Research Article

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Preparation and spectroscopic studies of Fe(II), Ru(II), Pd(II) and Zn(II) complexes of Schiff base containing terephthalaldehyde and their transfer hydrogenation and Suzuki-Miyaura coupling reaction

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Abstract: This study describes synthesis, spectroscopic characterization and catalytic activities of Fe(II), Ru(II), Pd(II) and Zn(II) complexes with a novel Schiff base ligand (L) derived from methyl 2-amino-5,5,7,7-tetramethyl-4,5,6,7-tetrahydrobenzo[b]thiophene-3-carboxylate and terephthalaldehyde. We used spectroscopic techniques including IR, UV-Vis, ^1H -NMR, ^{13}C -NMR, elemental analysis and also mass analysis and magnetic susceptibility measurements to identify the products. The Pd(II) complex was used as a potential catalyst for Suzuki-Miyaura coupling reaction of some aryl halides under optimized conditions. The effect of various bases such as NaOH, KOH, and KOBu^t was investigated in transfer hydrogenation (TH) of ketones by isopropyl alcohol as the hydrogen source. Ru(II) and Pd(II) complexes showed catalytic activity while Zn(II) and Fe(II) metal complexes failed to do that.

Keywords: Catalysis; Metal complexes; Thiophene carboxylate; Terephthalaldehyde; Schiff base.

1 Introduction

Schiff bases belong to a prominent class of compounds and they draw significant attention in many different fields because of their characteristic features [1]. The main advantages of Schiff bases are their ease of formation under mild conditions and the linking of additional functional groups for developing new structures and chemo-physical properties. They play an important role in inorganic chemistry since they can easily form stable complexes with most transition metal ions. Metal complexes of Schiff bases possess a wide range of implementation such as catalysts, drugs and magnetic or luminescent materials [2-5].

The high thermal and moisture stabilities of Schiff base complexes render them valuable for applications like catalysts in reactions at high temperatures. The activity of Schiff bases frequently increases by complexation. Therefore, a comprehensive understanding of the properties of ligands and metal complexes may result in the synthesis of highly active compounds. The most important advantages of using Schiff base ligands in metal complexes are that they include the hydrogenation of olefins and carbonyl groups, the transfer of an amino group and their capability to form complexes against toxic metals and other applications [6-12].

Transition metal complexes, mainly those containing ruthenium, are very significant catalyst precursors [13]. The center of attraction in ruthenium complexes containing Schiff bases remains unchanged owing to their multi-electron transfer properties, their ability to exhibit a large oxidation state, and their potential catalytic activity [14-20]. Palladium-catalyzed Heck-Mizoroki or Suzuki-Miyaura coupling reactions are important tools for construction of aryl-carbon bond. Currently, researchers

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have focused on these coupling reactions using more active catalysts or using ones that can be recycled. The goal is to reduce the cost, produce higher purity products and develop more productive and less wasteful processes with more efficient methodologies for such coupling reactions [21-29].

The synthesis, spectroscopic and catalytic properties of the Schiff base ligand and its $[\text{Zn}_2\text{L}\cdot 2\text{Cl}_2\cdot 2\text{H}_2\text{O}]$, $[\text{Fe}_2\text{L}\cdot 2\text{Cl}_2\cdot 2\text{H}_2\text{O}]\cdot 3\text{H}_2\text{O}$, $[\text{Ru}_2\text{Cl}_2(p\text{-cymene})_2\text{L}]$, $[\text{Pd}_2\text{L}\cdot 2\text{Cl}_2]\cdot 4\text{H}_2\text{O}$ complexes were described in this study. The catalytic activities of the Pd(II) complex for Suzuki-Miyaura coupling reactions were investigated. Further, the transfer hydrogenation of acetophenone was carried out by Ru(II) complex of reduced Schiff base ligand. The Ru(II) complex was found to be an active catalyst. The Pd(II) complex showed efficient catalytic activity in Suzuki-Miyaura cross-coupling reaction between various aryl halides and aryl boronic acids.

2 Experimental

2.1 Materials and methods

Every chemicals used were of reagent grade. Solvents were purified and distilled for synthesis and physical measurements. The IR spectra were recorded in KBr discs in the wave number range of 4000-400 cm^{-1} on a Perkin Elmer Model 65 FTIR Spectrophotometer. The ^1H and ^{13}C -NMR spectras were recorded in DMSO- d_6 solvent on Perkin Elmer 400 MHz NMR spectrometer using tetramethylsilane as the internal standard. Chemical shifts have been expressed in ppm. Electronic spectra were recorded on a UV-Visible Shimadzu 1800 in the wavelength 1100-190 nm. Mass spectra were recorded on Varian Inc, Anadolu University made Liquid Chromatography-Mass Spectrometer. Elemental analyses were performed on a LECO 932 CHNS analyzer. Magnetic susceptibility measurements were carried out using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as calibrant by Gouy balance. GC-MS measurements for catalytic experiments were applied using an Agilent 7890 B GC and Agilent 5977 M MS (GC-MS) system by GC-FID with an HP-5 column of 30 m length, 0.32 mm diameter, and 0.25 mm film thickness. The GC parameters were as follows: oven: 80°C (isothermal); carrier gas: He (Split ratio 1:10); flow rate: 4 mL/min; injector port temperature: 200°C; detector temperature: 260°C; injection volume: 2.0 μL .

2.2 Synthesis and characterization of ligand and its complexes

Sulfur (0.32 g, 0.01 mol), triethylamine (1.01 g, 0.01 mol) and methyl-2-cyanoacetate (0.99 g, 0.01 mol) were put to 50 mL of ethyl alcohol in the presence of 3,3,5,5-tetramethylcyclohexanone (1.13 g, 0.01 mol). The mixture was heated at 50°C under reflux for 3 h. Some water was added to precipitate the resulting solids in the mixture. Crystallization of filtrate with ethyl alcohol afforded the starting material.

The terephthalaldehyde (0.01 mol) dissolved in ethanol (20 mL) was put to the solution of the starting material (0.02 mol) in ethanol (20 mL). The mixture was refluxed for 10 h. Finally, the product was filtered off, washed with diethylether and dried at room temperature.

Ligand: Yield: 78%. Anal. Calc. for $\text{C}_{36}\text{H}_{44}\text{N}_2\text{O}_4\text{S}_2$ (formula weight 632.88 g/mol): C, 68.26; H, 6.95; N, 4.42; S, 10.11. Found: C, 68.28; H, 6.90; N, 4.35; S, 10.23%. IR (KBr, cm^{-1}) v.: 3100, 3000 (Ar-CH), 2903, 2831 (Aliph.-CH, CH_3), 1729 (C=O), 1605, 1602 (CH=N), 1579, 1562 (Ar-C=C), 777 (C-S-C). ^1H -NMR (400 MHz, DMSO- d_6): δ (ppm) = 8.55 (s, 2H, N=CH), 7.53-7.19 (m, 4H, Ar-H), 3.59 (s, 6H, -CO-O- CH_3), 2.52 (s, 4H, 2 CH_2), 1.48 (s, 4H, 2 CH_2), 1.48 (s, 6H, C-(CH_3) $_2$), 1.34 (s, 6H, C-(CH_3) $_2$). ^{13}C -NMR (400 MHz, DMSO- d_6): δ (ppm) = 162.76 (2C=O), 158.85 (2CH=N), 141.23, 137.64 (2C_{thiophene}), 133.17, 113.82 (C_{benzene}), 53.50, 24.59 (C_{cyclohexane}), 51.49 (O- CH_3), 31.38, 29.38 (-8 CH_3). UV-Vis (λ_{max} /nm, ($\epsilon/\text{L mol}^{-1}\text{ cm}^{-1}$)): $\pi \rightarrow \pi^*$, 204 (2400), 257 (3494); $n \rightarrow \pi^*$, 300 (361), 309 (387). Mass Spectrum [ESI]: m/z 631.88 (Calc.), 631.04 (Found) [L-H]. Color: Pale Brown.

The metal complexes were prepared adding stoichiometric proportion into a hot ethanol solution (20 mL) including 0.01 mol of ligand and a hot ethanol solution (20 mL) containing 0.02 mol metal chlorides (ZnCl_2 and $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$). The mixture was refluxed for 4 h. The precipitate was filtered off, washed with diethyl ether three times and finally dried at air room temperature.

$[\text{Zn}_2\text{L}\cdot 2\text{Cl}_2\cdot 2\text{H}_2\text{O}]$ complex: Yield: 75%. IR (KBr, cm^{-1}) v.: 3495, 3385 (OH), 3210, 3100 (Ar-CH), 2960, 2869 (Aliph.-CH, CH_3), 1690 (C=O), 1641, 1607 (CH=N), 1577, 1522 (Ar-C=C), 770 (C-S-C), 575, 535 (M-O), 480, 453 (M-N). ^1H -NMR (400 MHz, DMSO- d_6): δ (ppm) = 8.59 (s, 2H, 2N=CH), 7.55-7.19 (m, 4H, Ar-H), 4.26 (4H, 2 H_2O). Anal. Calc. for $\text{C}_{36}\text{H}_{48}\text{N}_2\text{S}_2\text{O}_6\text{Cl}_4\text{Zn}_2$ (formula weight 941.54 g/mol): C, 45.88; H, 5.10; N, 2.97; S, 6.80. Found: C, 45.87; H, 5.12; N, 2.99; S, 6.83%. UV-Vis (λ_{max} /nm, ($\epsilon/\text{L mol}^{-1}\text{ cm}^{-1}$)): $\pi \rightarrow \pi^*$, 217 (868), 252 (284); $n \rightarrow \pi^*$, 299 (282), 349 (538), 364 (530); L $\rightarrow$ M, 408 (547). MS [ES]: m/z 940.54 (Calc.), 940.00 (Found) [M-H]. Color: Orange.

Figure 1: Synthesis scheme of dimethyl 2,2'-(1*E*-1'*E*)-(1,4-phenylenebis(methan-1-yl-1-ylidene))bis(azan-1-yl-1-ylidene)bis(5,5,7,7-tetramethyl-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carboxylate (L).

Figure 2: Suggested structure of the $[Zn_2L \cdot 2Cl_2 \cdot 2H_2O]$ complex.

Figure 3: Suggested structure of the $[Fe_2L \cdot 2Cl_2 \cdot 2H_2O] \cdot 3H_2O$ complex

$[Fe_2L \cdot 2Cl_2 \cdot 2H_2O] \cdot 3H_2O$ complex: Yield: 80%. IR (KBr, cm^{-1}) ν : 3487, 3343 (OH), 3180, 3032 (Ar-CH), 2956, 2876 (Alip-CH), 1725, 1694 (C=O), 1663, 1641 (CH=N), 1599 (Ar-C=C)_{broad}, 787 (C-S-C), 592, 561 (M-O), 482, 457 (M-N). Anal. Calc. for $C_{36}H_{54}N_2S_2O_9Cl_4Fe_2$ (formula weight 976.38 g/mol): C, 44.25; H, 5.53; N, 2.87; S, 6.55. Found: C, 44.27; H, 5.53; N, 2.88; S, 6.54%. UV-Vis (λ_{max}/nm , ($\epsilon/L mol^{-1} cm^{-1}$)): $\pi \rightarrow \pi^*$, 203 (315), 218 (377); $n \rightarrow \pi^*$, 299 (117), 307 (107), 349 (258), 363 (257); L $\rightarrow$ M, 408 (272). MS [ES]: m/z 921.38 (Calc.), 921.77 (Found) $[M-3H_2O-H]^+$. Color: Black.

A toluene solution of ligand (0.01 mol) was mixed with $PdCl_2(CH_3CN)_2$ (0.02 mol) maintaining metal-ligand ratio 2:1. The mixture was refluxed for 8 h. The solid product, precipitated after cooling, was collected through filtration, washed with diethyl ether and recrystallized from methylene chloride. Similar synthesis were conducted for the Ru(II) complex using $[RuCl_2(p\text{-cymene})_2]$ (0.01 mol).

$[Ru_2Cl_2(p\text{-cymene})_2L]$ complex: Yield: 78%. IR (KBr, cm^{-1}) ν : 3062, 3036 (Ar-CH), 2960, 2872 (Alip-CH), 1694 (C=O), 1643, 1600 (CH=N), 1571 (Ar-C=C), 1372, 1170 (Ru-Cl), 776 (C-S-C), 576, 537 (M-O), 472, 453 (M-N). 1H -NMR (400 MHz, $DMSO-d_6$): δ (ppm) = 8.61 (s, 2H, 2N=CH), 7.58-7.20 (m, 4H, Ar-H), 2.30, 2.10 (m, H, -CH (*p*-cymene, methine), 2.16 (s, 3H, (*p*-cymene, methyl), 1.20, 1.10 (d, 6H, $(CH_3)_2CH$ (*p*-cymene). Anal. Calc. for $C_{56}H_{72}N_2S_2O_4Cl_2Ru_2$ (formula weight 1173.14 g/mol): C, 57.28; H, 6.13; N, 2.38; S, 5.46. Found: C, 57.27; H, 6.12; N, 2.38; S, 5.48%. UV-Vis (λ_{max}/nm , ($\epsilon/L mol^{-1} cm^{-1}$)): $\pi \rightarrow \pi^*$, 216 (1813); $n \rightarrow \pi^*$, 293 (351), 307 (332), 346 (541); L $\rightarrow$ M, 407 (523). MS [ESI+]: m/z

Figure 4: Suggested structure of the $[\text{Ru}_2\text{Cl}_2(\text{p-cymene})_2\text{L}]$ complex.

Figure 5: Suggested structure of the $[\text{Pd}_2\text{L}\cdot 2\text{Cl}_2]\cdot 4\text{H}_2\text{O}$ complex.

1018.14 Calc.), 1018.68 (Found) $[\text{M}-2\text{Cl}-2(-\text{C}_3\text{H}_7)]^{2+}$. Color: Brown.

$[\text{Pd}_2\text{L}\cdot 2\text{Cl}_2]\cdot 4\text{H}_2\text{O}$ complex: Yield: 80%. IR (KBr, cm^{-1}) ν : 3567, 3457 (OH), 3062, 3036 (Ar-CH), 2956 (Alip-CH), 1722 (C=O), 1612 (CH=N), 1573 (Ar-C=C), 775 (C-S-C), 578, 540 (M-O), 504 (M-N). Anal. Calc. for $\text{C}_{36}\text{H}_{52}\text{N}_2\text{S}_2\text{O}_8\text{Cl}_4\text{Pd}_2$ (formula weight 1059.48 g/mol): C, 40.77; H, 4.91; N, 2.64; S, 6.04. Found: C, 40.78; H, 4.93; N, 2.64; S, 6.05%. UV-Vis ($\lambda_{\text{max}}/\text{nm}$, ($\epsilon/\text{L mol}^{-1}\text{ cm}^{-1}$)): $\pi \rightarrow \pi^*$, 218 (607), 260 (335); $n \rightarrow \pi^*$, 347 (178); $\text{L} \rightarrow \text{M}$, 403 (110). MS [ESI⁺]: m/z 1058.48 (Calc.), 1058.69 (Found) $[\text{M}-\text{H}]^+$. Color: Black.

2.3 General experimental procedure for Suzuki-Miyaura coupling reaction

Pd(II) complex was utilized in a preliminary test to have the best reaction conditions (i.e., temperature, base, solvent, amount of catalyst). The cross coupling of 4-bromoacetophenon and phenylboronic acid was

selected to be the model reaction, and all reactions were conducted under aerobic conditions. After that, the optimal parameters were investigated in order to have the best reaction conditions (Table 3-5). The conversions were collected at different times. The yields were recorded by GC-MS analysis to examine the progress of the reaction.

2.4 General procedure for the transfer hydrogenation reaction

The hydrogen transfer reaction was performed in a closed Schlenk flask under argon atmosphere. Ketone (1 mmol), catalyst Ru(II) complex (0.01 mmol), and isopropyl alcohol (5 mL) were added into a Schlenk flask. KOH (2 mmol) was then put into the obtained mixture, and it was heated at 80°C for 10 h. Then the solvent was evaporated at reduced pressure. The precipitate was extracted by hexane/ethyl acetate (2:4), filtered by a pad of silica gel with multiple washings and purified by flash chromatography on silica gel. The yields were recorded using ^1H -NMR spectroscopy and GC-MS.

Ethical approval: The conducted research is not related to either human or animal use.

3 Results and discussion

3.1 Spectroscopy analysis

The characteristic absorption band 1729 cm^{-1} attribute to C=O stretching frequency of the ester carbonyl [30], sharp CH=N bands seen were in the range of 1605, 1602 cm^{-1} [31]. We observed that the stretching frequency of CH=N slightly shifted to lower or high wave numbers (1663-1600 cm^{-1}), which suggests that the azomethine nitrogen was involved in coordination to the metal ion in all metal complexes. Thiophene C-S-C stretching vibration was appeared at 777 cm^{-1} in the free ligand [32,33]. This band shifted to higher and lower stretching frequency (770-787 cm^{-1}) in the Fe(II) and Zn(II) complexes. That revealed the coordination of thiophene sulfur to the metal center [34,35]. The new bands seen at 1690-1725 cm^{-1} in the spectra of complexes were assigned to ester carbonyl group, which indicated the joining of oxygen atom of ester carbonyl group in coordination with metal ions [36]. The two new bands appeared in the far infrared region at 592-535 cm^{-1} and 504-453 cm^{-1} were attributed to $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{N})$ respectively. This confirmed the attachment of ligand to the center metal ions through the carbonyl

oxygen atoms and the azomethine nitrogen [37,38]. The infrared broad bands ($3567\text{--}3343\text{ cm}^{-1}$) of Fe(II), Zn(II) and Pd(II) complexes assigned to bonding of water molecules [39].

Electronic spectra were taken in the 1100–190 nm range and 1.0×10^{-4} mol/L in ethanol for all compounds. The spectra of the ligand indicated four high-intensity absorption bands: at 309, 300, 257 and 204 nm. These bands were attributed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of the ligand [40]. The spectra of the complexes showed four bands at 203–260, 293–299 and 307–364 nm which were assigned to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively, within the ligand. The spectra of the complexes showed bands in the range of 403–408 nm, which might be appointed to $L \rightarrow M$ charge transfer transitions [41–43].

The recorded magnetic moment value of Fe(II) complex was 4.92 B.M. and that confirmed octahedral geometry of Fe(II) metal center [44]. Zn(II) complex was diamagnetic and had an octahedral geometry [45]. The structured absorption bands between 260 and 347–403 nm for Pd(II) complex were assigned to $^1A_{1g} \rightarrow ^1B_g$ and $^1A_{1g} \rightarrow ^1E_g$ transitions, respectively in a square-planar configuration [46]. And also, the other high-intensity bands in the 293–346 nm could be attributed to ($^1A_{1g} \rightarrow ^1T_{2g}$) and $d \rightarrow d$ transition, occurring within ligand orbitals. The electronic spectra was similar to that of Ru(II) octahedral complexes [46,47].

The ^1H and ^{13}C NMR spectras of the ligand was given in experimental section. The protons of $\text{HC}=\text{N}$ group were observed at 8.55 ppm as singlet. The singlet peak of azomethines in the ligand was shifted to lower value at 8.59 ppm in Zn(II) complex, which shows the participation of $\text{HC}=\text{N}$ group in the complexation [48]. The signal showed at 4.26 ppm in Zn(II) assigned to two water molecules [49].

The ^{13}C NMR spectra of the ligand showed a peak at 158.85 ppm because of characteristic azomethine carbons. This signal shifted upfield in Zn(II) complex spectrum (148.70 ppm) which indicated the participation of $\text{HC}=\text{N}$ groups in complex formation. The ligand also showed signal at 162.76 ppm ($2\text{C}=\text{O}$). This signal was shifted to 158.10 ppm in Zn(II) complex spectrum because of bonding formation ester carbonyl oxygen. Based on the above spectroscopic data, the structures were proposed for complexes, as shown in Figures 2–5.

3.2 Transfer hydrogenation of ketones

In this study, KOH, NaOH, NaOAc, KOBu^t and K_2CO_3 were investigated in TH. Among the different bases used for

Table 1: Effect of bases for transfer hydrogenation.

Entry	Base	Conversion (%)
1	KOH	84
2	NaOH	55
3	K_2CO_3	51
4	KOBu^t	42
5	NaOAc	37
6	none	-

^aReaction conditions: Ketones (1 mmol), bases (2 mmol), isopropyl alcohol (5 mL), stirring for 10 h, 80 °C. ^bYield is determined by GC-MS.

this studies (Table 1), the KOH was the most suitable base and the conversion of yield was increased to 100% (Table 2, entry 6). However, more time was needed for reasonable conversions. In the condition of not using a base, TH of the ketones was not seen (Table 1, entry 6). The TH reactions of a variety of substituted acetophenone derivatives were applied with Ru(II) complex as the model catalyst, using *i*-PrOH/KOH, and the results were given in Table 2. Corresponding alcohols were obtained with very good results by using various acetophenone derivatives. The variety substituents present on the acetophenone ring were seen that it didn't influence on catalytic conversion.

The presence of an electron-withdrawing substituent (bromo, chloro) on the aryl ring showed higher conversions (Table 2, entries 2, 3). When compared with acetophenone (Table 2, entry 1), *p*-methoxyacetophenone and pentamethylacetophenone reacted very clearly and in good yields with isopropyl alcohol (Table 2, entries 4, 6). The maximum conversion to corresponding alcohol of 4-bromoacetophenone was accomplished over a period of 10 hours (Table 2, entry 3). We also tested this reaction on benzophenone. As a result of this reaction, benzophenone had a high conversion ratio in comparison to the acetophenone and methoxy group bearing *p*-position acetophenone (Table 2, entries 1, 4, 5). For the substituted acetophenones, Ru(II) complex showed more conversion than cyclicketones (Table 2, entries 1–7). Among the tested substrates, the tertiary butylcyclohexanone used as a ketone was observed to perform worse in TH (Table 2, entry 7). Ru(II) complex was highly efficient in the TH. This shows that air is not involved in the TH reaction and arene Ru(II) complexes are air-stable [50].

In the catalytic activity of Suzuki-Miyaura coupling reaction, 4-bromoacetophenone and phenylboronic acid

Table 2: Catalytic activity for transfer hydrogenation of ketones catalyzed by Ru(II) complex.

Entry	Ketone	Alcohol	Catalyst	Base	Yield (%) ^b
1			2a	KOH	84
2			2a	KOH	95
3			2a	KOH	98
4			2a	KOH	88
5			2a	KOH	97
6			2a	KOH	100
7			2a	KOH	44

^aReaction conditions: Ketones (1 mmol), bases (2 mmol), isopropyl alcohol (5 mL), stirring for 10 h, 80 °C. ^bYield is determined by GC-MS.

Table 3: Effect of bases for the Suzuki-Miyaura reaction.

Entry	Base	Time (h)	Conversion (%)
1	NaOH	3	52
2	Cs ₂ CO ₃	3	42
3	Na ₂ CO ₃	3	19
4	K ₂ CO ₃	3	90
5	KOBu ^t	3	12

Reaction conditions: 4-Bromoacetophenone (0.3 mmol), phenylboronic acid (0.45 mmol), catalyst (0.001 mmol) and base (1.5 mmol), solvent (5 mL)

Table 4: Effect of solvents for the Suzuki-Miyaura reaction.

Entry	Solvents	Time (h)	Conversion (%)
1	H ₂ O	20	-
2	Ethanol	3	92
3	Methanol	8	19
4	DMF	8	10
5	Toluen	8	12
6	Dioxane	8	32
7	THF	8	17
8	DMF+H ₂ O	8	10
9	THF	8	45

Reaction conditions: 4-Bromoacetophenone (0.3 mmol), phenylboronic acid (0.45 mmol), catalyst (0.001 mmol) and base (1.5 mmol), solvent (5 mL)

was chosen as a model substrate. Different parameters examined and the results were summarized in Table 3, 4. The cross-coupling of 4-bromoacetophenone with phenylboronic acid in ethanol medium under aerobic condition was chosen as the model reaction. The impacts of the temperature and base on the reaction were also examined. Various bases like K₂CO₃, Na₂CO₃, NaOH, KOBu^t, and Cs₂CO₃ were also examined. The results indicated organic bases were less effective than inorganic bases such as KOBu^t (Table 3, entries 4, 5). Therefore, K₂CO₃, which was more cost-effective, was chosen as a base for Suzuki-Miyaura coupling reactions [51]. The results are given in Table 3.

Subsequently, the effects of solvents such as H₂O, THF, EtOH, MeOH, dioxane, toluene and DMF were studied in the presence of Pd(II) complex (0.01 mmol) at 80 °C for 3 h. It is seen in Table 4 that when temperature increased to

80 °C, yield of product was not obtained in 20 h (Table 4, entry 1). The best solvent was found to be ethanol solvent with the highest yield, but DMF were obtained with the lowest yield (Table 4, entries 2-7). This solvent is less efficient to coordinate to the palladium center, because the *O*-donor atoms in dioxane are harder base than the *N*-donor atom in DMF and therefore catalyst performance is poor [52]. Since *N*-donor atoms of DMF coordinate to palladium ion, the catalyst activity of DMF is smaller than in other solvents [53].

Table 5 may suggest that various aryl halides, like those containing -CH₃, -OCH₃, -COCH₃ and -CHO substituent group, reacted smoothly under optimized conditions and provided the demanded products with quantitative yields.

Arylbromides with various functional groups reacted efficiently with boronic acids (Table 5, entries 1-5) using K₂CO₃ and 5 mL ethanol at reflux temperature in presence of Pd(II) catalyst for 3 h to yield Suzuki-Miyaura products in good conversions. The reaction of *p*-bromoacetophenone with boronic acid showed a very high conversion (Table 5, entry 1, 92%). In *p*-bromotoluene, the conversions were good in these conditions (Table 5, entry 2, 79%). *p*-methoxy, *p*-benzaldehyde substrates also showed an excellent conversion (Table 5, entries 3, 5, 82-86%). As expected, *p*-bromobenzene showed a medium conversion (Table 5, entry 4, 76%). Catalytic activity of Pd(II) depended on electronic properties of arylbromide substituent used. In the presence of electron withdrawing group on aryl ring increase the yield [54].

4 Conclusion

New ligand and its complexes were synthesized and characterized. The bidentate or tridentate coordination of ligand through carbonyl oxygen, azomethine nitrogen and thiophene sulfur was confirmed using spectral data analysis. The metal complexes had octahedral geometry except for the palladium complex. The ruthenium complex was shown to be an effective catalyst for the transfer hydrogenation of the different aromatic ketones to their corresponding secondary alcohols. It was found that a series of electronically diversified, different aryl halides of the Pd(II) complex was a highly effective catalyst for Suzuki-Miyaura cross-coupling reaction with phenylboronic acid. In conclusion, the catalytic activity of palladium complex influenced the Suzuki-Miyaura cross-coupling reaction while ruthenium complex influenced the transfer hydrogenation of ketones.

Table 5: Suzuki-Miyaura reactions with different substituent catalyzed by Pd(II) complex under optimized reaction conditions.

Entry	Catalyst	ArX	Time (h)	Yield(%)
1	4a	Br-C ₆ H ₄ -COCH ₃	3	92
2	4a	Br-C ₆ H ₄ -CH ₃	3	79
3	4a	Br-C ₆ H ₄ -OCH ₃	3	82
4	4a	Br-C ₆ H ₄	3	76
5	4a	Br-C ₆ H ₄ -CHO	3	86

Reaction conditions: R-C₆H₄-Br-*p*-bromoacetophenone (1 mmol), phenylboronic acid (1.5 mmol), K₂CO₃ (2 mmol), Pd(II) complexes (0.005 mmol), ethanol (3 mL), purity of compounds is checked by GC and NMR yields are based on *p*-aryl bromide. All reactions were monitored by GC-MS. Temperature 80 °C, 3 h.

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References

- [1] De Araújo E.L., Barbosaa H.F.G., Dockal E.R., Cavalheiro É.T.G., Synthesis, characterization and biological activity of Cu(II), Ni(II) and Zn(II) complexes of biopolymeric Schiff bases of salicylaldehydes and chitosan, *Int. J. Biol. Macromol.*, 2017, 95, 168-176.
- [2] Kleij A.W., Nonsymmetrical salen ligands and their complexes: Synthesis and applications, *Eur. J. Inorg. Chem.*, 2009, 193-205.
- [3] Das P., Linert W., Schiff base-derived homogeneous and heterogeneous palladium catalysts for the Suzuki-Miyaura reaction, *Coord. Chem. Rev.*, 2016, 311, 1-23.
- [4] Talouki S.A., Grivani G., Crochet P., Cadierno V., Half-sandwich ruthenium(II) complexes with water-soluble Schiff base ligands: Synthesis and catalytic activity in transfer hydrogenation of carbonyl compounds, *Inorg. Chim. Acta*, 2017, 456, 142-148.
- [5] Alshaheri A.A., Tahir M.I.M., Rahman M.B.A., Begum T., Saleh T.A., Synthesis, characterisation and catalytic activity of dithiocarbazate Schiff base complexes in oxidation of cyclohexane, *J. Mol. Liq.*, 2017, 240, 486-496.
- [6] Henrici G., Olive S., *The Chemistry of the Catalyzed Hydrogenation of Carbon Monoxide*, Springer, Berlin, 1984, pp. 152.
- [7] Manikandan R., Viswanathamurthi P., Muthukumar M., Ruthenium(II) hydrazone Schiff base complexes: Synthesis, spectral study and catalytic applications, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, 2011, 83, 297-303.
- [8] McGarrigle E.M., Gilheany D.G., Chromium and manganese salen promoted epoxidation of alkenes, *Chem. Rev.*, 2005, 105, 1563-1602.
- [9] Schenkel L.B., Ellman J.A., Metal complexes of ONO donor Schiff base ligand as a new class of bioactive compounds; Synthesis, characterization and biological evolution, *J. Org. Chem.*, 2004, 69, 1800-1808.
- [10] Buldurun K., Turan N., Savcı A., Çolak N., Synthesis, structural characterization and biological activities of metal(II) complexes with Schiff bases derived from 5-bromosalicylaldehyde: Ru(II) complexes transfer hydrogenation, *J. Saudi Chem. Soc.* 2019, 23, 205-214.
- [11] Turan N., Buldurun K., Alan Y., Savcı A., Çolak N., Mantarcı A., Synthesis, characterization, antioxidant, antimicrobial and DNA binding properties of ruthenium(II), cobalt(II) and nickel(II) complexes of Schiff base containing o-vanillin, *Res. Chem. Intermediat.* 2019, 45, 3525-3540.
- [12] Kumar N., Selvaraj S., Nagaraja N., Metal complexes of ONO donor Schiff base ligand as a new class of bioactive compounds; Synthesis, characterization and biological evolution, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, 2014, 131, 599-605.
- [13] Pandiarajan D., Ramesh R., Ruthenium(II) half-sandwich complexes containing thioamides: Synthesis, structures and catalytic transfer hydrogenation of ketones, *J. Organomet. Chem.*, 2013, 723, 26-35.

- [14] Suganthi P.K., Prabhu R.N., Sridevi V.S., Synthesis, structural characterization and catalytic transfer hydrogenation of ruthenium(II) carbonyl complexes bearing N,N,O pincer type benzoylhydrazone ligands, *Polyhedron*, 2015, 88, 57-62.
- [15] Everaere K., Mortreux A., Carpentier J.F., Ruthenium(II)-catalyzed asymmetric transfer hydrogenation of carbonyl compounds with 2-propanol and ephedrine-type ligands, *Adv. Synth. Catal.*, 2003, 345, 67-77.
- [16] Samec J.S.M., Backvall J.E., Andersson P.G., Brandt P., Mechanistic aspects of transition metal-catalyzed hydrogen transfer reactions, *Chem. Soc. Rev.*, 2006, 35, 237-248.
- [17] Ikariya T., Blacker A.J., Asymmetric transfer hydrogenation of ketones with bifunctional transition metal-based molecular catalysts, *Acc. Chem. Res.*, 2007, 40, 1300-1308.
- [18] Caprio V., Williams J.M.J., *Catalysis in Asymmetric Synthesis*, second ed., Wiley, Chichester, UK, 2009.
- [19] Tao L., Miao Q., Tehrani A.A., Hajiashrafi T., Hu M.L., Morsali A., Cationic half-sandwich Ru(II) complexes containing (N,N)-bound Schiff-base ligands: Synthesis, crystal structure analysis and spectroscopic studies, *J. Mol. Struct.*, 2016, 1118, 48-55.
- [20] Singh A.K., Pandey D.S., Xu Q., Braunstein P., Recent advances in supramolecular and biological aspects of arene ruthenium(II) complexes, *Coord. Chem. Rev.*, 2014, 31, 270-271.
- [21] Kalita M., Tamuli K.J., Barman P., Sarma B., Baruah R., Boruah H.P.D., Synthesis, crystal structure, bioactivities of Ni(II), Cu(II), Co(II) and Pd(II) complexes with unsymmetrical thioether donor Schiff base: Phosphine free Pd(II) complex catalyzed Suzuki reaction, *Polyhedron*, 2015, 97, 140-147.
- [22] Buldurun K., Özdemir İ., 5-Nitrobenzimidazole containing Pd(II) catalyzed C-C cross-coupling reactions: The effect of the N-substituent of the benzimidazole structure on catalyst activity, *J. Mol. Struct.*, 2019, 1192, 172-177.
- [23] Whitcombe N.J., Hii K.K., Gibson S.E., Advances in the Heck chemistry of aryl bromides and chlorides, *Tetrahedron*, 2001, 57, 7449-7476.
- [24] Dawood K.M., Microwave-assisted Suzuki-Miyaura and Heck-Mizoroki cross-coupling reactions of aryl chlorides and bromides in water using stable benzothiazole-based palladium(II) precatalysts, *Tetrahedron*, 2007, 63, 9642-9251.
- [25] Kawasaki I., Tsunoda K., Tsuji T., Yamaguchi T., Shibuta H., Uchida N., Yamashita M., Ohta S., A recyclable catalyst for asymmetric transfer hydrogenation with a formic acid-triethylamine mixture in ionic liquid, *Chem. Commun.*, 2005, 0, 2134-2136.
- [26] Fujii A., Hashiguchi S., Uematsu N., Ikariya T., Noyori R., Ruthenium(II)-catalyzed asymmetric transfer hydrogenation of ketones using a formic acid-triethylamine mixture, *J. Am. Chem. Soc.*, 1996, 118, 2521-2522.
- [27] Zheng C., You S.L., Transfer hydrogenation with Hantzsch esters and related organic hydride donors, *Chem. Soc. Rev.*, 2012, 41, 2498-2518.
- [28] Maytum H.C., Tavassoli B., Williams J.M., Reduction of aldehydes and ketones by transfer hydrogenation with 1,4-butanediol, *J. Org. Lett.*, 2007, 9, 4387-4389.
- [29] Azua A., Mata J.A., Peris E.A., Iridium NHC based catalysts for transfer hydrogenation processes using glycerol as solvent and hydrogen donor, *Organometallics*, 2011, 30, 5532-5536.
- [30] Mavrova A.T., Dimov S., Yancheva D., Rangelov M., Wesselinova D., Tsenov J.A., Synthesis, anticancer activity and photostability of novel 3-ethyl-2-mercapto-thieno[2,3-d]pyrimidin-4(3H)-ones, *Eur. J. Med. Chem.*, 2016, 123, 69-79.
- [31] Yadav V.K., Kar S., Mishra L., Reactivity of triazolyl Schiff bases with Ru(II)-2,2'-bipyridyl: Synthesis, spectroscopic characterization of isomers and their photo-physical properties, *Polyhedron*, 2009, 28, 121-125.
- [32] Abdel-Kader N.S., El-Ansarya A.L., El-Tayeb T.A., Elnagdi M.M.F., Synthesis and characterization of Schiff base complexes derived from cephradine: Fluorescence, photostability and photobiological applications, *J. Photochem. Photobiol. A: Chem.*, 2016, 321, 223-237.
- [33] Elsayed S.A., Noufal A.M., El-Hendawy A.M., Synthesis, structural characterization and antioxidant activity of some vanadium(IV), Mo(VI)/(IV) and Ru(II) complexes of pyridoxal Schiff base derivatives, *J. Mol. Struct.*, 2017, 1144, 120-128.
- [34] El-Shafiy H.F., Saif M., Mashaly M.M., Halim S.A., Eid M.F., Nabeel A.I., Fouad R., New nano-complexes of Zn(II), Cu(II), Ni(II) and Co(II) ions; spectroscopy, thermal, structural analysis, DFT calculations and antimicrobial activity application, *J. Mol. Struct.*, 2017, 1147, 452-461.
- [35] Saadeh S.M., Synthesis, characterization and biological properties of Co(II), Ni(II), Cu(II) and Zn(II) complexes with an SNO functionalized ligand, *Arabian J. Chem.*, 2013, 6, 191-196.
- [36] Mohamed G.G., El-Gamel N.E.A., Structural, spectroscopic and thermal characterization of 2-tert-butylaminomethylpyridine-6-carboxylic acid methylester and its Fe(III), Co(II), Ni(II), Cu(II), Zn(II) and UO₂(II) complexes, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, 2005, 61, 1089-1096.
- [37] Nakamoto K., *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley, New York, 1970.
- [38] Belal A.A.M., El-Deen I.M., Farid N.Y., Zakaria R., Refat M.S., Synthesis, spectroscopic, coordination and biological activities of some transition metal complexes containing ONO tridentate Schiff base ligand, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, 2015, 149, 771-787.
- [39] Abdel-Rahman L.H., Abu-Dief A.M., Newair E.F., Hamdan S.K., Some new nano-sized Cr(III), Fe(II), Co(II), and Ni(II) complexes incorporating 2-((E)-(pyridine-2-ylimino)methyl)naphthalen-1-ol ligand: Structural characterization, electrochemical, antioxidant, antimicrobial, antiviral assessment and DNA interaction, *J. Photochem. Photobiol. B: Biol.*, 2016, 160, 18-31.
- [40] Orojloo M., Zolgharnein P., Solimannejad M., Amani S., Synthesis and characterization of cobalt(II), nickel(II), copper(II) and zinc(II) complexes derived from two Schiff base ligands: Spectroscopic, thermal, magnetic moment, electrochemical and antimicrobial studies, *Inorg. Chim. Acta*, 2017, 467, 227-237.
- [41] Monika M., Karishma T., Kumar S.A., Vinod S.P., Synthesis, structural and corrosion inhibition studies on Mn(II), Cu(II) and Zn(II) complexes with a Schiff base derived from 2-hydroxypropiophenone, *Polyhedron*, 2014, 77, 57-65.
- [42] Shafaatian B., Ahmad S., Nasim K.O., Behrouz N.S., Ahmad R., Synthesis, crystal structure, fluorescence and electrochemical studies of a new tridentate Schiff base ligand and its nickel(II) and palladium(II) complexes, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, 2014, 128, 363-369.
- [43] Gup R., Kirkan B., Synthesis and spectroscopic studies of copper(II) and nickel(II) complexes containing hydrazonic ligands and heterocyclic coligand, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, 2005, 62, 1188-1195.

- [44] Turan N., Buldurun K., Gündüz B., Çolak N., Synthesis and structures of Fe(II), Zn(II) and Pd(II) complexes with a Schiff base derived from methyl 2-amino-6-methyl-4,5,6,7-tetrahydrothieno[2,3-c]pyridine-3-carboxylate and comparison of their optical constants for different solvents and molarities, *J. Nanoelectron. Optoe.*, 2017, 12, 1028-1040.
- [45] Mohamed G.G., Zayed M.A., Abdallah S.M., Metal complexes of a novel Schiff base derived from sulphametrole and varelaldehyde. Synthesis, spectral, thermal characterization and biological activity, *J. Mol. Struct.*, 2010, 979, 62-71.
- [46] El-Asmy H.A., Butler I.S., Mouhri Z.S., Jean-Claude B.J., Emmamc M.S., Mostafa S.I., Zinc(II), ruthenium(II), rhodium(III), palladium(II), silver(I), platinum(II) and MoO₂²⁺ complexes of 2-(2'-hydroxy-5'-methylphenyl)-benzotriazole as simple or primary ligand and 2,2'-bipyridyl, 9,10-phenanthroline or triphenylphosphine as secondary ligands: Structure and anticancer activity, *J. Mol. Struct.*, 2014, 1059, 193-201.
- [47] Mostafa S.I., Synthesis, characterization and antineoplastic activity of 5-chloro-2,3-dihydropyridine transition metal complexes, *J. Coord. Chem.*, 2008, 61, 1553-1567.
- [48] Nagesh G.Y., Mahendra Raj K., Mruthyunjayaswamy B.H.M., Synthesis, characterization, thermal study and biological evaluation of Cu(II), Co(II), Ni(II) and Zn(II) complexes of Schiff base ligand containing thiazole moiety, *J. Mol. Struct.*, 2015, 1079, 423-432.
- [49] Turan N., Savcı A., Buldurun K., Alan Y., Çolak N., Synthesis and Chemical Structure Elucidation of Two Schiff Base Ligands, Their Iron(II) and Zinc(II) Complexes, and Antiradical, Antimicrobial, Antioxidant Properties, *Lett. Org. Chem.*, 2016, 13, 343-351.
- [50] Turan N. and Buldurun K., Synthesis, characterization and antioxidant activity of Schiff base and its metal complexes with Fe(II), Mn(II), Zn(II), and Ru(II) ions: Catalytic activity of ruthenium(II) complex, *Eur. J. Chem.* 2018, 9, 22-29.
- [51] Islam S.M., Mondal D., Roy A.S., Mondal S., Hossain D., Heterogeneous Suzuki and copper-free Sonogashira cross-coupling reactions catalyzed by a reusable palladium(II) complex in water medium, *Tetrahedron Lett.*, 2010, 51, 2067-2070.
- [52] Mahamo T., Mogorosi M.M., Moss J.R., Mapolie S.F., Slootweg J.C., Lammertsma K., Smith G.S., Neutral palladium(II) complexes with P,N Schiff-base ligands: synthesis, characterization and application as Suzuki-Miyaura coupling catalysts. *J. Organomet. Chem.*, 2012, 703, 34-42.
- [53] Beigi Z., Ali Hossein K., Gholamhossein M., Helmar G., Winfried P., Palladium(II) complexes with diaminomaleonitrile-based Schiff-base ligands: Synthesis, characterization and application as Suzuki-Miyaura coupling catalysts, *Polyhedron*, 2017, 134, 65-72.
- [54] Rao G.K., Kumar A., Bhunia M., Singh M.P., Singh A.K., Complex of 2-(methylthio)aniline with palladium(II) as an efficient catalyst for Suzuki-Miyaura C-C coupling in eco-friendly water, *J. Hazard. Mater.*, 2014, 269, 18-23.