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Pd(II) complexes of Schiff bases and their application as catalysts in Mizoroki–Heck and Suzuki–Miyaura cross-coupling reactions

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Schiff bases of 2-(phenylthio)aniline, $(C_6H_5)SC_6H_4N{=}CR$ (R = (o-CH_3)(C_6H_5), (o-OCH_3)(C_6H_5) or (o-CF_3)(C_6H_5)), and their palladium complexes ($PdLCl_2$) were synthesized. The compounds were characterized using ^1H NMR and ^{13}C NMR spectroscopy and micro analysis. Also, electrochemical properties of the ligands and Pd(II) complexes were investigated in dimethylformamide–$LiClO_4$ solution with cyclic and square wave voltammetry techniques. The Pd(II) complexes showed both reversible and quasi-reversible processes in the −1.5 to 0.3 V potential range. The synthesized Pd(II) complexes were evaluated as catalysts in Mizoroki–Heck and Suzuki–Miyaura cross-coupling reactions. Copyright © 2015 John Wiley & Sons, Ltd.

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Keywords: Schiff base; palladium; Mizoroki–Heck coupling; Suzuki–Miyaura coupling; electrochemistry

Introduction

The palladium-catalysed cross-coupling reactions of aryl halides with arylboronic acids (Suzuki–Miyaura reaction)[1] and olefins (Heck–Mizoroki reaction)[2] provide a powerful methodology for constructing C(sp^2)–C(sp^2) bonds. The reason for the active research is the fact that C–C coupling reactions have many areas of usage in fields such as pharmacological agents, herbicides and the synthesis of natural products.[3] Consequently, researchers have been working on developing better catalysts and increasing yields in these areas which are important for both industrial and scientific purposes.[4]

In Mizoroki–Heck and Suzuki–Miyaura reactions, phosphine compounds are active due to their excellent donor capability. Nevertheless, they have some disadvantages like natural toxicity, sensitivity to air, high cost, synthetic difficulties and limitations of use.[5] Within this scope, nitrogen-based ligands are generally advantageous as they are usually stable to air, inexpensive and easier to handle than their phosphine counterparts.[6] Recently, Schiff bases and their palladium complexes have been shown to have such catalytic activity in Mizoroki–Heck and Suzuki–Miyaura cross-coupling reactions that they can become possible alternatives to phosphine.[7] Researchers have been developing these types of ligands and their palladium complexes which provide more effective and easier oxidative addition.

In the study reported here, we prepared several new Schiff base ligands containing hard nitrogen and soft sulfur donor atoms (**1–3**) and their Pd(II) complexes (**1a–3a**). The Pd(II) complexes were used in Mizoroki–Heck (Scheme 1) and Suzuki–Miyaura (Scheme 2) cross-coupling reactions. The Schiff bases and their palladium complexes were easily synthesized and the results demonstrate that these compounds are also ideal catalysts and highly efficient complexes for the C–C cross-coupling reaction.

Results and discussion

Ligands **1–3** were synthesized by treating 2-(phenylthio)aniline with appropriate aldehydes, i.e. 2-methylbenzaldehyde, 2-methoxybenzaldehyde and 2-trifluoromethylbenzaldehyde (Scheme 3). The Pd(II) complexes of these Schiff bases (**1a–3a**) were prepared under nitrogen atmosphere as shown in Scheme 4. It is found that although the Pd(II) complexes are soluble in dichloromethane, chloroform, ethanol, methanol and acetone, they are insoluble in *n*-hexane and diethyl ether.

FT-IR analysis of Schiff bases and Pd(II) complexes

The FT-IR spectra of the synthesized ligands show a characteristic peak in the region 1632–1640 cm^{-1} indicating the formation of Schiff bases. At the end of the reaction ν_{N-H} and $\nu_{C=O}$ stretching bands of amines and aldehydes disappear and new $\nu_{C=N}$ stretching bands appear with medium intensity at 1632 cm^{-1} (**1**), 1635 cm^{-1} (**2**) and 1640 cm^{-1} (**3**). The FT-IR spectral bands of Pd(II) complexes related to stretching vibrations shift towards lower frequencies when compared to the free ligands: 1624 cm^{-1} (**1a**), 1614 cm^{-1} (**2a**) and 1619 (**3a**) cm^{-1}.[8] The slight shift to lower frequencies after complexation discloses that the ligands are coordinated to Pd(II) through the nitrogen atom.[9] Also, the aromatic CH peaks for all compounds appear at 3060, 3050, 3047, 3027, 3043 and 3051 cm^{-1}, and aliphatic CH_3 bands for **1** and **2** and their Pd(II) complexes **1a** and **2a** are observed at 2967, 2982, 2939 and 2961 cm^{-1}, respectively.

NMR spectra

The structures of compounds were characterized using ^1H NMR and ^{13}C NMR spectroscopy. The ^1H NMR signals of $CH{=}N$ proton are at 8.05 (**1**), 8.19 (**2**) and 8.32 (**3**) ppm, respectively. The $CH{=}N$ peaks of

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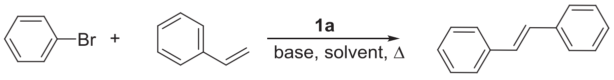
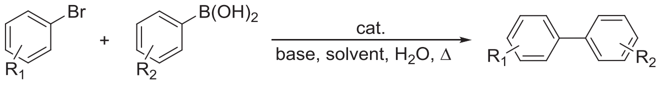
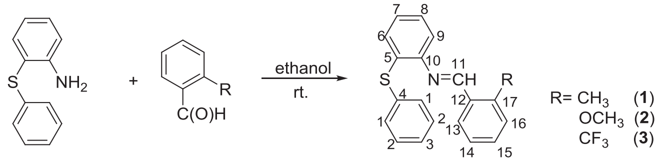


Scheme 1. Mizoroki–Heck reaction.

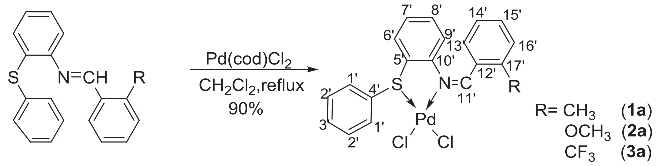


R_1= C(O)CH$_3$, C(O)H, C$_4$H$_3$-(m-OCH$_3$)
R_2= H, CH$_3$, C$_4$H$_4$

Scheme 2. Suzuki–Miyaura reaction.



Scheme 3. Synthesis of Schiff bases **1–3**.



Scheme 4. Synthesis of Pd(II) complexes **1a–3a**.

1a–3a slightly shift (by 0.23–0.11 ppm) when compared to the free ligands (**1a**, 8.28; **2a**, 8.30; **3a**, 8.45 ppm).[10] These results point to π-electrons of azomethine group being attracted to d orbitals of Pd(II). In the ^{13}C NMR spectra, the azomethine carbon (C^{11} and $C^{11'}$) resonances appear in the region of 156.4–162.3 ppm: 159.5 (**1**), 159.5 (**2**), 156.4 (**3**), 162.3 (**1a**), 160.3 (**2a**) and 160.0 (**3a**) ppm. These signals are assigned to *C*H=N resonances. The shifting of ^{13}C NMR spectra occurring after complexation proves that Pd(II) coordinates to the ligands via nitrogen atoms.[11] The ^{1}H NMR spectra of ligands and their Pd(II) complexes **1**, **2**, **1a** and **2a** show signals at 2.50–3.86 ppm, corresponding to aliphatic CH_3 protons. The peaks of aliphatic *C*H$_3$ carbons occur in the range 19.7–55.5 ppm in ^{13}C NMR spectra. The peaks observed in the region of 6.98–7.75 ppm as multiplets in ^{1}H NMR spectra belong to the aromatic protons of the phenyl rings.[12] In the ^{13}C NMR spectra of the ligands and complexes, the phenyl carbon signals appear in the region of 111.0–156.4 ppm. No substantial change is noticed in the NMR values of the aromatic protons and carbons when ligands are exchanged with complexes.

As a result of micro analysis, it is understood that all the ligands and complexes have few impurities due to the organic solvent. Micro analysis for C, H, N and S of ligands **1**, **2**, **3** and their Pd(II) metal complexes **1a**, **2a**, **3a** indicates that the metal-to-ligand ratio of complexes is 1:1. The NMR, FT-IR and micro analysis results prove that Pd (II) coordinates through nitrogen and sulfur atoms of the ligands.

Molar conductivity

The molar conductivity of the complexes was investigated and observed to be 2.3 (**1a**), 2.1 (**2a**) and 3.1 (**3a**) mS cm^2 mol^{-1} in acetonitrile. The values reveal that all the Pd(II) complexes behave as non-electrolytes.[13]

Electronic spectra

The electronic spectra of the ligands and their Pd(II) complexes were investigated in acetonitrile solvent (1×10^{-4} M). The absorption spectra show two π–π* transitions attributed to phenyl rings and azomethine chromophore in the range 286–290 nm. After complexation with Pd(II) the absorption bands are shifted to lower energy (408 (**1a**), 404 (**2a**) and 394 (**3a**) nm).[14]

Electrochemical studies of ligands and their Pd(II) complexes

Electrochemical properties of the Schiff base ligands (**1**, **2**, **3**) and their Pd(II) complexes (**1a**, **2a**, **3a**) were studied using cyclic voltammetry and square wave voltammetry in DMF with 0.1 M LiClO$_4$ as the supporting electrolyte within the potential range −1.5 to 0.3 V. The obtained electrochemical data are summarized in Table 1. None of the studied Schiff base ligands **1**, **2**, **3** show discernible responses under identical conditions except in the potential range −0.7 to −0.8 V. The value observed at this potential range corresponds to the intramolecular reduction/oxidation coupling of the imine groups.

Figure 1 shows the cyclic voltammetric responses of **1** and **1a**. It is seen that the Pd(II) complex **1a** exhibits an irreversible redox

Table 1. Electrochemical parameters for Pd(II) complexes in DMF–0.1 M LiClO$_4$ solution

Compound	Redox couple	E_{pc} (V)	E_{pa} (V)	ΔE_p (mV)^a	$E_{1/2}$ (V)^b
1a	Pd^{+2}/Pd^{+1}	−0.475	—	—	—
2a	Pd^{+2}/Pd^{+1}	−0.674	−0.417	257	−0.546
	Pd^{+1}/Pd^0	−1.158	−1.084	74	−1.121
3a	Pd^{+2}/Pd^{+1}	−0.285	−0.322	37	−0.304
	Pd^{+1}/Pd^0	−1.291	—	—	—

$^a\Delta E_p = E_{pa} - E_{pc}$.
$^bE_{1/2} = (E_{pa} + E_{pc})/2$.

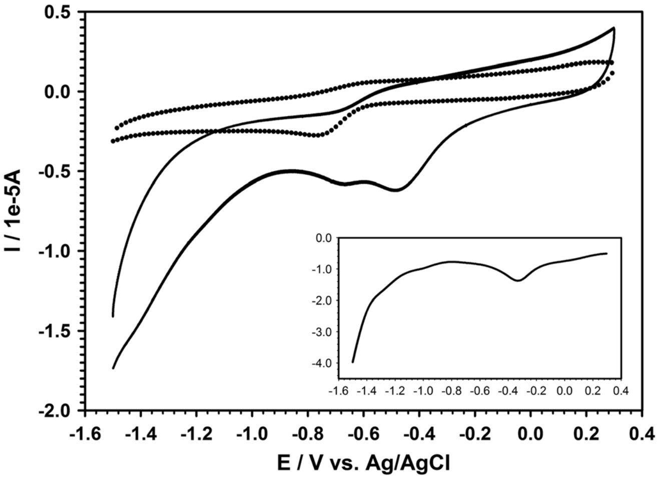


Figure 1. Cyclic voltammograms of Schiff base ligand **1** (dotted curve) and Pd(II) complex **1a** (solid curve) in DMF–LiClO$_4$ using glassy carbon electrode with 0.1 V s^{-1} scan rate (inset: square wave voltammogram of **1a**: amplitude, 50 mV; frequency, 15 Hz; glassy carbon working electrode).

process during the negative scan. The cathodic reduction peak at $E_{pc} = -0.475$ V corresponds to the Pd(II)/Pd(I) redox pair.[14] The reduction of Pd(II) to Pd(I) is clearly observed in the square wave voltammogram of the inset.

Complex **2a** shows a well-defined reversible electrochemical response at $E_{pa} = -1.084$ V and $E_{pc} = -1.158$ V which correspond to Pd(I)/Pd(0) redox pair (Fig. 2). This couple is found to be a reversible process. This behaviour is similar to that reported previously in cyclic voltammetric studies of Pd(II) complexes.[15] A quasi-reversible process is also observed in the cyclic voltammetric response of **2a** which is assigned to Pd(II)/Pd(I) couple at $E_{pa} = -0.417$ V and $E_{pc} = -0.674$ V.[16] Only a weak wave is observed in the anodic square wave voltammogram of this redox couple (Fig. 2, inset).

The cyclic voltammograms of 1×10^{-3} M Schiff base ligand **3** and Pd(II) complex **3a** are presented in Fig. 3. Complex **3a** shows an anodic peak at $E_{pa} = -0.322$ V. On the reverse scan, two cathodic peaks are observed at $E_{pc} = -0.285$ and -1.291 V, respectively. The reversible process in the -0.3 V potential range is assigned to Pd(II)/Pd(I) redox couple.[13,17] Pd(II)/Pd(I) redox process is clearly observed in both the cyclic voltammogram and the square wave voltammogram, whereas the process at -1.291 V in the cathodic scan is irreversible and not observed in the square wave voltammogram. This reductive response can be assigned as Pd(I) to Pd(0).[14]

According to Table 1, the cathodic peak potentials (E_{pc}) of Pd(II)/Pd(I) become less negative due to electron-withdrawing group $-CF_3$. In the case of compounds **1a** and **2a**, the presence of $-CH_3$ and $-OCH_3$ (electron donating) makes the potentials more negative than that of **3a**.[18]

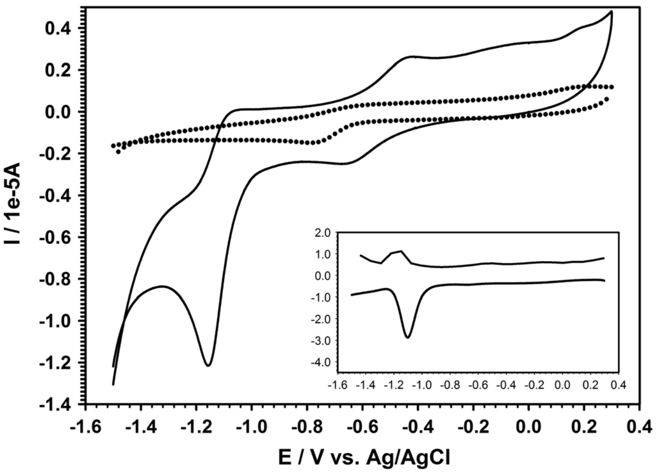


Figure 2. Cyclic voltammograms of Schiff base ligand **2** (dotted curve) and Pd(II) complex **2a** (solid curve) in DMF–$LiClO_4$ using glassy carbon electrode with 0.1 V s^{-1} scan rate (inset: square wave voltammogram of **2a**: amplitude, 50 mV; frequency, 15 Hz; glassy carbon working electrode).

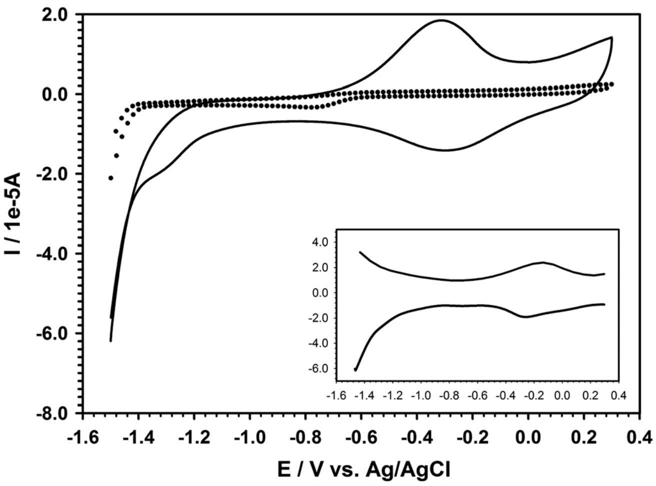


Figure 3. Cyclic voltammograms of Schiff base ligand **3** (dotted curve) and Pd(II) complex **3a** (solid curve) in DMF–$LiClO_4$ using glassy carbon electrode with 0.1 V s^{-1} scan rate (inset: square wave voltammogram of **3a**: amplitude, 50 mV; frequency, 15 Hz; glassy carbon working electrode).

Mizoroki–Heck reaction

Palladium complexes are active catalysts for C–C coupling reactions.[19,1] Because of this, complexes **1a–3a** were tested in Mizoroki–Heck and Suzuki–Miyaura reactions.

Firstly, the Mizoroki–Heck reaction of bromobenzene and styrene was chosen as a model reaction, and the optimal conditions were identified as shown in Scheme 1. Determination of the optimum conditions is achieved by testing organic and inorganic bases (NEt_3, Na_2CO_3, NaOAc and K_2CO_3), various temperatures (80, 100, 120 and 140 °C) and various solvent systems (toluene, 1,4-dioxane, DMF and *N*-methylpyrrolidone) in the presence of **1a** (substrate/catalyst: 250), with the samples taken at the end of the reaction being analysed using GC. In polar solvents, the conversions generally appear to be higher than those obtained in non-polar solvents, and the best conversion is found in 1,4-dioxane and K_2CO_3 at 140 °C. The Mizoroki–Heck reaction was carried out with catalysts **1a–3a** between derivatives of aryl bromides and styrenes or acrylates substituted in various positions (Tables 2 and 3) using the conditions mentioned above.

Under the typical reaction conditions, non-activated neutral substrates such as bromobenzene give moderate yields. Low conversion is obtained with styrenes only in one reaction with catalyst **1a** (Table 2, entry 1). High conversion is observed in the presence of **3a** (Table 2, entry 1). In the reaction between activated electron-deficient substrates such as 4-bromobenzaldehyde with styrenes, all three catalysts show high activity (Table 2, entries 5–7). In addition, the presence of electron-donating groups such as methyl or methoxy moiety on the aryl bromide leads to lower

Table 2. Results of reaction between olefins and aryl bromides[a]

			Conversion (%)[b]		
Entry	R_1	Aryl bromide	**1a**	**2a**	**3a**
1	H	Phenyl bromide	22	57	88
2	2-CH_3	Phenyl bromide	9	21	24
3	4-OCH_3	Phenyl bromide	5	54	52
4	4-Br	Phenyl bromide	20	26	33
5	H	4-Bromobenzaldehyde	99	99	99
6	2-CH_3	4-Bromobenzaldehyde	99	99	99
7	4-OCH_3	4-Bromobenzaldehyde	99	99	99
8	4-Br	4-Bromobenzaldehyde	67	70	70
9	H	6-Methoxynaphthyl bromide	30	60	41
10	2-CH_3	6-Methoxynaphthyl bromide	3	13	11
11	4-OCH_3	6-Methoxynaphthyl bromide	23	19	25
12	4-Br	6-Methoxynaphthyl bromide	15	10	10

[a] Reaction conditions: aryl bromide (0.1 mmol), olefin (0.12 mmol), K_2CO_3 (0.12 mmol), catalyst (4×10^{-4} mmol), 1,4-dioxane (3 ml), 140 °C, 6 h.
[b] Analyses were made using GC and in accordance to aryl bromide.

Table 3. Results of reaction between olefins and aryl bromides[a]

Entry	R_1	Aryl bromide	Conversion (%)[b] 1a	2a	3a
1	CH_3	Phenyl bromide	3	37	37
2	CH_2CH_3	Phenyl bromide	7	36	59
3	$(CH_2)_3CH_3$	Phenyl bromide	23	53	83
4	CH_3	4-Bromobenzaldehyde	5	37	70
5	CH_2CH_3	4-Bromobenzaldehyde	50	84	99
6	$(CH_2)_3CH_3$	4-Bromobenzaldehyde	99	99	99
7	CH_3	6-Methoxynaphthyl bromide	—	10	12
8	CH_2CH_3	6-Methoxynaphthyl bromide	6	90	69
9	$(CH_2)_3CH_3$	6-Methoxynaphthyl bromide	99	30	20

[a] Reaction conditions: aryl bromide(0.1 mmol), olefin (0.12 mmol), K_2CO_3 (0.12 mmol), catalyst (4×10^{-4} mmol), 1,4-dioxane (3 ml), 140 °C, 6 h.

[b] Analyses were made using GC and in accordance to aryl bromide.

Table 4. Results of reaction between aryl bromides and boronic acids[a]

Entry	R_1	R_2	Conversion (%)[b] 1a	2a	3a
1	2-C(O)CH_3	H	99	94	95
2	4-C(O)H	H	92	89	91
3	2-C(O)H	H	94	≥99	≤99
4	C_4H_3(*m*-OCH_3)	H	89	90	92
5	2-C(O)CH_3	C_4H_4	87	86	95
6	4-C(O)H	C_4H_4	93	94	98
7	2-C(O)H	C_4H_4	≤99	99	96
8	C_4H_3(*m*-OCH_3)	C_4H_4	74	30	31
9	2-C(O)CH_3	2-CH_3	89	78	89
10	4-C(O)H	2-CH_3	88	89	86
11	2-C(O)H	2-CH_3	99	99	99
12	C_4H_3(*m*-OCH_3)	2-CH_3	65	40	66

[a] Reaction conditions: aryl bromide (0.1 mmol), boronic acid (0.12 mmol), K_2CO_3 (0.12 mmol), catalyst (4×10^{-4} mmol), 1,4-dioxane (3 ml)–H_2O (3 ml), 100 °C, 6 h.

[b] Analyses were made using GC and in accordance to aryl bromide.

reaction rates and results in low conversions with styrenes. In the reaction of 2-bromo-6-methoxynaphthalene with olefins, **1a–3a** show a lower activity compared to other aryl bromides. This is probably because, unlike other aryl bromides, 2-bromo-6-methoxynaphthalene is sterically hindered (Table 2, entries 9–12).

Carbon–carbon coupling reactions were also tested with acrylates under the same reaction conditions as described above, and higher conversions are obtained when compared with styrenes. All catalysts show high activity in the reaction of 4-bromobenzaldehyde with butyl acrylate (Table 3, entry 6). In the reaction between 4-bromobenzaldehyde and ethyl acrylate, only two reactions show high activity (Table 3, entries 5 (**3a**) and 8 (**2a**)). Meanwhile, aryl bromides bearing electron-withdrawing groups such as aldehyde (Table 3, entries 5 and 6) give excellent conversions within 6 h. The reactions of 2-bromo-6-methoxynaphthalene with acrylates (Table 3, entries 8 (**2a**) and 9 (**1a**)) also result in high conversions. Other conversions listed in Table 3 are low and moderate because 2-bromo-6-methoxynaphthalene is sterically hindered and catalysts cannot approach the active site when compared to other aryl halides.

Suzuki–Miyaura reaction

The same approach was followed for the Suzuki–Miyaura reaction as for the Mizoroki–Heck reaction. For this purpose, inorganic and organic bases (NEt_3, Na_2CO_3, NaOAc, NaOH and K_2CO_3), various temperatures (80 and 100 °C) and various solvent systems (toluene, 1,4-dioxane and DMF with water) were tested in the reaction of aryl bromides and phenylboronic acids in the presence of catalyst **1a**, and samples taken at the end of the reaction were analysed using GC (Scheme 2). The GC results confirm that the conversion at 80 °C is low when compared to that at 100 °C (Table 4).

Catalytic experiments were conducted with various aryl halides and boronic acid derivatives at 100 °C using catalysts **1a–3a** (K_2CO_3, 1,4-dioxane–water (3:3 ml)). The reactions of 3-bromobenzaldehyde with boronic acids were performed with substrate-to-catalyst ratio of 250 at 100 °C and they give excellent yields (Table 4, entries 3, 7, 11). The lowest conversion is observed in the reaction of 2-naphthaleneboronic acid and 2-bromo-6-methoxynaphthalene (Table 4, entry 8). The reason for this low conversion can be explained as follows. Due to 2-naphthaleneboronic acid and 2-bromo-6-methoxynaphthalene being sterically bulky, the catalysts cannot come close to these compounds, an effect that has an influence on the reaction rates in these conditions. Therefore the catalysts show less activity in these reactions than in those reactions with other olefins and aryl halides. Whereas in the synthesis of carbaldehyde derivative compounds the same catalysts give high yields when coupling 2-bromo-6-methoxynaphthalene with benzeneboronic acid (Table 4, entry 4).

Experimental

Materials and methods

All reactions were carried out under nitrogen atmosphere using conventional Schlenk glassware. Solvents were dried using established procedures and then immediately distilled under nitrogen atmosphere prior to use. 2-(Phenylthio)aniline and aldehydes purchased from Sigma-Aldrich Chemie GmbH (Steinheim, Germany) were used without further purification. Pd(cod)Cl_2 was prepared as described in the literature.[20]

Micro analysis (C, H, N and S) was performed using a LECO CHNS 932 instrument. Infrared spectra of synthesized compounds were recorded with a PerkinElmer RX1 spectrophotometer in the range 650–4000 cm^{-1}. All ^1H NMR (400.1 MHz) data were obtained at 25 °C with deuterated DMSO and $CDCl_3$ using a Bruker NMR spectrometer. ^{13}C NMR spectra were obtained with a Varian Mercury 100.6 MHz NMR spectrometer. UV–visible spectra were recorded with a PG T80+ spectrophotometer at room temperature. Conductivities were measured with a Hanna EC-215 conductivity meter. The coupling products were analysed using a PerkinElmer Clarus 500 series gas chromatograph equipped with a flame ionization detector and a 30 m × 0.25 mm × 0.25 μm film thickness β-Dex capillary column. TLC was used for monitoring the reactions.

Cyclic voltammetry and square wave voltammetry data were obtained with a CHI 6094D electrochemical analyser controlled by an external PC. All electrochemical experiments were performed using a conventional three-electrode electrochemical cell system consisting of a glassy carbon electrode (3.0 mm in diameter) as working electrode, a platinum wire as auxiliary electrode and Ag/AgCl electrode as reference.

Voltammetric experiments were performed in extra-pure DMF (Merck) containing 0.1 M $LiClO_4$ as the supporting electrolyte. High-purity argon was used for deoxygenating the solution at least 15 min prior to each run and to maintain an argon blanket during the measurements. In order to obtain a reproducible active surface, the glassy carbon electrode was polished with alumina suspension with a particle size of 0.05 μm. Square wave voltammetry settings were: step potential, 4 mV; amplitude, 50 mV; frequency, 15 Hz. The concentration of the Pd(II) complexes was 1×10^{-3} M during the voltammetric experiments. Scans were performed in the potential range −1.5 to 0.3 V starting from negative potential. All electrochemical measurements were carried out at room temperature.

Preparation of ligands and complexes

*Preparation of $(C_6H_5)SC_6H_4N{=}C{-}(o\text{-}CH_3)(C_6H_5)$ (**1**)*

2-(Phenylthio)aniline (580 mg, 2.90 mmol) and 2-methylbenzaldehyde (350 mg, 2.90 mmol) were mixed and stirred for 1 h in ethanol (10 ml) at room temperature. The reaction was monitored using TLC (hexane–ethyl acetate, 3:1). The yellow precipitate product was washed with cold ethanol and dried under vacuum. The yellow product was crystallized from methanol at −20 °C. Yield 0.70 g (81%), m.p. 71 °C. ^1H NMR (400.2 MHz, $CDCl_3$, δ, ppm): 8.61 (s, H^{11}, HC=N), 7.44 (d, 1H, $J = 6.9$ Hz, H^{13}), 7.28 (d, 1H, $J = 7.7$ Hz, H^{16}), 7.18 (d, 2H, $J = 7.5$ Hz, H^1), 7.11 (d, 1H, $J = 7.4$ Hz, H^6), 7.20–6.98 (m, 8H, $H^{2,3,7-9,14,15}$), 2.55 (s, 3H, CH_3). ^{13}C NMR (100.6 MHz, $CDCl_3$, δ, ppm): 159.5 (s, C^{11}, CH=N), 150.8 (C^{10}), 138.9 (C^4), 134.2 (C^5), 133.9 (C^8), 133.1 (C^{16}), 131.8 (C^{17}), 131.1 (C^1), 131.0 (C^{14}), 129.3 (C^2), 129.0 (C^{12}), 128.8 (C^{15}), 127.7 (C^6), 127.1 (C^7), 126.3 (C^3), 126.2 (C^{13}), 118.4 (C^9), 19.7 (s, CH_3). FT-IR (KBr, cm^{-1}): 3060 (CH_{ar}), 2967 (CH_3), 1632 (C=N). Anal. Calcd for $C_{20}H_{17}NS$ (%): C, 79.17; H, 5.65; N, 4.62; S, 10.57. Found (%): C, 77.17; H, 5.69; N, 4.47; S, 10.52.

*Preparation of Ligands **2** and **3***

The Schiff bases **2** and **3** were prepared using a procedure similar to that for ligand **1**.

Ligand **2**. Yellow solid; yield 0.67 g (73%); m.p. 60.0 °C. ^1H NMR (400.2 MHz, DMSO-d_6, δ, ppm): 8.83 (s, 1H, HC=N), 7.53 (d, 1H, $J = 7.7$ Hz, H^{13}), 7.43 (d, 1H, $J = 7.0$ Hz, H^{16}), 7.31 (d, 2H, $J = 7.1$ Hz, H^1), 7.10 (d, 1H, $J = 7.3$ Hz, H^6), 7.33–7.17 (m, 8H, $H^{2,3,7-9,14,15}$), 3.86 (s, 3H, CH_3). ^{13}C NMR (100.6 MHz, $CDCl_3$, δ, ppm): 159.5 (C^{11}, CH=N), 156.4 (C^{10}), 150.5 (C^4), 133.9 (C^5), 133.4 (C^8), 132.8 (C^{17}), 132.4 (C^{16}), 129.2 (C^1), 128.5 (C^{14}), 127.9 (C^2), 127.7 (C^{12}), 126.8 (C^{15}), 125.9 (C^6), 124.6 (C^7), 120.8 (C^3), 118.4 (C^{13}), 111.0 (C^9), 55.5 (s, OCH_3). FT-IR (KBr, cm^{-1}): 3050 (CH_{ar}), 2982 (OCH_3), 1635 (C=N). Anal. Calcd for $C_{20}H_{17}NOS$ (%): C, 75.20; H, 5.36; N, 4.39; S, 10.04. Found (%): C, 73.87; H, 5.19; N, 4.62; S, 9.76.

Ligand **3**. Yellow solid; yield 0.95 g (92%); m.p. 72 °C. ^1H NMR (400.2 MHz, DMSO-d_6, δ, ppm): 8.73 (s, 1H, HC=N), 7.61 (d, 1H, $J = 7.8$ Hz, H^{13}), 7.53 (d, 1H, $J = 7.82$ Hz, H^{16}), 7.44 (d, 2H, $J = 7.1$ Hz, H^1), 7.32 (d, 1H, $J = 7.4$ Hz, H^6), 7.28–7.02 (m, 8H, $H^{2,3,7-9,14,15}$). ^{13}C NMR (100.6 MHz, $CDCl_3$, δ, ppm): 156.4 (C^{11}, CH=N), 149.5 (C^{10}), 134.0 (C^4), 133.8 (C^5), 133.1 (C^8), 132.6 (C^{17}), 132.2 (C^{16}), 129.7 (C^1), 129.5 (C^{14}), 129.3 (C^2), 129.1 (C^{12}), 128.9 (C^{15}), 127.8 (C^6), 127.1 (C^7), 125.7 (C^3), 125.1 (C^{13}), 123.3 (C^9), 118.2 (s, CF_3). FT-IR (KBr, cm^{-1}): 3047 (CH_{ar}), 1640 (C=N). Anal. Calcd for $C_{20}H_{14}F_3NS$ (%): C, 67.21; H, 3.95; N, 3.92; S, 8.97. Found (%): C, 66.27; H, 3.80; N, 4.07; S, 9.31.

*Preparation of $[PdCl_2(o\text{-}PPh_2)C_6H_4CH{=}N(o\text{-}CH_3)(p\text{-}OH)C_6H_3]$ (**1a**)*

Ligand **1** (155 mg, 0.51 mmol) was added to a solution of $Pd(cod)Cl_2$ (145 mg, 0.51 mmol) in dry CH_2Cl_2 (10 ml). The mixture was stirred for 2 h at reflux. Then, addition of diethyl ether caused the formation of a dark yellow precipitate which was filtered off and dried to afford the title compound **1a**. Yield 0.22 mg (90%), m.p. 244 °C. ^1H NMR (400.2 MHz, DMSO-d_6, δ, ppm): 8.28 (s, 1H, HC=N), 7.74 (d, 1H, $J = 7.8$ Hz, $H^{13'}$), 7.54 (d, 1H, $J = 6.9$ Hz, $H^{16'}$), 7.53–7.03 (m, 11H, $H^{1'-3',6'-9',14',15'}$), 2.50 (s, 3H, CH_3). ^{13}C NMR (100.6 MHz, $CDCl_3$, δ, ppm): 162.3 ($C^{11'}$, CH=N), 149.9 ($C^{10'}$), 146.4 ($C^{4'}$), 136.9 ($C^{5'}$), 136.6 ($C^{8'}$), 132.5 ($C^{17'}$), 132.3 ($C^{16'}$), 131.7 ($C^{1'}$), 131.0 ($C^{14'}$), 130.7 ($C^{2'}$), 129.8 ($C^{12'}$), 128.9 ($C^{15'}$), 127.6 ($C^{6'}$), 126.3 ($C^{7'}$), 125.4 ($C^{3'}$), 116.9 ($C^{13'}$), 115.0 ($C^{9'}$), 30.8 (s, CH_3). FT-IR (KBr, cm^{-1}): 3027 (CH_{ar}), 2939 (CH_3), 1624 (C=N). Anal. Calcd for $C_{20}H_{17}Cl_2NSPd$ (%): C, 49.97; H, 3.56; N, 2.91; S, 6.67. Found (%): C, 50.45; H, 3.86; N, 3.20; S, 7.40.

*Preparation of Complexes **2a** and **3a***

Complexes **2a** and **3a** were prepared using a procedure similar to that for complex **1a**.

Complex **2a**. Orange solid; yield 0.20 g (78%); m.p. 214 °C. ^1H NMR (400.2 MHz, DMSO-d_6, δ, ppm): 8.30 (s, 1H, HC=N), 7.52 (d, 1H, $J = 7.5$ Hz, $H^{13'}$), 7.42 (d, 1H, $J = 7.7$ Hz, $H^{16'}$), 7.73–7.03 (m, 11H, $H^{1'-3',6'-9',14',15'}$), 3.42 (s, 3H, OCH_3). ^{13}C NMR (100.6 MHz, $CDCl_3$, δ, ppm): 160.3 ($C^{11'}$), 146.6 ($C^{10'}$), 136.9 ($C^{4'}$), 136.6 ($C^{5'}$), 132.8 ($C^{8'}$), 132.3 ($C^{17'}$), 131.7 ($C^{16'}$), 131.4 ($C^{1'}$), 131.0 ($C^{14'}$), 130.7 ($C^{2'}$), 129.9 ($C^{12'}$), 129.0 ($C^{15'}$), 127.6 ($C^{6'}$), 127.4 ($C^{7'}$), 126.3 ($C^{3'}$), 125.4 ($C^{13'}$), 116.8 ($C^{9'}$), 54.8 (s, OCH_3). FT-IR (KBr, cm^{-1}): 3043 (CH_{ar}), 2961 (OCH_3), 1614 (C=N). Anal. Calcd for $C_{20}H_{17}Cl_2ONSPd$ (%): C, 48.36; H, 3.45; N, 2.82; S, 6.45. Found (%): C, 47.45; H, 3.96; N, 3.08; S, 7.40.

Complex **3a**. Orange solid; yield 0.24 g (88%); m.p. 239 °C. ^1H NMR (400.2 MHz, DMSO-d_6, δ, ppm): 8.45 (s, 1H, HC=N), 7.72 (d, 1H, $J = 7.7$ Hz, $H^{13'}$), 7.42 (d, 1H, $J = 6.2$ Hz, $H^{16'}$), 7.75–7.10 (m, 11H, $H^{1'-3',6'-9',14',15'}$). ^{13}C NMR (100.6 MHz, $CDCl_3$, δ, ppm): 160.0 ($C^{11'}$, CH=N), 149.9 ($C^{10'}$), 136.9 ($C^{4'}$), 136.1 ($C^{5'}$), 134.3 ($C^{8'}$), 131.8 ($C^{17'}$), 131.5 ($C^{16'}$), 131.1 ($C^{1'}$), 131.0 ($C^{14'}$), 130.4 ($C^{2'}$), 129.9 ($C^{12'}$), 128.6 ($C^{15'}$), 127.6 ($C^{6'}$), 125.4 ($C^{7'}$), 123.5 ($C^{3'}$), 120.6 ($C^{13'}$), 119.1 ($C^{9'}$), 114.8 (s, CF_3). FT-IR (KBr, cm^{-1}): 3051 (CH_{ar}), 1619 (C=N). Anal. Calcd for $C_{20}H14F_3Cl_2NSPd$ (%): C, 44.92; H, 2.64; N, 2.62; S, 6.00. Found (%): C, 45.45; H, 2.96; N, 2.20; S, 6.40.

General procedure for Mizoroki–Heck coupling reaction

In a typical experiment, an oven-dried Schlenk tube was charged with K_2CO_3 (1.2 mmol) and organic solvent (3 ml) under nitrogen atmosphere followed by addition of aryl halide (0.1 mmol), olefin (0.12 mmol) and Pd(II) catalyst (4×10^{-4} mmol). The flask was placed in an oil bath and the reaction mixture was stirred at appropriate temperatures for the required times. After completion of the reaction, the mixture was cooled and extracted with ethyl acetate (3 × 20 ml). The extracts were collected and washed with brine and dried over $MgSO_4$, and then the solvent was evaporated. The residue was purified by flash column chromatography on a silica gel column.

General procedure for Suzuki–Miyaura coupling reaction

An oven-dried Schlenk tube was charged with base (0.2 mmol) and organic solvent–H_2O (3:3 ml) under nitrogen atmosphere followed by aryl halide (0.1 mmol), phenylboronic acid (0.12 mmol) and Pd (II) catalyst (4×10^{-4} mmol). The flask was placed in an oil bath and then the reaction mixture was stirred at appropriate temperatures for required times. The reaction mixture was cooled and poured into water (5 ml) and extracted with $CHCl_3$ (3 × 20 ml). The extracts were washed with brine and dried over $MgSO_4$ and the solvent was evaporated.

Conclusions

New bidentate Schiff bases and their Pd(II) complexes were prepared. The complexes were tested as catalysts for Mizoroki–Heck and Suzuki–Miyaura reactions. High conversions were obtained in the Suzuki–Miyaura reaction when carried out at 100 °C in K_2CO_3 media. These results indicate that all the examined catalysts were effective for these reactions. Ligands with CH_3, OCH_3 and CF_3 had no influence on the catalytic activity because no significant difference was noticed in the resulting conversions when the catalysts were compared with one another. Electrochemical properties of the Pd(II) complexes investigated and $E_{1/2}$ values of reversible redox processes were determined. E_p values of irreversible processes have also been reported.

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