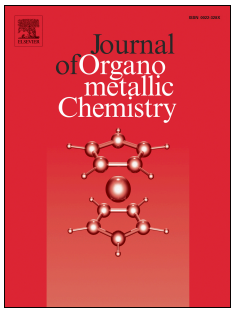
Accepted Manuscript



Ruthenium(II) 8-quinolinolates: Synthesis, characterization, crystal structure and catalysis in the synthesis of 2-oxazolines

P. Anitha, R. Manikandan, G. Prakash, B. Pachiyappan, P. Viswanathamurthi, J.G. Malecki

PII: S0022-328X(15)30032-2

DOI: 10.1016/j.jorganchem.2015.06.005

Reference: JOM 19107

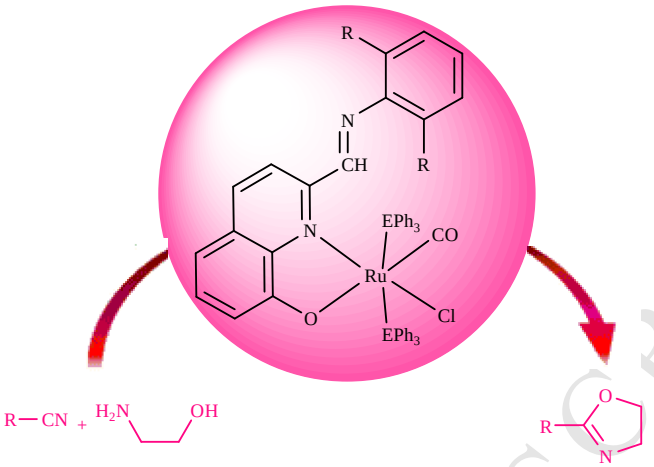
To appear in: *Journal of Organometallic Chemistry*

Received Date: 16 April 2015

Revised Date: 1 June 2015

Accepted Date: 3 June 2015

Please cite this article as: P. Anitha, R. Manikandan, G. Prakash, B. Pachiyappan, P. Viswanathamurthi, J.G. Malecki, Ruthenium(II) 8-quinolinolates: Synthesis, characterization, crystal structure and catalysis in the synthesis of 2-oxazolines, *Journal of Organometallic Chemistry* (2015), doi: 10.1016/j.jorganchem.2015.06.005.



Ruthenium(II) 8-quinolinolates: Synthesis, characterization, crystal structure and catalysis in the synthesis of 2-oxazolines

P. Anitha[a], R. Manikandan[a,1], G. Prakash[a], B. Pachiyappan[a], P. Viswanathamurthi[a,*], J.G. Malecki[b]

[a]Department of Chemistry, Periyar University, Salem-636011, Tamil Nadu, India.

[b]Department of Crystallography, Silesian University, Szkolna 9, 40-006 Katowice, Poland.

Abstract

New octahedral ruthenium(II) complexes (**1-4**) have been synthesized from the reaction of ruthenium(II) precursors [$RuHCl(CO)(EPh_3)_3$] (E = P or As) with the bidentate Schiff base ligands, 2-((2,6-dimethylphenylimino)methyl)quinolin-8-ol (**L_1**) and 2-((2,6-diisopropylphenylimino)methyl)quinolin-8-ol (**L_2**) in ethanol. These complexes have been characterized by elemental analyses, IR, UV-Vis, ^1H, ^{13}C and ^{31}P NMR and ESI-Mass spectroscopy. The molecular structure of the complex [$RuCl(CO)(PPh_3)_2(L_2)$] (**2**) was determined by single-crystal X-ray diffraction, which reveals a distorted octahedral geometry around ruthenium(II) ion. The catalytic activity of the new complexes was evaluated for the condensation of nitriles with ethanolamine under solvent free conditions. The processes were operative with aromatic and heteroaromatic nitriles and tolerated several substitutional groups. The studies on the effect of substitution over ligands, coligands, reaction time, temperature and catalyst loading were carried out in order to find the best catalyst in this series of complexes and favorable reaction conditions. A probable mechanism for the catalytic condensation of nitrile has also been proposed. The catalyst was recovered and recycled up to five times without significant loss of its activity.

Keywords:

Ru(II) carbonyl complexes

Crystal structure

2-Oxazolines

Recyclable catalyst

* Corresponding author. Fax: +91 427 2345124.

E-mail address: viswanathamurthi72@gmail.com (P. Viswanathamurthi).

[1]Present address: Department of Chemistry, KSR College of Arts and Science, Tiruchengode-637 215, India.

Introduction

Heterocyclic compounds are of great importance as pharmaceuticals, agrochemicals and ligands for organometallic chemistry [1]. Among the various heterocycles, 2-oxazoline has drawn tremendous attention due to their extensive applications in chemistry, biochemistry and pharmacology [2-5]. This heterocycle is found in the structure of many biologically active natural products [6]. It is also known as important intermediates in organic transformations [7]. Therefore, a great deal of attention, in recent years, has been devoted to the development of efficient methodologies for the preparation of such compounds. A number of methods have been developed for the preparation of 2-oxazolines from carboxylic acids [8], carboxylic esters [9], nitriles [10,11], aldehydes [12], hydroxyamides [13] and olefins [14]. Although these methods are valuable, most of them involve one or more disadvantages including harsh reaction conditions, long reaction times, low yields of products, use of stoichiometric amounts of catalysts, use of excess amounts of reagents and relatively expensive reagents and/or toxic solvents. So, the development of an efficient, simple and environmentally benign catalytic procedure for synthesis of the heterocycles is still in high demand.

There has been considerable interest in the chemistry of transition metal complexes of Schiff bases [15-18], as these ligands offer opportunities for inducing substrate chirality, tuning the metal-centered electronic factor and enhancing the solubility and stability of either homogeneous or heterogeneous catalysts [19-22]. Among the various Schiff bases, the coordination compounds of 8-hydroxyquinoline are well known due to their applications particularly in OLED (organic light emitting diode) materials [23,24]. But the study on catalytic behavior of such species is rather limited. It is well known that a small variation in the environment around Schiff base ligand affect its structure, chelate ring size and significantly properties of the complexes. By introducing appropriate substituents, one could in principle, fine tune the electronic structure, suitably to design a desired compound. A feasible approach in this work is to extend the degree of π-conjugation in 8-hydroxyquinoline molecule.

On the other hand, among the transition metals, the ruthenium complexes have received considerable attention due to their reactivity and efficiency as catalysts in wide spectrum of reactions [25-30]. Stimulated by the success of both Schiff bases and ruthenium complexes in catalytic activity, we have combined both types to prepare two new classes of hydroxyquinoline-Schiff base ligands and their ruthenium complexes.

So, based on the above facts and our continuous efforts in developing efficient transition metal catalysts [31], herein, we have reported the synthesis, spectral characterization and crystal structure of ruthenium(II) complexes containing substituted 8-hydroxyquinolinolate ligands with triphenyl phosphine/arsine and carbonyl as co-ligands. In addition, the catalytic performance of the ruthenium(II) complexes was studied towards the condensation of nitriles with ethanolamine under solvent-free conditions to generate various 2-oxazolines.

Experimental

Materials and methods

All the reagents used were chemically pure and AR grade. The solvents were purified and dried according to standard procedures. The ligands and the starting complexes [$RuHCl(CO)(PPh_3)_3$], [$RuHCl(CO)(AsPh_3)_3$] were prepared according to literature procedures [32-34]. Microanalyses of carbon, hydrogen and nitrogen were carried out using Vario EL III Elemental analyzer at SAIF - Cochin India. The IR spectra of the ligand and their complexes were recorded as KBr pellets on a Nicolet Avatar model spectrophotometer in 4000-400 cm^{-1} range. Electronic spectra of the ligand and their complexes have been obtained in dichloromethane using a Shimadzu UV - 1650 PC spectrophotometer in 800-200 nm range. ^{1}H, ^{13}C and ^{31}P NMR spectra were measured in Jeol GSX - 400 instrument using DMSO-d_6 as the solvent at room temperature. ^{1}H, ^{13}C and ^{31}P NMR spectra were obtained using TMS and *o*-phosphoric acid as the reference respectively. The ESI-MS spectra were performed by LC-MS Q-ToF Micro Analyzer (Shimadzu) in the SAIF, Panjab University, Chandigarh. Melting points were checked on a Technico micro heating table and were uncorrected.

Preparation of ligands (**HL_1, HL_2**)

2-Formyl-8-hydroxyquinoline (1 mM) was dissolved in dried and degassed ethanol (10 mL) and treated with ethanolic (10 mL) solution of 2,6-dimethylaniline/2,6-diisopropylaniline (1 mM) in 1:1 molar ratio. A drop of acetic acid was added and the reaction mixture was subsequently refluxed for 4 h. On cooling to room temperature, the yellow product obtained was purified by column chromatography using dichloromethane and petroleumether (1:3) solvent mixture.

2-((2,6-dimethylphenylimino)methyl)quinolin-8-ol (**HL_1**)

Yield: 85%; MP: 252 °C; Anal. calc. for $C_{18}H_{16}N_2O$ (%): C, 78.24; H, 5.84; N, 10.14. Found (%): C, 78.36; H, 5.78; N, 10.25. IR (KBr, cm^{-1}): 3372 (phenolic O-H), 1641 (azomethine CH=N), 1627 (ring C=N), 1324 (phenolic C-O). UV-Vis (λmax, nm): 355, 305. ^{1}H NMR (DMSO-d_6, ppm): 9.32 (s, phenolic O-H), 8.48 (s, azomethine CH=N), 7.69 (d, 1H, quin-H), 7.64 (d, 1H, quin-H), 7.40 (t, 1H, quin-H), 7.36 (d, 1H, quin-H), 7.27 (d, 1H, quin-H), 6.90 (d, 2H, Ar-H), 6.81 (d, 1H, Ar-H), 2.28 (s, 6H, CH_3).

2-((2,6-diisopropylphenylimino)methyl)quinolin-8-ol (**HL_2**)

Yield: 88%; MP: 238 °C; Anal. calc. for $C_{22}H_{24}N_2O$ (%): C, 79.48; H, 7.28; N, 8.43. Found (%): C, 79.36; H, 7.47; N, 8.25. IR (KBr, cm^{-1}): 3470 (phenolic O-H), 1636 (azomethine CH=N), 1632 (ring C=N), 1326 (phenolic C-O). UV-Vis (λmax, nm): 359, 304. ^{1}H NMR (DMSO-d_6, ppm): 9.02 (s, phenolic O-H), 8.35 (s, azomethine CH=N), 7.72 (d, 1H, quin-H), 7.69 (d, 1H, quin-H), 7.44 (t, 1H, quin-H), 7.41 (d, 1H, quin-H), 7.38 (d, 1H, quin-H), 7.01 (d, 2H, Ar-H), 6.98 (d, 1H, Ar-H), 3.68 (m, 2H, CH-^{i}Pr), 1.28 (d, 12H, CH_3-^{i}Pr).

General procedure for the synthesis of new ruthenium(II) complexes (**1-4**)

To a solution of [RuHCl(CO)(EPh_3)$_3$] (E = P or As) (0.1 mM) in ethanol (20 mL), the appropriate ligand (0.1 mM) was added in 1:1 molar ratio. The mixture was refluxed for 5 h in a water bath, whereby the solution turned from pale yellow to red. After reducing the content to half volume and standing for a day, the complex was obtained as a red precipitate. It was filtered and washed several times with ether and dried under vacuum. Crystals suitable for X-ray diffraction were obtained by slow evaporation of a concentrated solution of complex **2** in ethanol.

[RuCl(CO)(PPh_3)$_2$(L_1)] (**1**)

Yield: 84%; MP: 251 °C; Anal. calc. for $C_{55}H_{45}ClN_2O_2P_2Ru$ (%): C, 68.50; H, 4.70; N, 2.90. Found (%): C, 68.39; H, 4.61; N, 2.78. IR (KBr, cm^{-1}): 1932 (C≡O), 1639 (azomethine CH=N), 1584 (ring C=N), 1432 (phenolic C-O). UV-Vis (λmax, nm): 502, 362, 310. ^{1}H NMR (DMSO-d_6, ppm): 8.36 (s, azomethine CH=N), 7.88 (d, 1H, quin-H), 7.84 (d, 1H, quin-H), 7.53 (t, 1H, quin-H), 7.49 (d, 1H, quin-H), 7.45 (d, 1H, quin-H), 7.19 (d, 2H, Ar-H), 7.15 (d, 1H, Ar-H), 7.11-7.02 (m,

30H, PPh_3), 2.20 (s, 6H, CH_3). ^{13}C NMR (DMSO-d_6, ppm): 202.80 (C≡O), 164.14 (phenolic C-O), 152.13 (azomethine CH=N), 149.11 (quinoline ring C=N), 136.17, 135.81, 135.62, 134.47, 133.03, 132.15, 130.23, 128.70, 128.54, 127.35, 126.88, 126.39, 125.86, 124.38, 123.81 (Ar-C), 19.82 (CH_3). ^{31}P NMR (DMSO-d_6, ppm): 30.22. ESI-Mass (*m/z*) = 928.7 $[M\text{-}Cl]^+$.

[RuCl(CO)(PPh_3)$_2$(L_2)] (**2**)

Yield: 81%; MP: 278 °C; Anal. calc. for $C_{59}H_{53}ClN_2O_2P_2Ru$ (%): C, 69.44; H, 5.23; N, 2.74. Found (%): C, 69.56; H, 5.50; N, 2.86. IR (KBr, cm^{-1}): 1942 (C≡O), 1633 (azomethine CH=N), 1590 (ring C=N), 1367 (phenolic C-O). UV-Vis (λmax, nm): 485, 374, 320. ^1H NMR (DMSO-d_6, ppm): 8.20 (s, azomethine CH=N), 7.91 (d, 1H, quin-H), 7.86 (d, 1H, quin-H), 7.50 (t, 1H, quin-H), 7.46 (d, 1H, quin-H), 7.41 (d, 1H, quin-H), 7.06 (d, 2H, Ar-H), 7.02 (d, 1H, Ar-H), 6.93-6.84 (m, 30H, $AsPh_3$), 3.72 (m, 2H, CH-^{i}Pr), 1.29 (d, 12H, CH_3-^{i}Pr). ^{13}C NMR (DMSO-d_6, ppm): 204.40 (C≡O), 163.17 (phenolic C-O), 152.34 (azomethine CH=N), 148.82 (quinoline ring C=N), 136.67, 136.21, 135.63, 135.32, 134.58, 133.71, 132.86, 131.40, 130.58, 129.96, 129.62, 128.77, 128.25, 127.60, 127.31 (Ar-C), 28.53 (CH-^{i}pr), 22.92 (CH_3-^{i}pr). ^{31}P NMR (DMSO-d_6, ppm): 29.84. ESI-Mass (*m/z*) = 985.4 $[M\text{-}Cl]^+$.

[RuCl(CO)($AsPh_3$)$_2$(L_1)] (**3**)

Yield: 84%; MP: 268 °C; Anal. calc. for $C_{55}H_{45}ClN_2O_2As_2Ru$ (%): C, 62.77; H, 4.31; N, 2.66. Found (%): C, 62.54; H, 4.19; N, 2.52. IR (KBr, cm^{-1}): 1948 (C≡O), 1640 (azomethine CH=N), 1578 (ring C=N), 1431 (phenolic C-O). UV-Vis (λmax, nm): 467, 365, 307. ^1H NMR (DMSO-d_6, ppm): 8.26 (s, azomethine CH=N), 7.96 (d, 1H, quin-H), 7.91 (d, 1H, quin-H), 7.52 (t, 1H, quin-H), 7.48 (d, 1H, quin-H), 7.44 (d, 1H, quin-H), 7.23 (d, 2H, Ar-H), 7.19 (d, 1H, Ar-H), 7.15-7.08 (m, 30H, $AsPh_3$), 2.31 (s, 6H, CH_3). ^{13}C NMR (DMSO-d_6, ppm): 203.41 (C≡O), 164.43 (phenolic C-O), 152.77 (azomethine CH=N), 148.72 (quinoline ring C=N), 136.82, 136.53, 135.71, 135.26, 134.84, 134.40, 133.29, 132.75, 131.93, 131.17, 129.22, 128.58, 126.36, 125.82, 124.70 (Ar-C), 20.35 (CH_3). ESI-Mass (*m/z*) = 1016.6 $[M\text{-}Cl]^+$.

[RuCl(CO)($AsPh_3$)$_2$(L_2)] (**4**)

Yield: 81%; MP: 234 °C; Anal. calc. for $C_{59}H_{53}ClN_2O_2As_2Ru$ (%): C, 63.93; H, 4.82; N, 2.53. Found (%): C, 63.70; H, 4.95; N, 2.39. IR (KBr, cm^{-1}): 1938 (C≡O), 1634 (azomethine CH=N), 1580

(ring C=N), 1403 (phenolic C-O). UV-Vis (λmax, nm): 474, 368, 304. ^{1}H NMR (DMSO-d_6, ppm): 8.18 (s, azomethine CH=N), 7.77 (d, 1H, quin-H), 7.74 (d, 1H, quin-H), 7.43 (t, 1H, quin-H), 7.40 (d, 1H, quin-H), 7.38 (d, 1H, quin-H), 7.22 (d, 2H, Ar-H), 7.18 (d, 1H, Ar-H), 7.15-7.07 (m, 30H, $AsPh_3$), 3.78 (m, 2H, CH-^{i}Pr), 1.23 (d, 12H, CH_3-^{i}Pr). ^{13}C NMR (DMSO-d_6, ppm): 203.56 (C≡O), 162.77 (phenolic C-O), 153.07 (azomethine CH=N), 149.21 (quinoline ring C=N), 137.16, 136.94, 135.68, 135.40, 134.97, 133.46, 133.19, 132.62, 131.30, 130.68, 129.94, 129.26, 127.75, 127.12, 126.83 (Ar-C), 28.13 (CH-^{i}pr), 23.07 (CH_3-^{i}pr). ESI-Mass (*m/z*) = 1072.5 $[M-Cl]^{+}$.

X-ray crystallographic study

Crystal of **2** was mounted on glass fibers and used for data collection. Crystal data were collected at 295(2) K using a Gemini A Ultra Oxford Diffraction automatic diffractometer. Graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) was used throughout. The absorption corrections were performed by the multi-scan method. Corrections were made for Lorentz and polarization effects. The structure was solved by direct methods using the program SHELXS. Refinement and all further calculations were carried out using SHELXL [35]. The H atoms were included in calculated positions and treated as riding atoms using the SHELXL default parameters. The non-hydrogen atoms were refined anisotropically, using weighted full-matrix least squares on F^2. Atomic scattering factors were incorporated in the computer programs.

Condensation of nitriles with ethanolamine

Nitrile (1 mM), ethanolamine (3 mM) and ruthenium(II) complex (4 M%) were mixed and stirred for 5 h at 90 °C. After completion of the reaction, the mixture was cooled to room temperature, diluted with ethyl acetate (10 mL) and filtered. The solid material (catalyst) was washed with ethyl acetate, dried and then reused in the next run. The filtrate was concentrated and the resulting residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (50:50) as eluent, to afford the desired product. The products were characterized by ^{1}H NMR [36].

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-(4-Acetylphenyl)-4,5-dihydrooxazole. ^{1}H NMR (DMSO-d_6, ppm): 8.24-8.32 (d, 2H, aromatic CH), 7.92-8.01 (d, 2H, aromatic CH), 4.42-4.48 (t, 2H, CH_2), 4.23-4.29 (t, 2H, CH_2), 2.70 (s, 3H, $COCH_3$).

2-(4-Formylphenyl)-4,5-dihydrooxazole. ^{1}H NMR (DMSO-d_6, ppm): 8.28-8.36 (d, 2H, aromatic CH), 8.02-8.09 (d, 2H, aromatic CH), 4.33-4.38 (t, 2H, CH_2), 4.17-4.22 (t, 2H, CH_2), 10.04 (s, 1H, CHO).

4-(4,5-Dihydrooxazol-2-yl)benzoicacid. ^{1}H NMR (DMSO-d_6, ppm): 8.26-8.37 (d, 2H, aromatic CH), 8.15-8.23 (d, 2H, aromatic CH), 4.38-4.45 (t, 2H, CH_2), 4.21-4.29 (t, 2H, CH_2), 10.92 (s, 1H, COOH).

2-(4-methylphenyl)-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-Methoxyphenyl)-4,5-dihydrooxazole. ^{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).

2-(4-Hydroxyphenyl)-4,5-dihydrooxazole. ^{1}H NMR (DMSO-d_6, ppm): 7.10-7.22 (d, 2H, aromatic CH), 6.74-6.85 (d, 2H, aromatic CH), 4.40-4.48 (t, 2H, CH_2), 4.16-4.25 (t, 2H, CH_2), 10.30 (s, 1H, OH).

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).

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-(Thiophen-2-yl)-4,5-dihydrooxazole. ^{1}H NMR (DMSO-d_6, ppm): 7.53-7.81 (m, 3H, aromatic CH), 4.28-4.35 (t, 2H, CH_2), 4.02-4.09 (t, 2H, CH_2).

2-(4,5-Dihydrooxazol-2-yl)aniline. ^{1}H NMR (DMSO-d_6, ppm): 7.28-7.42 (m, 4H, aromatic CH), 4.38-4.43 (t, 2H, CH_2), 4.04-4.12 (t, 2H, CH_2), 3.83 (s, 2H, NH_2).

2-(2-Methylphenyl)-4,5-dihydrooxazole. ^{1}H NMR (DMSO-d_6, ppm): 7.32-7.70 (m, 4H, aromatic CH), 4.42-4.50 (t, 2H, CH_2), 4.06-4.14 (t, 2H, CH_2), 2.39 (s, 3H, CH_3).

2-(2-Chlorophenyl)-4,5-dihydrooxazole. ^{1}H NMR (DMSO-d_6, ppm): 7.31-7.64 (m, 4H, aromatic CH), 4.53-4.60 (t, 2H, CH_2), 4.21-4.30 (t, 2H, CH_2).

Results and discussion

The quinolinolate ligands ($HL_{1,2}$) were expected to act as tridentate NNO donors when it treated with [$RuHCl(CO)(EPh_3)_3$] (E = P or As) in 1:1 molar ratio (Scheme 1) (product 1). Unexpectedly, the quinolinolate ligands involved in this work deceived our expectations and formed stable six coordinated metal complexes in which they act as bidentate NO donors (product 2). The isolated complexes were stable at room temperature, non-hygroscopic in nature and highly soluble in common organic solvents such as dichloromethane, chloroform, benzene, acetonitrile, ethanol, methanol, dimethylformamide and dimethylsulfoxide. All the complexes were structurally characterized by elemental analyses, IR, electronic, NMR and ESI-Mass spectra. For further confirmation, the structure of complex **2** was elucidated by X-ray crystallographic analysis.

Spectroscopic studies

The IR spectra of free ligands were compared with that of new complexes in order to confirm the coordination of ligands to ruthenium metal. The band at 1632-1641 cm^{-1} in the free ligands can be assigned to azomethine, which remains unaltered in the complexes. This suggests that the non-participation of azomethine group in bonding. In the spectra of free ligands, a strong band was observed at the region 1627-1636 cm^{-1} which is characteristics of the C=N group of quinoline ring and this band has been shifted to lower frequency (1578-1590 cm^{-1}) in complexes indicating the participation of quinoline nitrogen in bonding with ruthenium atom [37]. A strong band appeared around the region 1324-1326 cm^{-1} in free ligands was assigned to the phenolic C-O stretching which has been shifted to higher frequency (1367-1432 cm^{-1}) in the complexes,

showing that the other coordination is through the phenolic oxygen atom [38]. This has been further confirmed by the disappearance of the broad O-H band around 3372-3470 cm^{-1} in all the complexes due to the binding of phenolic –OH group to ruthenium after deprotonation [39]. The strong absorption band around 1932-1948 cm^{-1} was due to the terminally coordinated carbonyl group. In addition, the other characteristic absorption due to triphenylphosphine or triphenylarsine was present in the expected region [40]. The electronic spectra of ligands and the complexes have shown two to three bands in dichloromethane solvent. The bands obtained in the region 304-374 nm in both the ligands and the complexes can be attributed to the intra-ligand electronic transitions such as $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ of free azometine group. The band in the region of 467-502 nm can be assigned to charge transfer transition from t_{2g} orbital of metal to the unfilled π^* molecular orbital of ligand [41-44].

The ^1H NMR spectra of the ligands and their complexes showed the signals in the expected regions. The spectra of free ligands exhibited a peak in the region 9.02-9.32 ppm which is characteristic of phenolic O-H group. This peak was disappeared in their corresponding complexes which confirmed that the binding of ligand with metal ion via deprotonation of phenolic hydroxyl group. The ligands and their complexes exhibited a peak in the region of 8.18-8.48 ppm was due to azomethine proton. The ligand $\mathbf{L_1}$ and their corresponding complexes showed singlet in the region 2.20-2.28 ppm was assigned to methyl group protons attached to benzene ring. The ligand $\mathbf{L_2}$ and their corresponding complexes showed doublet in the region 2.20-2.28 ppm and multiplet in the region 3.68-3.78 ppm were assigned to methyl and methine protons of isopropyl group which are attached to benzene ring. Further, the spectra of ligands and all the complexes showed a multiplet for aromatic protons at 6.81-7.96 ppm.

The ^{13}C NMR spectra of all the complexes showed a sharp peak at 202.80-204.40 ppm region, which has been attributed to terminal C≡O carbon. The phenolic carbon (C-O) and azomethine (CH=N) carbon have exhibited peaks at 162.77-164.43 and 152.13-153.07 ppm regions respectively. One sharp peak at 148.72-149.21 ppm region was correspond to C=N group of quinoline ring. A sharp singlet at 19.82 and 20.35 ppm was observed in the spectra of complexes **1** and **3** respectively, have been assigned to methyl carbon. A peak around 22.92-23.01 and 28.13-28.53 ppm region was observed for complexes 2 and 4 respectively and these

peaks were due to methyl and methine carbon of isopropyl group. In addition, all the aromatic carbon atoms exhibited their corresponding peaks in the region 123.81-137.16 ppm as expected. ^{31}P NMR spectra of complexes **1** and **2** were recorded to confirm the presence of triphenylphosphine group and its geometry in the complexes. One sharp singlet at 30.22 and 29.84 ppm was observed for complexes **1** and **2** respectively which confirmed the *trans* triphenylphospine geometry in both the complexes due to their symmetrical and chemically identical nature.

ESI-Mass spectra of the complexes (**1**-**4**) show the molecular ion peak with the loss of a chloride ion at *m/z* = 928.7, 985.4, 1016.6 and 1072.5. The calculated molecular mass correspond to these complexes was 928.9, 985.0, 1016.8 and 1072.9. The obtained molecular mass of complexes was in good agreement with that of the calculated molecular masses.

X-ray crystallography

Single crystal of **2** was obtained by the slow evaporation of ethanolic solution of compound at room temperature. A red crystal of approximate dimensions 0.44 × 0.14 × 0.12 mm was isolated and the single crystal X-ray diffraction experiment was carried out at 295 K. From the unit cell dimensions, it was clear that the crystal was triclinic belonging to the *P-1* space group. Ellipsoidal plot of complex **2** labeled with atom numbering scheme was shown in Fig. 1. The crystal data and structure refinement parameters of complex **2** was summarized in Table 1 and selected bond lengths and bond angles are depicted in Table 2. The ruthenium(II) ion exhibits a hexa coordination with an octahedral geometry, where equatorial coordination comes from ring nitrogen and phenolic oxygen of bidentate chelating ligand, a chloride and a carbonyl carbon. A pair of triphenylphosphines completes the axial coordination. Though the PPh_3 ligands usually prefer to occupy mutually *cis* position for better π -interaction [45], but in this complex the presence of CO, a stronger π-acidic ligand, might have forced the bulky PPh_3 ligands to take *trans* position for steric reasons. The +2 oxidation state of the complex is compensated by chloride ion and deprotonated phenolic oxygen. The N(1)-Ru(1)-Cl(1) and O(2)-Ru(1)-C1(1) bond angle is 168.40(9)° and 176.81(14)° respectively showing that Cl atom lies *trans* to ring nitrogen and carbonyl lies *trans* to phenolic oxygen atom. The *cis* angles N(1)-Ru(1)-O(2) = 79.74(10)°, Cl(1)-Ru(1)-O(2) = 88.77(7)°, Cl(1)-Ru(1)-C(1) = 88.92(13)°, Cl(1)-Ru(1)-P(1) = 89.79(3)°, Cl(1)-Ru(1)-P(2) = 87.46(3)°, O(2)-Ru(1)-P(1) = 87.59(7)° and O(2)-Ru(1)-P(2) =

88.86(7)° are acute, whereas the other *cis* angles N(1)-Ru(1)-C(1) = 102.62(15)°, P(1)-Ru(1)-C(1) = 90.21(13)°, P(2)-Ru(1)C(1) = 93.24(13)°, P(1)-Ru(1)-N(1) = 91.29(8)° and P(2)-Ru(1)-N(1) = 90.71(8)° are obtuse. The *trans* angles N(1)-Ru(1)-Cl(1) = 168.40(9)°, P(2)-Ru-P(1) = 175.55(4)° and O(2)-Ru(1)-C(1) = 176.81(14)° deviate from linearity. The variations in bond angles lead to a significant distortion from an ideal octahedral geometry for the complex. The Ru(1)-C(1), Ru(1)-Cl(1) Ru(1)−P(1) and Ru(1)−P(2) distances are 1.830(4), 2.4089(9), 2.4037(10) and 2.4108(10) Å. The observed bond distances are comparable with those found in other reported ruthenium complexes containing PPh_3 [46].

Synthesis of 2-oxazolines

Optimization of reaction conditions

Benzonitrile and ethanolamine were chosen as model substrates using complex **1** as catalyst to optimize the reaction conditions including reaction time, temperature, catalyst loading and the ratio of benzonitrile to ethanolamine (Table 3). The first set of reactions were run at constant concentration of catalyst at various time intervals at 70 °C using 1:2 molar ratio of benzonitrile and ethanolamine (entries 1-6). The yield increased with reaction time and total reaction time of 5 h gave a constant conversion of 39%. Next, we focused on the effect of reaction temperature on the catalyst activity (entries 7-12). The highest yield of 2-oxazoline was obtained at 90 °C. Further, the reaction was carried out at different concentration of catalyst (entries 13-16). A good yield was obtained for 4 M% of catalyst. It is noteworthy that the reaction was not able to proceed smoothly without the use of a catalyst, giving only 8% yield (Entry 17). Finally, to optimize the molar ratio of substrates, several ratios (1 : 1 to 1 : 5) were employed. As shown in Table 3, the ratio of benzonitrile to ethanolamine imposed important effects on the yield of 2-phenyloxazoline. The yield of product was gradually increased from 46 to 87% as the ratio of benzonitrile to ethanolamine was raised from 1 : 1 to 1 : 3 (entries 18-21). In addition, we observed that the newly synthesized complex containing bidentate ligand exhibited higher catalytic activity than that of pure ligand and the precursor complex (entries 22,23).

Selection of favorable catalyst

In order to choose the best catalyst among the synthesized complexes, the condensation reaction of benzonitrile with ethanolamine was carried out using the catalysts **1**, **2**, **3** and **4** under the above optimized conditions (Table 4). The results showed that the complexes bearing triphenylphospine (**1** and **2**) showed better activity compared to the rest of complexes (**3** and **4**) due to the higher leaving property of triphenylphospine. In addition, the effect of substituent has also slightly responsible for the catalytic activity. The complexes with methyl substituent exhibited good activity than isopropyl substituent. It may due to the steric hindrance of bulkier isopropyl substituent. Therefore, collectively, the complex that bearing both triphenylphospine coligands and methyl substituent (complex **1**) showed higher catalytic activity up to 87 % and so it has been chosen as the favorable catalyst.

Condensation of various nitriles with ethanolamine

Upon the above optimization, the optimal reaction conditions were identified as follows: solvent-free, 1 : 3 molar ratio of nitrile to ethanolamine, 4 M% of catalyst with a reaction time of 5 h at 90 °C. With the optimized reaction conditions in hand, a great number of nitrile substrates were tested by combining with standard amino alcohol and it was observed that various substitutions on the aromatic ring were allowed (Table 5). For example, electron-withdrawing group (nitro, chloro, acetyl, formyl or carboxyl) substituted benzonitriles (entries 2-6) displayed better performance with excellent yields 90-97%. On the other hand, the presence of an electron donating group (methyl, methoxyl, amino or hydroxyl) in the ring of the benzonitriles gave similar yields 81-87% (entries 7-10) as for unsubstituted benzonitrile (entry 1). The reaction of 2-naphthonitrile performed significantly well to give good yield (entry 11). Heteroaromatic compounds such as isonicotinonitrile and thiophene-2-carbonitrile reacted with ethanolamine to give better yields (entries 12,13). The reaction of aryl nitrile bearing *ortho* substituents gave moderate yields as a result of steric hindrance (entries 14-16). In comparison with other reported catalytic systems, our catalysts have been found to exhibit the best activity in terms of low catalyst loading [47-49], low reaction time [50-53] and high yield without any side products [53,54]. 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.

Catalyst recycling

Recovery and reusability of catalyst is an important theme in catalysis. This means the catalyst can be used in many catalytic cycles and thereby more commercial for industrial catalysis. For this purpose, the reaction of benzonitrile with ethanolamine was chosen as a model reaction in the presence of 4 M% of complex **1** as catalyst. At the end of reaction, catalyst was recovered from the reaction mixture by dilution of the mixture with ethyl acetate and filtered. The catalyst was washed with ethyl acetate, dried and then reused in the next run. More than 90% of catalyst from the quantity initially used could be regenerated in its pure form using this method. The isolated catalyst was reused up to five times without significant loss of its activity. The filtrate was concentrated and the residue was purified by silica gel chromatography to afford the pure 2-oxazoline.

Possible mechanism

The possible catalytic reaction mechanism [55] for the above reactions is proposed as follows (Scheme 2). Firstly, the nitrile molecule replaces the PPh_3 group and binds to the Ru(II) centre of complex, producing the intermediate I. Secondly, the intermediate I combines with ethanolamine to give the intermediate II through the nucleophilic addition. In the next step the intermediate II undergoes intramolecular cycloaddition to generate III. Then the intermediate III eliminates the tandem reaction product that loses one equivalent of NH_3, producing the 2-oxazoline and thus furnishing the catalytic cycle.

Conclusion

New ruthenium(II) 8-hydroxyquinolinolate complexes incorporating carbonyl and triphenylphosphine/arsine have been synthesized and characterized. X-ray diffraction study of complex **2** confirms the ON coordination mode of the ligands and reveals a distorted octahedral geometry around the ruthenium(II) ion. The new complexes act as excellent recyclable catalysts for the synthesis of 2-oxazolines with good to excellent isolated yields. All these complexes were screened for their catalytic activity in condensation reaction and the complex **1** has been found to be the most active one. This method offers several advantages including short reaction time, excellent yields, simple work-up, ease for separation and recyclability of the catalyst, as well as the ability to tolerate a wide variety of substitutions in the nitriles and environmentally-benign

reaction conditions. The reusability of this catalyst was high and can be reused up to five times without significant decrease from its initial activity. These advantages, in general, highlight this protocol as a useful and attractive methodology for the rapid synthesis of biologically active 2-oxazolines.

Supplementary material

CCDC 1047556 contains the supplementary crystallographic data for the complex **2**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data request/cif.

References

[1] (a) R. W. DeSimone, K. S. Currie, S. A. Mitchell, J. W. Darrow, D. A. Pippin, Comb. Chem. High Throughput Screening 7 (2004) 473.
(b) L. Kollar, G. Keglevich, Chem. Rev. 110 (2010) 4257.

[2] T.G. Gant, A.I. Meyers, Tetrahedron 50 (1994) 2297.

[3] J.A. Frump, Chem. Rev. 71 (1971) 483.

[4] M.R. Grimmett, in: A.R. Katritzky, C.W. Rees, E.F.V. Scriven (Eds.), Comprehensive Heterocyclic Chemistry, Pergamon, Oxford, 3 (1996).

[5] A.G. Gilman, L.S. Goodman, The Pharmacological Basis of Therapeutics, 10th edn, McGraw-Hill, NY (2001).

[6] J.V. Greenhill, L. Lue, in: G.P. Ellis, D.K. Luscombe (Eds.), Progress in Medicinal Chemistry, Elsevier, NY 3 (1993) 170.

[7] K. Puntener, M.D. Hellman, E. Kuester, L.S. Hegedus, J. Org. Chem. 65 (2000) 8301.

[8] A. Cwik, Z. Hell, A. Hegedus, Z. Finta, Z. Horvath, Tetrahedron Lett. 43 (2002) 3985.

[9] P. Zhou, J.E. Blubaum, C.T. Burns, N.R. Natale, Tetrahedron Lett. 38 (1997) 7019.

[10] D.S. Clarke, R. Wood, Synth. Commun. 26 (1996) 1335.

[11] I. Mohammadpoor-Baltork, A.R. Khosropour, S.F. Hojati, Synlett (2005) 2747.

[12] J.G. Badiang, J. Aube, J. Org. Chem. 61 (1996) 2484.

[13] E.J. Corey, K. Ishihara, Tetrahedron Lett. 33 (1992) 6807.

[14] S. Minakata, M. Nishimura, T. Takahashi, Y. Oderaotoshi, M. Komatsu, Tetrahedron Lett. 42 (2001) 9019.

[15] (a) Y. Sunatsuki, Y. Motoda, N. Matsumoto, Coord. Chem. Rev. 226 (2002) 199.
(b) C.M. Che, J.S. Huang, Coord. Chem. Rev. 242 (2003) 27.

[16] (a) H. Khanmohammadi, S. Amani, H. Lang, T. Rueffer, Inorg. Chim. Acta 360 (2007) 579.
(b) P. DiBernardo, P.L. Zanonato, S. Tamburini, P.A. Vigato, Inorg. Chim. Acta 360 (2007) 1083.

[17] (a) R.T. Ruck, E.N. Jacobsen, J. Am. Chem. Soc. 124 (2002) 2882.
(b) S. Adsule, V. Barve, D. Chen, F. Ahmed, Q.P. Dou, S. Padhye, F.H. Sarkar, J. Med. Chem. 49 (2006) 7242.

[18] (a) D.J. de Geest Andy Noble, B. Moubaraki, K.S. Murray, D.S. Larsen, S. Brooker,

Dalton Trans. (2007) 467.

(b) U. Beckmann, S. Brooker, Coord. Chem. Rev. 222 (2003) 17.

(c) S. Brooker, Coord. Chem. Rev. 222 (2001) 33.

[19] B. De Clercq, F. Verpoort, Macromolecules 35 (2002) 894.

[20] T. Opstal, F. Verpoort, Angew. Chem. Int. Ed. 42 (2003) 2876.

[21] C. Carlini, S. Giaiacopi, F. Marchetti, C. Pinzino, A.M.R. Galleti, G. Sbrana, Organometallics 25 (2006) 3659.

[22] S.N. Pal, S. Pal, Inorg. Chem. 40 (2001) 4807.

[23] J.-F. Moulin, M. Brinkmann, A. Thierry, J.-C. Wittmann, Adv. Mater. 14 (2002) 436.

[24] L.S. Sapochak, F.E. Benincasa, R.S. Schofield, J.L. Baker, K.K.C. Riccio, D. Fogarty, H. Kohlmann, K.F. Ferris, P. Burrows, J. Am. Chem. Soc. 124 (2002) 6119.

[25] L. Salvi, A. Salvini, F. Micoli, C. Bianchini, W. Oberhauser, J. Organomet. Chem. 692 (2007) 1442.

[26] C. Po Lau, S. Man Ng, G. Jia, Z. Lin, Coord. Chem. Rev. 251 (2007) 2223.

[27] C. Jun Yue, Y. Liu, R. He, J. Mol. Catal. A 259 (2006) 17.

[28] F. Nipa Haque, A.J. Lough, R.H. Morris, Inorg. Chim. Acta 361 (2008) 3149.

[29] P. Buskens, D. Giunta, W. Leitner, Inorg. Chim. Acta 357 (2004) 1969.

[30] J. Bravo, J. Castro, S. Garcia-Fontana, M.C. Rodriguez-Martinez, G. Albertin, S. Antoniutti, A. Manera, J. Organomet. Chem. 692 (2007) 5481.

[31] (a) N. Dharmaraj, P. Viswanathamurthi, P.K Suganthy, K Natarajan, Transition met. Chem. 23 (1998) 129.

(b) R. Karvembu, R. Prabhakaran, K. Senthilkumar, P. Viswanathamurthi, React. Kinet. Catal. Lett. 86 (2005) 211.

(c) R. Ramachandran, G. Prakash, S. Selvamurugan, P. Viswanathamurthi, J.G. Malecki, V. Ramkumar, Dalton Trans. 43 (2014) 7889.

(d) R. Manikandan, P. Anitha, G. Prakash, P. Vijayan, P. Viswanathamurthi, R.J. Butcher, and J.G. Malecki, J. Mol. Catal. A 398 (2015) 312.

[32] W.-H. Sun, M. Shen, W. Zhang, W. Huang, S. Liu, C. Redshaw, Dalton Trans. 40 (2011) 2645.

[33] N. Ahmed, J.J. Levison, S.D. Robinson, M.F. Uttley, Inorg. Synth. 15 (1974) 45.

[34] R.A. Sanchez-Delgado, W.Y. Lee, S.R. Choi, Y. Cho, M.J. Jun, Trans. Met. Chem. 16

(1991) 241.

[35] G. M. Sheldrick, Acta Crystallogr. A 64 (2008) 112.

[36] X. Li, B. Zhou, J. Zhang, M. She, S. An, H. Ge, C. Li, B. Yin, J. Li, Z. Shi, Eur. J. Org. Chem. (2012) 1626.

[37] V.P. Singh, A. Singh, Russ. J. Coord. Chem. 34 (2008) 374.

[38] K. Nareshkumar, R. Ramesh, Polyhedron 24 (2005) 1885.

[39] M. Muthukumar, P. Viswanathamurthi, Spectrochim. Acta A 74 (2009) 454.

[40] M. Mishra, Monicasani, Metal-Based Drugs. 10 (2008) 1155.

[41] H.S. Abbo, S.J.J. Titinchi, R. Prasad, S. Chand, J. Mol. Catal. A 23 (2005) 225.

[42] G. Csjernyik, A.H. Ell, L. Fadini, B. Pugin, J. Backvall, J. Org. Chem. 67 (2003) 1657.

[43] R. Ramesh, M. Sivagamasundari, Synth. React. Inorg. Met. Org. Chem. 33 (2003) 899.

[44] B.P. Lever, Inorganic Electronic Spectroscopy, 2nd Edn. Elisevier, New York (1984).

[45] F. Basuli, S.M. Peng, S. Bhattacharya, Inorg. Chem. 40 (2001) 1126.

[46] (a) L.D. Brown, S.D. Robinson, A. Sahajpal, J.A. Ibers, Inorg. Chem. 16 (1977) 2728.
(b) M.I. Bruce, J. Howard, I.W. Nowell, G. Shaw, P. Woodward, J. Chem. Soc. Chem. Commun. (1972) 1041.
(c) A.C. Skapski and P. G. H. Troughton, Chem. Commun. (London) (1968) 1230.

[47] X. Fernandez, R. Fellous, E. Dunach, Tetrahedron Lett. 41 (2000) 3381.

[48] I. Mohammadpoor-Baltork, A.R. Khosropour, S.F. Hojati, Catal. Commun. 8 (2007) 200.

[49] A. Shaabani, M. Seyyedhamzeh, A. Maleki, F. Rezazadeh, Appl. Catal. A 358 (2009) 146.

[50] S. Kumar, K. Kandasamy, H.B. Singh, R.J. Butcher, New J. Chem. 28 (2004) 640.

[51] T. Bodner, L. Ellmaier, V. Schenk, J. Albering, F. Wiesbrock, Polym. Int. 60 (2011) 1173.

[52] G.K. Jnaneshwara, V.H. Deshpande, M. Lalithambika, T. Ravindranathan, A.V. Bedekar, Tetrahedron Lett. 39 (1998) 459.

[53] H. Witte, W. Seeliger, Angew. Chem. Int. Ed. 11 (1972) 287.

[54] J.A. Seijas, M.P. Vazquez-Tato, J. Crecente-Campo, Tetrahedron 64 (2008) 9280.

[55] X.N. Li, B.Y. Zhou, J. Zhang, M.Y. She, S.J. An, H.X. Ge, C. Li, B. Yin, J.L. Li, Z. Shi, Eur. J. Org. Chem. (2012) 1626.

Table 1

Crystal data and structure refinement parameters for the complex **2.**

	2
Empirical formula	$C_{59}H_{53}ClN_2O_2P_2Ru$
Formula weight	1020.49
Colour	Red
Crystal dimensions (mm^3)	0.44 × 0.14 × 0.12
Temperature (K)	295(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	*P-1*
Unit cell dimensions (Å, °)	a = 10.16019(16) b = 15.0903(2) c = 17.1169(3) α = 90.5681(13) β = 103.4832(14) γ = 95.6632(13)
Volume $Å^3$	2538.10(7)
Z	2
Calculated density (Mg/m^3)	1.337
Absorption coefficient (mm^{-1})	0.469
F(000)	1056
Theta range for data collection (°)	3.0811-34.6078
Absorption correction	Multi-scan
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	8804/0/608
Goodness-of-fit on F^2	1.109
R indices [$I>2\sigma(I)$]	R_1 = 0.0493, wR_2 = 0.1143
R indices (all data)	R_1 = 0.0635, wR_2 = 0.1200

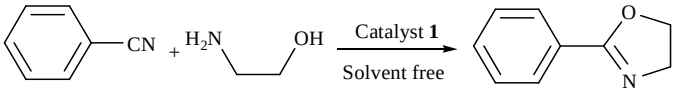
Table 2

Selected bond lengths (Å) and angles (°) for the complex **2.**

Ru1-P1	2.4037(10)	P1-Ru1-P2	175.55(4)
Ru1-P2	2.4108(10)	P1-Ru1-C1	90.21(13)
Ru1-O2	2.083(2)	P2-Ru1-C1	93.24(13)
Ru1-N1	2.123(3)	P1-Ru1-Cl1	89.79(3)
Ru1-C1	1.830(4)	P2-Ru1-Cl1	87.46(3)
Ru1-Cl1	2.4089(9)	P1-Ru1-N1	91.29(8)
O1-C1	1.148(5)	P2-Ru1-N1	90.71(8)
O2-C9	1.305(4)	P1-Ru1-O2	87.59(7)
N1-C2	1.333(5)	P2-Ru1-O2	88.86(7)
N1-C10	1.386(5)	N1-Ru1-O2	79.74(10)
		N1-Ru1-C1	102.62(15)
		N1-Ru1-Cl1	168.40(9)
		O2-Ru1-C1	176.81(14)
		O2-Ru1-Cl1	88.77(7)
		O2-Ru1-N1	79.74(10)
		C1-Ru1-Cl1	88.92(13)

Table 3

Optimization of reaction conditions.



Entry	Time (h)	Temp (°C)	Catalyst loading (M%)	Substrate ratio	Yield (%)[a]
1	2	70	2	1 : 2	14
2	3	70	2	1 : 2	20
3	4	70	2	1 : 2	31
4	5	70	2	1 : 2	39
5	6	70	2	1 : 2	39
6	7	70	2	1 : 2	39
7	5	50	2	1 : 2	04
8	5	60	2	1 : 2	11
9	5	80	2	1 : 2	44
10	5	90	2	1 : 2	57
11	5	100	2	1 : 2	57
12	5	110	2	1 : 2	58
13	5	90	1	1 : 2	32
14	5	90	3	1 : 2	64
15	5	90	4	1 : 2	72
16	5	90	5	1 : 2	72
17	5	90	-	1 : 2	08
18	5	90	4	1 : 1	46
19	5	90	4	1 : 3	87
20	5	90	4	1 : 4	87
21	5	90	4	1 : 5	88
22[b]	5	90	4	1 : 3	-
23[c]	5	90	4	1 : 3	38

[a]Isolated yield.

[b]In presence of quinolinolate ligand, **HL_1**.

[c]In presence of precursor complex, [$RuHCl(CO)(PPh_3)_3$].

Table 4

Selection of favorable catalyst[a].

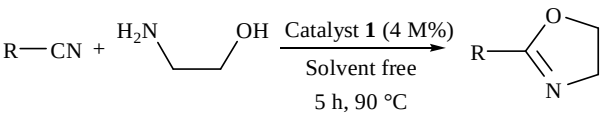
Entry	Catalyst	Yield (%)[b]
1	**1**	87
2	**2**	83
3	**3**	77
4	**4**	72

[a]Reaction conditions: Benzonitrile (1 mM), ethanolamine (3 mM) and catalyst (4 M%) refluxed at 90 °C for 5 h.

[b]Isolated yield.

Table 5

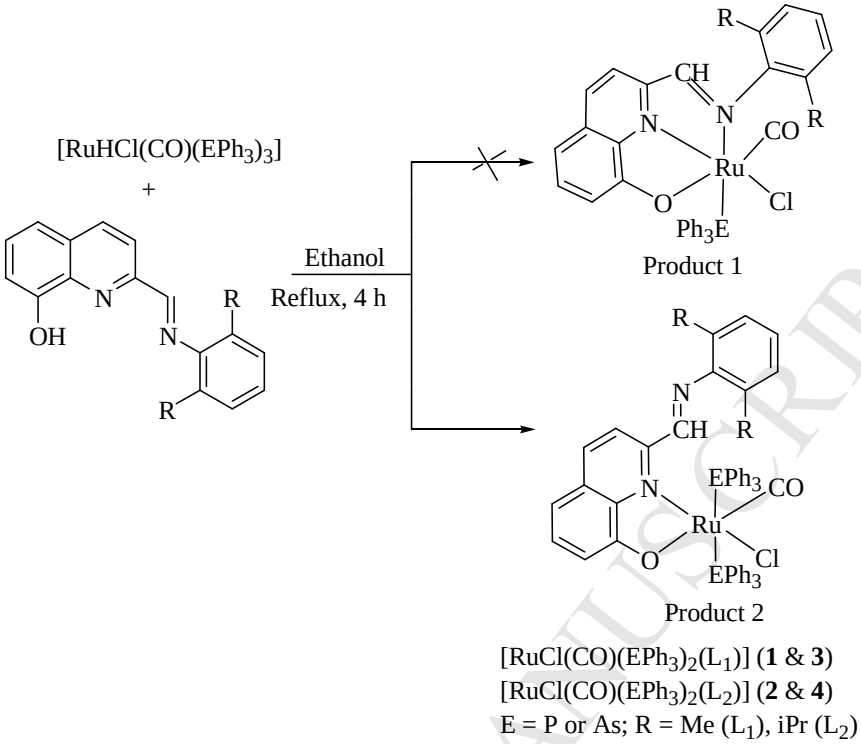
Synthesis of 2-oxazolines by ruthenium(II) catalyst[a].



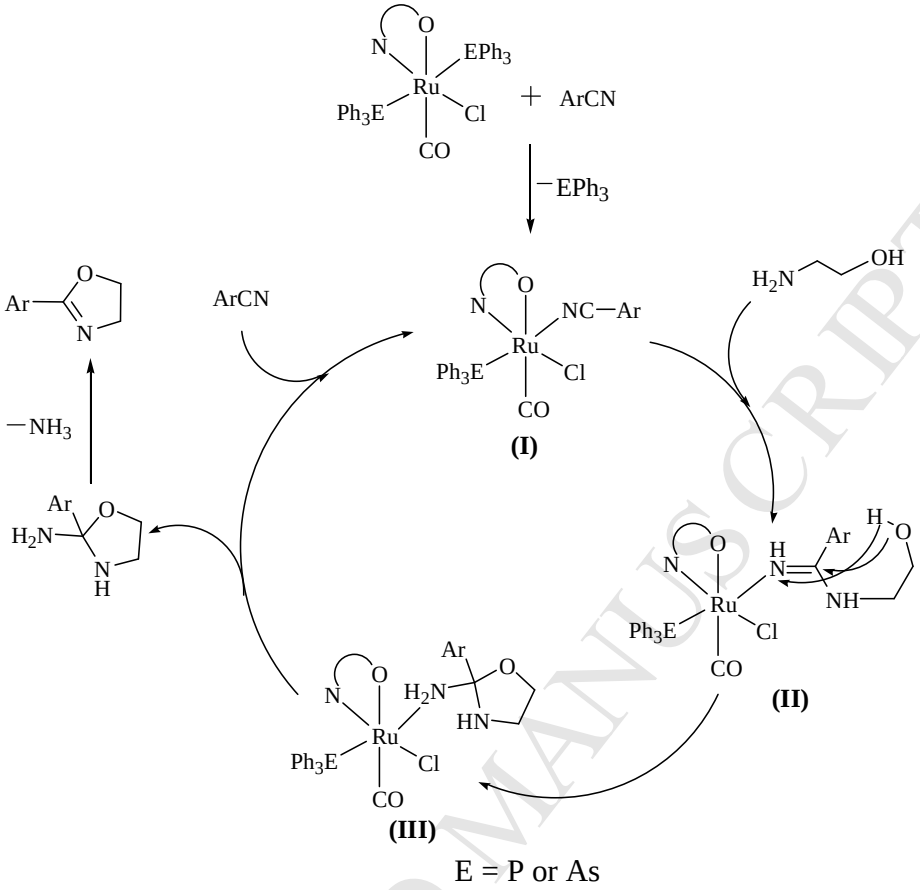
Entry	R	Yield (%)[b]
1	Phenyl	87
2	4-Nitrophenyl	97
3	4-Chlorophenyl	90
4	4-Acetylphenyl	92
5	4-Formylphenyl	95
6	4-Carboxylphenyl	94
7	4-Methylphenyl	83
8	4-Methoxyphenyl	81
9	4-Aminophenyl	87
10	4-Hydroxyphenyl	86
11	2-Naphthyl	91
12	4-Pyridyl	89
13	2-Thiophenyl	87
14	2-Aminophenyl	63
15	2-Methylphenyl	60
16	2-Chlorophenyl	68

[a]Reaction conditions: Nitrile (1 mM), ethanolamine (3 mM), catalyst (4 M%) refluxed at 90 °C for 5 h.

[b]Isolated yield.



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



Scheme 2. Possible mechanism for ruthenium(II) catalyzed synthesis of 2-oxazoline.

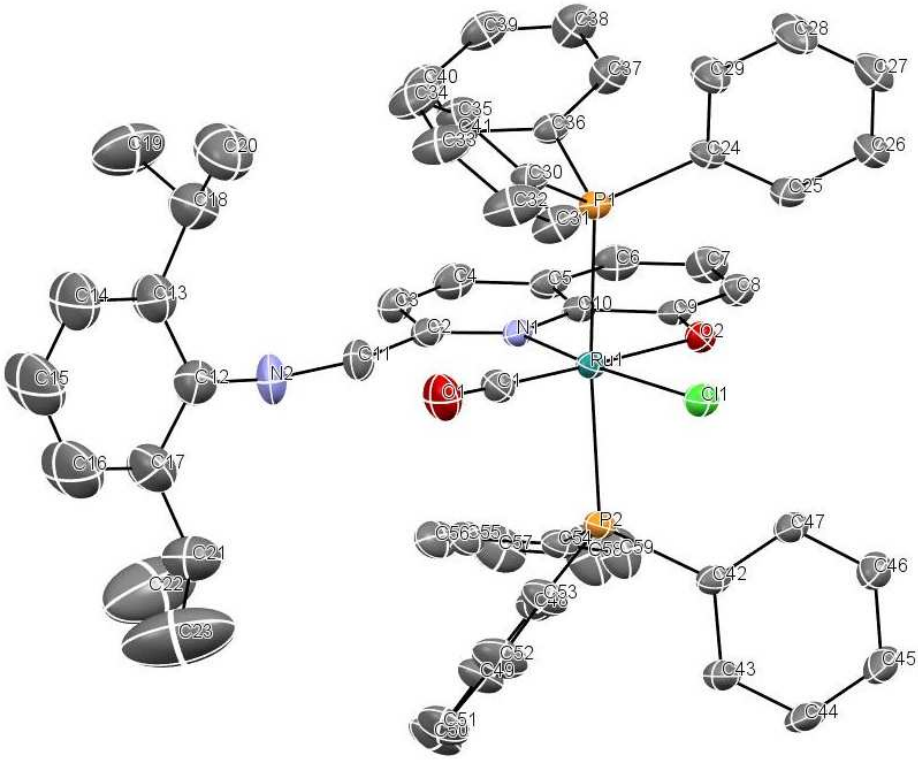


Figure 1. ORTEP view of complex **2.** Thermal ellipsoids were drawn at 25% probability level. The hydrogen atoms were omitted for clarity.

Research Highlights

- Synthesis of new ruthenium(II) carbonyl complexes.
- Spectral characterization and crystal structure determination of the complexes.
- Catalytic evaluation of Ru(II) complexes in the synthesis of 2-oxazolines.
- Recovery and recycling of catalyst.