared without heated under reflux. The solid was filtered off, washed with ice-cold ethanol and air-dried at room temperature with 82.7% yield.

Synthesis of Complexes

(a) Synthesis of HapbamPd

The ligand, Hapbam, (5 mmol, 1.1271 g) was dissolved in hot ethanol (20 mL) in a round-bottomed flask. Palladium(II) acetate (2.5 mmol, 0.5618 g) was dissolved separately in hot ethanol (40 mL) and added into the flask containing the ligand solution. The mixture was stirred and refluxed for 5 hours upon which green solid was formed. It was isolated by gravity filtration, washed with ice-cold ethanol and air dried at room temperature. The solid product was recrystallized from chloroform yielding yellow crystals with 87.8% yield.

(b) Synthesis of HapFbamPd

The ligand, HapFbam, (2 mmol, 0.4877 g) was dissolved in acetonitrile (30 mL) in a round-bottomed flask. Palladium(II) acetate (1 mmol, 0.2251 g) was dissolved separately in acetonitrile (20 mL) and added into the flask containing the ligand solution. The mixture was stirred and refluxed 5 hours upon which turmeric yellow solid was formed. It was isolated by gravity filtration, washed with ice-cold acetonitrile and air dried at room temperature with 48.5% yield.

General Procedure for The Suzuki Coupling Reaction

The general procedure was as followed: iodobenzene (1 mmol, 0.2 g), phenylboronic acid (0.2 mmol, 0.24 g), triethylamine (2.4 mmol, 0.24 g), Et₃N, palladium(II) Schiff base (1 mmol%) (HapbamPd, HapFbamPd) and solvent DMA (10 mL) were mixed together in Radley's 12-placed reaction carousel and refluxed (100°C) whilst being purged with nitrogen. The reaction was monitored regularly using GC.

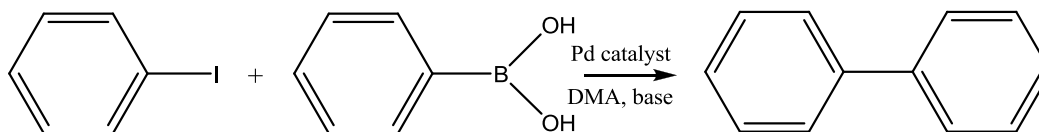


Figure 2: Suzuki reaction catalyzed by Pd catalysts

Results and Discussion

Elemental Analysis

The analytical data of the compounds are presented in Table 1 and are in good agreement with the theoretical values.

Table 1: Analytical data for the Hap-ligands series and their complexes

Ligand/Complex	Empirical Formula	Colour	Melting Point (°C)	Elemental Analysis (%)			Λ_M^a
				(found)			
				C	H	N	
Hapbam	C ₁₅ H ₁₅ NO	Yellow	120-122	79.97 (79.42)	6.71 (6.36)	6.22 (6.15)	-
HapbamPd	C ₃₀ H ₂₈ N ₂ O ₂ Pd	Moss green	248-257	63.82 (64.58)	4.59 (4.97)	5.32 (4.94)	0.00
HapFbam	C ₁₅ H ₁₄ FNO	Yellow	140-142	74.06 (73.65)	5.80 (5.46)	5.76 (5.78)	-
HapFbamPd	C ₃₀ H ₂₆ F ₂ N ₂ O ₂ Pd	Turmeric yellow	235-237	60.97 (60.81)	4.43 (4.49)	4.74 (4.66)	0.00

Based on the elemental analysis results, the structures of the ligands and palladium(II) complexes were indicated to be as those predicted (Figure 1). The melting points of the parent ligands were typically lower than those of the complexes.

FTIR Spectroscopy

Infrared spectra of ligands and complexes are presented in Figure 3 and 4 while the data of the compounds are presented in Table 2. The strong bands around 1619-1586 cm⁻¹ are assignable to $\nu(\text{C}=\text{N})$ while the $\nu(\text{Pd}-\text{O})$ and $\nu(\text{Pd}-\text{N})$ bands in Pd(II) complexes appeared in the regions of 700-500 cm⁻¹ and 440-500 cm⁻¹, respectively. The IR frequencies are in agreement with those previously reported [5]. Comparing the $\nu(\text{C}=\text{N})$ and $\nu(\text{C}-\text{O})$ values for Hapbam/HapbamPd and HapFbam/HapFbamPd, it was observed generally that the peaks experienced a redshift i.e. shifted to a lower frequency upon complexation to Pd(II). The shifting indicated that both the N and O donor atoms in the ligands were involved in the chelation to the metal centre. The nature of this interaction is such that it reduces the electron density on the C=N and C-N moieties as shown by the reduction of the frequency implying the reducing strength of the C=N and C-N bonds. It is also observed that the C-OH peaks in both the ligands disappeared upon complexation with Pd that indicated the participation of the phenolic oxygen on bonding with the metal centre. The phenolic protons were replaced by the Pd²⁺ cations forming an ionic bond of O-Pd.

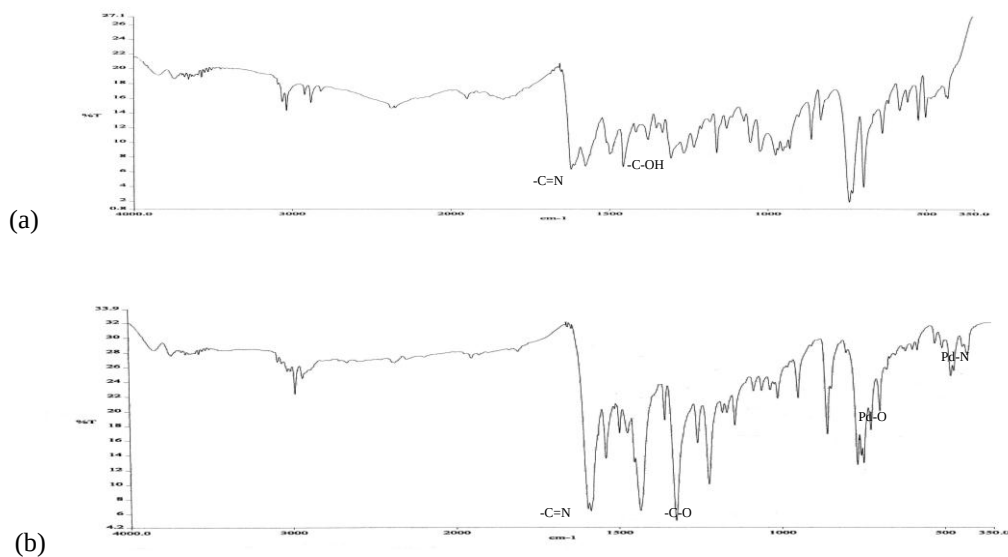


Figure 3: Infrared spectra of (a) Hapbam and (b) HapbamPd

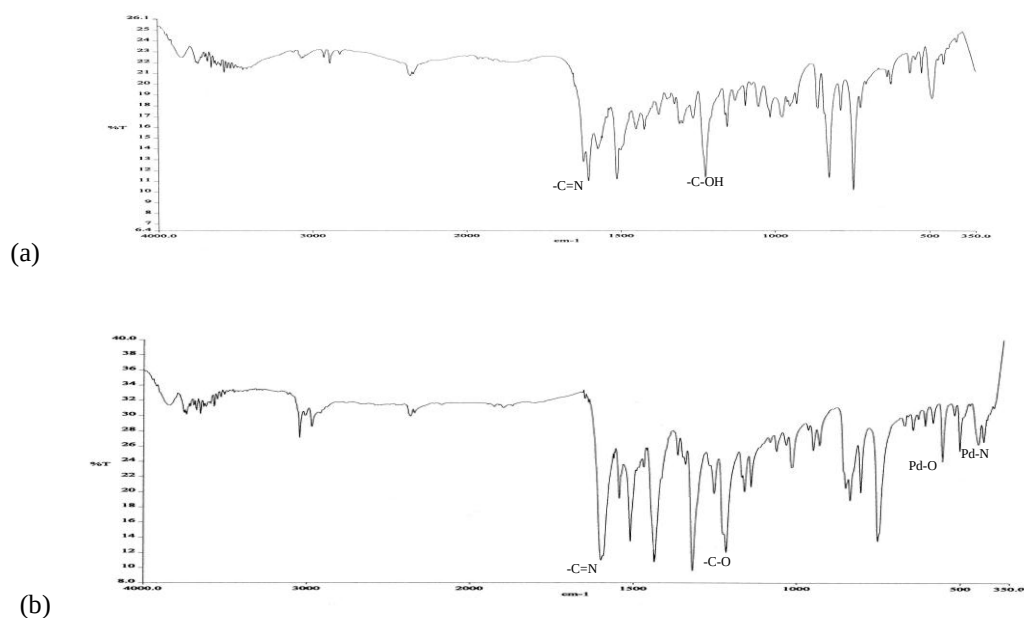


Figure 4: Infrared spectra of (a) HapFbam and (b) HapFbamPd

Table 2: Infrared spectra data for ligands and palladium(II) complexes

Ligand/Complex	Frequency (cm ⁻¹)					
	C≡N	C-N	-CH	C-OH	Pd-O	Pd-N
Hapbam	1619 (s)	1376 (w)	2878 (w)	1304 (w)	-	-
HapbamPd	1586 (s)	1355 (w)	2977 (w)	-	695 (w)	476 (w)
HapFbam	1604 (s)	1310 (w)	2879 (w)	1226 (s)	-	-
HapFbamPd	1598 (s)	1319 (s)	2969 (w)	-	556 (w)	446 (w)

Nuclear Magnetic Resonance (NMR) Spectroscopy

The ¹H NMR data and spectra of Hapbam and HapFbam are presented in Table 3 and Figure 5 and 6, respectively. The OH peaks in Hapbam and HapFbam that were expected to appear in the downfield region (10-14 ppm) [6] of the spectra were not observed as the labile phenolic ¹H may have undergone a rapid exchange with the deuterium in the solvent. The presence of the methyl groups attached to the C≡N was confirmed by the singlet appearing at 2.41 ppm. The ¹H of methylene and aromatic moieties were observed in 4.75-4.80 and 6.76-7.57 ppm, respectively.

Table 3: Significant ^1H NMR spectral data for ligands

Ligand/Complex	Assignment (ppm)			
	H-C-aromatic ^(m)	-CH ₂ ^(s)	H ₃ C-C=N ^(s)	C-OH ^(s)
Hapbam	6.76-7.56	4.80	2.41	N.D.
HapFbam	6.81-7.57	4.75	2.41	N.D.

s, singlet; m, multiplet; N.D., Not Detected

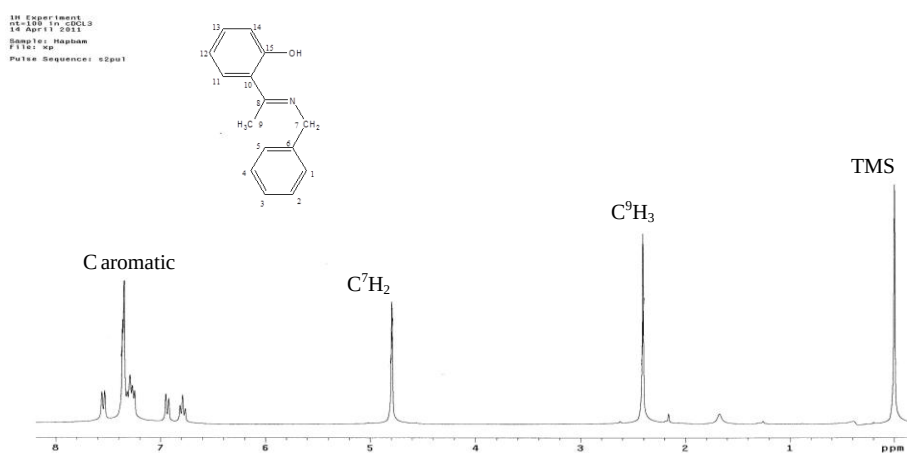


Figure 5: ^1H NMR spectrum of Hapbam

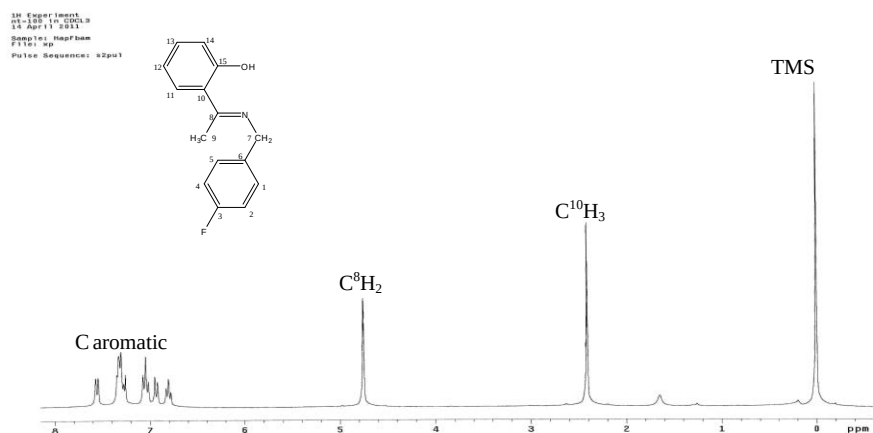


Figure 6: ^1H NMR spectrum of Hapbam

Molar Conductance and Magnetic Moment

The molar conductance values for the synthesized complexes were determined using $1 \times 10^{-3} \text{ M}$ CHCl_3 solutions, as shown in Table 1. Molar conductivity measurements conducted on the palladium(II) complexes revealed the non-conductivity nature of the solution at room temperature indicating the absence of any electrolytes [7]. These values show that there are no ions existing in the outer sphere coordination of the complexes. As expected, the magnetic susceptibility measurements showed diamagnetic behaviour reflected in the zero effective magnetic moment, $\mu_{\text{eff}} = 0$, in all of the complexes consistent with the 0 unpaired electrons of Pd(II) d^8 species having square planar geometry [8].

Single x-ray Crystallography

Structure of HapbamPd is shown in Figure 7 and selected bond lengths and angles are listed in Table 4.

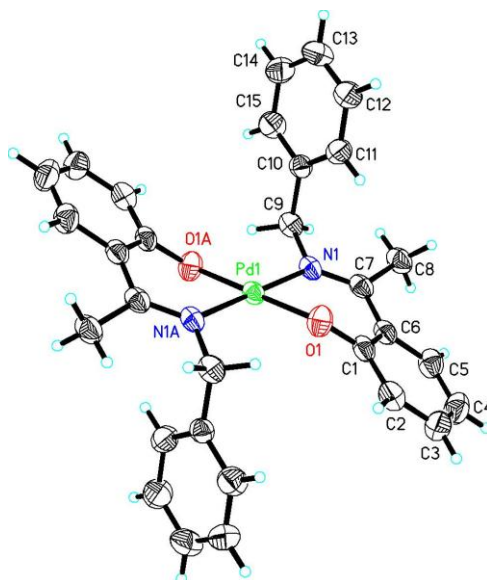


Figure 7: ORTEP diagram of HapbamPd with 50% probability ellipsoids [9]

Table 4: Bond lengths [Å] and angles [°] around Pd atom in HapbamPd

Atom1 - Atom2	Bond Length (Å)	Atom1 - Atom2	Bond Angle (°)
Pd1-O1	1.981 (2)	O1—Pd1—O1 ⁱ	180.00 (8)
Pd1-O1 ⁱ	1.981 (2)	O1—Pd1—N1	90.97 (10)
Pd1-N1	2.039 (2)	O1 ⁱ —Pd1—N1	89.03 (10)
Pd1-N1 ⁱ	2.039 (2)	O1—Pd1—N1 ⁱ	90.97 (10)
		O1 ⁱ —Pd1—N1 ⁱ	89.03 (10)
		N1—Pd1—N1 ⁱ	180.00 (11)
		C1—O1—Pd1	120.0 (2)

The palladium atom lies on an inversion center and is coordinated to two ligand molecules through the oxygen and nitrogen atoms in a bidentate manner to form a perfect square planar geometry. The Pd1—O and Pd1—N bond lengths of 1.981 (2) and 2.039 (2) Å, respectively, in a square planar geometry are typical of square planar Pd(II) of Schiff bases. The dihedral angle between the benzene rings is 76.5 (2)°.

Catalytic Studies

The palladium complexes that have been prepared in this study were tested as catalysts in the Suzuki reactions of iodobenzene with phenylboronic acid in the presence of triethylamine (Et_3N) as base in N,N -dimethylacetamide at 100°C .

Triethylamine was chosen as a base due its capability to give the highest conversion compared to other bases. The reaction was monitored by measuring the % conversion of the aryl iodide starting material using gas chromatography [10]. The results are summarized in the Table 5. Phenylboronic acid was found to couple smoothly with iodobenzene providing excellent yields that were more than 90% after a 12-hour reaction. All these data indicate that the palladium complexes may be utilized as catalysts in the Suzuki reaction.

Table 5: Activities of palladium catalyst on Suzuki reaction between iodobenzene and phenylboronic acid

Catalyst	% Conversion After 12 hours
HapbamPd	94
HapFbamPd	99
$\text{Pd}(\text{OAc})_2$	96

Conclusion

Two ligands and their palladium(II) complexes have been successfully synthesized as confirmed by the characterization via various physico-spectral techniques. X-ray crystallography investigation of HapbamPd revealed that the Schiff bases behave as singly charged bidentate ligands, coordinating to the palladium centre in the ratio of ligand:metal of 2:1. The geometry of the palladium centre was a perfect square planar. The coordination occur through the azomethine nitrogen and phenyl oxygen, indicated by the redshift of the $\nu(\text{C}=\text{N})$ and appearance $\nu(\text{C}-\text{O})$ upon complexation. It was observed that both $\text{Pd}(\text{II})$ complexes displayed properties of good catalysts for the reaction, indicated by more than 90% conversion of the starting materials to the biphenyl product after 12 hours of reaction time at 100°C in inert conditions.

Acknowledgement

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