Pd(II) Complexes with Nitrogen-oxygen Donor Ligands: Synthesis, Characterization and Catalytic Activity for Suzuki-Miyaura Cross-coupling Reaction

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Inexpensive bidentate Schiff base ligands (O1, O3) and their Pd(II) complexes (OPd1, OPd3) were successfully synthesized and characterized using CHN elemental analysis, FTIR, ¹H and ¹³C NMR, melting point determination, molar conductivity and magnetic moment. It revealed that these Schiff bases behaved as bidentate ligands in their complexes. The spectral data indicated that the ligands co-ordinated through the phenolic oxygen and the azomethine nitrogen atoms. Magnetic moment data suggested the existence of square planar Pd(II) complexes, while non-electrolytic behaviour indicated the absence of counter ions in chloroform. The Pd(II) complexes showed good catalytic activities for Suzuki-Miyaura cross-coupling reaction between iodobenzene with phenylboronic acid at 1.0 mmol% catalyst loading.

Key words: Bidentate Schiff base; nitrogen-oxygen donor ligands; Pd(II); Suzuki-Miyaura cross-coupling reaction; synthesis; physicochemical properties; catalytic activity; characterization

Schiff base ligands are considered 'privileged ligands' and are attractive because they are easily prepared by the condensation between aldehyde/ketone and imines both of which are relatively cheap and easily available. Stereogenic centres or other elements of chirality such as planes and axes can be introduced in the synthetic design (Cozzi 2004) as well as benzene rings containing electron donating or withdrawing substituents. The mono-, di-, tri- and multi-dentate chelating Schiff base ligands can be designed according to the binding environments of metal ions. The metal complexes of chiral Schiff base ligands showed stereoselectivity in organic transformation, hence the synthesis of chiral complexes become an important area of current research in co-ordination chemistry (Gupta & Sutar 2008).

Schiff base ligands are able to co-ordinate many different metals (Osman 2006; Sallam 2006) and to stabilize them in various oxidation states. The Schiff base complexes have been used in catalytic reactions (Dhara *et al.* 2010; Tamizh & Karvembu 2012) and as models for biological systems (Singh *et al.* 2012; Mohamed *et al.* 2010). Many Schiff base complexes show excellent catalytic activity in various reactions at high temperature (>100°C) and in the presence of moisture (Gupta & Sutar 2008).

The Suzuki-Miyaura cross-coupling reaction is a powerful method for the synthesis of biaryl bonds. The importance of biaryl units as molecular components in pharmaceuticals, herbicides and natural products, as well as in engineering materials such as conducting polymers, molecular wires and liquid crystals,

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has attracted enormous interest (Paul & Clark 2003). Numerous variants (Gillis & Burke 2009), optimizations and applications (McGlacken & Fairlamb 2009) have been disclosed in the literature. The robust nature of this reaction has led to its widespread use in the pharmaceutical industry (Torborg & Beller 2009). The relative thermal stability, insensitivity to air or moisture, and low toxicity (Miyaura & Suzuki 1995) of boronic acid constitute a highly valuable practical advantage for both academic and industrial applications.

As a part of our interest in designing new, inexpensive ligands and studying their co-ordination behaviour and catalytic application, we report herein the synthesis and characterization of a new type of ligands and their Pd(II) complexes as catalysts in Suzuki-Miyaura cross-coupling reaction.

MATERIALS AND METHODS

Experimental Sections

Materials. All reagents and chemicals used in this investigation were laboratory pure grade available from Acros, Merck and Sigma-Aldrich. The solvents for the spectral study were spectroscopic grade and used without further purification.

Techniques. Microanalyses for carbon, hydrogen and nitrogen were determined using a Thermo Finnigan Flash Elemental Analyzer 2000. The IR spectra were obtained on a Perkin Elmer 1750X FTIR spectrophotometer ($4000\text{ cm}^{-1} - 400\text{ cm}^{-1}$) with samples prepared as KBr pellets. Melting points of the products were determined using Buchii-B454 and are uncorrected. Proton (^1H) and carbon (^{13}C) NMR (300 MHz) spectra were recorded on a Bruker Varian spectrometer in CDCl_3 and reported in p.p.m. (δ) from the internal standard TMS. The magnetic susceptibilities were determined on Sherwood Auto Magnetic Susceptibility Balance at room temperature (25°C) using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as a calibrant; the diamagnetic

corrections were calculated from Guoy method. Molar conductance measurements of freshly prepared Schiff base ligands and their transition metal complexes solutions were determined in chloroform ($\sim 10^{-3}\text{ M}$) at room temperature using a Mettler Toledo Inlab 730 conductivity meter. The formation of products from catalytic testing was monitored using Gas Chromatography (GC) technique (Bhunja *et al.* 2010). Yields were calculated for a specific set of parameters at a specific time according to the product ratios.

Synthesis of Schiff base ligands.

Figure 1. General reaction for the synthesis of Ovan-series ligands.

Synthesis of (E)-2-[(benzylimino)methyl]-6-methoxyphenol [O1]

To *o*-vanillin (50 mmol, 7.6091 g) was dissolved in ethanol (25 ml), an ethanolic solution of benzylamine (50 mmol, 5.3869 g) was added and the mixture was stirred for overnight. The ethanol was allowed to evaporate slowly at room temperature. Orange-coloured solid product was evident after a week. The solid residue was filtered, washed with ice-cold ethanol and air-dried at room temperature. The yield was 36.8%.

Synthesis of (E)-2-methoxy-6-[(4-methoxybenzylimino)methyl]phenol [O3]

To *o*-vanillin (2 mmol, 0.3075 g) was dissolved in ethanol (5 ml), an ethanolic solution of 4-methoxybenzylamine (2 mmol, 0.2744 g) was added dropwise and the mixture was heated under reflux for 2 h. Upon cooling, there was

no formation of solid materials. Ethanol was removed using rotary evaporator. The ligand was used in complexation with Pd(II) metal salt.

Synthesis of Pd(II) complexes.

Figure 2. General reaction for the synthesis of Pd-Ovan-series complexes.

Synthesis of Bis(2-((E)-(benzylimino)methyl)-6-methoxyphenoxy)palladium(II) [OPd1]

The ligand, O1, (5 mmol, 1.2064 g) was dissolved in acetonitrile (10 ml) in a round-bottomed flask. Palladium(II) acetate (2.5 mmol, 0.5612 g) was dissolved separately in acetonitrile (10 ml) and added into the flask containing the ligand solution. The mixture was stirred and refluxed for 4 h upon which brown solids were formed. It was isolated by gravity filtration, washed with ice-cold acetonitrile and air dried at room temperature. The yield was 90.6%.

Synthesis of Bis(2-methoxy-6-((E)-(4-methoxybenzylimino)methyl)phenolato)palladium(II) [OPd3]

The ligand, O3, (2 mmol, 0.5426 g) was dissolved in acetonitrile (5 ml) in a round-bottomed flask. Palladium(II) acetate (1 mmol, 0.2246 g) was dissolved separately in acetonitrile (5 ml) and added into the flask containing the ligand solution. The mixture was stirred and refluxed for 4 h upon which a brown solid was formed. It was isolated by gravity filtration, washed with ice-cold acetonitrile and air dried at room temperature. The yield secured was 80.8%.

General reaction of Suzuki-Miyaura cross-coupling reaction. The palladium(II) Schiff base complexes were tested as homogeneous catalysts in a series of Suzuki-Miyaura cross-coupling reaction, between iodobenzene and phenylboronic acid to produce biphenyl. The general procedure (Figure 1) is as follows: Iodobenzene (1 mmol), phenylboronic acid (2 mmol), triethylamine, Et₃N (2.4 mmol), palladium(II) Schiff base (0.01 mmol) and solvent DMA (7 ml) were mixed in Radley's 12-placed reaction carousel and refluxed whilst being purged with nitrogen. The reaction was monitored every 6 h and sampling was done at 6 h, 12 h and 24 h.

Figure 3. Catalytic reaction of iodobenzene with phenylboronic acid.

RESULTS AND DISCUSSION

Physicochemical Properties of the Synthesized Compounds

All of these bidentate Schiff base ligands and their Pd(II) complexes were intensely coloured, air and moisture free. The ligands and their metal complexes were very stable solids at room temperature, without undergoing decomposition. Yields of the complexes were higher than those of the ligands. The ligands had very high solubility in almost all polar solvents attributable to their polar nature. The complexes however, had very low solubility in polar organic solvents such as Et₃OH, MeOH, DMSO, CH₂Cl₂, etc. but soluble in relatively less polar CHCl₃. These synthesized ligands contained both polar and non-polar groups such as -OH, -OCH₃, -CH₃ etc. The C, H and N percentages were theoretically calculated and the measured values were in accordance to the suggested formula. The physical and analytical data of the Schiff base ligands and their complexes are shown in Table 1.

Table 1. Physical and analytical data for ovan-series ligands and their complexes.

Ligand/ Complex	Empirical formula	Colour	Melting point (°C)	Elemental Analysis (%) (Found)		
				C	H	N
O1	C ₁₅ H ₁₅ NO ₂	Yellow	62–65	74.67 (74.77)	6.27 (6.31)	5.81 (5.91)
OPd1	C ₃₀ H ₂₈ N ₂ O ₄ Pd	Brown	259–261	61.39 (61.47)	4.81 (4.79)	4.77 (4.74)
O3	C ₁₆ H ₁₇ NO ₃	Yellow	–	70.83 (71.08)	6.32 (6.32)	5.23 (5.23)
OPd3	C ₃₂ H ₃₂ N ₂ O ₆ Pd	Brown	204–205	59.40 (59.12)	4.98 (4.99)	4.33 (4.35)

IR Spectral Studies

In general, all infrared spectra presented the same general characteristics. The appearance of the C=N (azomethine) peaks in the range 1620–1634 cm⁻¹ could be clearly seen in the spectra, indicating the formation of the Schiff bases. The broad band at 2300 cm⁻¹–3300 cm⁻¹ could be attributed to the intramolecular hydrogen-bonded O-H group (Zolezzi *et al.* 1999). This band was absent in the spectra of complexes due to deprotonation of the phenolic moiety upon complexation. The Pd(II) ion was co-ordinated through the nitrogen and oxygen atoms of the hydroxyl group. The azomethine C=N bands were seen to be shifted to lower frequencies, 1612 cm⁻¹–1623 cm⁻¹ in all Pd(II) complexes due to the withdrawal

of electron density from the nitrogen atom owing to co-ordination (Zolezzi *et al.* 1999). A similar effect was observed in the stretching vibration of the Schiff base phenolic C-O and methoxy groups, with respect to the same group in the complexes where it was shifted to a lower frequency, strongly indicating oxygen co-ordination to the metal centre. The appearance of new bands at 462 cm⁻¹–544 cm⁻¹ and 581 cm⁻¹–660 cm⁻¹, that ascribed Pd-O and Pd-N vibrations, support the evidence of 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 (Ouf *et al.* 2010; Mustafa *et al.* 2009). The significant bands of ligands and their Pd(II) complexes and their spectra are summarized in Table 2 and Figure 4.

Figure 4. FTIR Spectra of O1, O3, OPd1 and OPd3.

Table 2. Infrared data for ligands and their Pd(II) complexes.

Ligand/ Complex	Frequency (cm ⁻¹)					
	$\nu(\text{C}=\text{N})$	$\nu(\text{C}-\text{N})$	$\nu(\text{C}-\text{O})$	$\nu(\text{OCH}_3)$	$\nu(\text{C}-\text{OH})$	$\nu(\text{M}-\text{O}, \text{M}-\text{N})$
O1	1634(<i>s</i>)	1344(<i>w</i>)	1254(<i>s</i>)	1054(<i>w</i>)	2300–3300(<i>b</i>)	–
OPd1	1622(<i>s</i>)	1316(<i>s</i>)	1241(<i>s</i>)	1095(<i>w</i>)	–	657 416(<i>w</i>)
O3	1630(<i>w</i>)	1344(<i>w</i>)	1251(<i>s</i>)	1033(<i>w</i>)	2500–3200(<i>b</i>)	–
OPd3	1620(<i>s</i>)	1320(<i>s</i>)	1239(<i>s</i>)	1032(<i>w</i>)	–	567 515(<i>w</i>)

(s) = Strong; (b) = Broad; (w) = Weak.

¹H and ¹³C NMR Studies

In the ¹H NMR of the ligands (Table 3), the chemical shift for methylene appear at 4.74 p.p.m.–4.82 p.p.m. as singlets and slightly shifted to higher values of 5.04 p.p.m.–5.12 p.p.m. in their respective Pd(II) complexes. The methoxy peaks for ligands appear at 3.88 p.p.m.–3.90 p.p.m. while in complexes, they appear at 3.75 p.p.m.–3.76 p.p.m., slightly shifted to lower values. Upon co-ordination, there is an upfield shift of peaks for azomethine protons from 8.38 p.p.m.–8.42 p.p.m. to 7.69 p.p.m.–7.72 p.p.m.. This upfield shift is attributed to the conformational change that occurs in the ligand upon chelation (Mahamo *et al.* 2012). The phenolic proton appears at 13.85 p.p.m. in O1 and

disappeared upon complexation, indicating that the complexation was successfully achieved through deprotonation of the phenol. The OH peak in O3 that was expected to appear in the downfield region (10 p.p.m.–14 p.p.m.) (Saheb & Sheikhshoaei 2011) of the spectra was not observed as the labile phenolic proton may have undergone a rapid exchange with the deuterium in the solvent.

The ¹³C singlet signals for the imine carbons (C=N) in complexes are found in the region 162.3 p.p.m.–162.8 p.p.m. (Table 4). This is an upfield shift from 165.2 p.p.m.–165.6 p.p.m. observed for the free ligands, further affirming the co-ordination of the ligand through the imine group to the metal centre. There is

Table 3. Chemical shift of ¹H NMR for ligands and their Pd(II) complexes.

Assignments	Chemical shifts (p.p.m.)			
	O1	OPd1	O3	OPd3
C-CH ₂	4.82(<i>s</i>)	5.12(<i>s</i>)	4.74(<i>s</i>)	5.04(<i>s</i>)
N=CH	8.42(<i>s</i>)	7.72(<i>s</i>)	8.38(<i>s</i>)	7.69(<i>s</i>)
C ³ -H (Ar)	6.84–6.89(<i>d</i>)	6.76–6.81(<i>d</i>)	6.92–6.93(<i>d</i>)	6.78–6.79(<i>d</i>)
C ⁴ -H (Ar)	6.81–6.84(<i>t</i>)	6.47–6.52(<i>t</i>)	6.86–6.89(<i>t</i>)	6.83–6.84(<i>t</i>)
C ⁵ -H (Ar)	6.89–6.91(<i>d</i>)	7.26–7.29(<i>d</i>)	7.21–7.24(<i>d</i>)	7.36–7.39(<i>d</i>)
C ¹³ -H (Ar)	6.91–7.26(<i>t</i>)	7.29(<i>t</i>)	–	–
C ¹¹ , C ¹⁵ -H (Ar)	7.32(<i>d</i>)	7.44–7.46 (<i>d</i>)	6.76–6.79(<i>d</i>)	6.47–6.52(<i>d</i>)
C ¹² , C ¹⁴ -H (Ar)	7.26–7.32(<i>t</i>)	7.22–7.26(<i>t</i>)	7.29–7.30(<i>d</i>)	6.77–6.86(<i>d</i>)
C ¹³ -OCH ₃	–	–	3.79(<i>s</i>)	3.77(<i>s</i>)
Ar-OCH ₃	3.90(<i>s</i>)	3.75(<i>s</i>)	3.88(<i>s</i>)	3.76(<i>s</i>)
C ¹ -OH	13.85(<i>b</i>)	–	N.D.	–

(s) = Singlet; (d) = Doublet; (t) = Triplet; (b) = Broad; N.D. = Not detected; Ar = Aromatic.

Table 4. Chemical shift of ^{13}C NMR for ligands and their Pd(II) complexes.

Assignments	Chemical shifts (p.p.m.)			
	O1	OPd1	O3	OPd3
$\text{C}-\underline{\text{C}}\text{H}_2$	62.68(s)	58.85(s)	64.40(s)	58.33(s)
$\text{N}=\underline{\text{C}}\text{H}$	165.6(s)	162.8(s)	165.2(s)	162.3(s)
$\underline{\text{C}}^3\text{-H (Ar)}$	113.9(s)	114.0(s)	114.0(s)	113.8(s)
$\underline{\text{C}}^4\text{-H (Ar)}$	117.9(s)	120.2(s)	117.8(s)	113.8(s)
$\underline{\text{C}}^5\text{-H (Ar)}$	122.9(s)	125.4(s)	122.9(s)	125.4(s)
$\underline{\text{C}}^{13}\text{-H (Ar)}$	127.3(s)	127.1(s)	158.8(s)	158.8(s)
$\underline{\text{C}}^{11}, \underline{\text{C}}^{15}\text{-H (Ar)}$	127.5(s)	127.1(s)	129.9(s)	129.8(s)
$\underline{\text{C}}^{12}, \underline{\text{C}}^{14}\text{-H (Ar)}$	128.6(s)	128.4(s)	114.2(s)	114.0(s)
$\text{C}^{13}\text{-O}\underline{\text{C}}\text{H}_3$	–	–	55.30(s)	55.24(s)
$\text{Ar-O}\underline{\text{C}}\text{H}_3$	56.01(s)	55.90(s)	56.04(s)	55.95(s)
$\underline{\text{C}}^1\text{-OH}$	151.7(s)	–	151.9(s)	–

(s) = Singlet; Ar = Aromatic.

also an upfield shift from 62.68 p.p.m.–64.40 p.p.m. to 58.33 p.p.m.–58.85 p.p.m. and from 56.01 p.p.m.–56.04 p.p.m. to 55.90 p.p.m.–55.95 p.p.m. with respect to the free ligand in the signals for the methylene and methoxy carbons, respectively, upon co-ordination to the metal centre as per reported by Mahamo *et al.* (2012) and Dilworth *et al.* (1994). In the free ligands, C-OH signals appear at 151.7 p.p.m.–151.9 p.p.m. (Şenol *et al.* 2011) and disappeared upon complexation where the phenolic moiety was deprotonated.

Molar Conductance and Magnetic Moment

The molar conductance values of the Pd(II) complexes was found to be $0 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ suggesting their non-electrolytic nature (Ben-Saber *et al.* 2005). The magnetic moment of the complexes revealed their diamagnetic nature where $\mu_{\text{eff}} = 0$, consistent with the expected square planar geometry (Raman *et al.* 2007).

Catalytic Activity

The Pd(II) complexes namely OPd1 and OPd3 were tested as catalysts in the Suzuki-Miyaura 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 . Et_3N that is soluble in the reaction mixture was a good base for the reaction due to its capability to give high conversion, although in its presence trace quantities of palladium metal could occasionally be observed as a precipitate against the walls of the glass tubes.

In most of the cases, Et_3N was the base of choice to activate the boron species in order to increase its nucleophilicity and give a clean reaction. This is because the organoborons compounds are highly covalent in character (Matos & Soderquist 1998). Solubility of the bases plays a great rule in Suzuki-Miyaura coupling reaction (Papp *et al.* 2006).

The reaction was monitored using GC-FID by percentage conversion of iodobenzene at every 3 h and sampling was done at 3, 6, 9, 12 and 24 h. A control reaction without catalyst had been set up and there was no indication of iodobenzene conversion after 24 h.

The results are summarized in the *Figure 5*. It is observed, with increasing time, the %

Figure 5. Percentage conversion of Iodobenzene using OPd1 and OPd3 as catalysts within 24 h.

conversion of iodobenzene also increased. OPd1 showed its ability to convert iodobenzene faster than OPd3 in the early hours. At the end of the reaction, phenylboronic acid was found to couple smoothly with iodobenzene providing excellent yields up to 100% after 24 h for both catalysts.

CONCLUSION

Two ligands and their Pd(II) complexes were successfully synthesized as confirmed by the characterization via various physico-spectral techniques. The Schiff base ligands co-ordinated through phenolic oxygen and azomethine nitrogen atoms as bidentate chelates as indicated by the spectral data. It was observed that both Pd(II) complexes, OPd1 and OPd3 displayed properties of good catalysts for the reaction, with up to 100% conversion of iodobenzene after 24 h of reaction time at 100°C in inert conditions.

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