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

https://doi.org/10.1515/chem-2019-0074
received February 12, 2018; accepted October 7, 2018.

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, $^1$H-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...
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 [ZnL⋅2Cl⋅2H₂O], [FeL⋅2Cl⋅2H₂O]⋅3H₂O, [RuCl₂(p-cymene)]₂, [PdL⋅2Cl₂]⋅4H₂O 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 chemical used was 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 ¹³C-NMR spectra were recorded in DMSO-d₆ 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 range 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 Hg[Co(SCN)]₂ 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 C₅₆H₄₁N₅O₇S₂ (formula weight 632.88 g/mol): C, 68.28; 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) ν: 3100, 3000 (Ar–CH), 2903, 2831 (Aliph.–CH), 1729 (C=O), 1605, 1602 (CH=N), 1579, 1562 (Ar–C=C), 777 (C–S–C). ¹H-NMR (400 MHz, DMSO-d₆): δ (ppm) = 8.55 (s, 2H, N=CH), 7.53-7.19 (m, 4H, Ar–H), 3.59 (s, 6H, -CO–O–CH₃), 2.52 (s, 4H, 2CH₂), 1.48 (s, 4H, 2CH₂), 1.48 (s, 6H, C–(CH₂)₆), 1.34 (s, 6H, C–(CH₂)₆). ¹³C-NMR (400 MHz, DMSO-d₆): δ (ppm) = 162.76 (2C=O), 158.85 (2CH=N), 141.23, 137.64 (CH=N), 157.7, 160.2 (C–C=C), 1729 (C=O), 1641, 1607 (CH=N), 1577, 1522 (Aliph.–CH), 2.52 (s, 4H, 2CH₂), 1.48 (s, 4H, 2CH₂), 1.48 (s, 6H, C–(CH₂)₆), 1.34 (s, 6H, C–(CH₂)₆).

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 (ZnCl₂ and FeCl₃⋅4H₂O). The mixture was refluxed for 4 h. The precipitate was filtered off, washed with diethylether three times and finally dried at room temperature.

[ZnL⋅2Cl₂⋅2H₂O] complex: Yield: 75%. IR (KBr, cm⁻¹) ν: 3495, 3385 (OH), 3210, 3100 (Ar–CH), 2960, 2869 (Aliph.–CH, CH₃), 1690 (C=O), 1641, 1607 (CH=N), 1577, 1522 (Ar–C=C), 770 (C–S–C), 575, 535 (M–O), 480, 453 (M–N). "H-NMR (400 MHz, DMSO-d₆): δ (ppm) = 8.59 (s, 2H, N=CH), 7.55-7.19 (m, 4H, Ar–H), 3.59 (s, 6H, -CO–O–CH₃), 2.52 (s, 4H, 2CH₂), 1.48 (s, 4H, 2CH₂), 1.48 (s, 6H, C–(CH₂)₆), 1.34 (s, 6H, C–(CH₂)₆). UV-Vis (λ_max/nm, (ε/L mol⁻¹ cm⁻¹)) (ε/L mol⁻¹ cm⁻¹): π→π* ε = 204 (2400), 257 (394), n→π* 300 (361), 309 (387). Mass Spectrum [ESI]: m/z 631.88 (Calc.), 631.04 (Found) [L+H]. Color: Pale Brown.

The precipitate was filtered off, washed with diethylether three times and finally dried at room temperature.

[ZnL⋅2Cl₂⋅2H₂O] complex: Yield: 75%. IR (KBr, cm⁻¹) ν: 3495, 3385 (OH), 3210, 3100 (Ar–CH), 2960, 2869 (Aliph.–CH, CH₃), 1690 (C=O), 1641, 1607 (CH=N), 1577, 1522 (Ar–C=C), 770 (C–S–C), 575, 535 (M–O), 480, 453 (M–N). "H-NMR (400 MHz, DMSO-d₆): δ (ppm) = 8.59 (s, 2H, N=CH), 7.55-7.19 (m, 4H, Ar–H), 3.59 (s, 6H, -CO–O–CH₃), 2.52 (s, 4H, 2CH₂), 1.48 (s, 4H, 2CH₂), 1.48 (s, 6H, C–(CH₂)₆), 1.34 (s, 6H, C–(CH₂)₆). UV-Vis (λ_max/nm, (ε/L mol⁻¹ cm⁻¹)) (ε/L mol⁻¹ cm⁻¹): π→π* ε = 204 (2400), 257 (394), n→π* 300 (361), 309 (387). Mass Spectrum [ESI]: m/z 631.88 (Calc.), 631.04 (Found) [L+H]. Color: Pale Brown.
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**Figure 1:** Synthesis scheme of dimethyl 2,2'-((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[θ]thiophene-3-carboxylate (L)).

**Figure 2:** Suggested structure of the [Zn₂L•2Cl₂•2H₂O] complex.

**Figure 3:** Suggested structure of the [Fe₂L•2Cl₂•2H₂O]•3H₂O complex.

[Fe₂L•2Cl₂•2H₂O]•3H₂O complex: Yield: 80%. IR (KBr, cm⁻¹): v₁, 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 C₃₆H₅₄N₂S₂O₉Cl₄Fe₂ (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 (λₘₐₓ/nm, (ε/L mol⁻¹ cm⁻¹)): π → π*, 203 (315), 218 (377); n → π*, 299 (117), 307 (107), 349 (258), 363 (257); L → M, 408 (272). MS [ES]: m/z 921.38 (Calc.), 921.77 (Found) [M-3H₂O-H]. Color: Black.

A toluene solution of ligand (0.01 mol) was mixed with PdCl₂(CH₃CN)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 [RuCl₂(p-cymene)]₂ (0.01 mol).

[RuCl₂(p-cymene),L] complex: Yield: 78%. IR (KBr, cm⁻¹): v₁, 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-d₆): 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, –CH (p-cymene, methyl), 1.20, 1.10 (d, 6H, (CH₃)₂CH (p-cymene). Anal. Calc. for C₅₆H₇₂N₂S₂O₄Cl₂Ru₂ (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 (λₘₐₓ/nm, (ε/L mol⁻¹ cm⁻¹)): π → π*, 216 (1813); n → π*, 293 (351), 307 (332), 346 (541); L → M, 407 (523). MS [ESI+]: m/z
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 ν(M–O) and ν(M–N) respectively. This confirmed the attachment of ligand to the center metal ions through the carbonyl

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

Figure 4: Suggested structure of the [Ru₂Cl₂(p-cymene),L] complex.

Figure 5: Suggested structure of the [Pd₂L∙2Cl₂]∙4H₂O complex.
oxygen atoms and the azomethine nitrogen [37,38]. The infrared broad bands (3567-3343 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 1.0x10\(^{-4}\) 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→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 \(^1A_g\rightarrow^1B_g\) and \(^1A_g\rightarrow^1E_g\) transitions, respectively in a square-planar configuration [46]. And also, the other high-intensity bands in the 293-346 nm could be attributed to \((^1A_g\rightarrow^1T_{2g})\) and d-d transition, occurring within ligand orbitals. The electronic spectra was similar to that of Ru(II) octahedral complexes [46,47].

The \(^1\)H and \(^{13}\)C NMR spectra of the ligand was given in experimental section. The protons of HC=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 HC=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 HC=N groups in complex formation. The ligand also showed signal at 162.76 ppm (2C=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' and K\(_2\)CO\(_3\) were investigated in TH. Among the different bases used for 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.

| Entry | Base       | Conversion (%) |
|-------|------------|----------------|
| 1     | KOH        | 84             |
| 2     | NaOH       | 55             |
| 3     | K\(_2\)CO\(_3\) | 51            |
| 4     | KOBu'      | 42             |
| 5     | NaOAc      | 37             |
| 6     | none       |                 |

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

The TH reactions of a variety of substituted acetophenone derivatives were 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 cyclciketones (Table 2, entries 17). 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 (%)<sup>b</sup> |
|-------|--------|---------|----------|------|----------------------|
| 1     | ![Ketone_1](image1) | ![Alcohol_1](image2) | 2a       | KOH  | 84                   |
| 2     | ![Ketone_2](image3) | ![Alcohol_2](image4) | 2a       | KOH  | 95                   |
| 3     | ![Ketone_3](image5) | ![Alcohol_3](image6) | 2a       | KOH  | 98                   |
| 4     | ![Ketone_4](image7) | ![Alcohol_4](image8) | 2a       | KOH  | 88                   |
| 5     | ![Ketone_5](image9) | ![Alcohol_5](image10) | 2a       | KOH  | 97                   |
| 6     | ![Ketone_6](image11) | ![Alcohol_6](image12) | 2a       | KOH  | 100                  |
| 7     | ![Ketone_7](image13) | ![Alcohol_7](image14) | 2a       | KOH  | 44                   |

<sup>a</sup>Reaction conditions: Ketones (1 mmol), bases (2 mmol), isopropyl alcohol (5 mL), stirring for 10 h, 80 °C. <sup>b</sup>Yield is determined by GC-MS.
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 K$_2$CO$_3$, Na$_2$CO$_3$, NaOH, KOBu', and Cs$_2$CO$_3$ were also examined. The results indicated organic bases were less effective than inorganic bases such as KOBu'. Therefore, K$_2$CO$_3$, 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 H$_2$O, 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 –CH$_3$, –OCH$_3$, –COCH$_3$ and –CHO substituent group, reacted smoothly under optimized conditions and provided the demanded products with quantitative yields.

 Aryl bromides with various functional groups reacted efficiently with boronic acids (Table 5, entries 1-5) using K$_2$CO$_3$ 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-bromacetophenone 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].

### 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'      | 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     | Toluene  | 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)

### 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.
Acknowledgment: Thank to Scientific Research-Publications and Projects Research and Practice Center (BAYPUAM) under research project no MŞÜ15-FEF-G01 for their support.

Conflict of interest: Authors declare no conflict of interest.

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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 COCH₃  | 3        | 92       |
| 2     | 4a       | Br CH₃   | 3        | 79       |
| 3     | 4a       | Br OCH₃  | 3        | 82       |
| 4     | 4a       | Br CHO   | 3        | 76       |
| 5     | 4a       | Br CHO   | 3        | 86       |

Reaction conditions: R-C₆H₄Br-p (4-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-arylbromide. All reactions were monitored by GC-MS. Temperature 80 °C, 3 h.
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