Research Article

Tetradentate N_2O_2 Chelated Palladium(II) Complexes: Synthesis, Characterization, and Catalytic Activity towards Mizoroki-Heck Reaction of Aryl Bromides

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Four air and moisture-stable palladium(II)-Schiff base complexes, N,N' -bis(α -methylsalicylidene)propane-1,3-diamine palladium(II) (**2a**), N,N' -bis(4-methyl- α -methylsalicylidene)propane-1,3-diamine palladium(II) (**2b**), N,N' -bis(3,5-di-*tert*-butylsalicylidene)propane-1,3-diamine palladium(II) (**2c**), and N,N' -bis(4-methoxy-salicylidene)propane-1,3-diamine palladium(II) (**2d**), have been successfully synthesised and characterised by CHN elemental analyses and conventional spectroscopic methods. These complexes were investigated as catalysts in the phosphine-free Mizoroki-Heck cross-coupling reactions of aryl bromides with methyl acrylate.

1. Introduction

Palladium catalysed carbon-carbon coupling reactions are regarded as one of the most employed organic transformations [1, 2] and have been used extensively for the agrochemical industry [3] pharmaceutical intermediates, conducting polymers, pesticides, and liquid crystals as well [4, 5]. Among these transformations, the coupling of aryl, vinyl, benzyl or allylic halides, acetates, or triflates with alkenes (via the Mizoroki-Heck reaction) is an interesting example of C-C coupling reactions in organic synthesis [6–9]. These reactions are generally carried out in the presence of palladium catalysts associated with broad structural variation such as electron rich tertiary phosphine ligands, phosphoramidites, NHCs (*N*-heterocyclic carbenes), diamines, P, N- and N,O-donor ligands [10–13] which could stabilize the active palladium intermediates [14, 15]. However, due to the difficulty to make and the high cost of phosphines in addition to their propensity to oxidize, there is a current surge in the search of alternative cheap and relatively stable

phosphine-free catalysts that could offer comparable activity [16, 17]. Therefore catalysis under phosphine-free conditions represents a challenge of high importance.

The development of simple, mild, efficient, and more ecologically friendly applications has become a common goal for many researchers [18]. Among the later, Schiff bases have been extensively studied and proved suitable for palladium species. In our attempt to evaluate the phosphine-free system in the Mizoroki-Heck reaction, N_2O_2 -tetradentate Schiff base ligand was chosen. N_2O_2 -tetradentate ligands possess many advantages such as facile approach, readily adjusted ancillary ligand, and electronic environments on the metal centre [19]. Active and well-defined Schiff base metals complexes have been widely studied due to the versatility of their steric and electronic properties, which can be fine-tuned by choosing the amine precursors and ring substituents [20, 21]. Due to these properties, N_2O_2 -tetradentate ligands and their transition metal complexes often act as catalyst.

In this present paper, we wish to report the synthesis and spectroscopic characterization of four palladium(II)

SCHEME 1: Synthesis of tetradentate N_2O_2 -Schiff base ligands.

complexes with Schiff bases derived from the condensation between 2-hydroxyacetophenone, 2-hydroxy-4-methylacetophenone, 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde, and 2-hydroxy-4-methoxybenzaldehyde with 1,3-diaminopropane. The performances of these phosphine-free systems as catalyst have been evaluated in the homogenous Mizoroki-Heck cross-coupling reaction.

2. Experimental

All reactions were carried out under an inert atmosphere of dry nitrogen. Commercial grade solvents were distilled according to normal procedures and dried over molecular sieves (4 Å) prior to use. All reagents were obtained commercially and were used without further purification.

The melting points were measured in capillary tubes using a Electrothermal Digital Melting Point Apparatus and were uncorrected. IR spectra were recorded as KBr matrix on a Perkin Elmer Spectrum One FTIR spectrometer in the range of $4000\text{--}400\text{ cm}^{-1}$. NMR spectra were recorded in CDCl_3 on a Bruker Avance 400 MHz spectrometer operating at the appropriate frequencies. The chemical shifts are reported in ppm using tetramethylsilane (TMS) as internal standard. Elemental analyses were performed on a Thermo Finnigan CE 125 CHN analyzer.

Gas chromatography (GC) analyses were carried out on a GC-Hewlett-Packard 5890 series II gas chromatograph equipped with a $30\text{ m} \times 250\text{ }\mu\text{m} \times 0.25\text{ }\mu\text{m}$ nominal capillary column (ULTRA-1.0.05, 100% dimethylpolysiloxane) and Flame Ionization Detector (FID). The microliter samples are injected at 50°C . The temperature increment is at 15°C per minute and the final temperature was 300°C .

2.1. Synthesis of the Ligands. The N_2O_2 -Schiff base ligands **1a**, **1c**, and **1d** were synthesized according to the literature methods [22–26]. The spectroscopic characterizations of these ligands were in agreement with literature values.

2.2. Synthesis of N,N' -Bis(4-methyl- α -methylsalicylidene)propane-1,3-diamine (1b**).** Stoichiometric amount of 1,3-diaminopropane (5.0 mmol) with two equivalents of 2-hydroxy-4-methylacetophenone are mixed together in 10 mL anhydrous ethanol (Scheme 1). The resulting mixture was refluxed under N_2 atmosphere for 5 hours after which

a yellow solid had precipitated out. This was separated by vacuum filtration, washed with cold ethanol, and dried in vacuum. Yield: 85%, mp: $111\text{--}112^\circ\text{C}$. Calc. for $\text{C}_{21}\text{H}_{26}\text{N}_2\text{O}_2$: C, 74.52; H, 7.74; N, 8.28%. Found: C, 74.70; H, 7.69; N, 8.32%. IR (KBr) $\nu_{\text{max}}\text{ cm}^{-1}$: 3436 (OH), 1611 (C=N), 1154 (C–O). ^1H NMR (ppm, CDCl_3), δ_{H} : 12.30 (s, 2H, OH), 7.40–7.38 (d, 2H, $J = 8.0\text{ Hz}$, Ar–H), 6.74 (s, 2H, Ar–H), 6.60–6.58 (d, 2H, $J = 8.0\text{ Hz}$, Ar–H), 3.74–3.71 (t, 4H, C=N–CH₂), 2.33 (s, 6H, Ar–CH₃), 2.31 (s, 6H, N=C–CH₃) and 2.26–2.20 (m, 2H, C–CH₂–C). ^{13}C NMR (ppm, CDCl_3), δ_{C} : 172.1 (C=N), 164.6 (C–OH), 143.5, 127.9, 119.1, 118.2, 116.7 (arom. C), 46.1 (N–CH₂), 30.8 (C–CH₂), 21.6 (Ar–CH₃), and 14.4 (C–CH₃).

2.3. Synthesis of the Palladium(II) Complexes **2a–2d.** All Pd(II) complexes were synthesized following the standard methods [23, 27–29]. The complex **2c** was prepared by treating an equivalent molar amount of the corresponding ligand with $\text{Pd}(\text{OAc})_2$ in acetonitrile. The spectroscopic data (^1H , ^{13}C NMR, and FTIR) of this complex are in agreement with those reported recently by Ulusoy et al. [30].

2.4. Synthesis of N,N' -Bis(α -methylsalicylidene)propane-1,3-diamine Palladium(II) (2a**).** A solution of ligand **1a** (0.5 mmol) in acetonitrile (10 mL) was added to a solution of palladium(II) acetate (0.5 mmol) in acetonitrile (10 mL) in a three necked round bottom flask (Scheme 2). The resulting mixture was refluxed under N_2 atmosphere for 5 hours after which it was allowed to cool, filtered and evaporated to low volume. Yield: 77%, mp: $335\text{--}336^\circ\text{C}$. Calc. for $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_2\text{Pd}$: C, 55.02; H, 4.86; N, 6.75%. Found: C, 54.86; H, 4.77; N, 6.79%. IR (KBr) $\nu_{\text{max}}\text{ cm}^{-1}$: 1597 (C=N), 1141 (C–O). ^1H NMR (ppm, CDCl_3), δ_{H} : 7.31–7.28 (dd, 2H, $J = 8.0\text{ Hz}$, Ar–H), 7.18–7.14 (t, 2H, $J = 8.0\text{ Hz}$, Ar–H), 7.07–7.06 (d, 2H, $J = 8.0\text{ Hz}$, Ar–H), 6.56–6.52 (t, 2H, $J = 8.0\text{ Hz}$, Ar–H), 3.35–3.33 (t, 4H, C=N–CH₂), 2.78–2.76 (m, 2H, C–CH₂–C), 2.35 (s, 6H, N=C–CH₃). ^{13}C NMR (ppm, CDCl_3), δ_{C} : 169.2 (C=N), 166.5 (C–O), 133.4, 129.9, 127.0, 121.8, 114.8 (arom. C), 53.4 (N–CH₂), 32.1 (C–CH₂), 19.8 (C–CH₃).

2.5. Synthesis of N,N' -Bis(4-methyl- α -methylsalicylidene)propane-1,3-diamine Palladium(II) (2b**).** The corresponding

SCHEME 2: Synthesis of palladium(II)-Schiff base complexes.

palladium complex **2b** was prepared and isolated as brown solid in 75% yield after treating palladium(II) acetate with one mole equivalent of ligand **1b** in a similar manner to the method described for **2a**. mp: 341–343°C. Calc. for $\text{C}_{21}\text{H}_{24}\text{N}_2\text{O}_2\text{Pd}$: C, 56.96; H, 5.46; N, 6.33%. Found: C, 56.64; H, 5.42; N, 6.61%. IR (KBr) ν_{max} cm^{-1} : 1607 (C=N), 1165 (C–O). ^1H NMR (ppm, CDCl_3), δ_{H} : 7.20–7.18 (d, 2H, $J = 8.0$ Hz, Ar–H), 6.90 (s, 2H, Ar–H), 6.37–6.35 (d, 2H, $J = 8.0$ Hz, Ar–H), 3.34–3.32 (t, 4H, C=N–CH₂), 2.76–2.74 (m, 2H, C–CH₂–C), 2.33 (s, 6H, Ar–CH₃) and 2.22 (s, 6H, N=C–CH₃). ^{13}C NMR (ppm, CDCl_3), δ_{C} : 168.8 (C=N), 166.5 (C–O), 144.3, 129.7, 124.5, 121.8, 116.5 (arom. C), 53.3 (N–CH₂), 32.2 (C–CH₂), 21.4 (Ar–CH₃), and 19.6 (C–CH₃).

2.6. Synthesis of *N,N'*-Bis(4-methoxy-salicylidene)propane-1,3-diamine Palladium(II) (2d**).** The palladium complex **2d** was obtained as brown microcrystalline in 80% yield by treating **1d** with one mole equivalent of palladium(II) acetate in a similar way as **2a**. mp: 310–311°C. Calc. for $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_4\text{Pd}$: C, 51.08; H, 4.51; N, 6.27%. Found: C, 51.22; H, 4.50; N, 6.08%. IR (KBr) ν_{max} cm^{-1} : 1606 (C=N), 1169 (C–O). ^1H NMR (ppm, CDCl_3), δ_{H} : 7.45 (s, 2H, N=CH), 7.01–6.99 (d, 2H, $J = 8.0$ Hz, Ar–H), 6.61 (s, 2H, Ar–H), 6.21–6.19 (d, 2H, $J = 8.0$ Hz, Ar–H), 3.80 (Ar–OCH₃), 3.69–3.67 (t, 4H, C=N–CH₂) and 2.07–2.03 (m, 2H, C–CH₂–C). ^{13}C NMR (ppm, CDCl_3), δ_{C} : 166.9 (C–OCH₃), 164.3 (C–O), 161.3 (C=N), 134.8, 113.3, 106.5, 101.7, (arom. C), 60.3 (N–CH₂), 55.3 (Ar–OCH₃), and 29.6 (C–CH₂).

2.7. General Procedure for Catalytic Mizoroki-Heck Reaction. Aryl bromide (1 mmol), methyl acrylate (3 mmol), base (2.4 molar equiv.), palladium complex **2a**, (1 mmol%; 0.01 mmol), and *N,N*-dimethylacetamide (DMA) (2.5 mL) were mixed together in a Radley's 12-placed reaction carousel whilst purging with nitrogen (Scheme 3). The reaction carousel was then heated to 120°C with the temperature carefully controlled by a contact thermometer ($\pm 1^\circ\text{C}$) for 3 and 6 hours. The conversion of reactants was monitored by GC-FID. After the reaction completed, the catalyst was then separated from the reaction mixture. The filtrate was poured into 2% hydrochloric acid (HCl) solution. On cooling to 0°C, a white precipitate was formed. The precipitate was filtered, washed with distilled water, and dried to give the

final product [31]. The identity of the isolated compound was checked by ^1H NMR spectroscopy. The Heck cross-coupling reaction was repeated by using complex **2b**, **2c**, and **2d** as catalyst.

2.8. Characterization of the Methyl-4-acetoxycinnamate. The product was isolated as pale yellow solid in 78% yield. mp: 66–67°C. ^1H NMR (ppm, CDCl_3), δ_{H} : 7.98 (d, H, $J = 8.0$ Hz, Ar–H), 7.72 (d, 1H, $J = 16.0$ Hz, C=CH), 7.62 (d, H, $J = 8.0$ Hz, Ar–H), 6.54 (d, 1H, $J = 16.0$ Hz, C=CH), 3.83 (s, 3H, O–CH₃) and 2.63 (s, 3H, C–CH₃). ^{13}C NMR (ppm, CDCl_3), δ_{C} : 197.3 (C–C=O), 166.9 (O–C=O), 143.4 (C=CH), 138.7, 138.1, 128.7, 128.1 (arom. C), 120.3 (C=CH), 51.9 (O–CH₃), and 26.7 (C–CH₃).

2.9. Characterization of the Methyl-4-nitrocinnamate. The cross coupling product was obtained as yellow solid in 76% yield. mp: 162–163°C. ^1H NMR (ppm, CDCl_3), δ_{H} : 8.27 (d, 2H, $J = 9.0$ Hz, Ar–H), 7.74 (d, 1H, $J = 16.2$ Hz, C=CH), 7.69 (d, 2H, $J = 9.0$ Hz, Ar–H), 6.58 (d, 2H, $J = 16.2$ Hz, C=CH), 3.83 (s, 3H, O–CH₃). ^{13}C NMR (ppm, CDCl_3), δ_{C} : 164.2 (O–C=O), 148.1 (C–N), 141.9 (C=CH), 141.1, 128.5, 123.9 (arom. C), 119.2 (C=CH), and 50.3 (O–CH₃).

2.10. Characterization of the Methyl-4-aminocinnamate. Methyl-4-aminocinnamate was obtained as yellow solid in 80% yield. mp: 73–74°C. ^1H NMR (ppm, CDCl_3), δ_{H} : 7.56 (d, 1H, $J = 16.2$ Hz, C=CH), 7.15 (d, 2H, $J = 7.8$ Hz, Ar–H), 6.52 (d, 2H, $J = 7.8$ Hz, Ar–H), 6.34 (d, 1H, $J = 16.2$ Hz, C=CH), 4.08 (s, 2H, NH₂), 3.65 (s, 3H, O–CH₃). ^{13}C NMR (ppm, CDCl_3), δ_{C} : 167.3 (O–C=O), 147.2 (C–N), 142.4 (C=CH), 128.1, 125.6, 117.0 (arom. C), 121.3 (C=CH), and 52.2 (O–CH₃).

3. Results and Discussion

3.1. Synthesis of Ligands and Palladium(II) Complexes. The Schiff base ligands **1a–1d** were synthesised by condensation reaction between 1,3-diaminopropane with 2 mole equivalent of the corresponding carbonyl compounds according to the step shown in Scheme 1. The condensation reactions were rapid and complete. Meanwhile, the corresponding

SCHEME 3: Heck coupling reaction of aryl bromide with methyl acrylate.

palladium(II) complexes **2a–d** were prepared under nitrogen atmosphere as shown in Scheme 2. The reaction of palladium(II) acetate with the appropriate Schiff base proceeds smoothly in refluxing acetonitrile, to give the brownish complexes **2a** (77%), **2b** (75%), **2c** (78%), and **2d** (80%). All the ligands and the palladium(II) complexes were fully characterised. Elemental analytical, FTIR, ¹H, and ¹³C NMR data are given in the Experimental section. Microanalytical data for the ligands and the palladium complexes are consistent with the calculated empirical formula values.

The FTIR spectra of the Schiff bases **1a–d**, each showed the appearance of a very strong azomethine (C=N) stretching band at 1615, 1611, 1633, and 1622 cm^{−1}, respectively. These values are consistent and are in agreement with other similar imine compounds [32]. Besides that, the absorption bands for the ν(−NH₂) stretching mode from 1,3-diaminopropane and the ν(C=O) stretching mode from 2-hydroxyacetophenone, 2-hydroxy-4-methylacetophenone, 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde, and 2-hydroxy-4-methoxybenzaldehyde have totally disappeared, demonstrating that in each case, the condensation is complete, confirming that the ligands have been successfully synthesized.

Meanwhile, the IR spectra of the palladium(II) complexes **2a–d**, each exhibit a strong and sharp ν(C=N) stretching band at 1597, 1607, 1613, and 1606 cm^{−1}, respectively. The slight displacement of the ν(C=N) band from 1615, 1611, 1633, and 1622 cm^{−1} in the free ligands suggested the coordination of the azomethine nitrogen atoms to the palladium metal in the complexes. This results show that the contribution of the C=N stretching have been reduced as the nitrogen atoms are involved in bond formation with the metal ion. Besides, the broad ν(O–H) band at 3445, 3436, 3426, and 3432 cm^{−1} in the ligands **1a–d**, respectively, are absent in the IR spectrum of the complexes, suggesting the deprotonation of the O–H groups and subsequent coordination of the phenolic oxygen atoms to the metal centre.

The NMR spectra of the complexes further supported the assigned structures. The signal of the acidic OH proton for **1a–d** in the ¹H NMR spectra of the free ligands, each appeared as single resonance at low field at δ 12.28, 12.30, 13.81, and 13.90 ppm, respectively. These signals have totally disappeared in the ¹H spectra of the complexes, indicating the coordination of the phenolic oxygen atoms to the palladium metal due to the participation of OH groups in chelating to metal ion through proton displacement [33]. Meanwhile, the ¹³C NMR spectral data showed the displacement to low field of the imine carbon (C=N) resonance from δ 172.4, 172.0, 166.5, and 163.6 ppm for **1a–d** in the free ligands to δ 169.2,

168.8, 163.8, and 161.3 ppm, respectively in the complexes which further support the coordination of the azomethine nitrogen atoms to the palladium metal.

3.2. Catalytic Studies. The palladium complexes **2a–d** were tested as catalysts for the Heck coupling reaction of methyl acrylate with 4-bromoacetophenone. The reactions were carried out under nitrogen atmosphere in DMA in the presence of base at 120 °C (Scheme 3). 4-bromoacetophenone is chosen as it is economical and more readily available substrate. Owing to the stability and commercial availability of this aryl bromide, the development of a general procedure for the direct coupling of inexpensive aryl bromide with methyl acrylate still represents a challenging and important goal in coupling chemistry [34]. The use of this electron-deficient bromide was also beneficial for the conversion as well [35]. In addition, methyl acrylate has been chosen as the only olefin investigated in this study because the resulting cinnamic ester derivatives are usually used as UV absorbers [36], as anti-oxidants in plastics, and as intermediates for pharmaceuticals [37].

All the complexes were found to catalyse the coupling of methyl acrylate with 4-bromoacetophenone to form exclusively *trans*-acid methyl ester as established by ¹H NMR analysis. No other coupling products (*cis* or *gem*-isomers) were observed. This is in agreement with previous studies by Ojwach et al. [17] and Yasar et al. [35] which reported that in all cases only the *trans* products were selectively obtained as confirmed by ¹H NMR spectroscopy.

Our initial exploration of reaction conditions focused on the effect of bases. The results are shown in Table 1. Catalytic loading was kept to 1.0 mmol%, so as to give an expected turnover number of 100 if 100% conversion was achieved. The main function of base in the Heck cross-coupling reaction mechanism is to neutralize the acidic condition of hydrogen halide in the reductive elimination step and regeneration of catalyst to continue the catalytic cycle [16]. After screening a variety of bases, NaOAc was found to be most effective base as highest conversion was obtained (entries 7, 22, and 23). In contrast, low conversion was achieved when using Na₂CO₃ (entries 12 and 26), probably due to the insolubility of Na₂CO₃.

In the case of an organic base, low conversion was also observed for Et₃N (entries 1 and 17) which may due in part to steric effects exerted by competitive coordination of amine to palladium center [38, 39]. It may also in part due to the formation of gaseous Et₃N at 120 °C that may lead to poor contact with the reaction mixture.

TABLE 1: Effect of the base on the catalytic performance^a.

Entry	Catalyst	Base	Time (h)	Conversion ^b (%)	TON ^c
1	2a	Et ₃ N	3	29	29
2	2b	Et ₃ N	3	44	44
3	2c	Et ₃ N	3	57	57
4	2d	Et ₃ N	3	31	31
5	2a	NaOAc	3	60	60
6	2b	NaOAc	3	48	48
7	2c	NaOAc	3	69	69
8	2d	NaOAc	3	33	33
9	2a	Na ₂ CO ₃	3	29	29
10	2b	Na ₂ CO ₃	3	36	36
11	2c	Na ₂ CO ₃	3	41	41
12	2d	Na ₂ CO ₃	3	27	27
13	2a	NaHCO ₃	3	60	60
14	2b	NaHCO ₃	3	65	65
15	2c	NaHCO ₃	3	43	43
16	2d	NaHCO ₃	3	30	30
17	2a	Et ₃ N	6	58	58
18	2b	Et ₃ N	6	76	76
19	2c	Et ₃ N	6	100	100
20	2d	Et ₃ N	6	75	75
21	2a	NaOAc	6	75	75
22	2b	NaOAc	6	100	100
23	2c	NaOAc	6	100	100
24	2d	NaOAc	6	83	83
25	2a	Na ₂ CO ₃	6	57	57
26	2b	Na ₂ CO ₃	6	44	44
27	2c	Na ₂ CO ₃	6	69	69
28	2d	Na ₂ CO ₃	6	48	48
29	2a	NaHCO ₃	6	97	97
30	2b	NaHCO ₃	6	98	98
31	2c	NaHCO ₃	6	83	83
32	2d	NaHCO ₃	6	46	46

^aReactions were carried out at 120°C with catalyst (1.0 mmol%), 4-bromoacetophenone (1.0 mmol), methyl acrylate (3.0 mmol), base (2.40 mmol), DMA (5.0 mL), in N₂ atmosphere.

^bDetermined by GC-FID.

^cTurnover number (TON): moles of substrate converted per mole of metal in the catalyst.

Complex **2c** showed slightly better catalytic performance than complexed **2a**, **2b**, and **2d** probably due the presence of the electron donating 3,5-di-*tert*-butyl group. In addition, the bulkier ligands are also believed to accelerate the oxidative addition of aryl bromides under homogeneous conditions [30]. Hence, our further investigations only focussed on the catalytic performance of **2c**.

The effect of catalyst loading on the performance of the Heck coupling reactions using catalyst **2c** was then examined (Table 2). The yield of Heck products normally depended on the amounts of Pd(II) catalyst used. The Pd catalysts are important in the oxidative addition and the alkene insertion steps which were the rate-determining steps in the Heck cross-coupling reactions [40]. By controlling the amount of

TABLE 2: Effect of the amount of catalyst on the catalytic performance^a.

Entry	Catalyst. (mmol%)	Time (h)	Conversion ^b (%)	TON ^c
1	2c (0.5)	3	45	90
2	2c (0.5)	6	100	200
3	2c (1.0)	3	68	68
4	2c (1.0)	6	100	100
5	2c (1.5)	3	73	49
6	2c (1.5)	6	100	67
7	2c (2.0)	3	76	35
8	2c (2.0)	6	100	50

^aReactions were carried out at 120°C with 4-bromoacetophenone (1.0 mmol), methyl acrylate (3.0 mmol), NaOAc (2.40 mmol), DMA (5.0 mL), in N₂ atmosphere.

^bDetermined by GC-FID.

^cTurnover no (TON): moles of substrate converted per mole of metal in the catalyst.

TABLE 3: Effect of temperature on the catalytic performance^a.

Entry	Temperature (°C)	Time (h)	Conversion ^b (%)	TON ^c
1	100	3	64	128
2	100	6	68	136
3	120	3	45	90
4	120	6	100	200
5	140	3	59	118
6	140	6	100	200

^aReactions were carried out with catalyst **2c** (0.5 mmol%), 4-bromoacetophenone (1.0 mmol), methyl acrylate (3.0 mmol), NaOAc (2.40 mmol), DMA (5.0 mL), in N₂ atmosphere.

^bDetermined by GC-FID.

^cTurnover number (TON): moles of substrate converted per mole of metal in the catalyst.

Pd catalyst (mmol%), higher turnover number (TON) can be achieved to maximize the percentage conversion of the desired products.

As shown in Table 2, it is apparent that the highest TON value of 200 (entry 2) was achieved even at low catalyst loading (0.5 mmol%). There is considerable activity with a conversion of 100% after 6 hours of reaction time. Thus, we conclude that the choice of 0.5 mmol% Pd-catalyst loading is suitable since it can give higher TON at the same reaction time.

Having established the optimum catalytic conditions, using NaOAc as a base and with 0.5 mmol% catalyst loading, the performance of catalyst **2c** was further screened at different reaction temperatures (Table 3). It is well known that the reaction temperature has a very strong influence on Heck cross-coupling reaction [41]. However, 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 [42]. From our studies, the optimum reaction temperature was found to be at 120°C which is suitable for the activation of aryl bromide (entry 4). The catalytic data obtained indicated that complex **2c** efficiently catalyse

TABLE 4: Effect of substituted aryl bromides on the catalytic performance^a.

Entry	Aryl bromide	Alkene	Product	Conversion ^b (%)	TON ^c
(1)				99.64	199.28
(2)				93.65	187.30
(3)				No conversion	—
(4)				No conversion	—

^a Reactions were carried out at 120 °C, 6 h with catalyst (0.5 mmol%), aryl bromide (1.0 mmol), methyl acrylate (3.0 mmol), NaOAc (2.40 mmol), DMA (5.0 mL), in N₂ atmosphere.

^b Determined by GC-FID.

^c Turnover number (TON): moles of substrate converted per mole of metal in the catalyst.

the Heck cross-coupling reaction of 4-bromoacetophenone with methyl acrylate, giving 100% conversion after 6 hours.

Under the optimisation reaction conditions, several of aryl bromides were tested with methyl acrylate (Table 4), affording the coupled products occurred in excellent yields. As expected, the results showed that the electron-deficient bromides (entries 1 and 2) were beneficial for the conversions. Attempts had been made to use an electron-donating bromide (entry 3) and electron neutral bromide (entry 4). However no conversions were achieved and no desirable coupled products were obtained. It is noted that the percentage of conversion observed for the amino substituted compound is significantly high (entry 2). Although the NH₂ group can also acts as electron donor through resonance, it is believed that the electron withdrawing effect of the electronegative nitrogen atom is more dominant in stabilising the electron rich reaction intermediates.

As stated above, the catalytic activity of palladium complex **2c** was found to be active and efficient catalyst for Heck cross-coupling reaction involving electron deficient aryl bromides with methyl acrylate in which under optimised reaction conditions, excellent conversion of coupled products could be obtained. It should be noted that in all cases only the *trans* products were selectively obtained as confirmed by ¹H NMR.

The application of aryl chlorides as substrates in the Mizoroki-Heck reactions is arguably most attractive due to their higher availability. However, the palladium-catalysed couplings of aryl chlorides were very uncommon and not favourable due to their low reactivity which has usually been attributed to the reluctance of the aryl chloride bond to undergo oxidative addition to Pd(0) [43]. It has been reported that treatment of aryl chlorides with alkenes resulted in low conversion of products formation and it was known that the

oxidative addition of aryl chlorides can only be achieved at elevated temperatures [44, 45].

4. Conclusion

We have successfully synthesised and characterised four chelated palladium(II) complexes with Schiff bases obtained from the condensation reaction between 2-hydroxyacetophenone, 2-hydroxy-4-methoxyacetophenone, 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde, or 2-hydroxy-4-methoxybenzaldehyde with 1,3-diaminopropane. Under our present experimental condition, these complexes efficiently catalyse the Heck cross-coupling reaction of electron-deficient aryl bromides with methyl acrylate.

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