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Syntheses, Characterisation and Application of Palladium(II) Complexes as Catalysts in Heck Cross-Coupling Reaction

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ABSTRACT

A new series of *N,O*-bidentate ligands, L1, L2, L3 and L4, and their Pd(II) complexes, PdL1, PdL2, PdL3 and PdL4 have been synthesised and characterised using various physico-chemical techniques, namely elemental analyses, IR and ^{1}H and ^{13}C NMR spectroscopies, and conductivity analysis. The molecular geometries of PdL2 and PdL4 have been elucidated through single crystal X-ray crystallography revealing 2:1 molar equivalence of ligand: Pd with the Schiff bases that exhibited bidentate ligands behaviour, in which they coordinated through the phenolic O donor atoms and imine N. Upon complexation, the ν(C=N) around 1629-1639 cm^{-1} and ν(C-O) around 1251 to 1252 cm^{-1} shifted to lower frequencies by 4 to 23 cm^{-1}. In this study, three parameters were chosen for the reaction conditions optimisation, which were types of bases, loadings for the catalyst, and temperatures of the reaction. Pd(II) complexes exhibited good catalytic activities for Heck coupling reaction with 100% conversion at 100°C within 12 hours of reaction time. Reducing the reaction temperature to 80°C reduced the conversion to a maximum of 80%.

Keywords: Bidentate Schiff base, Heck cross-coupling reaction, palladium(II), X-ray

INTRODUCTION

Schiff bases are compounds that have been extensively studied (He & Cai, 2011) for their selectivity and sensitivity toward various metal ions. Scientists in this field of study have put extensive work in synthesis, as well as characterisation of mono-nuclear and bi-nuclear transition metal complexes. It is reported that bidentate Schiff bases were the ligands of choice because they are known to be the most convenient and attractive ligands for metal centre complexations (Vigato & Tamburini, 2004; Drozdzak et al., 2005). The metal complexes of Schiff bases especially Pd(II) and Ni(II) containing nitrogen and other

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donor atoms have been given attention because of their stability, biological activity (Islam et al., 2013) and potential applications as catalysis (Kumar et al., 2009).

Currently, phosphines complexes are the most common catalysts applied for the cross-coupling of C—C bond formation due to the presence of strong P-donors such as tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$), which has resulted in high conversion rates catalysed by these complexes and comparative ease of modifying their properties. Nonetheless, it is also known that such low-valent, low-coordinate palladium complexes of phosphines can be extremely unstable in ambient conditions and their formation has been found to be energetically unfavourable. Furthermore, these types of compounds are not ecological friendly (Lai et al., 2005).

It is important to note that the catalysts used in Heck reaction for the formation on C—C bonds in laboratories are Pd(II) complexes with nitrogen-containing ligands (Pratihar et al., 2012). The catalytic activity of the bidentate Schiff base Pd(II) complexes not only rivals but may be better than the corresponding phosphines and sulphur equivalents. Thus, the practices of employing phosphine and sulphur-free palladium catalysts in Suzuki cross-coupling reactions are of interest to many (Lai et al., 2005).

The objective of the present work is to study the chelation behaviour of bidentate Schiff base ligands towards palladium(II) ion. Herein, some remarkable results of using several new types of *N,O*-bidentate ligands in palladium-catalysed Heck coupling reaction are presented. The efficiency of palladium(II) complexes are compared and discussed subsequently. A preliminary result of this investigation of Heck cross-coupling reaction is also reported in this paper.

MATERIALS AND METHOD

Materials

All operations were carried out under a dry nitrogen atmosphere. All reagents and chemical were laboratory pure grade and used without purification. A Thermo Finnigan Flash Elemental Analyser 2000 was used for microanalyses of C, H and N. The IR spectra were obtained using the Perkin Elmer 1750X FTIR spectrophotometer (4000-400 cm^{-1}) with KBr disc samples. Prior to use, KBr of Spectroscopic grade was dried in an oven at 110°C overnight and then stored in a desiccator. The spectra for proton (^1H) and carbon (^{13}C) NMR (300 MHz) were recorded on a Bruker Varian spectrometer in $CDCl_3$ and the results were reported in ppm (δ) relative to TMS, applying the residual solvent resonances as the internal references. Single-crystal x-ray diffraction investigations were carried out on Bruker SMART APEX CCD area-detector diffractometer. Analyses using gas chromatography were performed on Agilent 6890N Network GC System with a Flame Ionisation Detector (FID).

General Procedure of the Synthesis of Schiff Base Ligands

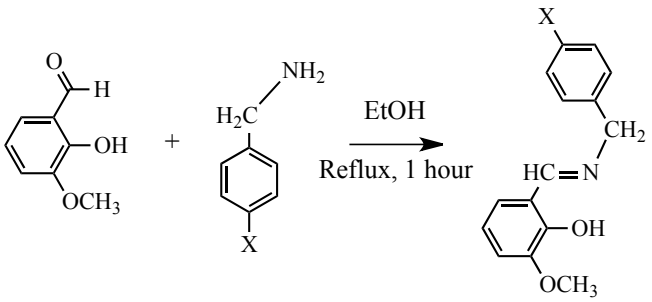

Figure 1. Synthesis of Schiff bases (L1-L4)

Schiff base ligand was synthesised by first dissolving *o*-vanillin (50 mmol, 7.6091 g) in ethanol. This was followed by adding the mixture into an ethanolic solution of benzylamine (50 mmol, 5.3869 g). The mixture was then stirred overnight to allow for it to react. Following that, the ethanol was evaporated slowly at room temperature. After a week, yellow solids appeared. The solids were collected, filtered off, and washed with ice-cold ethanol. Lastly, the sample was allowed to air-dry at room temperature and to give ligands of L1, L2, L3 and L4 (Figure 1).

(E)-2-((benzylimino)methyl)-6-methoxyphenol (L1)

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).

(E)-2-methoxy-6-((4-methylbenzylimino)methyl)phenol (L2)

Yellow liquid at room temperature. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.34 (s, 3H, CH_3), 4.78 (s, 2H, CH_2), 3.90 (s, 3H, Ar–OCH_3), 6.76-7.16 (phenylic hydrogen groups), 8.39 (s, 1H, =CH), 13.97 (b, 1H, OH). ^{13}C NMR (300MHz, $CDCl_3$): δ 21.1 (CH_3), 56.1 (Ar–OCH3), 62.25 (CH_2), 114.0, 117.9, 127.6, 122.9, 129.3, 127.6, 128.7 (ArC), 151.9 (C1), 134.9 (C13), 165.4 (N=CH). Anal. Calcd for $C_{16}H_{17}NO_2$: C, 75.27; H, 6.71; N, 5.49%; Found: C, 74.40; H, 6.67; N, 5.38%. IR (KBr, cm^{-1}): 3483 υ(OH), 1629 υ(C=N), 1335 υ(C–N), 1252 υ(C–O), 1039 υ(OCH_3).

(E)-2-methoxy-6-((4-methoxybenzylimino)methyl)phenol (L3)

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 (CH2), 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).

(E)-2-((4-fluorobenzylimino)methyl)-6-methoxyphenol (L4)

Yellow solid; yield, 52%; m.p. 54-56°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.78 (s, 2H, CH_2), 3.89 (s, 3H, Ar–OCH_3), 6.85-7.30 (phenylic hydrogen groups), 8.42 (s, 2H, =CH), 13.80 (b, 1H, OH). ^{13}C NMR (300 MHz, $CDCl_3$): δ 56.1 (Ar–OCH_3), 62.1 (CH_2), 115.4, 115.6, 118.1, 122.9, 129.2, 128.7 (ArC), 151.5 (C1), 160.4 (C13), 165.7 (N=CH). Anal. Calcd for $C_{15}H_{14}FNO_2$: C, 69.70; H, 5.48; N, 5.41%; Found: C, 69.63; H, 5.51; N, 5.49%. IR (KBr, cm^{-1}): 3461 υ(OH), 1636 υ(C=N), 1336 υ(C–N), 1252 υ(C-O), 1037 υ(OCH_3).

General Procedure of The Synthesis of Palladium(II) Complexes

In a round bottom flask, ligand, (L1) (5 mmol, 1.2064 g) was dissolved in acetonitrile (10 mL). Separately, palladium(II) acetate (2.5 mmol, 0.5612 g) was dissolved in MeCN (10 mL) and was then added into the ligand solution. The mixture was then stirred and refluxed for 4 hours to yield brown solids. The solids were filtered off followed by washing with ice-cold MeCN prior to air-drying at room temperature. The solids products were recrystallized from chloroform producing orange crystals. The recrystallization gave complexes of PdL1, PdL2, PdL3 and PdL4, respectively (Figure 2).

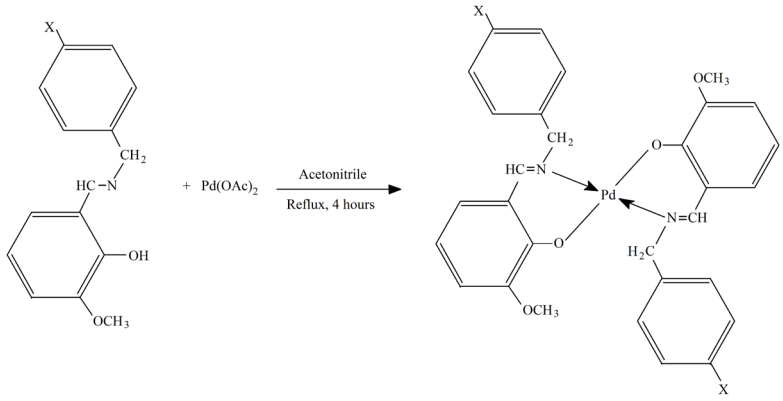

Figure 2. Synthesis of palladium(II) complexes (PdL1-PdL4)

Bis(2-((E)-(benzylimino)methyl)-6-methoxyphenoxy)palladium(II) (PdL1)

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). UV-Vis (CHCl3) λ_{max} (nm) = 252, 362, 473. μ_{eff} (B.M.) (298 K): diamagnetic.

Bis(2-methoxy-6-((E)-(4-methylbenzylimino)methyl)phenolato)palladium(II) (PdL2)

Dark yellow; yield, 91%; m.p. 236-238°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.30 (s, 3H, CH_3), 5.07 (s, 2H, CH_2), 3.75 (s, 3H, Ar-OCH_3), 6.76-7.34 (phenylic hydrogen groups), 7.69 (s, 1H, =CH). ^{13}C NMR (300 MHz, $CDCl_3$): 21.1 (CH_3), 55.9 (Ar–OCH_3), 62.25 (CH_2), 114.0, 120.4, 125.4, 128.4, 129.1 (ArC), 136.1 (C13), 162.6 (N=CH). Anal. Calcd for $C_{32}H_{32}N_2O_4Pd$: C, 62.49; H, 5.24; N, 4.55%; Found: C, 62.47; H, 5.29; N, 4.55%. IR (KBr, cm^{-1}): 1623 υ(C=N), 1316 υ(C–N), 1239 υ(C-O), 1092 υ(OCH_3), 660 υ(Pd-N), 416 υ(Pd–O). UV-Vis ($CHCl_3$) λ_{max} (nm) = 246, 292, 408. μ_{eff} (B.M.) (298 K): diamagnetic.

Bis(2-methoxy-6-((E)-(4-methoxybenzylimino)methyl)phenolato)palladium(II) (PdL3)

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, CH_2), 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.

Bis(2-((E)-(4-fluorobenzylimino)methyl)-6-methoxyphenoxy)palladium(II) (PdL4)

Turmeric yellow solid; yield, 97%; m.p. 253-256°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.06 (s, 2H, CH_2), 3.36 (s, 3H, Ar–OCH_3), 6.51-7.45 (phenylic hydrogen groups), 7.73 (s, 2H, =CH). ^{13}C NMR (300MHz, $CDCl_3$): δ 55.8 (Ar–OCH_3), 58.3 (CH_2), 114.0, 115.1, 115.4, 125.4, 130.1 (ArC), 150.9 (C13), 162.8 (N=CH). Anal. Calcd for $C_{30}H_{26}F_2N_2O_4Pd$: C, 57.84; H, 4.21; N, 4.50%; Found: C, 57.88; H, 4.21; N, 4.27%. IR (KBr, cm^{-1}): 1616 υ(C=N), 1328 υ(C–N), 1248 υ(C–O), 1084 υ(OCH_3), 581 υ(Pd–N), 495 υ(Pd–O). UV-Vis ($CHCl_3$) λ_{max} (nm) = 290, 340, 410. μ_{eff} (B.M.) (298 K): diamagnetic.

General Procedure for the Heck cross-coupling Reaction

Four catalytic reactions were performed with a similar procedure using PdL1-PdL4 complexes. Optimisation was done based on the three parameters of temperatures, catalyst loadings, and bases. The palladium(II) complexes were tested as homogeneous catalysts in a series of Heck coupling reactions between iodobenzene and methyl acrylate to produce methyl cinnamate. The mixtures 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 24 hours at 100°C and monitored using gas chromatography.

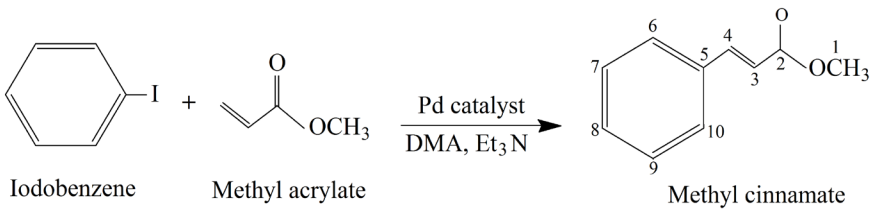

Figure 3. The Heck coupling reaction of iodobenzene with methyl acrylate

Heck Reaction using Different Bases

The previously explained procedure was repeated using 4 different types of bases while the refluxing at 100°C. The bases used were Et_3N, $NaHCO_3$, Na_2CO_3 and NaOAc.

Heck Reaction using Different Catalyst Loadings

Different catalyst loadings were studied by repeating the previously explained procedures with Et_3N as the base at 100°C. The palladium catalyst loadings were varied at 0.5, 1.0 and 1.5 mmol%, respectively.

Heck Reaction at Different Temperatures

Maintaining Et_3N as the base, the procedure was again repeated using palladium(II) Schiff base complex 1.0 mmol% and varying reaction temperatures at 30, 80, 100 and 120°C.

RESULTS AND DISCUSSION

Infrared Spectroscopy

The appearance of the C=N of azomethine in the range of 1629-1636 cm^{-1} can be clearly observed, indicating the formation of Schiff base. The azomethine C=N bands were observed to be shifted to lower frequencies, 1612 to 1623 cm^{-1}, in all the Pd(II) complexes. This phenomenon could be due to the withdrawal of electron density from the nitrogen atom upon coordination (Zolezzi, Decinti, & Spodine, 1999). A similar effect can also be observed in the stretching vibration of the Schiff base phenolic C–O and OCH3 groups, as regard to the same group in the complexes where it can be observed to be shifted to a lower frequency, hence confirming the oxygen coordination to the metal, as reported by Gupta and Sutar (2008). The spectra also confirmed the appearance of new bands, both at 462 to 544 cm^{-1} and 581 to 660 cm^{-1}, which ascribed Pd–N and Pd–O vibrations, respectively. This is the evidence of the participation of nitrogen atom of the azomethine group and oxygen atom of the of OH group presents in the ligand upon complexation with Pd(II) ion (Mustafa et al., 2009; Ouf et al., 2010).

NMR Spectroscopy

^{1}H NMR. It can be observed in the ^{1}H NMR spectra of the ligands, the evidence of chemical shifts of methylene; that for the metal complexes, CH_2 appeared at 4.70 to 4.85 ppm as singlets and shifted to higher values of 5.00 to 6.00 ppm. Also in the spectra, ligands exhibited chemical shifts of OCH_3 groups at 3.80 to 3.90 ppm, whereas for Pd(II) complexes, these peaks appeared to have shifted to the values of 3.60 to 3.80 ppm. The shifting can be caused by the involvement of the adjacent imine group, which was coordinated to the Pd centre (Mohamo et al., 2012), causing the CH_2 groups to be more pronounced than the OCH_3 group. This could be due to the closer proximity of the former group to the imine group.

There was an upfield shift of azomethine protons from 8.30 to 8.50 ppm for the ligands to 7.60 to 7.75 ppm for the complexes upon complexation. This upfield shift can be linked to, that upon chelation, the conformational change that has occurred in the ligand (Mohamo et al., 2012; Tsuno, Iwabe, & Brunner, 2013). The peaks for phenolic protons of the ligands, appearing at 13.80 to 14.00 ppm, have disappeared upon complexation, which is in agreement with the work by Gupta and Sutar (2008). They explained that this might be an indication of the occurrence of complexation through deprotonation of the phenolic moiety. The spectra also shown aromatic protons appearing as multiplets in free ligands and were more clearly resolved in complexes. These complexes have JHH values of 6 to 9 Hz, which are indicative of the presence of ortho aromatic protons. Lastly, although the OH peak in the L3 was initially expected to appear in the downfield region of 10 to 14 ppm (Saheb & Sheikhshoaie, 2011), no such peaks were observed. This might be due to the labile nature of phenolic protons, which had undergone rapid exchange with the deuterium present in the solvent.

^{13}C NMR. The imine carbons (C=N) in the Pd(II) complexes were discovered as singlets in the region of 162.3 to 162.9 ppm, and these are similar with what have been reported by Senol et al. (2011). The peaks were shifted upfield from the equivalent peaks in the respective ligands and appeared at 165.5 to 165.8 ppm. This further supports the suggestion of imine nitrogen coordination to the Pd(II) centre. In the free ligands, C–OH signals can be observed at 151.5 to 151.9 ppm, which disappeared upon complexation. This agrees with the work by Senol et al. (2011), which provides evidence that the complexation is successfully achieved through phenol deprotonation.

Further evidence of the coordination to Pd(II) centre can be observed in the position of the peaks representing aromatic carbons succeeding complexation, where the peaks shifted downfield in the complexes.

X-ray Crystallography. Suitable single crystals of PdL2 and PdL4 were subjected to X-ray crystallography investigation to determine their structures. All these crystals were obtained via slow evaporation of chloroform ($CHCl_3$) at room temperature. The ORTEP drawings of PdL2 and PdL4 are depicted in Figure 4.

The complex PdL2 (Bahron et al., 2014) was obtained as single crystals from slow evaporation of chloroform. The bond length of azomethine N1-C7 and N1-iC8 of PdL2 is 1.296(15) and 1.490(14) Å, respectively, which is consistent with the normal C=N bond lengths

observed in a similar complex, PdL4 (Bahron et al., 2011). The PdL2 crystals appeared to contain one solvated chloroform molecule used in the recrystallisation.

In the compound PdL4 (Bahron et al., 2011), the Pd^{II} atom is tetracoordinated by two N atoms and two O atoms from the two 2-[(4-fluorobenzyl)iminomethyl]-6-methoxyphenoxy ligands, forming a square-planar geometry. The two N atoms and two O atoms around the Pd^{II} atom are *trans* to each other. The dihedral angle between the two fluoro-substituted benzene rings is 39.03(6)°. The molecular structure is stabilised by an intramolecular C-H•••O hydrogen bond. In the crystal, weak intermolecular C-H•••π interactions occur.

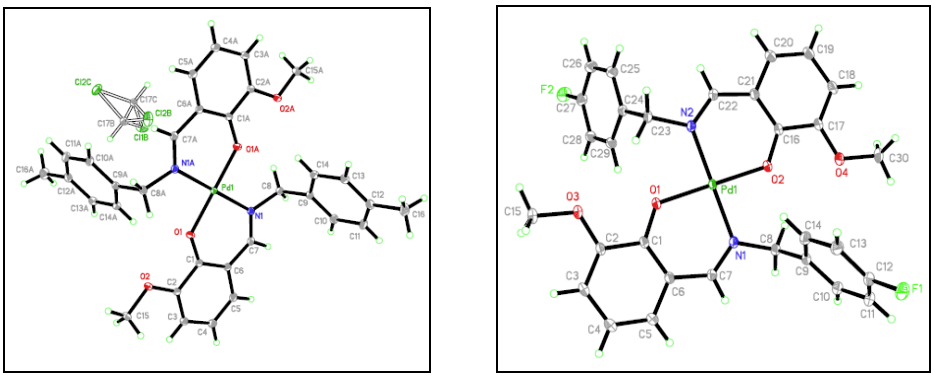

Figure 4. ORTEP diagram of: (a) PdL2; and (b) PdL4

Catalytic Activity

The Heck Cross-Coupling Reaction. The coupling reactions were carried out between methyl acrylate with iodobenzene at 100°C for 24 hours in *N,N*-dimethylacetamide (DMA) solvent under nitrogen conditions. A control experiment indicated that the coupling reaction did not occur in the absence of Pd(II) complexes. The conversions were calculated based on the GC peak areas of reactants and product. From these findings, PdL1-PdL4 were found to be suitable to catalyse Heck (Table 1, entries PdL1-PdL4) up to 100% yields after 24 hours of reactions.

Table 1
Activities of Pd(II) catalysts on the Heck reaction between iodobenzene and methyl acrylate

Entry	Catalyst[a] (mmol%)	Conversion[b] (%)	TON
PdL1	1.0	100	100
PdL2	1.0	100	100
PdL3	1.0	100	100
PdL4	1.0	100	100

[a]Reaction conditions: 1.0 mmol of iodobenzene, 2.0 mmol of methyl acrylate, 2.4 mmol Et_3N, 0.01 mmol Pd(II) complex, DMA (7 mL)
[b]Conversion is determined by GC. TON = mmol product/mmol catalyst used

Optimisation

Effect of Different Types of Bases. Base plays a significant role in both rate and product distribution of the Heck reaction. Hence, Et_3N, $NaHCO_3$, Na_2CO_3, and NaOAc (Figure 5) were used as the bases and investigated. Base can be used to neutralise the acid (HX) ensuing from the formal exchange of a hydrogen atom with an aryl or vinyl group (Biffis, Zecca, & Basato, 2001). Et_3N was found to be the most effective base.

All the catalysts tested for the Heck reaction using Et_3N as the base showed 100% conversion. Et_3N was found to be a good base for the reaction, even though there were occasionally trace quantities of palladium metal precipitate against the walls of the glass tubes observed. In most cases, Et_3N was the base to neutralise the hydrogen iodide by-product formed by the reaction (Gupta & Sutar, 2008). This is due to the solubility of Et_3N in the reaction mixture instead of other bases. Bases solubility plays an important role in Heck reaction. Moderate yield was obtained in the reaction of PdL4 as the catalyst when $NaHCO_3$ was used. However, longer reaction times were required to compare the reactions using other catalysts. Na_2CO_3 gave lower yields compared to other bases, even after 24 hours of reaction time.

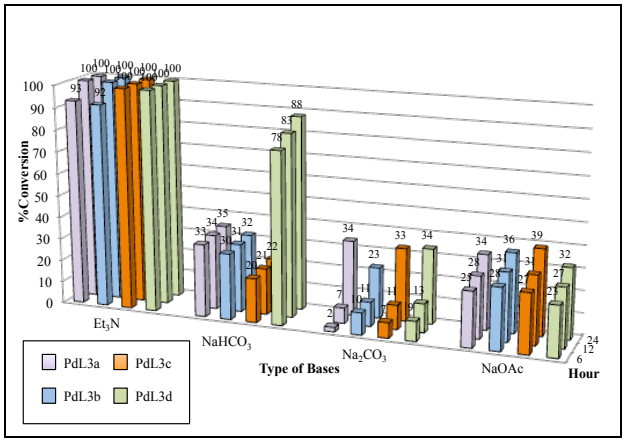

Figure 5. Effects of different types of bases on Heck reaction

Effects of Catalyst Loadings

It is ideal to have good yields using the most minimal amount of catalysts. Hence, this study examined the effects of catalyst loadings on a convenient coupling between iodobenzene and methyl acrylate. It is of impractical interest to use huge amounts of catalyst (Parida & Rath, 2009) unnecessarily. Other than the cost of utilising the catalyst for the reaction, the cost of removal and regeneration of the catalyst at the end of its life cycle is also substantial.

It was observed that higher amount of catalysts yielded higher product conversions when the amount of catalyst was increased from 0.5 to 1.5 mmol%. This might be due to the increased availability of more basic sites, which can be linked to the dispersion of more active species. The results showed that 100% conversion of iodobenzene was reached at the catalyst loading of 1.0 mmol% as early as 6 hours of reaction time. A lower loading of 0.5 mmol% produced

100% conversion for only one sample, i.e. PdL3, after 24 hours, which is the maximum reaction time. Therefore, it was decided that a catalyst loading of 1.0 mmol% was the optimum loading for the reaction.

Effects of Temperatures

Four different temperatures (30, 80, 100 and 120°C) were selected to study the optimum temperature for the catalysed reaction (Figure 6). By keeping other parameters fixed, the rate of conversion of iodobenzene at different temperatures was investigated through observation. Through this, a general increase in the percentage of iodobenzene conversion was observed upon increasing reaction temperature. However, at 120°C, a black precipitate of palladium metal (i.e., palladium black) was observed to have formed due to catalysts decomposition, thus inhibiting the catalytic cycle.

The lowest temperature, 30°C, yielded less than 10% conversion of iodobenzene for all the catalysts. This indicated that they were not highly active at this temperature. Upon comparing all the four catalysts, PdL1, PdL2 and PdL3 had the best performances with the highest catalytic activities recorded, even at 80°C with more than 80% conversion. On the contrary, PdL4 only produced 58% conversion at the same temperature. However, none of the catalysts managed to achieve 100% conversion even after 24 hours of reaction at 80°C. Even so, all the catalysts started to give 100% conversion of iodobenzene at only 12 hours of reaction time at 100oC. Therefore, it can be concluded that 100°C is the optimum reaction temperature for the catalysed Heck reaction.

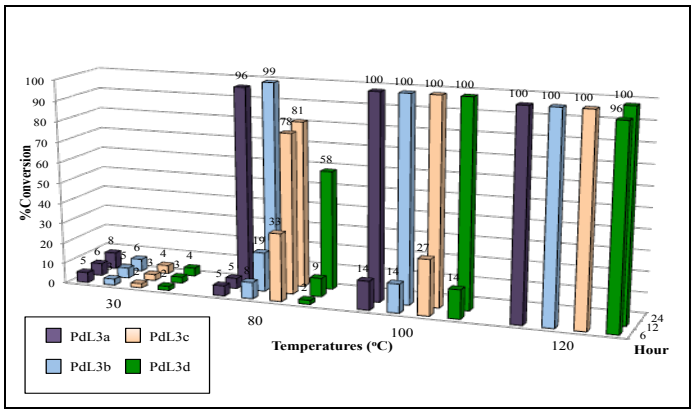

Figure 6. Effects of different reaction temperatures on the Heck reaction

CONCLUSION

Schiff base ligands, L1, L2, L3 and L4, have been successfully synthesised and characterised. From the studies, it can be concluded that the ligands act as bidentate chelating coordinates with Pd(II) ions upon complexations to produce Pd(II) complexes, PdL1, PdL2, PdL2 and PdL4, and give square planar geometries. The ligands and complexes are thermally and air

stable. PdL1, PdL2, PdL2 and PdL4 were explored for the homogeneous catalysis of the Heck cross-coupling reaction. The yields were up to 100% after 24 hours of reactions.

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