



## **Schiff Base and Its Fe(II), Zn(II), Ru(II), Pd(II) Complexes Containing ONS Donor Atoms: Synthesis, characterization and Catalytic Studies**

### **ONS Donor Atomları İçeren Schiff Bazı ve Fe(II), Zn(II), Ru(II), Pd(II) Kompleksleri: Sentez, Karakterizasyon ve Katalitik Çalışmalar**

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#### **Abstract**

The work include the synthesis, spectroscopic characterization and as well as catalytic activities of Fe(II), Zn(II), Ru(II), and Pd(II) complexes with a novel Schiff base ligand derived from methyl 2-amino-5,5,7,7-tetramethyl-4,5,6,7-tetrahydrobenzo[b]thiophene-3-carboxylate and salicylaldehyde. Spectroscopic techniques including IR, UV-Vis, NMR, and mass analysis as well as elemental analysis and magnetic susceptibility measurement were used to identify the compounds. Based on elemental and spectral studies octahedral geometry was proposed to Fe(II), Zn(II) and Ru(II) complexes and square planar geometry was proposed to Pd(II) complex. To improve more efficient and stable catalysts, we wanted to study if there is any influence the catalytic activity of ruthenium complex for the transfer hydrogenation of ketones and we wanted to examine the catalytic activities of palladium complex in Suzuki C-C cross coupling reactions under various conditions.

**Keywords:** Suzuki coupling, Metal complexes, Carboxylate, Spectroscopic techniques

#### **Öz**

Bu çalışma metil 2-amino-5,5,7,7-tetrametil-4,5,6,7-tetrahidrobenzo[b]tiyofen-3-karboksilat ve salisilaldehitten elde edilen yeni bir Schiff bazı ligandı ile Fe(II), Zn(II), Ru(II) ve Pd(II) komplekslerinin sentez, spektroskopik karakterizasyon ilaveten katalitik aktivitelerini içermektedir. Bileşikleri tanımlamak için element analiz ve manyetik süsseptibilite ölçümü dâhil olmak üzere IR, UV-Vis, NMR ve kütle analizi içeren spektroskopik teknikler kullanıldı. Elemental ve spektral çalışmalara dayanarak, Fe(II), Zn(II) ve Ru(II) komplekslerine oktahedral geometri ve Pd (II) kompleksine kare düzlem geometri önerildi. Daha etkili ve kararlı katalizörler geliştirmek için, rutenyum kompleksinin ketonların hidrojen transferindeki katalitik aktiviteyi etkileyip etkilemediğini ve paladyum kompleksinin çeşitli koşullar altında Suzuki C-C çapraz eşleşme tepkimelerindeki katalitik aktivitelerini incelemek istedik.

**Anahtar Kelimeler:** Suzuki eşleşme, Metal kompleksler, Karboksilat, Spektroskopik teknikler

## 1. Introduction

Schiff bases derived from substituted salicylaldehydes and various amines and their metal complexes have been widely investigated due to their wide applicability [1]. The applications of Schiff bases and transition metal complexes have been extensively studied in biochemistry [3,4], catalysis [5] medicinal, industrial [6], pharmaceutical [7] and analytical applications [8,9]. Since the first report of their metal complexes, simple di-, ter-, and tetra-Schiff base ligands have been extensively studied and used for the metal complexation. Extension of the study to include bidentate NO and tridentate ONP or ONS donor sets is capable of providing multi-choice coordination types, and it has been accordingly understood that a few polynuclear complexes bearing Schiff-base ligands are abundant in the literature, owing to the case that they can be modified by various functional groups [10].

Many Schiff base complexes of metal ions show high catalytic activity and played a significant role in various reactions to enhance their yield and product selectivity. The convenient route of synthesis and thermal stability of Schiff base ligands have contributed significantly for their possible applications in catalysis as metal complexes [11].

Recently, the palladium-catalyzed cross-linking reaction for the formation of carbon-carbon bonds has emerged as a powerful method in an organic synthesis [12]. In particular, the Suzuki-Miyaura coupling reaction, which is referred to as cross-coupling of palladium-catalyzed organic halides with arylboronic acids, is one of the most effective methods for forming C-C bonds [13]. The products obtained in these reactions have been taken into account for their high prevalence in a wide variety of fields, including industrial, for the pharmaceutical, polymer, liquid crystals, agricultural chemical industries [14-16]. They are also used as natural products, molecular organic materials and components for optical device production [17,18]. Until now, soluble palladium(II) complexes with various ligands such as oxazolines, thioureas, pyridines, pyrazoles [19], imidazole [20], Schiff bases [21,22] and N-heterocyclic carbines [23] have been used as effective catalysts. Among these ligands, Schiff base ligands have superior properties such as ease of obtaining, low cost, thermal and chemical stability [24]. Ruthenium(II)

complexes containing arene are usually the most important catalysts used in the transfer hydrogenation of ketones [25].

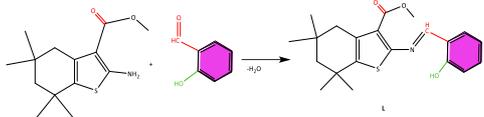
In view of above, we thought it was worthwhile to synthesis salicylaldehyde with thiophene moiety. In the present study, we describe synthesis of (*E*)-methyl-2-(2-hydroxybenzylideneamino)-5,5,7,7-tetramethyl-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carboxylate (L) and its complexes and characterization by elemental analysis, UV-Vis, IR, <sup>1</sup>H, <sup>13</sup>C NMR, mass analysis, magnetic susceptibility. The catalytic activities of Ru(II) and Pd(II) complexes were also reported.

## 2. Material ve Method

All the 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<sup>-1</sup> on a Perkin Elmer Model 65 FTIR Spectrophotometer. The <sup>1</sup>H, <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> solvent respectively 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 Shimadzu1800 in the wavelength 1100-190 nm. Mass spectra were recorded on Varian Inc, Anadolu University made Liquid Chromatography Mass Spectrometer. Elemental analyses (carbon, hydrogen, nitrogen and sulfur) were performed on a LECO 932 CHNS analyzer. Magnetic susceptibility measurements were carried out using Hg[Co (SCN)<sub>4</sub>] as calibrant by Gouy balance.

### 2.1. Synthesis and characterization of ligand and complexes

Ligand was prepared using standard procedures involving the condensation of methyl 2-amino-5,5,7,7-tetramethyl-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carboxylate (0.95 g, 0.004 mmol) and with salicylaldehyde (0.45 g, 0.004 mmol) in absolute ethanol (50 mL) in the presence of a few drops of glacial acetic acid. The mixture was stirred at reflux for 24 h. By slow cooling of the reaction mixture room temperature, a light brown crystal of Schiff base ligand was obtained.



**Figure 1.** Structural representation of the Schiff base ligand

Ligand-Empirical formula:  $(C_{21}H_{25}NO_3S)$ ; formula weight: 371.49 g/mol; yield: %72; FT-IR (KBr,  $\nu$  max  $(cm^{-1})$ ): 3346 (-OH), 3000 (Ar-CH), 2903, 2831 (Aliph.-CH,  $CH_3$ ), 1731 (C=O), 1602 (CH=N), 1586, 1515 (Ar-C=C), 1157 (C-O), 759 (C-S-C);  $^1H$ -NMR (400 Mz,  $CDCl_3$ ):  $\delta$  (ppm) = 11.20 (s, H, OH), 8.70 (s, H, N=CH), 7.60-7.00 (m, 4H, Ar-H), 3.39 (s, 3H, -CO-O- $CH_3$ ), 2.40-1.40 (s, 4H, cyclohexane), 1.40-0.98 (s, 12H, 4 $CH_3$ );  $^{13}C$ -NMR (400 MHz,  $CDCl_3$ ):  $\delta$  (ppm) = 159.00 (C=O), 160.00 (CH=N), 150.30-128.60 ( $C_{thiophene}$ ), 161.10-117.80 ( $C_{benzen}$ ), 51.50 (O- $CH_3$ ), 25.50-41.80 ( $C_{cyclohexane}$ ), 30.38-28.68 (- $CH_3$ ). Elem. analysis: calc. C, 67.83; H, 6.72; N, 3.76; S, 8.61. Found: C, 67.88; H, 6.80; N, 3.75; S, 8.63; UV-vis bands ( $\lambda_{max}$ , nm, ( $\epsilon$ ,  $M^{-1} cm^{-1}$ ):  $\pi \rightarrow \pi^*$ , 216 (2000), 257 (2000);  $n \rightarrow \pi^*$ , 391 (735.50). Color: Light brown.

A solution of ligand (0.74 g, 2 mmol) in 30 mL absolute ethanol was added to metal salts (1 mmol) namely,  $ZnCl_2$ , and  $FeCl_2 \cdot 6H_2O$ . The reaction mixture was refluxed for 18 h. The obtained colored solution was left standing at room temperature to crystallize. The product was removed by filtration, washed with cooled absolute ethanol, recrystallized from dichloromethane/ether mixture (1:1) and dried under vacuum. The analytical and physical data of the complexes are:

[ $ZnL_2 \cdot 2H_2O$ ] $\cdot 2H_2O$ -Empirical formula:  $(C_{42}H_{56}N_2S_2O_{10}Zn)$ ; formula weight: 877.37 g/mol; yield: %86; FT-IR (KBr,  $\nu_{max}$   $(cm^{-1})$ ): 3533, 3483 (OH), 3000 (Ar-CH), 2956, 2869 (Aliph.-CH,  $CH_3$ ), 1731 (C=O), 1610 (CH=N), 1547 (Ar-C=C), 1177 (C-O), 760 (C-S-C), 556, 523 (M-O), 499, 461 (M-N); Elem. analysis: calc. C, 57.44; H, 6.38; N, 3.19; S, 7.29. Found: C, 57.47; H, 6.45; N, 3.19; S, 7.30; UV-vis bands ( $\lambda_{max}$ , nm, ( $\epsilon$ ,  $M^{-1} cm^{-1}$ ):  $\pi \rightarrow \pi^*$ , 237 (72.40), 340 (55.700),  $L \rightarrow M$ , 963 (150); MS [ES]: m/z 875.37 (calcd.), 875.00 (found)  $[M-2H]^{-2}$ ; Color: Orange.

[ $FeL_2 \cdot 2H_2O$ ] $\cdot H_2O$ -Empirical formula:  $(C_{42}H_{54}N_2S_2O_9Fe)$ ; formula weight: 849.85 g/mol; yield: %76; FT-IR (KBr,  $\nu_{max}$   $(cm^{-1})$ ): 3445, 3404 (OH), 3005 (Ar-CH), 2948 (Aliph-CH), 1730 (C=O)<sub>broad</sub>, 1611 (CH=N), 1549 (Ar-

C=C), 1118 (C-O), 759 (C-S-C), 503 (M-O), 493, 478 (M-N); Elem. analysis: calc. C, 59.30; H, 6.35; N, 3.29; S, 7.53. Found: C, 59.37; H, 6.33; N, 3.27; S, 7.52; UV-vis bands ( $\lambda_{max}$ , nm, ( $\epsilon$ ,  $M^{-1} cm^{-1}$ ):  $\pi \rightarrow \pi^*$ , 240 (161.80);  $n \rightarrow \pi^*$ , 336 (90.450), 921 (750); MS [ES]: m/z 850.85 (calcd.), 850.80 (Found)  $[M+H]^+$ ; Color: Black.

A toluene solution of ligand (0.02 mmol) was mixed with  $[RuCl_2(p\text{-cymene})]_2$  (0.01 mmol) keeping metal ligand ratio 1:2. The mixture was refluxed for 4 h. The solid product precipitated on cooling was collected by filtration and washed with diethyl ether and recrystallized from  $CH_2Cl_2/Et_2O$  mixture. Similar synthesis were performed for the Pd(II) complex using bis(acetonitrile)dichloropalladium(II), (0.01 mmol).

[ $RuL^1Cl$ ] $\cdot 2H_2O$ -Empirical formula:  $(C_{31}H_{42}NSO_5ClRu)$ ; formula weight: 676.52 g/mol; yield: %75; FT-IR (KBr,  $\nu_{max}$   $(cm^{-1})$ ): 3440 (OH), 3054, 3032 (Ar-CH), 2960, 2925 (Aliph-CH), 1731 (C=O), 1594 (CH=N), 1526 (Ar-C=C), 1158 (C-O), 1365 (Ru-Cl), 759 (C-S-C), 569, 525 (M-O), 459 (M-N); Elem. analysis: calc. C, 54.98; H, 6.20; N, 2.06; S, 4.73. Found: C, 54.88; H, 6.19; N, 2.08; S, 4.78; UV-vis bands ( $\lambda_{max}$ , nm, ( $\epsilon$ ,  $M^{-1} cm^{-1}$ ):  $\pi \rightarrow \pi^*$ , 235 (200), 258 (200);  $n \rightarrow \pi^*$ , 347 (200), 374 (200); MS [ES]: m/z 674.52 (calcd.), 674.70 (Found):  $[M-2H]^{-2}$ ; Color: Dark Brown.

[ $PdL^2$ ]-Empirical formula:  $(C_{42}H_{48}N_2S_2O_6Pd)$ ; formula weight: 846.40 g/mol; yield: %65; FT-IR (KBr,  $\nu_{max}$   $(cm^{-1})$ ): 3525, 3407 (OH), 3043, (Ar-CH), 2952, 2857 (Aliph-CH), 1731 (C=O), 1615 (CH=N), 1539 (Ar-C=C), 1147 (C-O), 758 (C-S-C), 531 (M-O), 463 (M-N); Elem. analysis: calc. C, 59.54; H, 5.67; N, 3.30; S, 7.56. Found: C, 59.57; H, 5.60; N, 3.34; S, 7.58; UV-vis bands ( $\lambda_{max}$ , nm, ( $\epsilon$ ,  $M^{-1} cm^{-1}$ ):  $\pi \rightarrow \pi^*$ , 216 (200); 257 (200);  $n \rightarrow \pi^*$ , 381 (73.35); MS [ES]: m/z 845.40 (calcd.), 845.97 (Found)  $[M-H]^{-1}$ ; Color: Brown.

### 3. Results and Discussion

Ru(II), Fe(II), Zn(II) complexes were synthesized by treating  $PdCl_2(CH_3CN)_2$ ,  $[RuCl_2(p\text{-simen})]_2$ ,  $FeCl_2 \cdot 6H_2O$ ,  $ZnCl_2$ , and all the complexes were stable in air. The percentages of carbon, hydrogen nitrogen and sulfur were determined experimentally using CHNS analyzer. The physical and analytical data for the newly synthesized compounds was in good agreement with the proposed molecular formulae (Figure 1,2).

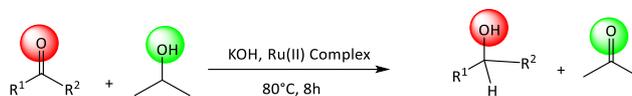
The IR spectrum of ligand showed a characteristic broad band centered in the 3346  $\text{cm}^{-1}$  and a sharp strong absorption at 1602  $\text{cm}^{-1}$ , attributable to phenolic OH and to the  $\nu(\text{CH}=\text{N})$  stretching mode, respectively. In the spectra of complexes, the former band disappeared and the latter was shifted to lower frequencies in the spectra of complexes (1594-1615  $\text{cm}^{-1}$ ), suggesting the coordination of the imine nitrogen and the deprotonated phenolic oxygen atoms to the metal atom [26]. The C-O stretching vibration showed that 1177-1118  $\text{cm}^{-1}$  for Fe(II), Pd(II), Ru(II) and Zn(II) metals were bound to the oxygen atom in the phenolate group [27]. In addition, these complexes showed new bands near 569-503 and 499-459  $\text{cm}^{-1}$ , which indicates the presence of  $\nu(\text{M}-\text{O})$  and  $\nu(\text{M}-\text{N})$  respectively. The coordination of azomethine nitrogen atom was further supported by the presence of a new band in the range, 499 and 459  $\text{cm}^{-1}$  were due to  $\nu(\text{M}-\text{N})$  mode [28]. The characteristic bands due to the  $\nu(\text{C}-\text{S}-\text{C})$  thiophene ring and  $\nu(\text{C}=\text{O})$  in ligand compared with the IR spectra of respective complexes were remain almost unshifted. This confirmed the thiophene sulfur and carbonyl oxygen did not coordinate to the metal center in case of all the metal complexes [29,30]. In Fe(II), Zn(II) complex, a band in the region 3483-3404  $\text{cm}^{-1}$  observed was assigned to  $\nu(\text{OH})$  of coordinated water, which was confirmed from [31]. These results showed that both Fe(II) and Zn(II) complexes contain two hydrate water molecule.

The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of all compounds are consistent with the proposed structures. The CH=N and OH groups protons resonances appeared as singlet peaks at 8.70 and 11.20 ppm, respectively. Azomethine protons were present in Pd(II), Ru(II) metal complexes which were appearance 8.78-8.75 ppm, respectively according to the substituent attached [32]. No appreciable change was seen in the peak positions corresponding to aromatic protons and cyclohexane protons and methylacetat protons in the complexes. Under complexation of complexes -OH protons did not appear anymore. After ligand [Ru(*p*-cymene)Cl<sub>2</sub>] was attached, the chemical shifts of the protons of *p*-cymene group shifted to the back region (1.10, 2.01, 2.60-2.80, 6.20 ppm, respectively). The ligand-bearing aromatic protons were observed at 7.70 and 7.10 ppm.

In the  $^{13}\text{C}$  NMR spectrum of ligand, two important signals were observed at 160.00 and 159.00 ppm, which are attributed to the imine (CH=N) and the free carbonyl (C=O) signals, respectively. After the chemical modification of Schiff base ligand, the free carbonyl signal of ligand disappeared, and a new azomethine signal appeared at 163.40 ppm in the spectrum of complexes. This signal showed the condensation of methyl 2-amino-5,5,7,7-tetramethyl-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carboxylate with salicylaldehyde was accomplished.

The electronic spectra of the Schiff base and its complexes were summarized in experimental section. The spectra of the ligand showed banded at about 216-257 nm and a broad shoulder at 391 nm. The first peak was attributed to  $\pi \rightarrow \pi^*$  transitions. This band was not significantly affected by chelation. The second band in the spectra of the ligand was assigned to  $n \rightarrow \pi^*$  transition. This band was disappeared via complexation and a new band attributed to the donation of the lone pairs of the nitrogen atoms of the Schiff base to the metal ion (N-M) appear [33]. In complexes the d-d transition could not be observed as it was obscured by strong charge transfer transition. The electronic spectra of the Zn(II) and Fe(II) complexes in the visible region showed intense absorption at 963-921 nm due to metal-to-ligand charge transfer (MLCT) transitions in addition to the  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  ligand centered transitions. Pd(II) was diamagnetic, suggesting a square-planar geometry for this complex [34]. The complex of Zn(II) was diamagnetic. In analogy with those described for complex that NO heteroatom having Schiff bases and according to the characterization data, we proposed an octahedral geometry for the Zn(II) complex [35].

The mass spectra of ligand and its metal complexes revealed the peaks at various positions of  $m/z$  values. The peak at  $m/z$  372.00 in the mass spectrum of ligand signifies molecular ion peak  $[\text{M}+\text{H}]^+$ . The metal complexes, such as, Fe(II), Zn(II), Ru(II) and Pd(II) deliver respective molecular ion peaks at  $m/z$  850.85, 875.37, 674.52 and 845.40, which strongly support proposed molecular formula of the complexes. These molecular mass values combined with other spectral studies are essential to generate the structure of the compounds.

**Table 1.** Catalytic activity for transfer hydrogenation of ketones catalyzed by Ru(II) complex

Entry	Ketone	Alcohol	Catalyst <sup>a</sup>	Base	Yield (%) <sup>b</sup>
1			<b>1c</b>	KOH	79
2			<b>1c</b>	KOH	2
3			<b>1c</b>	KOH	94
4			<b>1c</b>	KOH	91
5			<b>1c</b>	KOH	98
6			<b>1c</b>	KOH	96
7			<b>1c</b>	KOH	64

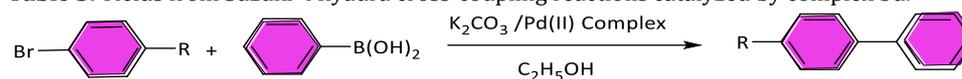
<sup>a</sup>Reaction conditions: Ketones (1 mmol), bases (4 mmol), i-PrOH (5 mL), stirring for 8 h, 80 °C.

<sup>b</sup>Yield is determined by GC-MS.

**Table 2.** Effect of solvents for the Suzuki-Miyaura reaction

Entry	Solvent	Base	Temp (°C)	Time (hrs)	Conversion
1	DMF	NaOH	100	24	10
2	DMF	K <sub>2</sub> CO <sub>3</sub>	100	24	32
3	DMF	Na <sub>2</sub> CO <sub>3</sub>	100	24	17
4	DMF	KOBu <sup>t</sup>	100	24	12
5	Ethanol	NaOH	80	24	52
6	Ethanol	K <sub>2</sub> CO <sub>3</sub>	80	24	92
7	Ethanol	Na <sub>2</sub> CO <sub>3</sub>	80	24	19
8	Ethanol	KOBu <sup>t</sup>	80	24	12
9	Toluene	NaOH	90	24	15
10	Toluene	K <sub>2</sub> CO <sub>3</sub>	90	24	12
11	Toluene	Na <sub>2</sub> CO <sub>3</sub>	90	24	20
12	Toluene	KOBu <sup>t</sup>	90	24	14
13	Dioxane	NaOH	90	24	18
14	Dioxane	K <sub>2</sub> CO <sub>3</sub>	90	24	48
15	Dioxane	Na <sub>2</sub> CO <sub>3</sub>	90	24	32
16	Dioxane	KOBu <sup>t</sup>	90	24	28

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

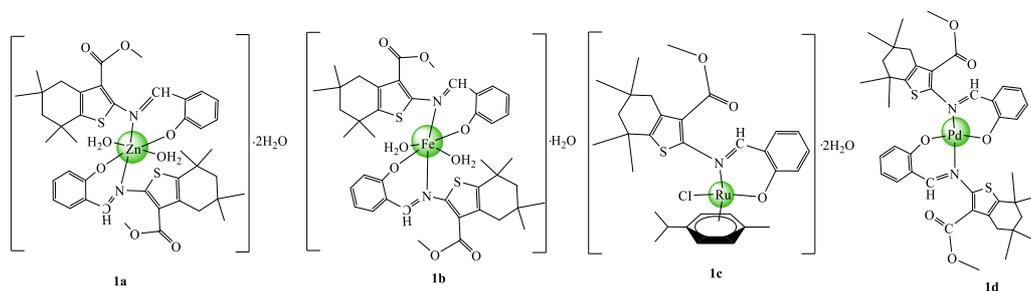
**Table 3.** Yields from Suzuki-Miyaura cross-coupling reactions catalyzed by complex 3d.

Entry	Catalysts <sup>a</sup>	R	Time	Yield(%) <sup>b,c</sup>
1	<b>1d</b>	-COCH <sub>3</sub>	3	92
2	<b>1d</b>	-CH <sub>3</sub>	3	79
3	<b>1d</b>	-OCH <sub>3</sub>	3	82
4	<b>1d</b>	-H	3	76
5	<b>1d</b>	-CHO	3	86

<sup>a</sup> Reaction conditions: 4-Bromoacetophenone (0.3 mmol), phenylboronic acid (0.45 mmol), catalyst (0.001 mmol) and base (1.5 mmol), ethanol (5 mL)

<sup>b</sup> All reactions were monitored by GC-MS.

<sup>c</sup> Isolated yield (purity of yield checked by NMR).



**Figure 2.** The proposed structure for metal complexes

As the base facilitates the formation of a ruthenium alkoxide by removing the proton from isopropanol, different bases were used as accelerators in the transfer hydrogenation of the ketones (Table 1). Benzophenone was retained as a test substrate and allowed to react with the Ru(II) complex in catalytic amount in isopropanol in the presence of different bases such as NaOH, KOH,  $\text{KOBU}^t$  and  $\text{Na}_2\text{CO}_3$ . Among the bases used, KOH had been shown to have the best conversions. For this reason, it was decided that the base KOH was the best choice between the optimum reaction rates in isopropanol and that it provides 98% conversion to benzophenone in 8 hours. In the same experimental condition, a number of substituents aromatic ketone had been investigated as Ru(II) complex catalyst via of the transfer hydrogenation. With the optimal reaction conditions in hand, we started to expand the scope and efficiency of this methodology. It had been observed that the catalytic activity varies with the substituent in the ketones. The electron donor substituent in the extracts showed a significant effect on the catalytic activity. Pentamethylacetophenone and 4-methoxyacetophenone, conversion to the corresponding alcohols was 96% and 91%, respectively (entries 4 and 5, Table 1). The substrate containing electron-withdrawing substituents such as Cl, Br, plays a role at the same level of hematogenesis on conversion of ketones to alcohols (entries 2, 3 and 6, Table 1) and was catalyzed with 92%, 94% and 96% good conversions, respectively. Under optimized conditions, was seen when the highest conversion with 98% benzophenone was used (entry 5, Table 1). This complex catalyzes the reduction of ketones to the corresponding alcohols when used to tertiary butylcyclohexanone and acetophenone shows less conversion of 64% and 79% respectively

(entries 1, 6, Table 1). Both electron withdrawing and releasing groups with acetophenone afforded the corresponding alcohols with high yields (Table 1). It was found that present Ru(II) complex exhibited higher conversions and yields for HT.

We have tried for the ability of the catalyst for optimization of coupling reaction between phenylboronic acid and 4-bromoacetophenone with different solvents, bases and at different temperatures (80, 90 and 100 °C) (Table 2). The effect of bases ( $\text{NaOH}$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{KOBU}^t$ ), solvents (DMF, 1,4-dioxane, ethanole, toluene) and reaction times were summarized (Table 2). Among the bases,  $\text{K}_2\text{CO}_3$  was found to be the most effective. The effect of solvents was studied under the optimum conditions, using the solvents toluene, DMF, 1,4-dioxane and ethanole. Ethanole was found to be the best solvent which gave conversions in excess of 92% in 3 h and 80 °C as the reaction temperature (entry 6, Table 2).

The presence of electron withdrawing or electron donating substituent on groups on the aryl bromide (entries 1 and 5, Table 3) afforded the corresponding products with high yields. The best results were obtained when carbonyl groups containing aryl bromides such as 4-bromoacetophenone (entry 1, Table 3) and 4-bromobenzaldehyde (entry 5, Table 3) were used. Respectively 92-86% conversion was reached within 3 hour for two substrates. Comparing the efficiency of the others aryl halides as electron donating (such as;  $-\text{OCH}_3$ ,  $-\text{CH}_3$ ) substrates in this reaction reveals that the good results were obtained when 4-bromoanisole and 4-bromotoluene were used (entries 2 and 3, Table 3) and the moderate result is obtained when bromobenzene was used as substrate (entry 4, Table 3). Using relatively electron-rich aryl bromides increased down the rate of reaction (entries 1 and 5, Table

3), with the poorest results 76% conversion obtained when 4-bromobenzene was used as substrate (entry 5, Table 3). The Pd(II) complex also showed tolerance for electron withdrawing and electron donating substituents on the aryl bromide. It was found that present catalyst exhibited higher conversions and yields [36,37].

#### 4. Conclusion

Four new complexes with tridentate Schiff base ligand were synthesized and characterized by physio-chemical analysis. As expected, Fe(II), Zn(II), Ru(II) complexes acquired a octahedral geometry coordinating via deprotonated hydroxyl oxygen, azomethine nitrogen and oxygene atoms of hydration water molecules of ligand. Pd(II) complex adopted square planar geometry by coordinating via deprotonated hydroxyl oxygen, azomethine nitrogen of ligand to the palladium centre and sulfur atoms remain unligated. The palladium complex showed good catalytic activity towards Suzuki reaction. Ru(II) complex showed efficient catalytic property for oxidation of both primary and secondary alcohols to the corresponding carbonyl compounds in the presence of KOH base in isopropanol, and also for transfer hydrogenation of substituted aromatic ketones with high conversions.

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