CHAPTER VI

Ruthenium(II) phenanthrenequinone thiosemicarbazone complexes: Synthesis, characterization and catalytic activity towards reduction and condensation of nitriles

There has been much interest in the chemistry of half-sandwich arene ruthenium(II) complexes since synthesis of new and highly active transition-metal based catalysts derived from arene ligands are used in different catalytic reactions including addition of carboxylic acids to alkynes, transfer hydrogenation of ketones, polymerization of norbornene and methyl methacrylate, isomerization of alkenes and dimerization of alkynes. Among the various arene ligands, the indenyl anion C9H7 belongs to six electron groups which form one of the most typical ligands in organometallic chemistry. In contrast to the extensively used cyclopentadienyl metal fragments [M(η5-C5H5)Lm], the analogous indenyl derivatives [M(η5-C9H7)Lm] have attracted comparatively less attention. However, during last decade, the chemistry of indenyl transition metal complexes raised due to well known enhanced reactivity of these derivatives.

The formation of carbon-nitrogen bonds is an important task for organic synthesis as a number of nitrogen-containing molecules are used industrially for the preparation of both bulk and fine chemicals and for pharmaceuticals. In addition, a plethora of naturally occurring compounds such as alkaloids, amino acids and nucleotides which contain amino groups are involved in biological processes. Catalytic methods offer efficient and versatile strategies towards the synthesis of amines and represent in general a key technology for the advancement of green chemistry, specifically in terms of waste prevention, reducing energy consumption, achieving high atom efficiency and generating advantageous economics. In this respect, several interesting methods have been developed, such as the palladium-catalyzed amination of aryl halides, hydroamination of olefins and alkynes, hydroaminomethylation of olefins and reductive amination of carbonyl compounds. In addition, the catalytic hydrogenation of nitriles represents an
atom-economic and valuable route to amines. However, compared to reductions of C=C, C=O and C=N bonds, the hydrogenation of nitriles has been less investigated.

2-Oxazolines are found in a wide variety of biologically active natural products and enzyme inhibitors. They also contribute to the flavors of a variety of foods. Substituted oxazolines are an important class of intermediates in modern organic synthesis. During the last years, chiral mono- and bis-oxazoline compounds have been shown to be very useful auxiliaries and ligands in asymmetric reactions. They are also found in the structure of optically active polymers which attracted much attention due to their unique functions. A number of methods have been developed for the preparation of 2-oxazolines from carboxylic acids, carboxylic esters, nitriles, aldehydes, hydroxyamides and olefins. Various reaction conditions and a variety of homogeneous and heterogeneous catalysts have been applied for this purpose. Although these methods are valuable, most of them involve one or more disadvantages including harsh reaction conditions, long reaction times, low yields of products, the use of stoichiometric amounts of catalysts and toxic solvents. So, the development of an efficient, simple and environmentally benign catalytic procedure for the synthesis of this heterocycle is still in high demand. Based on the above, this chapter describes the synthesis and spectral characterization of ruthenium(II) complexes containing 9,10-phenanthrenequinone-N-substituted thiosemicarbazone ligands with indenyl as co-ligand and their catalytic performance such as transfer hydrogenation of nitrile and synthesis of 2-oxazoline.

**Experimental**

**Materials and instruments**

All the reagents used were chemically pure and AR grade. The solvents were purified and dried according to standard procedures. RuCl₃·3H₂O was purchased from Loba Chemie Pvt Ltd. The starting complex [RuCl(Ph₃)₂(η⁵-C₅H₅)] was prepared according to literature. Microanalyses of carbon, hydrogen, nitrogen and sulfur were carried out using Vario EL III Elemental analyzer at SAIF-Cochin India. The IR spectra of the ligands and their complexes were obtained as KBr pellets on a Nicolet Avatar model spectrophotometer in 4000-400 cm⁻¹ range.
Electronic spectra of the complexes have been measured in dichloromethane using a Shimadzu UV-1650 PC spectrophotometer in 800-200 nm range. $^1$H and $^{13}$C NMR spectra were recorded in Jeol GSX-400 instrument using DMSO-$d_6$ as the solvent at room temperature with TMS as the internal standard. Mass spectra were recorded under HRMS (FAB) using a JEOL JMS600H mass spectrometer. Melting points were checked on a Technico micro heating table and were uncorrected.

**Preparation of ligands (HL$_{1-3}$)**

9,10-Phenanthrenequinonethiosemicarbazone (HL$_1$), 9,10-phenanthrene quinone methylthiosemicarbazone (HL$_2$) and 9,10-phenanthrenequinone phenylthiosemicarbazone (HL$_3$) were prepared as per chapter-II procedure.

**Synthesis of new ruthenium(II) complexes**

All the metal complexes were prepared according to the following general procedure. An ethanolic solution (10 mL) containing HL$_{1-3}$ (0.1 mM) was added to [RuCl(PPh$_3$)$_2$(η$^5$-C$_9$H$_7$)] (0.1 mM) in benzene (10 mL). The resulting green solution was refluxed for 4 h and then cooled to room temperature, resulting in a green precipitate. It was filtered off, washed with ethanol and recrystallized from CH$_2$Cl$_2$/petroleum ether mixture. The purity of the complex was checked by TLC.

[Ru(η$^5$-indenyl)(L$_1$)] (I)

Yield: 87%; Color: Green; M.p.: 198 °C. Anal. Calc. for C$_{24}$H$_{17}$N$_3$ORuS: C, 58.05; H, 3.45; N, 8.46; S, 6.46%. Found: C, 58.69; H, 3.01; N, 8.87; S, 6.98%. IR (KBr, cm$^{-1}$): 1612 (quinone C=O), 1584 (C=N), 1574 (C=N), 758 (C-S). UV-Vis ($\lambda_{max}$/nm): 476, 355, 275, 227. $^1$H NMR (DMSO-$d_6$, ppm): 9.48 (s, 2H, NH$_2$), 6.95-8.26 (m, 12H, aromatic protons of six membered ring of indenyl group and ligand), 5.41 (t, 1H, indenyl), 4.45 (d, 2H, indenyl). $^{13}$C NMR (DMSO-$d_6$, ppm): 181.3 (quinone C=O), 172.4 (C-S), 161.8 (C=N), 123.5-138.4 (aromatic carbons of ligand and six membered ring of indenyl), 75.2, 78.6, 92.4, 107.2, 109.1 (carbons of five membered ring of indenyl). FAB-MS ($m/z$) = 497.05 [M+H]$^+$. 161
[Ru(η⁵-indenyl)(L₂)] (2)

Yield: 84%; Color: Green; M.p.: 210 °C. Anal. Calc. for C₂₅H₁₉N₃ORuS: C, 58.81; H, 3.75; N, 8.23; S, 6.28%. Found: C, 58.29; H, 3.06; N, 8.87; S, 6.68%. IR (KBr, cm⁻¹): 1623 (quinone C=O), 1588 (C=N), 1560 (C=N), 758 (C=S). UV-Vis (λmax/nm): 448, 321, 252, 216. ¹H NMR (DMSO-d₆, ppm): 8.46 (s, 1H, NH-CH₃), 7.01-8.02 (m, 12H, aromatic protons of six membered ring of indenyl group and ligand), 5.46 (t, 1H, indenyl), 4.49 (d, 2H, indenyl), 3.09 (s, 3H, CH₃). ¹³C NMR (DMSO-d₆, ppm): 181.1 (quinone C=O), 173.2 (C=S), 162.3 (C=N), 123.6-135.9 (aromatic carbons of ligand and six membered ring of indenyl), 74.7, 78.1, 91.8, 107.1, 109.5 (carbons of five membered ring of indenyl). FAB-MS (m/z) = 511.92 [M+H]⁺.

[Ru(η⁵-indenyl)(L₃)] (3)

Yield: 79%; Color: Green; M.p.: 201 °C. Anal. Calc. for C₃₀H₂₁N₃ORuS: C, 62.92; H, 3.70; N, 7.34; S, 5.60%. Found: C, 63.29; H, 3.06; N, 7.89; S, 5.16%. IR (KBr, cm⁻¹): 1614 (quinone C=O), 1580 (C=N), 1558 (C=N), 746 (C=S). UV-Vis (λmax/nm): 468, 348, 250, 217. ¹H NMR (DMSO-d₆, ppm): 11.42 (s, 1H, NH-C₅H₅), 6.81-8.21 (m, 17H, aromatic protons of six membered ring of indenyl group and ligand), 5.43 (t, 1H, indenyl), 4.44 (d, 2H, indenyl). ¹³C NMR (DMSO-d₆, ppm): 182.1 (quinone C=O), 172.2 (C=S), 163.1 (C=N), 123.8-136.1 (aromatic carbons of ligand and six membered ring of indenyl), 74.8, 77.2, 92.1, 107.8, 109.3 (carbons of five membered ring of indenyl). FAB-MS (m/z) = 573.53 [M+H]⁺.

Transfer hydrogenation of nitriles

A flask (25 mL) containing ruthenium(II) complex (1 M%) and 2-butanol (5 mL) was stirred for 5 min under an argon atmosphere at room temperature. Afterwards, t-BuOK (0.05 mM) was added and the mixture was stirred for another 5 min. Then, the nitrile (0.5 mM) was added and placed on a hot plate at 120 °C for 30 min. After completion of reaction, the catalyst was removed from the reaction mixture by the addition of petroleum ether followed by filtration and subsequent neutralization with 1M HCl. The ether layer was filtered through a short path of silica gel by column chromatography. To the filtrate, hexadecane was added as a standard and the yield was determined by GC.

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Condensation of nitriles with aminoalcohol

Nitrile (1 mM), amino alcohol (3 mM) and ruthenium(II) complex (10 M%) were mixed and stirred for 6 h at 80 °C. After completion of the reaction, the mixture was cooled to room temperature, diluted with ethyl acetate (10 mL) and filtered. The filtrate was concentrated in vacuo and the resulting residue was purified by column chromatography to provide the desired product. All the products were characterized by $^1$H NMR spectra.

2-Phenyl-4,5-dihydrooxazole. $^1$H NMR (DMSO-$d_6$, ppm): 7.19-7.96 (m, 5H, aromatic CH), 4.40-4.51 (t, 2H, CH$_2$), 3.71-3.82 (t, 2H, CH$_2$).

2-(4-Nitrophenyl)-4,5-dihydrooxazole. $^1$H NMR (DMSO-$d_6$, ppm): 8.36-8.40 (d, 2H, aromatic CH), 8.09-8.12 (d, 2H, aromatic CH), 4.48-4.54 (t, 2H, CH$_2$), 4.31-4.38 (t, 2H, CH$_2$).

2-(4-Chlorophenyl)-4,5-dihydrooxazole. $^1$H NMR (DMSO-$d_6$, ppm): 7.62-7.78 (d, 2H, aromatic CH), 6.66-6.81 (d, 2H, aromatic CH), 4.41-4.48 (t, 2H, CH$_2$), 4.02-4.10 (t, 2H, CH$_2$).

2-(p-Tolyl)-4,5-dihydrooxazole. $^1$H NMR (DMSO-$d_6$, ppm): 7.68-7.74 (d, 2H, aromatic CH), 7.14-7.21 (d, 2H, aromatic CH), 4.51-4.68 (t, 2H, CH$_2$), 4.12-4.19 (t, 2H, CH$_2$), 2.41 (s, 3H, CH$_3$).

4-(4,5-Dihydroazol-2-yl)anisole. $^1$H NMR (DMSO-$d_6$, ppm): 8.38-8.50 (d, 2H, aromatic CH), 8.02-8.14 (d, 2H, aromatic CH), 4.70-4.88 (t, 2H, CH$_2$), 4.36-4.44 (t, 2H, CH$_2$), 4.08 (s, 3H, OCH$_3$).

4-(4,5-Dihydrooxazol-2-yl)aniline. $^1$H NMR (DMSO-$d_6$, ppm): 7.02-7.18 (d, 2H, aromatic CH), 6.88-6.92 (d, 2H, aromatic CH), 4.41-4.52 (t, 2H, CH$_2$), 4.10-4.21 (t, 2H, CH$_2$), 3.80 (s, 2H, NH$_2$).

1,4-bis(4,5-Dihydrooxazol-2-yl)benzene. $^1$H NMR (DMSO-$d_6$, ppm): 7.30-7.69 (m, 4H, aromatic CH), 4.52-4.59 (t, 2H, CH$_2$), 4.22-4.30 (t, 2H, CH$_2$).
2-(Pyridin-4-yl)-4,5-dihydrooxazole. $^1$H NMR (DMSO-$d_6$, ppm): 8.56-8.82 (d, 2H, aromatic CH), 8.08-8.18 (d, 2H, aromatic CH), 4.54-4.72 (t, 2H, CH$_2$), 4.18-4.29 (t, 2H, CH$_2$).

2-(Naphthalen-2-yl)-4,5-dihydrooxazole. $^1$H NMR (DMSO-$d_6$, ppm): 7.33-7.92 (m, 7H, aromatic CH), 4.46-4.53 (t, 2H, CH$_2$), 4.18-4.24 (t, 2H, CH$_2$).

**Results and Discussion**

The synthetic route for ruthenium(II) complexes was shown in scheme 1. All the complexes were stable at room temperature, non-hygroscopic in nature and highly soluble in common organic solvents such as dichloromethane, benzene, acetonitrile, chloroform and DMSO. The analytical data was in good agreement with proposed molecular formula of the complexes.

![Scheme 1. Synthetic route for ruthenium(II) complexes](image)

**Infrared spectra**

The ligands were monoanionic tridentate, forming two five-membered chelate rings around the ruthenium through a donor set comprising quinone carbonyl oxygen, imine nitrogen and thiolate sulfur as revealed from the corresponding shifts in IR frequencies of the respective vibrations.$^{27}$ The bands assigned to azomethine $\nu$(C=N) and quinone carbonyl $\nu$(C=O) vibrations appeared at 1596-1598 and 1630-1634 cm$^{-1}$ respectively in the spectra of free ligands are shifted to lower wave numbers while the bands at 3111-3148 and 807-843 cm$^{-1}$ ascribed to the $\nu$(N–H) and $\nu$(C=S) stretches respectively disappeared on metal
complexation confirming the thio enolization nature of the ligands and subsequent coordination through the deprotonated sulfur. This was further confirmed by the appearance of two new bands at 1580-1588 and 746-758 cm\(^{-1}\) corresponds to ν(C=N−N=C) and ν(C−S) stretches respectively.

**Electronic spectra**

Electronic spectra of the complexes showed four intense absorptions in the ultraviolet and visible region 209-476 nm. The less intense absorption in the region at 321-476 nm was probably due to metal-to ligand charge transfer transition. The high intensity bands below 300 nm regions were ligand-centered transitions, likely due to the chelating, tridentate ligands. The pattern of the electronic spectra of all the complexes indicated the presence of an octahedral environment around ruthenium(II), similar to that of other ruthenium complexes.

**NMR spectra**

The singlet at 14.41-14.81 ppm assigned to hydrazinic N-H proton indicates that the ligands exist in thionic forms. This peak was not found in the spectra of complexes, consistent with deprotonation of these ligands upon metal complexation. The terminal NH\(_2\) protons in ligand \(\text{HL}_1\) were magnetically non-equivalent, have shown two singlets at 9.07 and 9.36 ppm. These protons became equivalent upon formation of ruthenium complexes and observed as a singlet at 9.48 ppm. The ligands \(\text{HL}_2, \text{HL}_3\) and their corresponding complexes showed singlet in the region 8.35-11.42 ppm were assigned to NH methyl and NH phenyl protons. In complexes, the doublet and triplet present in the region 4.44-4.49 and 5.41-5.46 ppm respectively are assigned to five membered ring of indenyl protons. In the spectra of all the complexes, the multiplet at 6.81-8.81 ppm was assigned to aromatic protons of ligand and six membered ring of indenyl. Further, the methyl protons appeared in the region 2.98-3.09 ppm (Figure 1).
Figure 1. (i) $^1$H-NMR spectra
The $^{13}$C NMR spectra of the complexes (Figure 2) have a peak at 181.1-182.1 ppm region assigned to quinone carbonyl (C=O) carbon. The azomethine (C=N) carbon exhibited a peak at 161.8-163.1 ppm. A sharp peak at 31.7 ppm was assigned to methyl carbon.
Resonance at 172.2-173.2 ppm is assigned to C-S of thiosemicarbazone. The aromatic carbons of ligands and six membered ring of indenyl showed peaks in the region of 123.5-138.4 ppm. The resonance at 74.7-109.5 ppm is assigned to five membered ring of indenyl carbons.

**Figure 2. (ii) $^{13}$C-NMR spectra**
ESI-Mass Spectra

FAB-Mass spectra were also employed to check the composition of the complexes. The complexes (1-3) displayed molecular ion isotopic clusters at m/z = 497.05, 511.92 and 573.53 [M+H]^+ (Figure 3) respectively confirmed the stoichiometry of the complexes.

Figure 3. (i) FAB-Mass spectra
Catalytic transfer hydrogenation of nitriles

In order to find optimal reaction conditions, the influence of time, temperature, base and the catalyst concentration on the yield were investigated (Table 1). The initial studies on the development of new ruthenium(II) complexes for nitrile hydrogenations were carried out with benzonitrile as standard substrate using the complex 1 as catalyst. The first set of reactions was run at constant concentration of catalyst at various time intervals at 80 °C using NaOH as base (entries 1-5). The yield increased with reaction time and total reaction time of 30 min gave a constant conversion of 66%. Next, the effect of reaction temperature on the catalyst activity was focused (entries 6, 7). The highest yield of benzylamine was obtained at 120 °C. Next, the influence of different bases on the yield of benzylamine was examined (entries 8-14). The best result was observed by using potassium tert-butoxide with conversion of 93%. In the presence of organic bases such as pyridine and triethylamine, no product was observed. Furthermore, the reaction was carried out at different concentration of catalyst. An excellent yield was obtained for 1 M% of catalyst and it can be observed that even at very low catalyst loading of 0.0025 mM (entry 15), moderate yield was obtained. The yield
decreased with decrease in catalyst loading and reaches to the lowest value of 17% with 0.00125 mM of catalyst (entry 16). Notably, no primary amine was observed without catalyst under similar reaction conditions (entry 17).

Table 1. Screening of reaction time, temperature, base and catalyst concentration

\[ 
\text{Entry} & \quad \text{Catalyst (mM)} & \quad \text{Time (min)} & \quad \text{Temp (°C)} & \quad \text{Base} & \quad \text{Conversion (\%)}^\text{b} \\
1 & 0.005 & 10 & 80 & \text{NaOH} & 38 \\
2 & 0.005 & 20 & 80 & \text{NaOH} & 54 \\
3 & 0.005 & 30 & 80 & \text{NaOH} & 66 \\
4 & 0.005 & 40 & 80 & \text{NaOH} & 67 \\
5 & 0.005 & 50 & 80 & \text{NaOH} & 67 \\
6 & 0.005 & 30 & 100 & \text{NaOH} & 74 \\
7 & 0.005 & 30 & 120 & \text{NaOH} & 85 \\
8 & 0.005 & 30 & 120 & \text{t-BuOK} & 93 \\
9 & 0.005 & 30 & 120 & \text{Cs}_2\text{CO}_3 & 78 \\
10 & 0.005 & 30 & 120 & \text{Na}_2\text{CO}_3 & 51 \\
11 & 0.005 & 30 & 120 & \text{K}_2\text{CO}_3 & 30 \\
12 & 0.005 & 30 & 120 & \text{KOH} & 62 \\
13 & 0.005 & 30 & 120 & \text{Py} & - \\
14 & 0.005 & 30 & 120 & \text{NEt}_3 & - \\
15 & 0.0025 & 30 & 120 & \text{t-BuOK} & 52 \\
16 & 0.00125 & 30 & 120 & \text{t-BuOK} & 17 \\
\]

\(^a\)Reaction conditions: benzonitrile (0.5 mM), base (10 M%), 2-butanol (5 mL)
\(^b\)Yield determined by GC

Finally, the reduction of different nitriles was performed under optimized conditions such as 1 M% of catalyst with a reaction time of 30 min at 120 °C using potassium tert-butoxide as base to demonstrate the scope and limitation of substrates in presence of ruthenium(II) complexes (Table 2). Aromatic nitriles substituted with functional groups such as NH₂, CH₃, OCH₃, NO₂, Cl, Br were tolerated without eroding the product yields (entries 2-7). The reduction of hetero aromatic nitrile gave the respective product with moderate yield of 60-75% (entries 8, 9) whereas 1-naphthonitrile could be converted into primary amine in low yield of 37-45% (entry 10).
Table 2. Reduction of nitriles catalyzed by ruthenium(II) complexes

\[
\text{R} \equiv \text{N} \xrightarrow{\text{Catalyst (1 M\%)} \quad \text{r-BaOK (10 M\%)} \quad \text{2-butanol} \quad \text{30 min, 120 °C}} \quad \text{R} \equiv \text{NH}_2
\]

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<th>Entry</th>
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<sup>a</sup>Yield determined by GC

Furthermore, the catalytic activity of complexes in transfer hydrogenation of nitriles was different from one another due to the presence of different substitutions on the terminal part of thiosemicarbazone moiety and the order of reactivity of ruthenium(II) complexes with respect to the different substitutions on ligands given by, CH<sub>3</sub> > H > C<sub>6</sub>H<sub>5</sub>. Gratifyingly, side products were not formed under these conditions.
catalytic conditions. The regenerated catalyst exhibited all the characteristic peaks in its IR spectrum which confirm the stability of the catalyst under reaction conditions. Moreover, the present catalytic system works at mild reaction conditions with low reaction time, low catalyst loading and the efficiency in terms of the yield of products without side products was higher than the existing catalytic systems.\textsuperscript{36-43}

A proposed mechanism for the hydrogenation of nitrile using ruthenium(II) complexes has been shown in scheme 2. Ruthenium(II) complexes were hydrogen transfer agents in presence of a base which can efficiently transfer the proton from the solvent (2-butanol) to nitrile and convert it into their corresponding amine compound in two consecutive hydrogen transfer cycle as shown in the mechanism. The cleavage of M-S bond under catalytic condition opens up the coordination sphere for 2-butanol which leads to the formation of a thiol in I. It is evident by the presence of C-SH peak at 2576 cm\(^{-1}\) in the IR spectrum of reaction mass before the addition of nitrile.\textsuperscript{44} Then I undergoes \(\beta\)-elimination to give a ruthenium hydride II, which is the active catalyst; this mechanism was proposed by several workers on the studies of ruthenium complex catalyzed transfer hydrogenation reaction.\textsuperscript{45,46} Ruthenium hydride complex may form an intermediate III due to the interaction of substrate (nitrile). Then III results in the formation of IV by insertion of hydride, from which unstable imine intermediate ejects as shown. Further, the imine intermediate must then be immediately undergo another hydrogen transfer cycle with II and thus, forms the final product, primary amine.\textsuperscript{36}
Scheme 2. Possible mechanistic pathway for ruthenium(II) catalyzed transfer hydrogenation of nitriles

Synthesis of 2-oxazolines

Benzonitrile and 2-aminoalcohol were chosen as the model substrates to optimize the reaction conditions including reaction temperature, time, catalyst loading and the ratio of benzonitrile to 2-aminoalcohol (Table 3). The reaction temperature usually impacts such a reaction. At 30-50 °C, the reaction did not work (entries 1-3). When the reaction temperature was raised from 60 to 80 °C, the product yields raised from 42 to 76% (entries 4-6) while the yield of the product was decreased as the temperature was raised to 90 °C (entry 7). To optimize the molar ratio of benzonitrile to 2-aminoalcohol, several ratios (1 : 1, 1 : 2, 1 : 3, 1 : 4)
were employed. As shown in Table 3, the ratio of benzonitrile to 2-aminoalcohol imposed important effects on the yield of 2-phenyloxazoline. The yield of product was gradually increased from 31 to 88% as the ratio of benzonitrile to 2-aminoalcohol was raised from 1 : 1 to 1 : 3 (entries 6, 8 and 9) at 80 °C.

**Table 3. Optimization of reaction conditions**

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<tr>
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<td>1 : 3</td>
<td>10</td>
<td>7</td>
<td>88</td>
</tr>
</tbody>
</table>

aIsolated yield

Furthermore, the catalyst loading may also affect the catalytic activity to some extent. The product yield was gradually increased from 32 to 88% as the catalyst concentration was raised from 4 to 10 M% with respect to benzonitrile concentration (entries 11-14). It is noteworthy that the reaction was not able to proceed smoothly without using a catalyst, giving only a low yield (entry 15).
Finally to optimize the reaction time, regular interval of time (4-7 h) was employed. The yield increased with reaction time and total reaction time of 6 h at 80 °C gave a higher yield (entries 14 and 16-18).

Upon the above optimization, the optimal reaction conditions were identified as follows: solvent-free, 1 : 3 molar ratio of nitriles to 2-aminoalcohol, 10 M% of catalyst and with a reaction time of 6 h at 80 °C. With the optimized reaction conditions in hand, a variety of substituted nitrile derivatives were chosen as the substrates in this tandem reaction (Table 4). The ¹H NMR spectra of catalytic products were shown in figure 4.

**Table 4. Synthesis of 2-oxazolines by ruthenium(II) complexes**

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>K</th>
<th>Yield (%)</th>
<th>1 (%)</th>
<th>2 (%)</th>
<th>3 (%)</th>
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<tr>
<td>1</td>
<td>Ph</td>
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<td>87</td>
<td>80</td>
<td>78</td>
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<tr>
<td>2</td>
<td>4-NO₂-C₆H₄</td>
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<td>93</td>
<td>90</td>
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<tr>
<td>3</td>
<td>4-Cl-C₆H₄</td>
<td></td>
<td>89</td>
<td>85</td>
<td>81</td>
<td></td>
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<tr>
<td>4</td>
<td>4-Me-C₆H₄</td>
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<td>85</td>
<td>79</td>
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<tr>
<td>5</td>
<td>4-MeO-C₆H₄</td>
<td></td>
<td>83</td>
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<td>76</td>
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<tr>
<td>6</td>
<td>4-NH₂-C₆H₄</td>
<td></td>
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<td>7</td>
<td>4-CN-C₆H₄</td>
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<td>88</td>
<td>83</td>
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<td>9</td>
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</table>

*a*Reaction conditions: nitrile (1 mM), 2-aminoalcohol (3 mM), and catalyst loading = 10 M% at 80 °C for 6 h

*b*Isolated yield

The condensation reactions were performed and the desired products were isolated in moderate to excellent yields. As shown in table 4, aromatic nitrile containing electron withdrawing substituents proceed in higher yields than those
with electron-donating substituents. For example, higher yields (entries 2, 3) were obtained for aromatic benzonitrile bearing electron withdrawing group relative to those of electron donating ones (entries 4-6). The reaction of nitriles bearing heterocycle such as isonicotinonitrile or 2-naphthonitrile performed significantly well to give good yields (entries 8, 9). As shown in table 4, the complex 1 exhibited more efficient catalytic performance on the condensation of nitriles with 2-aminoalcohol than 2 and 3, which may be due to the steric hindrance caused by bulky methyl and phenyl groups on the terminal part of thiosemicarbazone ligands in 2 and 3 respectively. In comparison with other reported catalytic systems, the present catalytic system has been found to exhibit the best activity in terms of low catalyst loading, low reaction time and high yield without any side products. Moreover, the catalytic system works under solvent-free conditions and prevent the problems which may associate with use of solvent such as cost, handling, safety and pollution.

![2-Phenyl-4,5-dihydroxazole](image)

**Figure 4.** (i) $^1$H NMR spectrum
Figure 4. (ii) $^1$H NMR spectra
Figure 4. (iii) $^1$H NMR spectra
Figure 4. (iv) $^1$H NMR spectra
Figure 4. (v) $^1$H NMR spectra
Conclusion

In this chapter, the ligands 9,10-phenanthrenequinone-N(4)-substituted thiosemicarbazones and their ruthenium(II) complexes were synthesized and characterized by elemental and spectroscopic methods. The complexes showed efficient catalytic property for the transfer hydrogenation of nitriles with high conversions. Complexes also catalyze the synthesis of 2-oxazolines from the condensation of aromatic nitrile with 2-aminoalcohol. The change in catalytic activities of the complexes can be reasonably explained by the presence of different substitutions on the terminal part of thiosemicarbazone moiety. The present approach was remarkably simple, convenient and efficient compared to the previous reports.
References


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