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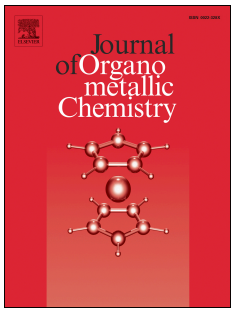

Ruthenium (II) complexes of NO ligands: Synthesis, characterization and application in transfer hydrogenation of carbonyl compounds

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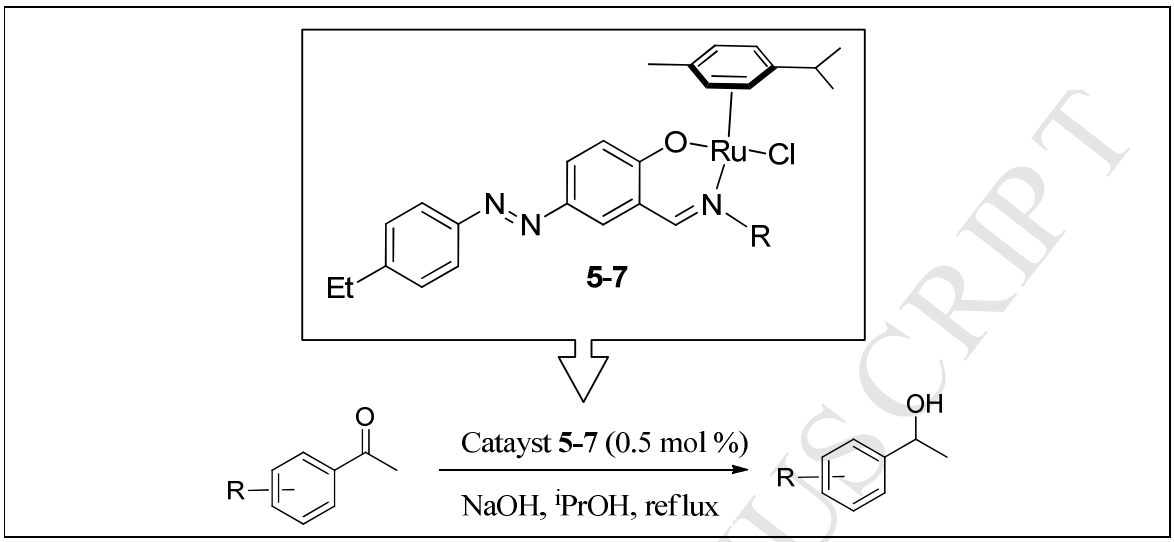

Ruthenium (II) complexes of NO ligands: Synthesis, characterization and application in transfer hydrogenation of carbonyl compounds

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Abstract:

New Schiff base ligands including azo group such as (4-((E)-(4-ethylphenyl)diazenyl)-2-((E)-(phenylimino)methyl)phenol **2**, 4-((E)-(4-ethylphenyl)diazenyl)-2-((E)-(naphthalen-1-ylimino)methyl)phenol **3**, 2-((E)-(benzylimino)methyl)-4-((E)-(4-ethylphenyl)diazenyl)phenol **4** and azo group-free ligand (E)-2-((benzylimino)methyl)phenol **8** and their ruthenium complexes **5-7** and **9** with [$RuCl_2$(*p*-cymene)] were synthesized and characterized by spectroscopic techniques including ^{1}H and ^{13}C NMR, FT-IR and UV-Vis. According to the UV-visible, IR and NMR data, the Ru (II) complexes **5-7** and **9** are formed by the coordination of *N, O* atoms of the ligands. Molecular structures of the complex **7** and complex **9** were determined by single crystal X-ray diffraction studies. These Ruthenium (II) complexes **5-7** and **9** were used as catalysts for the transfer hydrogenation of a series of ketones and benzaldehyde in 2-propanol. Following the comparison of complex **9** with the other three azo containing complexes **5-7**, it was observed that azo group has got remarkable increasing effect on the catalytic activity. The results showed that the complex **5** is efficient than the other Ru (II) complexes.

Keywords: Ruthenium, transfer hydrogenation, NO complex, azo compounds.

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Introduction

Transfer hydrogenation is one of the most important method for reduction of ketones and aldehydes, due to it is a valuable and atom-efficient reaction, more cost effective and simpler experimental procedure [1]. It is a useful method for the reduction of carbonyl compounds to their corresponding alcohols [2-4]. In addition to its use at important synthesis stages of products which have pharmaceutical, natural and industrial values, the hydrogenation reaction provides opportunity for such kind of studies to proceed rapidly because of high reaction yield [5-7].

Transition-metal catalyzed processes for transfer hydrogenation of a wide variety of functional groups by different hydrogen donors are interesting alternatives to molecular hydrogenation [1]. The studies to develop the new catalysts for transfer hydrogenation is still of considerable importance, in order to find more efficient catalysts [8]. The most active and selective catalysts for the transfer hydrogenation reactions are ruthenium [9], iridium [10] and rhodium [11] complexes containing NN, NNN, CNN, NO and PNP *etc*. type of ligands [12] (Scheme 1). Besides that the NN- and NO-donor attached ligands play important role in catalytic reactions [13].

Among the various ligand systems, Schiff base analogues have attracted great interest in recent years. Azo group show donor properties and play an important role in coordination chemistry [14]. Steric and electronic effects of substituent's in the coordination zone increases the activity of the metal and the other groups on ligands that not attended to coordination also may have an impact on this activity.

Complex formation studies of ruthenium with azo/azoimine ligands and their usage at transfer hydrogenation reaction, metal-carbon bond formation and catalytic transformations have been ongoing [15]. The ruthenium complexes formed by different types of ligands have significant importance. To design the new types of ruthenium (II) Schiff base complexes bearing oxygen and nitrogen donor atoms have importance due to their potential catalytic activities [5]. During recent years, half-sandwich (η^6-arene)ruthenium (II) complexes draw attention very much and proceed to be the subject of intense research in the field of organometallic chemistry emphatically [16-18].

In this context, our research group has focused on synthesis, characterization, and catalytic activity of ruthenium (II) NO-type complexes **5**-**7**, **9** that formed from Schiff base ligands bearing azo group on the ligand system. In addition to this, one of the aims of our study is to demonstrate that the azo group has got increasing effect on the catalytic activity. For this purpose the catalytic activities of the complexes **5**-**7** which have azo group have compared to the complex **9** without azo group. Also these ruthenium (II) NO-type Schiff base complexes were tested as catalysts for transfer hydrogenation reaction to reduce carbonyl compounds to their corresponding alcohols.

Experimental

Materials and methods

Reagents and solvents were purchased from chemical suppliers and purified to match the reported physical and spectroscopic data. The solvents were carefully dried using standard methods. Melting points were determined with an Electrothermal 9200 apparatus. IR spectra were obtained using KBr discs (4000–400 cm^{-1}) on a Shimadzu 8300 FTIR spectrophotometer. The electronic spectra in the 200–900 nm range were obtained using DMF on a Hithachi U-3900 spectrophotometer. ESI mass spectra were recorded on a ESI/MS Tandem mass spectrometry. ^{1}H and ^{13}C NMR spectra were recorded on a Varian AS-400 MHz instrument and Bruker 600 Mhz Ultrashield TM in $CDCl_3$.The conversions were determined by GC analysis with YL6500 Instrument.

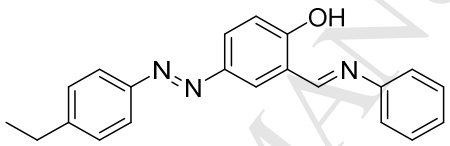
The diffraction data for complexes **(7** and **9**) were collected at room temperature on a Bruker APEX-II CCD diffractometer using graphite monochromated radiation (MoK_α, λ=0.71073 Å). ω/2θ scan mode was employed for data collection. The structures were solved by SHELXS-97[19] and refined with SHELXL-97 [20] software package. In complex **7** and **9**, all H atoms were refined using a riding model with distances of 0.93 Å (aromatic), 0.96 Å (CH_3), 0.97 Å (CH_2), 0.98 Å (CH), and $U_{iso}(H)=1.2U_{eq}(C)$ for methylene and aromatic, $1.50U_{eq}(C)$ for methyl. A summary of the key crystallographic information for both complexes are given in Table 1. Molecular drawings of the complexes indicating atom numbering scheme with thermal ellipsoids at %30 probabilities were obtained using ORTEP-III [21] The PLATON [22] program was used for geometrical calculation and conformational features of the complexes. Further experimental details have been deposited as supplementary material at the Cambridge Crystallographic Data Centre CCDC 1052112 and 1061609.

*General procedure for the synthesis of ligands **2-4***

Methanolic solutions (25 ml) of (*E*)-5-((4-ethylphenyl)diazenyl)-2-hydroxybenzaldehyde **1** (508.56 mg, 2.00 mmol) and aromatic amines (2 mmol) were stirred at reflux temperature for 8 h. After the end of reaction time, the mixtures were allowed to cool and resulting solids were collected. The crude products were recrystallised from hot methanol to yield pure crystalline products (Fig. 1).

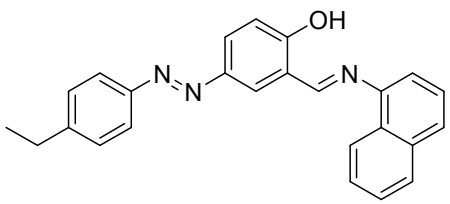
*Data for the ligands **2-4***

*For 4-((E)-(4-ethylphenyl)diazenyl)-2-((E)-(phenylimino)methyl)phenol **2***



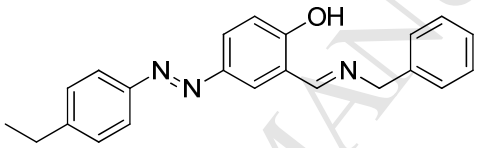
Color: Red. Yield: 545 mg (83%). m.p.119-120 °C. ^{1}H NMR (600 MHz, $CDCl_3$,δ, ppm): 13.85 (s, 1H), 8.77 (s, 1H), 8.06 (m, 2H), 7.86 (d, *J* = 8.3 Hz, 2H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.36 (m,5H), 7.17 (d, *J* = 8.5 Hz, 1H), 2.76 (q, *J* = 7.6 Hz, 2H), 1.32 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$,δ, ppm): 163.8, 162.2, 150.9, 147.8, 147.4, 145.6, 129.5, 128.6, 127.7, 127.5, 127.3, 122.7, 121.2, 118.9, 118.1, 28.8, 15.5. ESI (MeOH): 330 $[M+H]^+$. FT-IR (KBr, cm^{-1}): 3402, 3062, 1613 and 1567. UV-vis (λ_{max}, nm): 250, 352 (in 10^{-4} M DMF).

*For 4-((E)-(4-ethylphenyl)diazenyl)-2-((E)-(naphthalen-1-ylimino)methyl)phenol **3***



Color: Orange. Yield: 713.4 mg (94%). m.p. 162-163^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$,δ, ppm): 13.93 (s, 1H), 8.87 (s, 1H), 8.30 (m, 1H), 8.14 – 8.09 (m, 2H), 7.95 – 7.91 (m, 1H), 7.87 (d, *J* = 8.3 Hz, 2H), 7.85 (d, *J* = 8.3 Hz, 1H),7.63 – 7.58 (m, 2H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 7.2 Hz, 1H), 7.24 (d, *J* = 8.8 Hz, 1H), 2.77 (q, *J* = 7.6 Hz, 2H), 1.32 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$,δ, ppm): 163.8, 163.2, 150.9, 147.5, 145.8, 145.6, 134.0, 128.6, 128.2, 128.2, 127.8, 127.7, 127.4, 126.8, 126.7, 126.0, 123.1, 122.7, 119.2, 118.1, 114.2, 28.8, 15.4. ESI (MeOH): 380 $[M+H]^+$. FT-IR (KBr, cm^{-1}): 3420, 3049, 1626, and 1579. UV-vis (λ_{max}, nm): 253, 353(in 10^{-4} M DMF).

For 2-((benzylimino)methyl)-4-((E)-(4-ethylphenyl)diazenyl)phenol ***4***



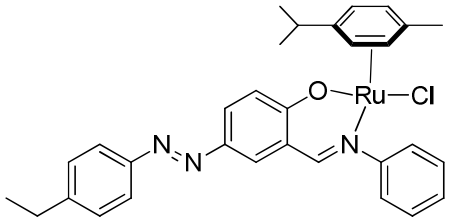
Color: Yellow. Yield: 612 mg (89 %). m.p.78-80^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$,δ, ppm): 14.04 (s, 1H), 8.55 (s, 1H), 8.00 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.94 (d, *J* = 2.4 Hz, 1H), 7.83 (d, *J* = 8.3 Hz, 2H), 7.41 (m, 2H), 7.38 – 7.32 (m, 5H), 7.09 (d, *J* = 8.8 Hz, 1H), 4.88 (s, 2H), 2.75 (q, *J* = 7.6 Hz, 2H), 1.31 (t, *J* = 7.6 Hz, 3H).^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 165.4, 164.5, 150.9, 147.2,145.3, 137.6, 128.8, 128.6, 127.9, 127.6, 127.1, 127.0, 122.6, 118.4, 118.1, 62.7, 28.8, 15.5. ESI (MeOH): 344 $[M+H]^+$. FT-IR (KBr, cm^{-1}): 3417, 3047, 1614, 1568.UV-vis (λ_{max}, nm): 255, 357(in 10^{-4} M DMF).

General procedure for the preparation of complexes ***5-7***

Dichloro(*p*-cymene)ruthenium(II) dimer (153 mg, 0. 25 mmol) and KOH (32 mg, 0.5mmol) were added to the solutions of ligands (0.50 mmol) in methanol (10 ml) in one portion and heated at 50 °C for 6 h under nitrogen atmosphere in a Schlenk tube. The precipitate was collected by filtration, washed with a large quantity of petroleum ether and diethyl ether and dried in vacuum.

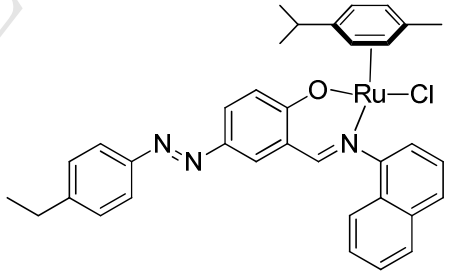
*Data for complexes **5-7***

*For complex **5***



Color: Orange. Yield: 222 mg (74%). m.p.224-225 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.92 (dd, *J* = 9.3, 2.5 Hz, 1H), 7.90 (s, 1H), 7.71(d, *J* = 8.3 Hz, 2H), 7.65 (m, 3H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.3 Hz, 1H), 7.27 (d, *J* = 8.2 Hz, 2H), 7.06 (d, *J* = 9.3 Hz, 1H), 5.39 (d, *J* = 6.1 Hz, 1H), 5.30 (d, *J* = 6.1 Hz, 1H), 5.03 (d, *J* = 5.7 Hz, 1H), 4.20 (d, *J* = 5.7 Hz, 1H), 2.77 – 2.57 (m, 3H), 2.14 (s, 3H), 1.26 (t, *J* = 7.6 Hz, 3H), 1.19 (d, *J* = 7.0 Hz, 3H), 1.14 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 168.3, 164.3, 158.3, 151.2, 146.1, 142.5, 134.8, 129.0, 128.4, 127.4, 127.3, 123.6, 123.5, 122.2, 117.8, 101.9, 98.2, 86.6, 83.8, 83.4, 80.7, 30.4, 28.7, 22.79, 21.6, 18.5, 15.5. ESI (MeOH): 564 $[M\text{-}Cl]^+$. FT-IR (KBr, cm^{-1}): 3047, 1613, 1589.UV-vis (λ_{max}, nm): 266, 408 (in 10^{-4} M DMF). Anal. Calcd. For: $[C_{31}H_{32}ClN_3ORu]$, C: 62.15, H. 5.38, N: 7.01. Found: C:62.01, H: 5.14, N: 7.04.

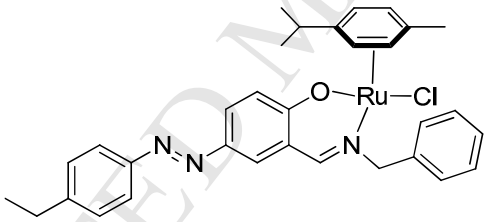
*For complex **6***



Color: Brown. Yield: 250 mg (77%). m.p.229-230°C. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 8.12 (dd, J = 7.4, 1.1 Hz, 1H), 8.06 – 7.92 (m, 1H), 7.89 (dd, J = 9.4, 5.1 Hz, 1H), 7.74

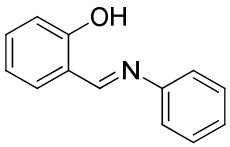
– 7.52 (m, 1H), 7.25 (d, J = 8.4 Hz, 1H), 7.11 (d, J = 9.3 Hz, 1H), 5.45 (d, J = 6.1 Hz, 1H), 5.12 (d, J = 6.2 Hz, 1H), 5.06 (d, J = 5.7 Hz, 1H), 3.89 (d, J = 5.7 Hz, 1H), 2.78 – 2.58 (m, 1H), 1.96 (s, 1H), 1.28 – 1.16 (m, 1H). 9.07 (d, J = 9.0 Hz, 1H, minor isomer), 7.06 (d, J = 9.3 Hz, 1H, minor isomer), 5.36 (d, J = 6.7 Hz, 1H, minor isomer), 5.22 (d, J = 6.3 Hz, 1H, minor isomer), 4.81 (d, J = 5.6 Hz, 1H, minor isomer), 3.59 (d, J = 5.5 Hz, 1H, minor isomer), 1.79 (s, 1H, minor isomer). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm) 168.6, 166.9, 154.0, 151.2, 146.1, 142.6, 134.9, 133.9, 129.0, 128.4, 127.7, 127.2, 127.1, 126.7, 125.9, 122.2, 121.9, 121.3, 117.5, 104.2, 94.5, 86.7, 85.8, 84.5, 30.4, 28.8, 22.9, 21.1, 17.9, 15.5. Minor isomer peaks: 170.0, 165.2, 154.1, 151.24, 146.0, 134.7, 134.1, 127.58, 127.56, 127.4, 127.17, 124.7, 123.2, 122.19, 119.6, 119.0, 102.6, 95.8, 85.5, 83.8, 80.4, 30.3, 21.2 and 18.0. ESI (MeOH): 614 [M-Cl]$^+$. FT-IR (KBr, cm^{-1}): 3048, 1620 and 1600. UV-vis (λ_{max}, nm): 266, 409 (in 10^{-4} M DMF). Anal. Calcd. For: [$C_{35}H_{34}ClN_3ORu$], C: 64.75, H. 5.28, N: 6.47. Found: C:64.61, H: 5.16, N: 6.27.

*For complex **7***



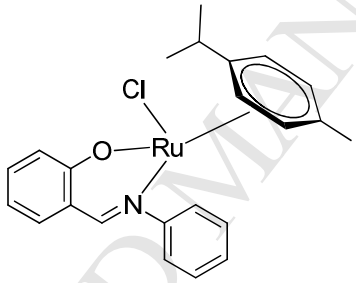
Color: Orange. The single crystal was collected from DCM-Ether (1:3) solution. Yield: 245 mg (80%). m.p.200-201°C. ^{1}H NMR (300 MHz, $CDCl_3$,δ, ppm): 7.88 (dd, *J* = 9.2, 2.5 Hz, 1H), 7.77 (s, 1H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 2.5 Hz, 1H), 7.54 – 7.38 (m, 5H), 7.27 (d, *J* = 8.5 Hz, 2H), 7.03 (d, *J* = 9.2 Hz, 1H), 5.38 (m, 3H), 5.30 (d, *J* = 6.1 Hz, 1H), 5.13 (d, *J* = 5.7 Hz, 1H), 4.94 (d, *J* = 5.7 Hz, 1H), 2.82 – 2.62 (m, 3H), 2.15 (s, 3H), 1.26 (t, *J* = 7.6 Hz, 3H), 1.20 (d, *J* = 6.9 Hz, 3H), 1.10 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.8, 165.6, 151.1, 146.2, 142.5, 137.0, 132.9, 129.3, 128.6, 128.4, 128.4, 127.5, 123.5, 122.2, 119.3, 102.8, 96.2, 84.49, 84.2, 81.8, 79.4, 71.9, 30.6, 28.8, 22.7, 21.6, 18.5, 15.5. ESI (MeOH): 579 [M-Cl]$^+$. FT-IR (KBr, cm^{-1}): 3047, 1607 and 1525. UV-vis (λ_{max}, nm): 268, 409 (in 10^{-4} M DMF). Anal. Calcd. For: [$C_{32}H_{34}ClN_3ORu$], C: 62.68, H. 5.59, N: 6.85. Found: C:62.54, H: 5.46, N: 6.75.

*Sythesis of (E)-2-((phenylimino)methyl)phenol **8***



25 mL 2-hydroxybenzaldehyde (508.5 mg, 2.00mmol) solution in methanol was added aniline (186.3 mg, 2 mmol) in methanol (5 mL) and refluxed for 8 hours. The solution was concentrated on air by removing solvent for two days and crystallized to give *(E)-2-((phenylimino)methyl)phenol* **8** as a yellow needle crystals. Yield: 545 mg (83 %).

*Synthesis of Complex **9***



Complex **9** was synthesized according to the general procedure for complexes. Dichloro(*p*-cymene)ruthenium(II) dimer (153 mg, 0. 25 mmol) and KOH (32 mg, 0.5mmol) were added to the solutions of (E)-2-((phenylimino)methyl)phenol **8** (99 mg, 0.50 mmol in methanol (10 ml) in one portion and heated at 50 °C for 6 h at nitrogen atmosphere in a Schlenk tube. The precipitate was collected by filtration, washed with a large quantity of petroleum ether and diethyl ether and dried in vacuum.

The complex **9** was obtained as orange crystals. Yield: 183 mg (78%). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.75 (s, 1H), 7.64 (d, *J* = 7.9, 2H), 7.45 (d, *J* = 7.8 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.22 (ddd, *J* = 8.6, 6.8, 1.8 Hz, 1H), 7.00 (d, *J* = 8.6 Hz, 1H), 6.95 (dd, *J* = 7.9, 1.8 Hz, 1H), 6.43 (dt,, *J* = 7.8, 0.9 Hz, 1H), 5.34 (d, *J* = 6.1 Hz, 1H), 5.25 (d, *J* = 6.1 Hz, 1H), 5.00 (d, *J* = 5.7 Hz, 1H), 4.20 (d, *J* = 5.7 Hz, 1H), 2.63 (hept, , *J* = 6.9 Hz,1H), 2.11 (s, 3H), 1.17 (d, *J* = 6.9 Hz, 3H), 1.12 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 165.2, 164.2, 158.5, 135.5, 135.4, 128.8, 126.9, 123.7, 122.7, 118.1, 114.2, 101.4, 97.9, 86.5, 83.6, 83.5, 80.3, 30.3, 22.8, 21.6, 18.5. ESI (MeOH): 433 $[M\text{-}Cl]^+$. FT-IR (KBr, cm^{-1}): 3047, 1607

and 1525. UV-vis (λ_{max}, nm): 265, 410 (in 10^{-4} M DMF). Anal. Calcd. For: [$C_{23}H_{24}ClNORu$], C: 59.16, H. 5.18, N: 3.00. Found: C:59.01, H: 5.14, N: 2.97.

Typical procedure for the transfer hydrogen reaction

Under nitrogen atmosphere, aromatic ketone (4 mmol), NaO^iPr (0.8 mL, 0.1 M) and complex **5** (1 mg, 0.0012 mmol) were dissolved in degassed 2-propanol (18 mL) with nitrogen and the mixture was refluxed for 24 h. The hydrogenation of the ketone began instantly, and the conversion and enantiomeric excess was determined by GC using HP-5 column.

Result and Discussion

*Synthesis and Characterization of ligands (**2-4, 8**) and complexes (**5-7, 9**)*

(E)-5-((4-ethylphenyl)diazenyl)-2-hydroxybenzaldehyde **1** was synthesized according to literature [23]. Three azo containing Schiff base ligands **2-4** and their Ru(II) complexes **5-7** were prepared as shown in Fig.1. The Schiff base ligands, **2**, **3** and **4** have been prepared by the condensation between (E)-5-((4-ethylphenyl)diazenyl)-2-hydroxybenzaldehyde **1** with aniline, 1-naphthylamine and 4-ethylaniline, respectively in MetOH. Also the ligand **8** and its Ru (II) complex **9** were synthesized as seen in Fig.1. The ligands are stable at room temperature and soluble in common organic solvents such as EtOH, MeOH, DMF and CH_2Cl_2. The complexes are also stable at room temperature in air.

The azo containing ligands **2-4** were completely characterized by IR, mass analyse, ^1H and ^{13}C NMR. The IR spectra of Schiff Base ligands **2-4** have similar signals. These ligands exhibit bands at 3402-3420 cm^{-1} and 3045-3062 cm^{-1} that are assignable to ν(OH) and ν(Ar-CH) [24]. Both of these three ligands **2-4** show characteristic bands at 1613-1626 range can be assigned to the azomethine ν(C=N) stretching. The distinctive bands of N=N group were observed at 1567-157 9 cm^{-1}range in ligands [8]. In complex this stretching shifted to lower frequency (1607-1620), thereby indicating coordination of azomethine nitrogen atoms [25]. Also disappearance of ν(OH) bands proves that coordination occurred with oxygen atoms as the other donor atom beside nitrogen atoms.

The electronic spectra of ligands and their Ruthenium (II) complexes **5-7** were recorded in DMF in the range 800-200 nm. The spectra of ligands **2-4** are very similar and display a strong band at 352-357 nm range. By comparing the spectra of the ligands **2-4** and the corresponding complexes **2-4**, the absorptions above 409 nm are assigned to ligand to

metal charge transfer transitions and the absorptions below 409 nm are attributed to ligand centered transitions [26].

In order to better understand the structure of the ligands **2-4** and **8,** ^{1}H and ^{13}C NMR analyses were studied. Ligands and complexes NMR spectra were given in Fig. S6-8 at supporting files. The ^{1}H NMR spectra of the ligands shows singlets in the 13.85-14.04 ppm range can be attributed to the proton of the –OH group [27]. The ^{1}H NMR resonance of azomethine proton (CH=N) in ligands are observed at 8.77, 8.55 and 8.87 ppm respectively. The quarted signals at 2.75-2.77 ppm range and the triplet signals at 1.31-1.32 ppm range corresponding to $–CH_2$ and $–CH_3$ protons. The multiplets of the aromatic protons were in the region of 8.00–7.09 ppm for ligands. Unlike other ligands, the peak at 4.88 ppm in the spectra of ligand **4** was attributed to CH_2 group.

The ^{1}H NMR spectra ($CDCl_3$) recorded during the reaction revealed formation of the two isomers in preparation of complex **6**. The spectrum exhibited one doublet at 8.12 ppm for major complex **6** and one doublet at 9.07 ppm for minor complex **6** at ratio 1:0.33. This ratio was also measured 5.45, 5.12, 5.06 and 3.89 ppm for major isomer and 5.36, 5.22, 4.81, and 3.59 ppm for minor isomer as doublets of p-cymene aromatic protons. Interestingly, the ratio of isomer which was recorded as 1:0.33 at room temperature was changed to 1:0.22 by dropping the temperature to -40 ℃ (233K).

Besides, the signals belonging to minor isomer at the low temperature disappeared in ^{31}C NMR spectrum (Fig. S10, 11).

The $[M+H]^+$ molecular ion peak for the ligand **2** is observed at m/z:330. The most intense peaks at 301 and 194 corresponds to $[C_{19}H_{14}N_3O]^+$ and $[C_{13}H_9N_2]^+$ fragments. Also the $[M+H]^+$ molecular ion peak for the ligand **3** is observed at m/z:380. The peak at 235 may be attributed to $[C_{15}H_{13}N_3]^+$. In the mass spectrum of the ligand **4**, the peak observed at m/z: 344 can be assigned to the molecular ions $[M+H]^+$. In the mass spectra of the complexes **5-7, 9**, the peaks at m/z**:** 564, m/z: 614, m/z: 579 and m/z: 433 can be assigned to the $[M-Cl]^+$ ion peaks respectively.

In the title complex **7**, Ru atom has a typical half-sandwich coordination environment with three-coordinated by O1, Cl1, N1 and six C atoms of the aromatic ring of the *p*-cymene ligand. Geometric parameters around Ru involving ring centroids are listed in Table 2. In complex **7**, the bond lengths of the configuration around the Ru1 atom are 2.4297(10) Å, 2.062(3) Å, 2.099(3) Å and 1.667(2) Å for the Ru1-Cl1, Ru1-O1, Ru1-N1 and Ru1-*Cg*4 (*Cg*4 is the centroid of C23-C28 ring) bonds, respectively, which are in good agreement with the

literature values. The bond angles of the geometry around Ru including ring centroid are 127.97(8)^{o}, 123.30(12)^{o} and 132.87(12)^{o} for the Ru1-*Cg*4-Cl1, Ru1-*Cg*4-O1 and Ru1-*Cg*4-N1, which are comparable with previously reported Ru complexes having similar coordination environment in the crystallographic studies [28-32]. In the complex **5**, Cl and O atoms involving in two C-H···Cl and a C-H···O inter-molecular hydrogen bonding interactions are observed [C7···Cl1=3.648(4) Å, C7-H7···Cl1=165.00^{o}; C24···Cl1=3.4965(5) Å, C24-H24···Cl1=140.00^{o}; C25···O1=3.5600 Å, C25-H25···O1=172.42^{o}] which help for stabilizing the molecular packing. In addition, three C-H···*Cg* (π-ring) interactions involving neighboring molecules in the unit cell (Table 3 and Fig.2) and a short aromatic π-π stacking interaction [*Cg*2-*Cg*2 (3-x, -y, 1-z) distance = 3.760(3) Å; *Cg*2 is the centroid of the C9-C14 ring] is available for forming three dimensional network (Fig.2).

The crystal structure of complex **9**, has also a half-sandwich geometry about the central Ru atom and its coordination geometry is quite similar to the complex **7** (Fig.3). In the asymmetric unit, the bond lengths and angles in complex **9** are comparable with complex **7** and those of the related structures reported in literature [28-32], except for shorter Ru1-O1, Ru1-N1 and Ru1-*Cg*3 (*Cg*3 is the centroid of C15-C20 ring) bond lengths (Table 2). In **9**, the Cl atom plays a vital role in the formation of dimeric units as a result C-H···Cl interactions (an intra-molecular contact with C9···Cl1<3.56 Å and three inter-molecular contacts with C···Cl<3.89 Å) which contribute the stability of the overall molecular structure. Besides a number of C-H···*Cg* (π-ring) interactions and some π-π stacking interactions [*Cg*1-*Cg*1 (1/2-x, 1/2+y, -z) = 5.203(3) Å, *Cg*2-*Cg*3 (x, y, z) = 4.869(3) Å, *Cg*3-*Cg*2 (-1/2+x, 1/2-y, z) = 5.009(3) Å; *Cg*1, *Cg*2 and *Cg*3 are the centroids of the C1-C6, C8-C13 and C15-C20 benzene rings, respectively] between the adjacent molecules may stabilize the molecular packing (Fig. S5 and Table 4). A comparison of Ru geometries, hydrogen bonding and short ring-interactions, complex **9** has grater hydrogen bonding effects and better stable geometry than complex **7**.

Catalytic Studies

All the ligands **2-4** and **8** were converted to ruthenium catalysts **5-7** and **9** with dichloro(*p*-cymene)ruthenium (II) dimer and these complexes were used as catalysts in transfer hydrogen reaction. Initially, to determine the catalytic performance of the ruthenium complexes **5-7** and **9**, they were examined in the reduction of acetophenone to 1-

phenylethanol as a chosen model reaction which was carried out at reflux temperature with 1000:3 substrat complex ratios in the presence of 0.1 M NaOH as a base. Transfer hydrogenation reaction was applied in ^{i}PrOH as a solvent and hydrogen source. Complex **5** was selected the best catalyst according to conversion of acetophenone to 1-phenylethanol for 24 hours (Table 5, entries 1-4). Following the selection of complex **5** amongst the other complexes, 12 test reactions have been performed with different base types, amounts and substrate/catalyst ratios to optimize and find out the best catalytic reaction conditions.

For this purpose, first of all the influence of base type was investigated by using 0.03 mmol 0.1 M NaOH, KOH, NaO^{i}Pr, NaO^{t}Bu and KO^{t}Bu base solutions and conversation rate occurred as, KO^{t}Bu < KOH < NaO^{i}Pr < NaO^{t}Bu < NaOH (Table 5, entries 1, 5-8). In the circumstances NaOH was selected as base in this system. The amount of base was increased from 0.03 mmol to 0.1 mmol but the catalytic activity in conversion did not change anymore (entries 9, 10). Besides, the ratio of substrate and complex was raised to 200 and 125 and the conversion ratio remained almost the same in 8 hours as well and these results showed a bit increase from 95 to 98 % as a result of enlarging the reaction time for 24 hours (entries 11, 12)

After the best conditions had been established for the complex **5**, a series of ketones and benzaldehyde were screened in transfer hydrogenation reaction. In all cases, the reaction was performed by transfer hydrogenation of carbonyl compounds to alcohols in ^{i}PrOH and in the presence of NaOH under the standard conditions (reflux temp., 200 substrate complex ratio and 24 h), which are displayed in Table 6. No significant changes in the yield were observed when the methyl-substituents were located in the *o*-, *m*- and *p*-positions of the acetophenone (entries 2-4). Although *m*-bromo acetophenone reduction was yielded to similar acetophenone with 91 % conversion (entry 6), the conversions of *o*- and *p*- bromo acetophenones were observed lower (entries 5-7). It was also found that the best conversion was obtained (99 %) in spite of steric effect of the *o*-methoxy substituent of the aromatic ring (entry 8). Nevertheless, that conversion was found to decrease from 99 to 85 % while proceeding towards *p*- position (entries 9 and 10). Besides, 2-acetonapthone was realized to have similar conversion when compared to acetophenone in transfer hydrogenation (entry 11). The use of sterically hindered ketones on aliphatic position of acetophenone such as 2-methyl-1-phenylpropan-1-one and propiophenone led to a dramatic decrease in conversion value (45 and 52 % respectively at 24 h.) and when a higher catalyst amount was used, higher conversion was obtained in comparison with substrate ratio (98 and 93 %, entries 12, 13). We

also tested this reaction on benzophenone and its derivatives. As a result of this reaction, *p*-methoxy on benzophenone had lower conversion ratio in comparison to the compounds which involved benzophenone and methyl group bearing *p*- position (entries 14-16). Furthermore, cyclohexanone as an aliphatic ketone and benzaldehyde as a simple aromatic aldehyde was performed in transfer hydrogenation with good conversions (entries 17, 18).

Conclusions

Azo containing Schiff base Ru (II) complexes were synthesized by the reaction of [$RuCl_2$(*p*-cymene)] with 4-((*E*)-(4-ethylphenyl)diazenyl)-2-((E)-(phenylimino)methyl)phenol **2**, 4-((*E*)-(4-ethylphenyl)diazenyl)-2-((E)-(naphthalen-1-ylimino)methyl)phenol **3** and 2-((benzylimino)methyl)-4-((*E*)-(4-ethylphenyl)diazenyl)phenol **4** at 50°C in methanol. According to the analytical, UV-visible, IR and NMR data, the Ru (II) complexes **5-7** and **9** are formed by the coordination of N and O atoms of the ligands.

These three Ruthenium (II) complexes **5-7** were used as catalysts for the transfer hydrogenation of a series of ketones and benzaldehyde in 2-propanol. Following the comparison of complex **9** with the other three complexes **5-7**, it was observed that azo group has got noticeably increasing effect on the catalytic activity. The results showed that the [RuCl(**2**)*p*-cymene] complex **5** is efficient than the other Ru (II) complexes. Investigation of side group effect of relevant complexes in transfer hydrogenation is under way.

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Table 1.
Crystal data and structure refinement for complex **5** and complex **9**.

Properties	Complex **5**	Complex **9**
Empirical Formula	$C_{32}H_{34}ClN_3ORu$	$C_{23}H_{24}ClNORu$
Formula weight	613.14	466.95
Temperature	296(2) K	296(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system, space group	Triclinic, P-1	Monoclinic, P21/c
Unit cell dimensions	a = 10.7316(4) Å b = 11.4017(4) Å c = 14.4256(6) Å α = 102.069(2) ° β = 108.783(2) ° γ = 106.907(2) °	a = 17.9196(3) b = 8.2451(1) c = 13.4869(2) α = 90.00 β = 94.7610(10) γ = 90.00
Volume	1506.93(10) $Å^3$	1985.80 $Å^3$
Z, Calculated density	2, 1.351 Mg/m^3	4, 1.562 Mg/m^3
Absorption coefficient	0.637 mm^{-1}	0.937 mm^{-1}
F(000)	632	952
Crystal size	0.40 x 0.35 x 0.10 mm	0.40 x 0.30 x 0.15 mm
Theta range for data collection (°)	1.58 to 30.84	2.28-39.71
Limiting indices	$-15\leq h\leq 15$ $-16\leq k\leq 16$ $-20\leq l\leq 9$	$-32\leq h\leq 32$ $-14\leq k\leq 14$ $-24\leq l\leq 23$
Reflections collected / unique	28805 / 8992 [R(int) = 0.0545]	45966 / 12032 [R(int)=0.0234]
Completeness to theta	94.8 %	99.5 %
Max. and min. Transmission	0.9391 and 0.7847	0.8723 and 0.7057
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8992 / 0 / 346	12032 / 0 / 247
Goodness-of-fit on F^2	1.051	1.050
Final R indices [I>2σ(I)]	R1 = 0.0630, wR2 = 0.1209	R1 = 0.0337, wR2 = 0.0773
R indices (all data)	R1 = 0.1150, wR2 = 0.1459	R1 = 0.0555, wR2 = 0.0881
Largest diff. peak and hole (e.$Å^3$)	1.330 and -0.704	0.973 and -0.608

Table 2.
Geometric parameters around Ru involving ring centroids (Å, °).

Complex **5**		Complex **9**	
*Cg*4-Ru1	1.667(2)	*Cg*3-Ru1	1.6643(12)
O1-Ru1	2.062(3)	O1-Ru1	2.0517(17)
Cl1-Ru1	2.4297(13)	Cl1-Ru1	2.4357(13)
N1-Ru1	2.099(3)	N1-Ru1	2.0874(17)
*Cg*4-Ru1-Cl1	127.97(8)	*Cg*3-Ru1-Cl1	129.33(3)
Cl1-Ru1-O1	86.59(11)	Cl1-Ru1-O1	85.20(4)
Cl1-Ru1-N1	82.62(11)	Cl1-Ru1-N1	85.06(4)
*Cg*4-Ru1-O1	123.30(12)	*Cg*3-Ru1-O1	124.11(4)
O1-Ru1-N1	88.65(14)	O1-Ru1-N1	88.62(4)
*Cg*4-Ru1-N1	132.87(12)	*Cg*3-Ru1-N1	130.02(4)

*Cg*4 is the centroid of the (C23-C28) ring for complex **5** and *Cg*3 is the centroid of the (C15-20) ring for complex **9**.

Table 3.
Hydrogen-bond geometry (Å, °) for Ru complex **5**.

D-H···*A*	*D*-H	*D*...*A*	H...*A*	*D*-H…*A*
C7-H7···Cl1^{i}	0.9300	3.648(4)	2.7400	165.00
C24-H24···Cl1^{ii}	0.9300	3.496(5)	2.7300	140.00
C25-H25···O1^{ii}	0.9300	3.5600	2.636(4)	172.42
C12-H12···*Cg*1	0.9300	3.914(7)	3.1409	141.79
C28-H28···*Cg*2^{iii}	0.9300	3.748(5)	3.0306	135.19
C31-H31B···*Cg*3^{iv}	0.9300	3.951(7)	3.0643	154.28

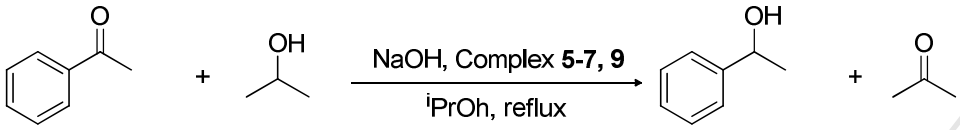
Symmetry codes: (i) 2-*x*,-*y*,1-*z*; (ii) 2-*x*,1-*y*,1-*z*; (iii) 1+*x*, *y*, *z*; (iv) 1+*x*,1+*y*, *z*.
*Cg*1, *Cg*2 and *Cg*3 are the centroids of the (C1-C6), (C9-C14) and (C15-C20) rings, respectively.

Table 4.
Hydrogen-bond geometry (Å, °) for Ru complex **9**.

D-H···*A*	*D*-H	*D*...*A*	H...*A*	*D*-H…*A*
C9-H9···Cl1^{i}	0.93	3.558(1)	2.801	139.38
C20-H20···*Cg*2^{i}	0.93	3.8223(16)	3.2845	118.96
C22-H22A···Cl1^{ii}	0.96	3.810(2)	2.903	157.84
C11-H11···Cl1^{iii}	0.93	3.886(2)	2.985	163.66
C10-H10···*Cg*2^{iv}	0.93	4.065(2)	3.3203	138.59
C13-H13···*Cg*3^{v}	0.93	3.7363(17)	2.9409	144.40
C14-H14C···*Cg*2^{vi}	0.96	3.812(3)	3.0056	142.50
C23-H23C···*Cg*1^{vii}	0.96	3.788(3)	3.2124	120.26

Symmetry codes: (i) x, y, z; (ii) *x*, *y-1*, *z*; (iii) 1+*x*, *y*-1/2, -*z*+1/2; (iv) 1-x, 1/2+y, 1/2-z; (v) x, 3/2-y, 1/2+z; (vi) x, 5/2-y, -1/2+z; (vii) x, -1+y, z.
*Cg*1, *Cg*2 and *Cg*3 are the centroids of the (C1-C6), (C8-C13) and (C15-C20) rings.

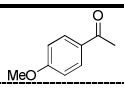
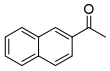
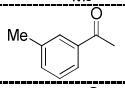
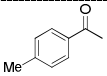
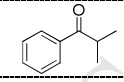
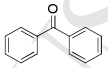
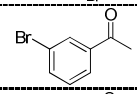
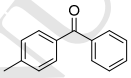
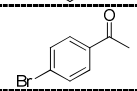
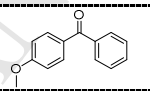
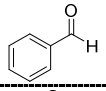
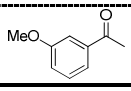
Table 5.
Reaction optimization for transfer hydrogenation of acetophenone



Entry	Acetophenone	S/C	Complex	Base[a]	Time (h)	Conversion %[d]
1	1 mmol	333	5	NaOH	24	95
2	1 mmol	333	6	NaOH	24	89
3	1 mmol	333	7	NaOH	24	79
4	1 mmol	333	9	NaOH	24	67
5	1 mmol	333	5	KOH	24	83
6	1 mmol	333	5	NaO^tBu	24	91
7	1 mmol	333	5	KO^tBu	24	72
8	1 mmol	333	5	NaO^iPr	24	86
9	1 mmol	333	5	NaOH[b]	24	94
10	1 mmol	333	5	NaOH[c]	24	94
11	1 mmol	200	5	NaOH[b]	24 (8)	98 (95)
12	1 mmol	125	5	NaOH[b]	8	95

a: 00.3 mmol, 0.1 M, b: 00.5 mmol, 0.1 M, c:0. 1 mmol, 0.1 M, d: Determined by GC (Agilent HP-5 column).

Table 6.
Catalytic transfer hydrogenation of ketones with ruthenium complex **5**

Entry	Substrate	S/C	Time (h)	Conversion (%)[a]	Entry	Substrate	S/C	Time (h)	Conversion %[a]
1		200	24	98	10		200	24	85
2		200	24	89	11		200	24	95
3		200	24	95	12		200 (100)	24 24	51 98
4		200	24	91	13		200 (100)	24 24	51 93
5		200	24	47	14		200	24	99
6		200	24	91	15		200	24	95
7		200	24	73	16		200	24	66
8		200	24	99	17		200	24	95
9		200	24	95	18		200	24	99

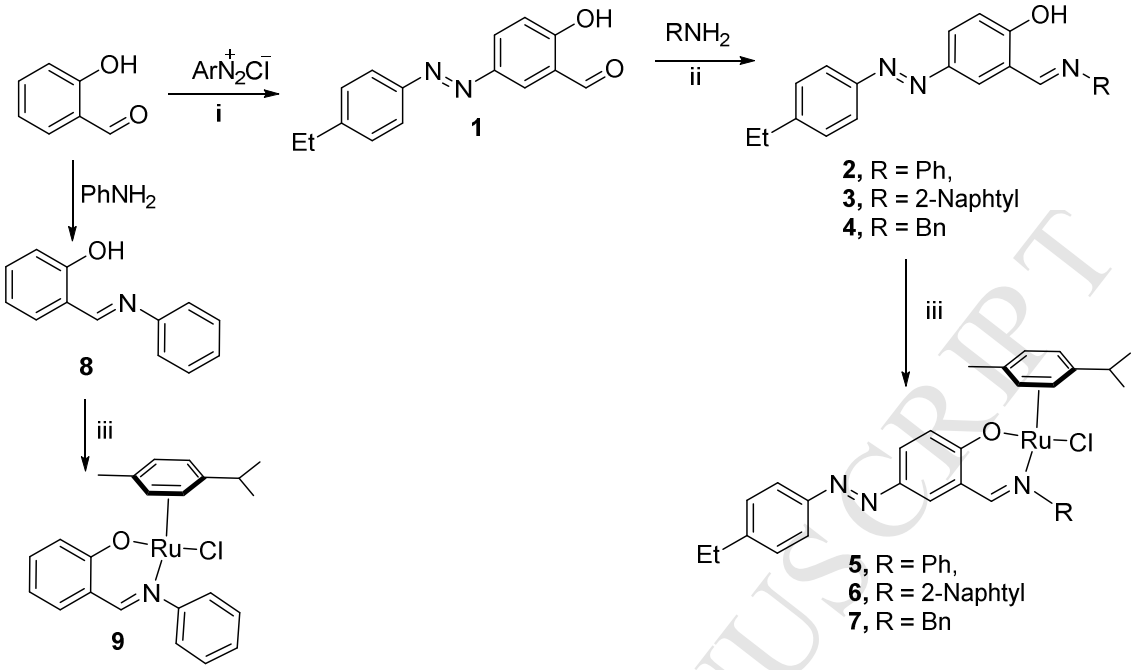


Fig. 1. Reagent and conditions: (i) $NaNO_2$, NaOH, H_2O, 0-5 °C; (ii) methanol, reflux, 8 h; (iii) KOH, $[RuCl_2(p\text{-cymene})]_2$, MeOH, 50 °C, 12 h;

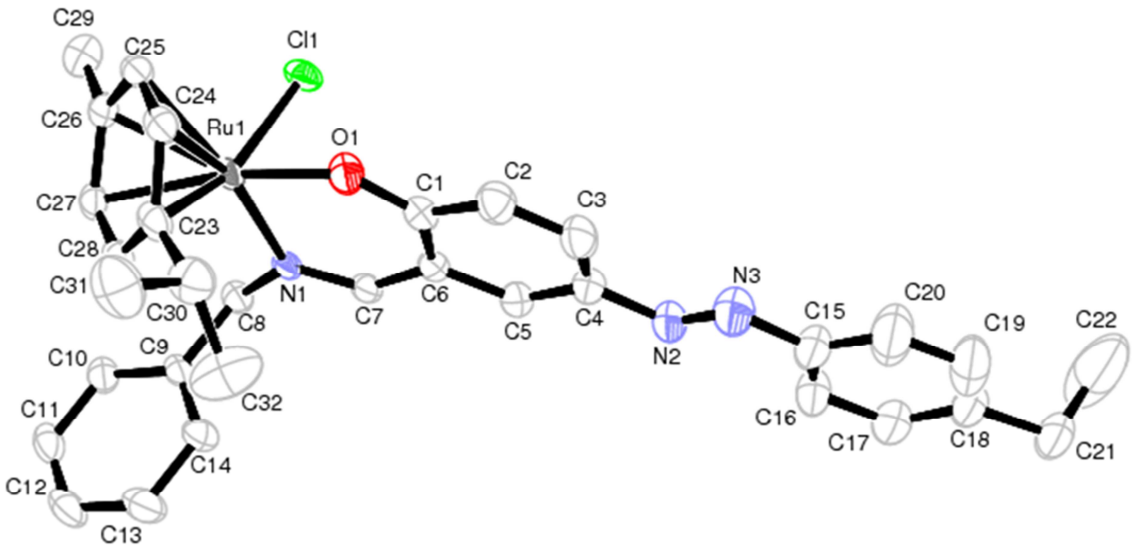


Fig.2. An *ORTEP* view of complex **7**, showing 30% probability displacement ellipsoids. Hydrogen atoms have been omitted for clarity.

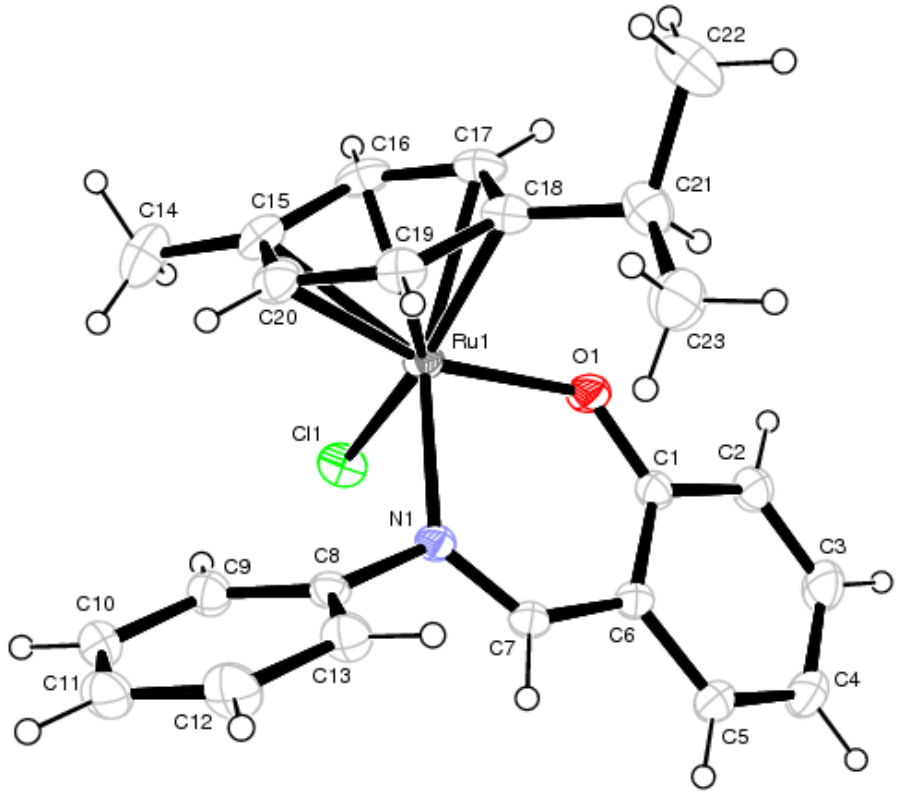
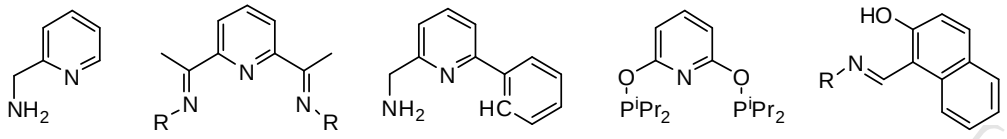


Fig.3. An *ORTEP* view of the complex **9**, showing 30% probability displacement ellipsoids.



NN NNN CNN PNP NO

Scheme 1

► Three new azo-containing Schiff Bases and their Ru (II) metal complexes were synthesized. And single-crystal X-ray analyses were performed for complex **7** and **9**.

► The synthesized metal complexes were performed as catalysts for the transfer hydrogenation of a series of ketone and benzaldehyde in 2-propanol.

► Following the comparison of complex **9** with the other three complexes **5-7**, it was observed that azo group has got remarkably increasing effect on the catalytic activity.

► Best active catalyst has found to be complex **5**.