Journal of Coordination Chemistry

ISSN: 0095-8972 (Print) 1029-0389 (Online) Journal homepage: http://www.tandfonline.com/loi/gcoo20

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To cite this article: Panneerselvam Anitha, Periasamy Viswanathamurthi, Devarayan Kesavan & Ray Jay Butcher (2015) Ruthenium(II) 9,10-phenanthrenequinone thiosemicarbazone complexes: synthesis, characterization, and catalytic activity towards the reduction as well as condensation of nitriles, Journal of Coordination Chemistry, 68:2, 321-334, DOI: 10.1080/00958972.2014.977269

To link to this article: http://dx.doi.org/10.1080/00958972.2014.977269

Journal of Coordination Chemistry, 2015
Vol. 68, No. 2, 321–334, http://dx.doi.org/10.1080/00958972.2014.977269

Ruthenium(II) 9,10-phenanthrenequinone thiosemicarbazone complexes: synthesis, characterization, and catalytic activity towards the reduction as well as condensation of nitriles

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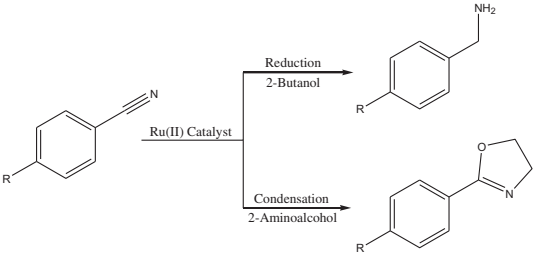
(*Received 8 May 2014; accepted 29 September 2014*)



The ligands 9,10-phenanthrenequinone-N^4-substituted thiosemicarbazones (HL_{1-3}) and their ruthenium(II) complexes were synthesized and characterized by elemental and spectroscopic methods. The ligands are tridentate, monobasic chelating ligands with O, N, and S as the donor sites and are in the thiol form in all the complexes. Catalytic studies showed that all the complexes displayed good catalytic activity towards the reduction of nitriles and also the condensation of nitriles with 2-aminoalcohol under solvent-free conditions.

Keywords: Ruthenium(II) complexes; Thiosemicarbazones; Catalytic activity; Reduction of nitriles; 2-Oxazolines

1. Introduction

Transition metal complexes containing mixed ligands with N and S or N, S, and O donors exhibit interesting stereochemical, electrochemical, and electronic properties [1,2]. Derivatives of semicarbazones and thiosemicarbazones are amongst the most widely studied nitrogen and oxygen/sulfur ligands [3, 4]. Particularly, thiosemicarbazones have emerged as an important class of sulfur donor ligands for transition metal ions because of their mixed

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hard–soft donor character and versatile coordination behavior [5]. Thiosemicarbazones of aromatic aldehydes or ketones as tridentate ligands can yield cyclometalated complexes having two fused five-membered chelate rings at the metal center [6].

There has been much interest in the chemistry of half-sandwich arene ruthenium(II) complexes [7, 8], since syntheses 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 [9], transfer hydrogenation of ketones [10], polymerization of norbornene and methyl methacrylate [11, 12], isomerization of alkenes [13], and dimerization of alkynes [14]. Among the various arene ligands, the indenyl anion $C_9H_7^-$ is a typical ligand in organometallic chemistry. In contrast to the extensively used cyclopentadienyl metal fragments [$M(\eta^5\text{-}C_5H_5)L_n$], the analogous indenyl derivatives [$M(\eta^5\text{-}C_9H_7)L_n$] have attracted less attention.

The formation of carbon–nitrogen bonds is an important task for organic synthesis as a number of nitrogen-containing molecules are used industrially for preparation of both bulk and fine chemicals and for pharmaceuticals. A plethora of naturally occurring compounds such as alkaloids, amino acids, and nucleotides which contain amino groups are involved in biological processes [15]. Catalytic methods offer efficient and versatile strategies towards the synthesis of amines and represent 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 [16]. In this respect, several interesting methods have been developed, such as palladium-catalyzed amination of aryl halides [17], hydroamination of olefins and alkynes [18], hydroaminomethylation of olefins [19], and reductive amination of carbonyl compounds [20]. 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 variety of biologically active natural products and enzyme inhibitors. They also contribute to the flavors of foods [21]. Substituted oxazolines are an important class of intermediates in modern organic synthesis [22]. Chiral mono- and bis-oxazoline compounds are useful auxiliaries and ligands in asymmetric reactions [23]. They are also found in the structure of optically active polymers which attracted attention due to their unique functions [24]. A number of methods have been developed for the preparation of 2-oxazolines from carboxylic acids [25], carboxylic esters [26], nitriles [27, 28], aldehydes [29], hydroxyamides [30], and olefins [31]. 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 facts and our continuous effort in developing efficient transition metal catalysts, herein, we have reported the synthesis and spectral characterization of ruthenium(II) complexes containing 9,10-phenanthrenequinone-N^4-substituted thiosemicarbazone ligands with indenyl as co-ligand. In addition, the catalytic performance of the ruthenium(II) complexes were tested for simple organic conversions such as transfer hydrogenation of nitrile and synthesis of 2-oxazoline.

2. Experimental

2.1. *Materials and methods*

All reagents used were chemically pure and AR grade. The solvents were purified and dried according to standard procedures. $RuCl_3 \cdot 3H_2O$ was purchased from Loba Chemie Pvt Ltd. HL_{1-3} and $[RuCl(PPh_3)_2(\eta^5\text{-}C_9H_7)]$ were prepared according to literature procedures [32, 33]. The ORTEP representation of HL_{1-3} is shown in figures S1–S3 (see online supplemental material at http://dx.doi.org/10.1080/00958972.2014.977269). Relevant data collection and details of the structure refinement are summarized in table S1. Selected bond lengths and angles for HL_{1-3} are given in table S2. Microanalyses of carbon, hydrogen, nitrogen, and sulfur were carried out using a Vario EL III Elemental analyzer at SAIF – Cochin, India. IR spectra of the ligands and their complexes were recorded as KBr pellets on a Nicolet Avatar model spectrophotometer from 4000 to 400 cm^{-1}. Electronic spectra of the complexes have been recorded in dichloromethane using a Shimadzu UV-1650 PC spectrophotometer from 800 to 200 nm. ^1H and ^{13}C NMR spectra were recorded in a 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 recorded on a Technico micro heating table and are uncorrected.

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

2.2.1. Synthesis of $[Ru(\eta^5\text{-indenyl})(L_1)]$ (1). An ethanolic solution (10 mL) containing HL_1 (0.1 mM) was added to $[RuCl(PPh_3)_2(\eta^5\text{-}C_9H_7)]$ (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_2Cl_2/petroleum ether mixture in order to remove the triphenylphosphine. The purity of the complex was checked by TLC. Our efforts to obtain single crystals of the complexes were unsuccessful. Yield 87%, m.p. 198 °C. Anal. Calcd for $C_{24}H_{17}N_3ORuS$ (%): 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 (λ_{max}/nm): 476, 355, 275, 227. ^1H NMR (DMSO-d_6, ppm): 4.45 (d, 2H, indenyl), 5.41 (t, 1H, indenyl), 6.95–8.26 (m, 12H, aromatic protons of six-membered ring of indenyl group and ligand), 9.48 (s, 2H, NH_2). ^{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 $[M + H]^+$.

2.2.2. Synthesis of $[Ru(\eta^5\text{-indenyl})(L_2)]$ (2). **2** was prepared using the same procedure as described for **1** with HL_2 (0.1 mM) and $[RuCl(PPh_3)_2(\eta^5\text{-}C_9H_7)]$ (0.1 mM). Green powder was obtained. Yield 84%, m.p. 210 °C. Anal. Calcd for $C_{25}H_{19}N_3ORuS$ (%): 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 (λ_{max}/nm): 448, 321, 252, 216. ^1H NMR (DMSO-d_6, ppm): 3.09 (s, 3H, CH_3), 4.49 (d, 2H, indenyl), 5.46 (t, 1H, indenyl), 7.01–8.02 (m, 12H, aromatic protons of six membered ring of indenyl group and ligand), 8.46 (s, 1H, NH–CH_3). ^{13}C NMR (DMSO-d_6, 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 $[M + H]^+$.

2.2.3. Synthesis of [Ru(η^5-indenyl)(L_3)] (3). **3** was prepared using the same procedure as described for **1** with HL_3 (0.1 mM) and $[RuCl(PPh_3)_2(\eta^5\text{-}C_9H_7)]$ (0.1 mM). Green powder was obtained. Yield 79%, m.p. 201 °C. Anal. Calcd for $C_{30}H_{21}N_3ORuS$: 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 (λ_{max}/nm): 468, 348, 250, 217. ^{1}H NMR (DMSO-d_6, ppm): 4.44 (d, 2H, indenyl), 5.43 (t, 1H, indenyl), 6.81–8.21 (m, 17H, aromatic protons of six-membered ring of indenyl group and ligand), 11.42 (s, 1H, NH–C_6H_5). ^{13}C NMR (DMSO-d_6, 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 $[M + H]^+$.

2.3. *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, KO*t*Bu (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 the reaction, the catalyst was removed from the reaction mixture by addition of petroleum ether followed by filtration and subsequent neutralization with 1 M 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.

2.4. *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.

2.4.1. 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).

2.4.2. 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).

2.4.3. 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).

2.4.4. 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).

2.4.5. 4-(4,5-Dihydrooxazol-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).

2.4.6. 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).

2.4.7. 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).

2.4.8. 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).

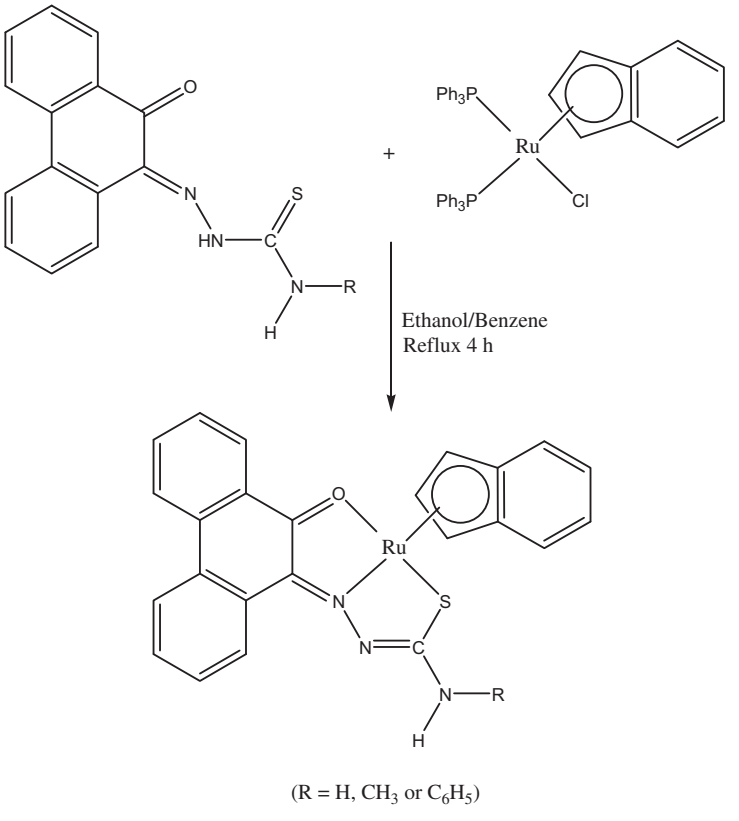
2.4.9. 2-(Naphthalen-2-yl)-4,5-dihydrooxazole. ^{1}H NMR (DMSO-d_6, ppm): 7.33–7.92 (m, 7H, aromatic CH), 4.46–4.53 (t, 2H, CH_2), 4.18–4.24 (t, 2H, CH_2).

3. Results and discussion

The synthetic route for ruthenium(II) complexes is shown in scheme 1. All the complexes are stable at room temperature, non-hygroscopic, and highly soluble in common organic solvents such as dichloromethane, benzene, acetonitrile, chloroform, and DMSO. The analytical data are in agreement with proposed molecular formula of the complexes. In addition, FAB-MS spectra were also employed to check the composition of the complexes. Complexes **1–3** displayed molecular ion isotopic clusters at $m/z = 497.05$, 511.92 and 573.53 $[M + H]^+$ (figures S4–S6), respectively, confirming the stoichiometry of the complexes.

3.1. *IR spectra*

The ligands are monoanionic tridentate, forming two five-membered chelate rings around 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 [34]. The bands assigned to azomethine (C=N) and quinone carbonyl (C=O) vibrations appeared at 1596–1598 and 1630–1634 cm^{-1}, respectively, in spectra of free ligands are shifted to lower wavenumbers, 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



Scheme 1. Synthetic route of ruthenium(II) complexes.

complexation confirming the thio enolization nature of the ligands and subsequent coordination through the deprotonated sulfur [35–37]. This was further confirmed by the appearance of two new bands at 1580–1588 cm^{-1} and 746–758 cm^{-1} corresponding to $\nu_{(C=N-N=C)}$ and $\nu_{(C-S)}$ stretches, respectively [38].

3.2. *UV–Vis absorption spectra*

Electronic absorption spectra of the complexes have been recorded in dichloromethane solution. The complexes showed four intense absorptions in the ultraviolet and visible region 209–476 nm. The less intense absorption at 321–476 nm is probably due to metal-to-ligand charge transfer transition [39]. The high intensity bands below 300 nm 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 [40].

3.3. *NMR spectra*

^{1}H NMR spectra of the ligands and the corresponding ruthenium(II) complexes were recorded in DMSO to confirm the presence of coordinated ligand in the complexes.

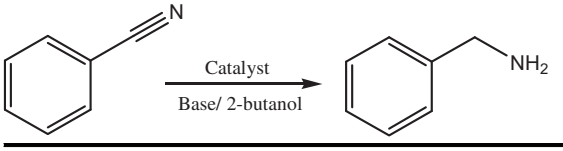
The singlet at 14.41–14.81 ppm assigned to hydrazinic N–H proton indicates that the ligands exist in thionic forms. These peaks are not found in the spectra of complexes, consistent with deprotonation of these ligands upon metal complexation [41]. The terminal NH_2 protons in HL_1 are magnetically non-equivalent, showing two singlets at 9.07 and 9.36 ppm. These protons became equivalent upon formation of ruthenium complexes as a singlet at 9.48 ppm [42]. HL_2, HL_3, and their corresponding complexes showed a singlet at 8.35–11.42 ppm 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 spectra of all the complexes, the multiplet at 6.81–8.81 ppm is assigned to aromatic protons of ligand and six-membered ring of indenyl. Further, the methyl protons are at 2.98–3.09 ppm (figures S7–S9).

The ^{13}C NMR spectra of the complexes (figures S10–S12) have a peak at 181.1–182.1 ppm region assigned to quinone carbonyl (C=O) carbon. The azomethine (C=N) carbon exhibits a peak at 161.8–163.1 ppm. A sharp peak at 31.7 ppm is expected to be 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 at 123.5–138.4 ppm. The resonance at 74.7–109.5 ppm is assigned to five-membered ring of indenyl carbons.

3.4. *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). Our initial studies on the development of new ruthenium(II) complexes for nitrile hydrogenations were carried out

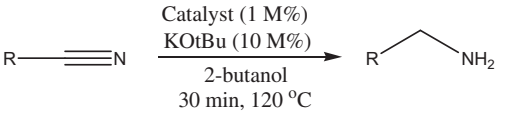
Table 1. Screening of reaction time, temperature, base, and catalyst concentration.[a]

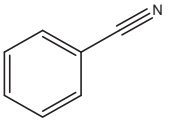
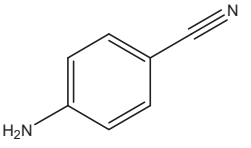
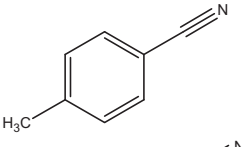
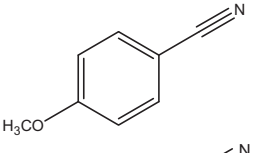
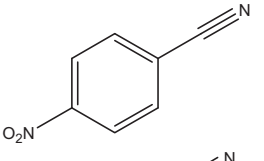
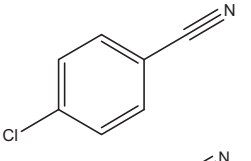
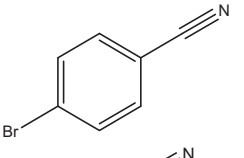
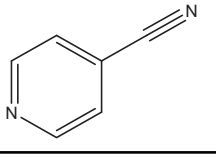


Entry	Catalyst (mM)	Time (min)	Temp. (°C)	Base	Conversion (%)[b]
1	0.005	10	80	NaOH	38
2	0.005	20	80	NaOH	54
3	0.005	30	80	NaOH	66
4	0.005	40	80	NaOH	67
5	0.005	50	80	NaOH	67
6	0.005	30	100	NaOH	74
7	0.005	30	120	NaOH	85
8	0.005	30	120	KO*t*Bu	93
9	0.005	30	120	Cs_2CO_3	78
10	0.005	30	120	Na_2CO_3	51
11	0.005	30	120	K_2CO_3	30
12	0.005	30	120	KOH	62
13	0.005	30	120	Py	–
14	0.005	30	120	NEt_3	–
15	0.0025	30	120	KO*t*Bu	52
16	0.00125	30	120	KO*t*Bu	17

[a]Reaction conditions: benzonitrile (0.5 mM), base (10 M%), and 2-butanol (5 mL).
[b]Yield determined by GC analysis with hexadecane as the internal standard.

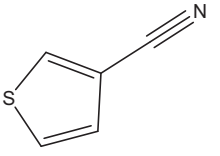
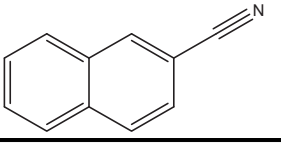
Table 2. Reduction of nitriles using ruthenium(II) complexes as catalysts.



Entry	Substrate	Yield (%)[a]		
		1	**2**	**3**
1		93	97	90
2		89	92	82
3		88	90	80
4		89	93	81
5		86	89	78
6		87	90	79
7		87	91	83
8		68	75	62

(*Continued*)

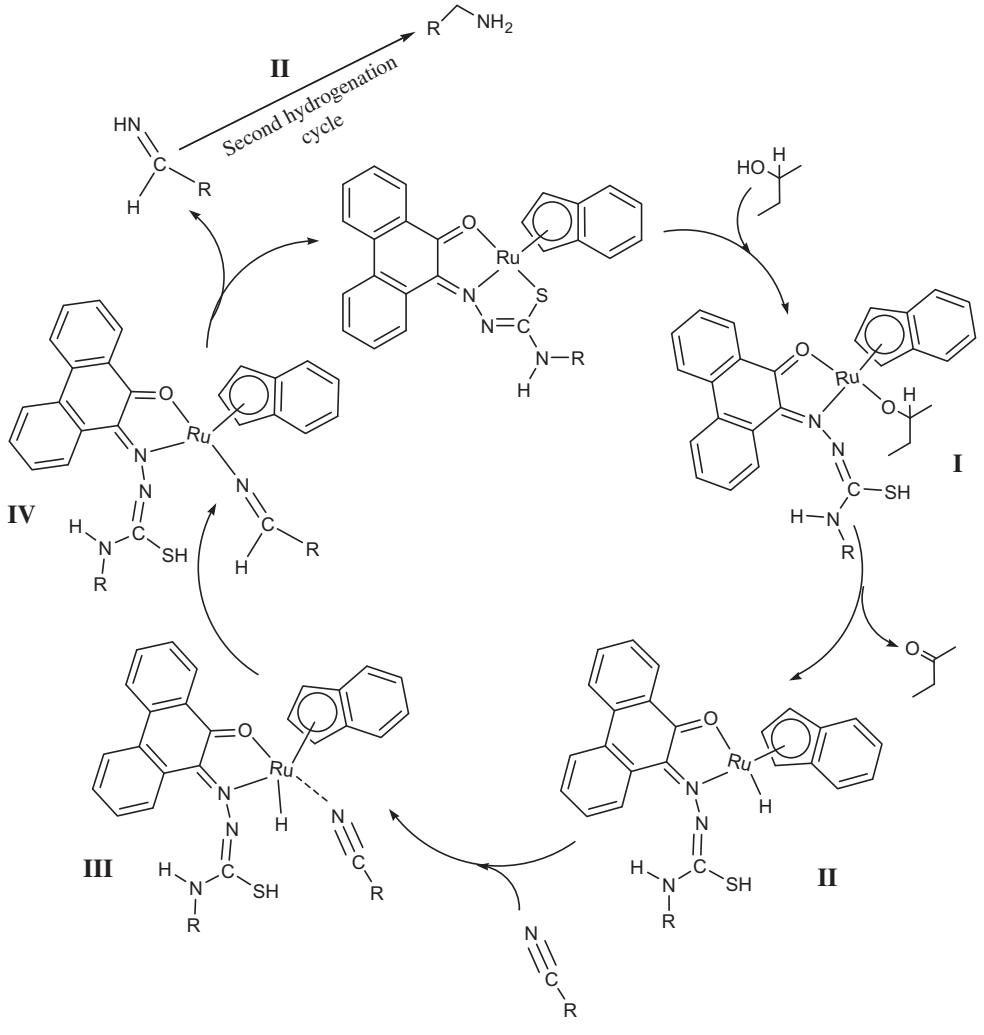
Table 2. (*Continued*).

Entry	Substrate	Yield (%)[a]		
		1	**2**	**3**
9		66	74	60
10		40	45	37

[a]Yield determined by GC analysis with hexadecane as the internal standard.

with benzonitrile as standard substrate using **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, we focused on the effect of reaction temperature on the catalyst activity (entries 6 and 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 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 concentrations 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 the lowest value of 17% with 0.00125 mM of catalyst (entry 16). No primary amine was observed without catalyst under similar reaction conditions (entry 17).

Finally, we performed the reduction of different nitriles 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 limitations of substrate in presence of ruthenium(II) complexes (table 2). Aromatic nitriles substituted with functional groups such as NH_2, CH_3, OCH_3, NO_2, Cl, and 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 and 9), whereas 1-naphthonitrile could be converted into primary amine in low yield of 37–45% (entry 10). Furthermore, the catalytic activity of complexes in transfer hydrogenation of nitriles is 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 is given by $CH_3 > H > C_6H_5$. Gratifyingly, side products are not formed under these catalytic conditions. The catalyst was regenerated after the completion of catalytic reaction and was subjected to IR spectral analysis. The characteristic peaks of the complex remained, indicating survival of our complexes under the catalytic 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 is higher than the existing catalytic systems [43–50].



Scheme 2. Possible mechanistic pathway for ruthenium(II)-catalyzed transfer hydrogenation of nitriles.

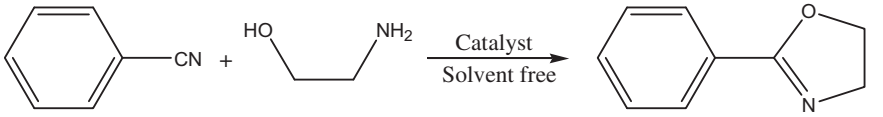
A proposed mechanism for the hydrogenation of nitrile using ruthenium(II) complexes is shown in scheme 2. Ruthenium(II) complexes are hydrogen transfer agents in the presence of a base which can efficiently transfer the proton from the solvent (2-butanol) to nitrile and convert it into the corresponding amine in two consecutive hydrogen transfer cycles as shown in the mechanism. The cleavage of the Ru–S bond under catalytic condition opens up the coordination sphere for 2-butanol which leads to 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 the reaction mass before the addition of nitrile [51]. Then **I** undergo β-elimination to give a ruthenium hydride **II** which is the active catalyst; this mechanism is proposed by several workers on the studies of ruthenium complex catalyzed transfer hydrogenation reactions [52, 53]. 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 immediately undergo another hydrogen transfer cycle with **II** and thus, forms the final product, primary amine [43].

3.5. *Synthesis of 2-oxazolines*

Benzonitrile and 2-aminoalcohol were chosen as 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 increased from 42 to 76% (entries 4–6), while the yield of the product is decreased as the temperature was raised up to 90 °C (entry 7). To optimize the molar ratio of benzonitrile to 2-aminoalcohol, several ratios (1 : 1, 1 : 2, 1 : 3, and 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. 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). The reaction gave only a low yield (entry 15) without using a catalyst. Finally to optimize the reaction time, several different time intervals (4–7 h) were 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).

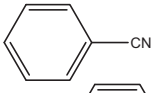
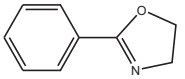
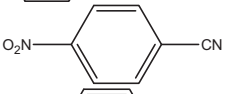
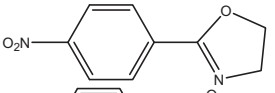
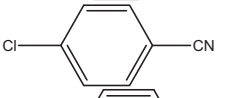
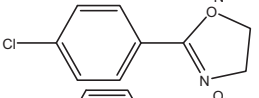
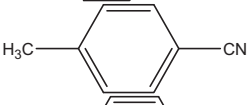
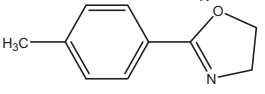
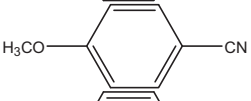
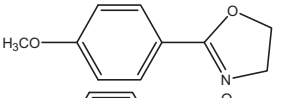
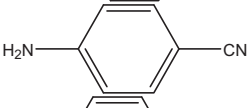
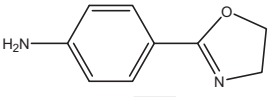
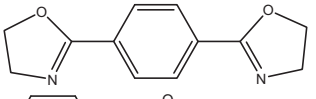
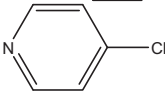
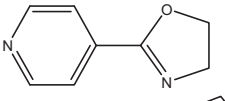
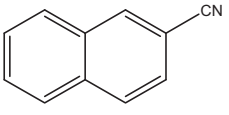
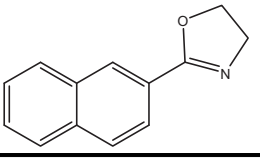
Table 3. Optimization of reaction conditions with respect to temperature, substrate ratio, catalyst concentration, and time.



Entry	Temp (°C)	Substrates ratio	Catalyst loading (M%)	Time (h)	Yield (%)[a]
1	30	1 : 2	12	6	–
2	40	1 : 2	12	6	–
3	50	1 : 2	12	6	–
4	60	1 : 2	12	6	42
5	70	1 : 2	12	6	68
6	80	1 : 2	12	6	76
7	90	1 : 2	12	6	52
8	80	1 : 1	12	6	31
9	80	1 : 3	12	6	88
10	80	1 : 4	12	6	86
11	80	1 : 3	4	6	32
12	80	1 : 3	6	6	53
13	80	1 : 3	8	6	74
14	80	1 : 3	10	6	88
15	80	1 : 3	–	6	24
16	80	1 : 3	10	4	59
17	80	1 : 3	10	5	70
18	80	1 : 3	10	7	88

[a]Isolated yield.

Table 4. Synthesis of 2-oxazolines catalyzed by ruthenium(II) complexes.[a]

Entry	Nitrile	Product	Yield (%)[b]		
			1	**2**	**3**
1			87	80	78
2			93	90	88
3			89	85	81
4			85	79	78
5			83	78	76
6			72	65	60
7			74	68	64
8			88	83	80
9			78	71	69

[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 optimal reaction conditions were identified as: 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, a variety of substituted nitrile derivatives were chosen as the substrates in this tandem reaction (table 4). The condensation reactions were performed and the desired products were isolated in moderate to excellent yields. As shown in table 4, aromatic nitriles-containing electron-withdrawing substituents proceed in higher yields than those with electron-donating substituents. For example, higher yields (entries 2 and 3) were obtained for aromatic benzonitrile-bearing electron-withdrawing group relative to those of electron-donating ones (entries 4–6). The reactions of isonicotinonitrile and 2-naphthonitrile performed well to give good yields (entries 8 and 9). As shown in table 4, **1** exhibited more efficient catalytic performance for 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 the thiosemicarbazone ligands in **2** and **3**, respectively. In comparison with other reported catalytic systems, our catalysts exhibit the

best activity in terms of low catalyst loading [54–56], low reaction time [57–60], and high yield without any side products [60, 61]. Moreover, the present catalytic system works under solvent-free conditions and prevent the problems which many associate with use of solvent such as cost, handling, safety, and pollution.

4. Conclusion

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

Supplementary material

CCDC 979369, 999390, and 999391 contain the supplementary crystallographic data for the compounds HL_1–HL_3. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223 336 033; or E-mail: deposit@ccdc.cam.ac.uk.

Acknowledgements

The authors express their sincere thanks to Council of Scientific and Industrial Research (CSIR), New Delhi [grant number 01(2437)/10/EMR-II] for financial support. One of the authors (PA) thanks CSIR for the award of Senior Research Fellowship.

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