Journal of Organometallic Chemistry 923 (2020) 121411

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Hydrazone complexes of ruthenium(II): Synthesis, crystal structures and catalytic applications in N-alkylation reactions

Kaliyappan Murugan [a], Subbarayan Vijayapritha [a], Muthukumaran Nirmala [a], Periasamy Viswanathamurthi [a,*], Karuppannan Natarajan [b]

[a] Department of Chemistry, Periyar University, Salem, 636 011, India
[b] Department of Chemistry, Sri Ramakrishna Mission Vidyalaya College of Arts and Science, Coimbatore, 64120, India

ARTICLE INFO

Article history:
Received 22 January 2020
Received in revised form
26 May 2020
Accepted 15 June 2020
Available online 12 July 2020

Keywords:
8-hydroxy quinoline-2-carboxyaldehyde hydrazide
Ru(II) complexes
Crystal structure
N-alkylation
N,C_3-dialkylation

ABSTRACT

A series of new Ru(II) complexes of 8-hydroxy quinoline-2-carboxyaldehyde hydrazone of the general formula [RuH(CO)(EPh_3)$_2$L] (**1**–**6**) (E = P or As, L = N'-((8-hydroxyquinolin-2-yl)methylene)thiophene-2-carbohydrazide (HQ-THy), N'-((8-hydroxyquinolin-2-yl)methylene)isonicotinohydrazide (HQ-IHy), N'-((8-hydroxyquinolin-2-yl)methylene) benzohydrazide (HQ-BHy)) have been synthesized. They have been characterized by elemental analysis, IR, NMR (^{1}H, ^{13}C & ^{31}P) and ESI-MS spectral methods. Further, structures of two of the complexes have been determined by single crystal X-ray diffraction technique which revealed a pseudo octahedral geometry with the coordination of the quinoline nitrogen and quinoline oxygen atoms of the ligand. All the new complexes have been employed as efficient catalysts in N-alkylation reactions for the synthesis of tertiary amines by the coupling of secondary amines with aromatic primary alcohols at low catalyst loading with maximum yields. In addition, the effects of substituents on the ligands, different solvents as well as bases and amounts of catalyst loading on the catalytic activity of the complexes have been thoroughly investigated. Complex **1** was found to be efficient catalyst towards N-alkylation of alcohols with the amine. Further, a variety of secondary amines and aromatic (hetero) primary alcohols with various functional groups have also been successfully used in the N-alkylation reactions and it has been found that only one equivalent of the alcohol was consumed in the process.

1. Introduction

Since the compounds with nitrogen functionalities are not only abundantly present in important biologically active molecules but also find extensive applications in pharmaceuticals, there has been an upsurge in research leading to the synthesis of compounds containing C–N bond. Various methods have been employed in the synthesis of compounds containing the C–N bond including amination of aryl halides [1], reductive amination of carbonyl compounds [2] hydro-amination [3], hydro amino-methylation of C–C multiple bonds [4] or N-alkylation [5] and typical compounds thus synthesized are shown in Fig. 1. Among the methods that have been used for the synthesis of new compounds, N-alkylation of amines/amides with alcohol is a significant one because it is not only a simple direct method but also due to the facts that alcohols are readily available, highly stable, low in toxicity, easily storable and very low in cost. Besides, the reaction falls in green chemistry and environmentally friendly since water is the sole byproduct [6,7]. In spite of the fact that both heterogeneous and homogeneous catalysts have been used for the effective N-alkylation of amine with alcohol, homogeneous catalysts have gained much prominence due to their high catalytic performance and greater product selectivity. In this connection, several iridium and ruthenium complexes containing phosphine ligands have been employed in the N-alkylation of amines with alcohols in good yields and selectivity [8–14]. Grigg [15] and Watanabe [16] independently reported the N-alkylation of amines using [$RuCl_2(PPh_3)_3$] and [$RhH(PPh_3)_4$] for the first time. Catalysts derived from other transition metals such as Fe [17], Os [18], Cu [19] and Rh [20] have also shown to be efficient in catalyzing the reaction with a good yield. However, they are not trouble free as most of the methods reported have some difficulties like the requirement of high temperature, pressure and prolonged reaction times up to few days. The drawbacks to the reported catalysts necessitate the synthesis of new catalysts.

* Corresponding author.
E-mail address: viswanathamurthi@gmail.com (P. Viswanathamurthi).

https://doi.org/10.1016/j.jorganchem.2020.121411
0022-328X/

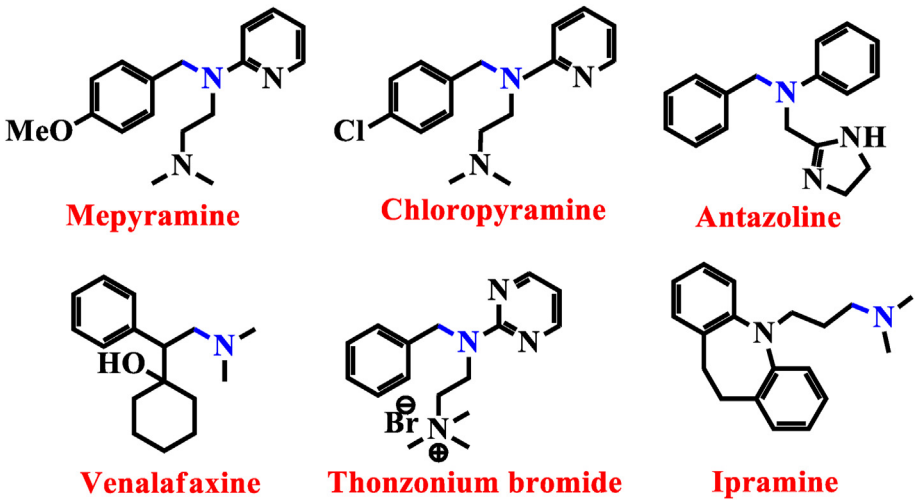


Fig. 1. Examples of important drugs with alkylated amine.

Generally, in the area of development of transition metal catalysts for a specific process, besides choosing the right metal ion, the design of ligand is also very important. Since nature of the ligand has a profound effect on the coordination chemistry of a metal complex, the designing and "tailoring" of ligand properties can lead to complexes with efficient homogeneous catalytic activities. In this connection, special interest has been shown on the use of hydrazone as ligands not only because of their various coordination modes but also due to their remarkable applications in catalytic and biological activities [21]. Moreover, hydrazones with an additional donor groups have become an important class of ligands due to the potential hemilability of the new donor groups can play a dual role in a catalyst since they can easily enable coordination sites in addition to at the same time, protect the coordination sites by a dynamic "on and off" chelating effect. Among the several donor groups that have been reported to functionalize hydrazones [22–24] hydroxy quinoline with the coincident presence of soft and hard donors received special interest.

Inspired by the high activity of Ru(II) complexes for N-alkylation reactions and from out of our systematic investigation on finding effective homogeneous catalysts [25], here in we report the design and synthesis of hydrazone ligands functionalized with 8-hydroxy quinoline-2-carboxyaldehyde group and their ruthenium(II) complexes. The coordination modes of the ligand with ruthenium metal were investigated using FT-IR, ^{1}H, ^{13}C & ^{31}P NMR spectroscopy and mass spectrometry. The solid-state structures of the catalysts were established by single-crystal X-ray diffraction. The impact of the newly synthesized complexes was studied in N-alkylation of secondary amine with aromatic and heteroaromatic alcohols. The role of co-ligands in determining the catalytic activity for N-alkylation was also investigated.

2. Experimental section

2.1. Starting materials and measurements

Chemically pure and AR grade reagents were used for all the reactions. The solvents were distilled and dried according to literature procedures [26]. $RuCl_3.3H_2O$ was purchased from Sigma Aldrich. Microanalyses of carbon, hydrogen, nitrogen and sulfur were carried out using a Vario EL III elemental analyzer. IR spectra were obtained with Bruker Alpha model FT-IR spectrophotometer in the 4000–600 cm^{-1} range. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker Advance 400 MHz FT-NMR instrument using $CDCl_3$ as solvent and tetramethyl silane or *o*-phosphoric acid as reference. Electrospray ionization mass spectra were measured by liquid chromatography–mass spectrometry quadrupole time-of-flight Micro Analyzer (Shimadzu) at Indian Institute of Technology Madras, Chennai. Melting points were recorded on a Technico micro heating table and are uncorrected. The catalytic yields were determined by gas chromatography–flame ionization detection (GC-FID) using an ACME 6000 series instrument with a DP-5 column of 30 m length, 0.53 mm diameter and 5.00 μm film thickness. The precursor complexes $[RuHCl(CO)(PPh_3)_3]$ [27], $[RuHCl(CO)(AsPh_3)_3]$ [28] and 8-hydroxyquinoline-2-carbaldehyde [29] were prepared according to literature procedures.

2.2. Synthesis of 8-hydroxyquinoline-2-carboxyaldehyde hydrazide ligands

8-hydroxyquinoline-2-carbaldehyde (1 mmol) was dissolved in ethanol (20 mL) and reacted with an equivalent of substituted hydrazide (1 mmol) in a mixture of ethanol (20 mL) and H_2O (1 mL). The reaction mixture was subsequently refluxed for 6 h. On cooling the resultant solution, a solid compound separated which was filtered and washed with ether and dried. All the three 8-hydroxyquinoline-2-carboxy aldehyde hydrazide ligands were obtained as yellow crystalline precipitate in good yield.

2.2.1. N'-((8-hydroxyquinolin-2-yl)methylene) thiophene-2-carbohydrazide (HQ-THy) ligand

It was prepared from 8-hydroxyquinoline-2-carbaldehyde (0.172 g, 1 mmol) and thiophene carboxylic acid hydrazide (0.142 g, 1 mmol). Yield: 77%. Yellow color solid. M.P. 240–244 °C. Anal. Calc. for $C_{15}H_{11}N_3SO_2$: C, 60.59; H, 3.73; N, 14.13; S, 10.78. Found: C, 60.67; H, 3.78; N, 14.19; S, 10.85. IR (ATR, ν cm^{-1}): 3401 (OH), 3113 (NH), 1613 (C=O), 1593 (C=N), 1560 ($C=N_{ring}$).^{1}H NMR (300.13 MH_Z, $CDCl_3$, ppm): 10.24 (s, OH), 9.54 (s, NH), 8.10 (s, CH=N), 7.92–7.12 (m, Ar–H). ^{13}C NMR (75.47 MH_Z, $CDCl_3$, ppm): 166.01 (C=O), 153.87 (C=N), 153.87 (C=N), 153.74 (C–O), 129.83 (Ar–C), 128.78 (Ar–C), 127.93 (Ar–C), 127.01 (Ar–C), 126.91 (Ar–C), 126.42 (Ar–C), 126.35 (Ar–C), 125.88 (Ar–C), 123.50 (Ar–C), 110.43 (Ar–C).

2.2.2. N'-((8-hydroxyquinolin-2-yl) methylene) isonicotinohydrazide (HQ-IHy) ligand

It was prepared from 8-hydroxyquinoline-2-carbaldehyde (0.170 g, 1 mmol) and isonicotinic hydrazide (0.137 g, 1 mmol).

Yield: 75%. Yellow color solid. M.P. 228–230 °C. Anal. Calc. for $C_{16}H_{12}N_4O_2$: C: 65.75; H, 4.39; N, 19.17. Found: C, 65.73; H, 4.42; N, 19.25. IR (ATR, ν cm^{-1}): 3396 (OH), 3041 (NH), 1680 (C=O), 1647 (C=N), 1545 (C=N_{ring}). ^{1}H NMR (400 MH_Z, $CDCl_3$, ppm): 12.42 (s, NH), 9.86 (s, OH), 8.68 (s, CH=N), 7.96–7.14 (m, Ar–H). ^{13}C NMR (75.47 MHz, $CDCl_3$, ppm): 162.10 (C=O), 153.57 (C=N), 153.45 (C=N), 150.40 (C–O), 129.16 (Ar–C), 121.82 (Ar–C), 121.95 (Ar–C), 121.63 (Ar–C), 120.95 (Ar–C), 120.95 (Ar–C), 113.04 (Ar–C), 113.04 (Ar–C), 111.97 (Ar–C).

2.2.3. N'-((8-hydroxyquinolin-2-yl)methylene)benzohydrazide (HQ-BHy) ligand

It was prepared from 8-hydroxyquinoline-2-carbaldehyde (0.170 g, 1 mmol) and benz hydrazide (0.136 g, 1 mmol). Yield: 78%. Yellow color solid. M.P. 236–239 °C. Anal. Calc. for $C_{17}H_{13}N_3O_2$: C, 70.09, H, 4.50; N, 14.42. Found: C, 70.15; H, 4.52; N, 14.47. IR (ATR, ν cm^{-1}): 3396 (OH), 3211 (NH), 1689 (C=O), 1642 (C=N), 1545 (C=N_{ring}). ^{1}H NMR (300.13 MH_Z, $CDCl_3$, ppm): 11.92 (s, OH), 9.58 (s, NH), 8.35 (s, CH=N), 7.41–6.92 (m, Ar–H). ^{13}C NMR (75.47 MH_Z, $CDCl_3$, ppm): 166.50 (C=O), 153.58 (C=N), 154.10 (C=N), 153.74 (C=O), 139.81 (Ar–C), 136.77 (Ar–C), 136.18 (Ar–C), 131.05 (Ar–C), 127.46 (Ar–C), 127.26 (Ar–C), 126.68 (Ar–C), 121.40 (Ar–C), 108.17 (Ar–C).

2.3. Synthesis of new ruthenium(II) hydroxyquinoline hydrazone complexes (**1**–**6**)

[RuHCl(CO)(EPh_3)$_3$] (E = P or As) (0.1 mmol) and 8-hydroxyquinolinehydrazide ligand (0.1 mmol) were taken in ethanol - chloroform mixture (20 mL, 1 : 1, v/v) and heated under reflux for 8 h during which the solution turned from pale yellow to reddish brown. After completion of reaction which was confirmed from thin layer chromatography (TLC), the solution was cooled to room temperature, a solid compound separated which was filtered and washed several times with ether and dried in vacuo. All the new ruthenium(II) hydroxyquinoline hydrazone complexes are obtained in good yields.

2.3.1. [RuH(CO)(PPh_3)$_2$(HQ-Thy)] (**1**)

The ligand HQ-Thy (0.029 g, 0.1 mmol) was reacted with [RuHCl(CO)(PPh_3)$_3$] (0.095 g, 0.1 mmol) to form complex **1**. Yield: 87%. Color: Reddish brown. M.P. 158–161 °C. Anal. Calc. for $C_{52}H_{41}N_3SO_3P_2Ru$: C, 65.67; H, 4.35; N, 4.42; S, 3.37. Found: C, 65.72; H, 4.39; N, 4.49; S, 3.43. IR (ATR, ν cm^{-1}): 3051 (NH), 1909 (CO), 1736 (C=O), 1630 (C=N), 1586 (C=N_{ring}). ^{1}H NMR (400 MH_Z, $CDCl_3$, ppm): −10.67 (Ru–H), 10.73 (s, NH), 8.24 (s, HC=N), 8.11–6.26 (m, Ar–H).^{13}C NMR (100 MH_Z, $CDCl_3$, ppm): 204.71 (CO), 174.62 (C=O), 151.67 (C=N), 148.62 (C=N_{ring}), 133.77–127.62 (Ar–C). ^{31}P NMR (162 MHz, $CDCl_3$, ppm): 29.41 (s, PPh_3). ESI-MS: m/z = 950.0 $[M - H]^+$. Crystals suitable for X-ray diffraction were obtained by slow evaporation of dichloromethane-ethanol solution of complex **1**.

2.3.2. [RuH(CO)(PPh_3)$_2$(HQ-IHy)] (**2**)

The ligand HQ-IHy (0.029 g, 0.1 mmol) was reacted with [RuHCl(CO)(PPh_3)$_3$] (0.095 g, 0.1 mmol) to form complex **2**. Yield: 82%. Color: Reddish brown. M.P. 125–128 °C. Anal. Calc. for $C_{53}H_{43}N_4O_3P_2Ru$: C, 67.22; H, 4.58; N, 5.92. Found: C, 67.29; H, 4.63; N, 5.96. IR (ATR, ν cm^{-1}): 3044 (NH), 1900 (CO), 1735 (C=O), 1623 (C=N), 1573 (C=N_{ring}). ^{1}H NMR (400 MH_Z, $CDCl_3$, ppm): −10.63 (s, Ru–H), 10.80 (s, NH), 8.66 (s, HC=N), 7.70–6.31 (m, Ar–H). ^{13}C NMR (100 MH_Z, $CDCl_3$, ppm): 202.23 (CO), 175.19 (C=O), 155.94 (C=N), 153.97 (C=N_{ring}), 139.18–125.99 (Ar–C). ^{31}P NMR (162 MHz, $CDCl_3$, ppm): 29.74 (s, PPh_3).

2.3.3. [RuH(CO)(PPh_3)$_2$(HQ-BHy)] (**3**)

The ligand HQ-BHy (0.029 g, 0.1 mmol) was reacted with [RuHCl(CO)(PPh_3)$_3$] (0.095 g, 0.1 mmol) to form complex **3**. Yield: 84%. Color: Reddish brown. M.P: 178–181 °C. Anal. Calc. for $C_{54}H_{44}N_3O_3P_2Ru$: C: 68.56; H, 4.69; N, 4.44. Found: C, 68.64; H, 4.73; N, 4.54. IR (ATR, ν cm^{-1}): 3048 (NH), 1908 (CO), 1730 (C=O), 1675 (C=N), 1543 (C=N_{ring}). ^{1}H NMR (400 MH_Z, $CDCl_3$, ppm): −10.56 (s-Ru-H), 10.70 (s, NH), 8.61 (s, HC=N), 7.88–6.33 (m, Ar–H).^{13}C NMR (100 MH_Z, $CDCl_3$, ppm): 204.49 (CO), 178.99 (C=O), 151.22 (C=N), 148.89 (C=N_{ring}), 132.82–126.81 (Ar–C). ^{31}P NMR (162 MHz, $CDCl_3$, ppm): 29.57 (s, PPh_3).

2.3.4. [RuH(CO)($AsPh_3$)$_2$(HQ-Thy)] (**4**)

The ligand HQ-Thy (0.029 g, 0.1 mmol) was reacted with [RuHCl(CO)($AsPh_3$)$_3$] (1.085 g, 0.1 mmol) to form complex **4**. Yield: 78%. Color: Reddish brown. M.P. 126–129 °C. Anal. Calc. for $C_{52}H_{42}N_3SO_3As_2Ru$: C, 60.06; H, 4.07; N, 4.04; S, 3.08. Found: C, 60.12; H, 4.14; N, 4.09; S, 3.13. IR (ATR, ν cm^{-1}): 3055 (NH), 1905 (CO), 1730 (C=O), 1627 (C=N), 1572 (C=N_{ring}). ^{1}H NMR (400 MH_Z, $CDCl_3$, ppm): −11.30 (s, Ru–H), 10.74 (s, NH), 8.30 (s, HC=N), 8.29–6.51 (m, Ar–H). ^{13}C NMR (100 MH_Z, $CDCl_3$, ppm): 201.62 (CO), 176.91 (C=O), 157.85 (C=N), 154.20 (C=N_{ring}), 134.07–121.87 (Ar–C). ESI-MS: m/z = 1040.0 $[M]^+$. Crystals suitable for X-ray diffraction were obtained by slow evaporation of dichloromethane-petroleum ether solution of complex **4**.

2.3.5. [RuH(CO)($AsPh_3$)$_2$(HQ-IHy)] (**5**)

The ligand HQ-IHy (0.029 g, 0.1 mmol) was reacted with [RuHCl(CO)($AsPh_3$)$_3$] (1.085 g, 0.1 mmol) to form complex **5**. Yield: 65%. Color: Reddish brown. M.P.132–134 °C. Anal. Calc. for $C_{53}H_{43}N_4O_3As_2Ru$: C, 61.54; H, 4.19; N, 5.41. Found: C, 61.63; H, 4.24; N, 5.49. IR (ATR, ν cm^{-1}): 3046 (NH), 1904 (CO), 1735 (C=O), 1630 (C=N), 1578 (C=N_{ring}). ^{1}H NMR (400 MH_Z, $CDCl_3$, ppm): -10.68 (s, Ru–H), 10.60 (s, NH), 8.20 (s, HC=N), 7.39–6.48 (m, Ar–H). ^{13}C NMR (100 MH_Z, $CDCl_3$, ppm): 201.80 (CO), 175.57 (C=O), 155.31 (C=N), 152.04 (C=N_{ring}), 135.49–127.81 (Ar–C).

2.3.6. [RuH(CO)($AsPh_3$)$_2$(HQ-BHy)] (**6**)

The ligand HQ-BHy (0.029 g, 0.1 mmol) was reacted with [RuHCl(CO)($AsPh_3$)$_3$] (1.085 g, 0.1 mmol) to form complex **6**. Yield: 77%. Color: Reddish brown. M.P. 110–112 °C. Anal. Calc. for $C_{54}H_{44}N_3O_3P_2As_2Ru$: C, 59.19; H, 4.05; N, 3.83. Found: C, 59.26; H, 4.12; N, 3.89. IR (ATR, ν cm^{-1}): 3052 (NH), 1907 (CO), 1732 (C=O), 1632 (C=N), 1572 (C=N_{ring}). ^{1}H NMR (400 MH_Z, $CDCl_3$, ppm): −11.09 (s, Ru–H), 10.62 (s, NH), 8.61 (s, HC=N), 8.18–6.45 (m, Ar–H). ^{13}C NMR (100 MH_Z, $CDCl_3$, ppm): 201.62 (CO), 175.81 (C=O), 156.49 (C=N), 151.12 (C=N_{ring}), 134.41–123.33 (Ar–C).

2.4. X-ray crystallographic study

Crystal data were collected for the complexes (**1** and **4**) at 296 K using a Gemini A Ultra Oxford Diffraction automatic diffractometer. Graphite monochromated Mo-Ka radiation (λ = 0.71073 Å) was used throughout. The absorption corrections were performed by multi-scan method. Corrections were made for Lorentz and polarization effects. The structure was solved by direct method using the program SHELXS 2018 [30]. Refinement and all further calculations were carried out using SHELXL. 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 F2. Atomic scattering factors were incorporated in the computer programs.

2.5. Typical procedure for catalytic N-alkylation of hetro cyclic secondary amines with primary alcohol

KOH (40 mol %) was added to a stirred solution of secondary amine (1 mmol) in 2 mL of toluene. After 1 min of stirring, the primary alcohol (2.5 mmol) and Ru(II) complex (1 mmol %) were added and the mixture was stirred at 110 °C for 12 h. The reaction mixture was cooled to room temperature and dichloromethane (6 mL) was added. The resulting suspension was filtered through Celite. The filtrate was subjected to GC analysis using dodecane as an internal standard. All of the data reported are averages of at least two runs.

3. Results and discussion

The 8-hydroxyquinoline-2-carboxyaldehyde hydrazide ligands (HQ-THy, HQ-IHy, HQ-BHy) were synthesized from the condensation reaction of 8-hydroxyquinoline -2-carbaldehyde with thiophenecarbohydrazide, isonicotinohydrazide or benzhydrazide (Scheme 1**).** The reaction between these hydrazides with [RuHCl(-CO)(EPh_3)$_3$] (E = P or As) yielded new Ru(II) complexes of the type [RuH(CO)(EPh_3)$_2$L] (E = P or As; L = HQ-THy, HQ-IHy or HQ-BHy) (Scheme 2). All the ruthenium hydrazone complexes have been found to be non-hygroscopic solids and soluble in all organic solvents such as dichloromethane, chloroform, THF, acetone, benzene, toluene, N,*N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO). All the new complexes were characterized by elemental analyses, spectral techniques (IR, ^{1}H, ^{13}C & ^{31}P NMR and ESI-mass) and single-crystal XRD studies (**1** and **4**). The ESI mass spectra of complexes **1** and **4** show molecular ion peak with *m/z* value 950.0 ($[M - H]^+$) and 1040.0 ($[M]^+$) respectively which are in agreement with calculated molecular masses 951.1 and 1039.8. (Figs. S1–2).

3.1. X-ray crystallography

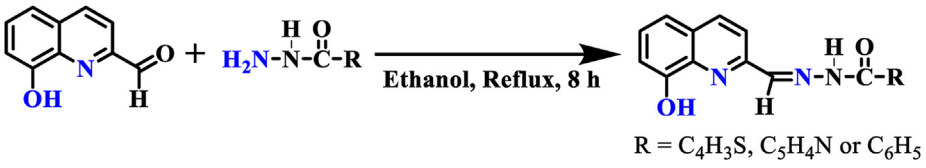
Though we attempted to grow crystals for all the six complexes, we could obtain good quality crystals suitable for X-ray diffraction for only two of them, namely [RuH(CO)(PPh_3)$_2$ (HQ-Thy)] **(1)** and [RuCl(CO)($AsPh_3$)$_2$ (HQ-Thy)] **(4)** and hence, we determined their structures by X-ray diffraction techniques. Crystals of suitable size of complexes **1** and **4** were obtained from dichloromethane-ethanol and dichloromethane-petroleum ether mixture and they both crystallized in monoclinic system with *P*21/*c* space group. The crystallographic data and structural refinement parameters as well as selected bond length and bond angle are shown in Tables 1 and 2. The ORTEP views of the complexes **1** and **4** have been depicted in Figs. 2 and 3. In both the complexes **1** and **4,** the 8-hydroxyquinoline-2-carboxyaldehyde hydrazide ligand behaves as monobasic bidentate N, O donors and binds to ruthenium ion via 8-hydroxyquinoline oxygen and nitrogen, form a five-membered chelate ring with a bite angle of O(1)–Ru(2)–N(1) of 77.14(7) and O(1)–Ru(2)–N(1) of 77.07(19) for complexes **1** and **4** respectively. Ru(2)–N(1) bond distance is 2.240(2) Å and Ru(2)–O(2) bond distance is 2.0876(17) Å for the complex **1** and the corresponding bond lengths for complex **4** are 2.239(5) and 2.096(5) Å. Further, the two triphenyl phosphine ligands (PPh_3) in **1** and triphenyl arsine ($AsPh_3$) ligands in **4** are present in *trans* position of distorted octahedral Ru(II) complexes. The two PPh_3 are slightly bent towards the hydride ligand in complex **1** due to the steric requirements of the 8-hydroxy quinoline hydrazone ligand. The Ru–C(1) bond distances in complex **1** and **4** have been observed as 1.812(3) and 1.798(7) Å which is comparable with the Ru–C bond lengths of previously reported carbonyl complexes [31]. The bond lengths of metal hydrogen bonds in complexes **1** and **4** have been obtained as 1.344 and 1.879 Å. Moreover, intra molecular hydrogen bonding was observed in complexes **1** and **4**.

3.2. Infrared spectroscopic analysis

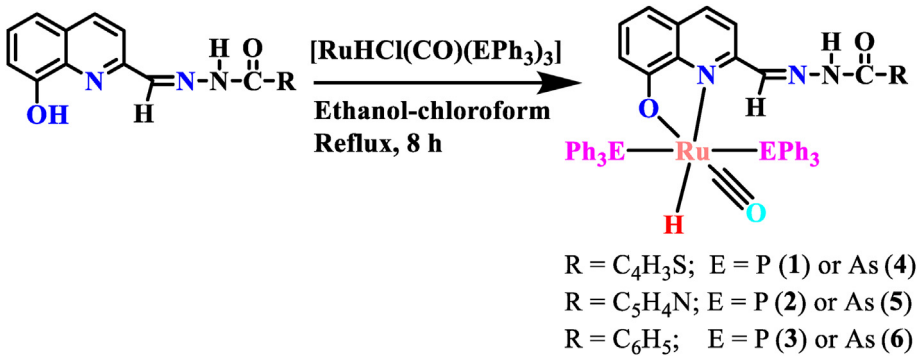
In order to confirm the coordination of ligands to ruthenium metal, the IR spectra of free ligands were compared with that of new ruthenium complexes. In the spectra of free ligands, a strong band has been observed in the region 1647–1593 cm^{-1} which is characteristics of the azomethine group and this band has been found in same frequency in the complexes indicates that the azomethine nitrogen of the ligand does not involve in the coordination with central metal ion. The bands due to NH and C=O which were observed around 3373–3305 and 1736–1630 cm^{-1} respectively in the free ligands have not shifted appreciably in the complexes indicate that neither N of NH nor O of C=O in the hydrazone ligands do not participate in binding of the ligand. A broad band appeared around 3214–3184 cm^{-1}for OH of the free ligands has completely disappeared in complexes shows the coordination of phenolic O atom after deprotonation. The band appeared around 1572–1551 cm^{-1} in the ligands for the ring C=N has got shifted to higher frequencies (1586-1556 cm^{-1}) in metal complexes reveals that the other coordination is through quinoline nitrogen. A band which appeared around 1909–1900 cm^{-1} in all the complexes clearly shows the presence of a terminal carbonyl ligand. Hence, from the infrared spectroscopic data, it has inferred that the quinoline nitrogen and phenolic oxygen atom of the hydrazone ligands coordinated to the metal ion in all the complexes.

3.3. ^{1}H NMR spectroscopic analysis

^{1}H NMR spectra of ligands and ruthenium complexes were recorded in $CDCl_3$ solvent to confirm the binding of hydrazide ligands with metal ion and they are shown in Fig. S3- S8. The spectra of free ligands show a singlet in the region 12.42–10.24 ppm, characteristic of phenolic OH group. This peak disappeared in their corresponding complexes confirming the binding of ligands with metal ion via phenolic O atom after deprotonation of phenolic hydroxyl group. The NH and azomethine peaks appear in the region 10.80–10.60 and 8.66–8.20 ppm respectively in the spectra of ligands do not change their position in the spectra of complexes indicate that they do not involve in the coordination to the metal ion. Multiplets were observed around 8.18–6.26 ppm in all the ligands and complexes due to aromatic protons. In addition, a singlet appeared at −11.30–10.56 ppm due to the Ru–H in all the complexes.



Scheme 1. Synthesis of 8-hydroxyquinoline-2-carboxyaldehyde hydrazide ligands.



Scheme 2. Synthesis of Ru(II) complexes.

Table 1
Crystal data and structure refinement of complexes **1** and **4.**

	$[RuH(CO)(PPh_3)_2(HQ\text{-}Thy)]$	$[RuH(CO)(AsPh_3)_2(HQ\text{-}Thy)]$
CCDC Number	1967465	1967467
Empirical formula	$C_{52}H_{41}N_3SO_3ClP_2Ru$	$C_{52}H_{41}N_3SO_3ClAs_2Ru$
Formula weight	986.40	1074.30
Temperature	296(2) K	296(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	*P* 21/*n*	*P* 21/*n*
Unit cell dimensions		
a	15.1624(5) Å	15.4143(4) Å
b	18.9080(6) Å	18.8694(4) Å
c	16.8310(6) Å	17.0411(4) Å
α	90°	90°.
β	95.7640(10)°	97.1850(10)°
γ	90°	90°
Volume	4800.9(3) $Å^3$	4917.6(2) $Å^3$
Z	4	4
Density (calculated)	1.420 Mg/m^3	1.450 Mg/m^3
Absorption coefficient	0.542 mm^{-1}	1.795 mm^{-1}
F(000)	2100	2160
Crystal size	0.288 × 0.277 × 0.162 mm^3	0.22 × 0.19 × 0.17 mm^3
Theta range for data collection	2.542–28.288°.	2.640–28.263°.
Index ranges	−20 ≤ h<=20 −18 ≤ k<=25 −20 ≤ l<=22	20 ≤ h<=20 −25 ≤ k<=25 −22 ≤ l<=22
Reflections collected	44854	45611
Independent reflections	11843 [R(int) = 0.0333]	12184 [R(int) = 0.0346]
Completeness to theta = 25.242°	99.5%	99.8%
Absorption correction	None	None
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	11843/0/599	12146/0/556
Goodness-of-fit on F^2	1.013	1.066
Final R indices [I > 2sigma(I)]	R1 = 0.0407, w*R*2 = 0.1074	R1 = 0.0500, w*R*2 = 0.2458
R indices (all data)	R1 = 0.0592, w*R*2 = 0.1168	R1 = 0.1027, w*R*2 = 0.1643

3.4. ^{13}C NMR spectroscopic analysis

The ^{13}C NMR spectra of complexes were recorded in order to confirm the formation of new ruthenium(II) with 8-hydroxyquinoline-2-carboxyaldehyde hydrazone (Figs. S9–S14). Peaks appear around at 139.18–121.87 ppm can be assigned to aromatic carbons. Azomethine carbon (>C═N) and amide group (NH–C═O) have shown their signals around at 157.85–151.22 and 178.99–175.11 ppm respectively. The appearance of peak at 204.71–201.62 ppm region is due to the terminal carbonyl carbon of the coordinated carbonyl.

3.5. ^{31}P NMR spectroscopic analysis

^{31}P NMR spectra were recorded for complexes **1**–**3** to confirm the coordination of triphenylphosphine group and its configuration around ruthenium atom. Appearance of peak around 29.74–29.41 ppm indicates the presence of triphenylphosphine group in the new complexes. The presence of single peak confirms the coordination of two triphenylphosphine groups in *trans* position (Figs. S15–S17).

3.6. Catalytic N-alkylation and N, C_3-dialkylation of cyclic amines with alcohols

It is very well known that ruthenium complexes have been used extensively as precatalysts for N-alkylation of amines with alcohols [32]. Though several enough examples are known in which hydrogen borrowing strategy has been employed for the construction of N-alkylation and N,C-dialkylated products arising from alcohols, no single step process for the simultaneous alkylation of both the N and the unactivated C_3 carbon of secondary amines

Table 2
Selected bond lengths [Å] and bond angles [°] for complexes **1** and **4.**

Complex 1		Complex 4	
Ru(1)-C (16)	1.812(3)	Ru (1)-C (16)	1.798(7)
Ru(1)-O (1)	2.0876(17)	Ru (1)-O (1)	2.096(5)
Ru(1)-N (1)	2.240(2)	Ru (1)-N (1)	2.239(5)
Ru(1)-P (1)	2.3635(7)	Ru (1)-As (1)	2.4414(9)
Ru(1)-P (2)	2.3683(7)	Ru (1)-As (2)	2.4423(8)
Ru(1)−H(1)	1.344	Ru(1)−H(1)	1.879
bond Angles [°]			
C(16)-Ru(1)-O(1)	173.54(10)	C(16)-Ru(1)-O(1)	173.4(3)
C(16)-Ru(1)-N(1)	109.18(11)	C(16)-Ru(1)-N(1)	109.4(3)
O(1)-Ru(1)-N(1)	77.14(7)	O(1)-Ru(1)-N(1)	77.07(19)
C(16)-Ru(1)-P(1)	92.06(9)	C(16)-Ru(1)-As(1)	92.4(3)
O(1)-Ru(1)-P(1)	86.54(6)	O(1)-Ru(1)-As(1)	86.46(15)
N(1)-Ru(1)-P(1)	89.75(6)	N(1)-Ru(1)-As(1)	88.27(14)
C(16)-Ru(1)-P(2)	90.73(9)	C(16)-Ru(1)-As(2)	91.6(3)
O(1)-Ru(1)-P(2)	90.08(6)	O(1)-Ru(1)-As(2)	89.00(15)
N(1)-Ru(1)-P(2)	94.48(6)	N(1)-Ru(1)-As(2)	94.62(14)
P(1)-Ru(1)-P(2)	173.87(2)	As(1)-Ru(1)-As(2)	173.95(3)
N(1)-Ru(1)-H(1)	168.44	C(1)-O(1)-Ru(1)	116.0(4)
O(1)-Ru(1)-H(1)	92.13	C(6)-N(1)-Ru(1)	109.4(4)
H(1)-Ru(1)-P(1)	85.27	H(1)-Ru(1)-As(1)	87.14
H(1)-Ru(1)-P(2)	89.15	H(1)-Ru(1)-As(2)	89.32

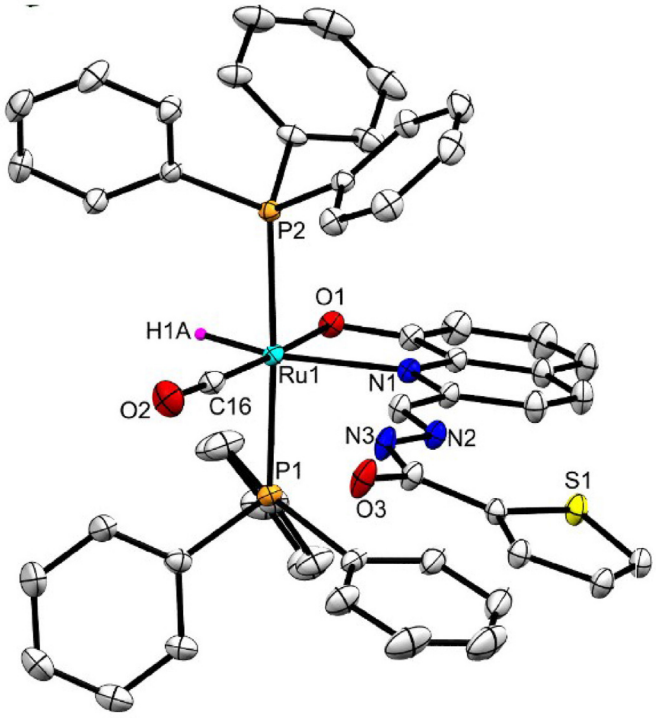


Fig. 2. Molecular structure of [RuH(CO)(PPh_3)$_2$(HQ-Thy)] (**1**). Ellipsoids are shown at the 50% probability level omitting the hydrogen, chlorine atoms and solvent molecule.

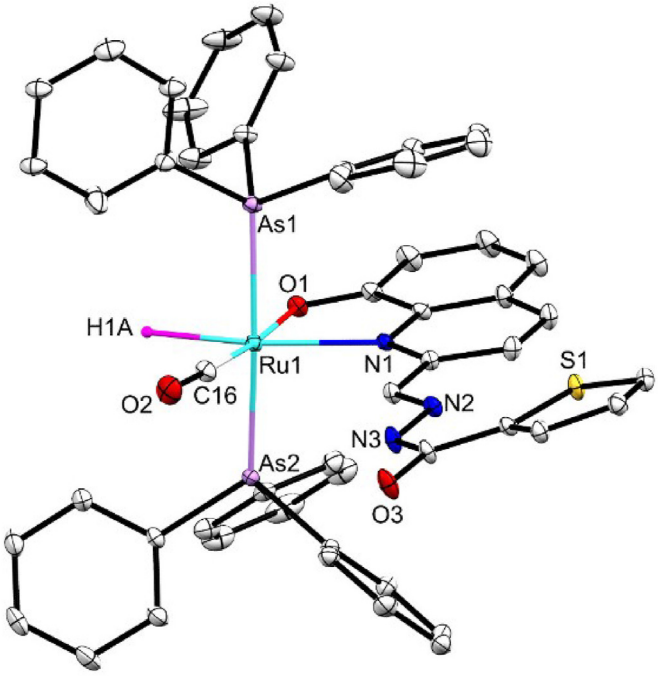


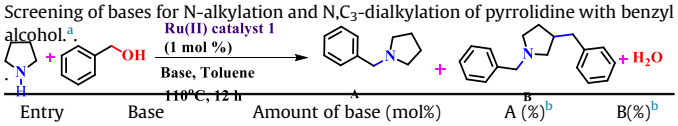
Fig. 3. Molecular structure of [RuH(CO)($AsPh_3$)$_2$(HQ-Thy)] (**4**). Ellipsoids are shown at the 50% probability level omitting the hydrogen and chlorine atoms.

corresponding to a formal C (sp^3)-H activation was known until Bruneau and co-workers reported the N-alkylation and N,C_3-dialkylation of saturated cyclic amines in the presence of ruthenium precatalysts [33]. Hence, we decided to test the catalytic activities of our new complexes in the N-alkylation and N,C_3-dialkylation of secondary amine with alcohols.

To start with, optimization of base and temperature were investigated for the N-alkylation and N,C_3-dialkylation of pyrrolidine with benzyl alcohol as a model reaction and obtained results are given in Table 3. It is to be noted that weak bases such as Na_2CO_3, K_2CO_3 and Cs_2CO_3 were not effective (Table 3 entries 1–3). However, the use of strong bases such as NaOH, NaOtBu and KOH lead to good yields of the desired product (Table 3, entries 6, 8–10). It is evident that with the use of KOH, the yield of the product was the highest indicate KOH as the best base (Table 3, entry 6). To determine the amount of KOH (mol %) required for effective transformation, the amount of KOH was increased from 20 mol % up to 40 mol % in the model reaction (Table 3, entries 4–6). The results show that the use of 40 mol % base has resulted not only the maximum yield for the N-alkylated product but also for N,C_3-dialkylated product.

After finding the need for a strong base to activate the catalyst, we were involved to examine the solvent dependent differences in activity of catalyst **1** by carry out the screening

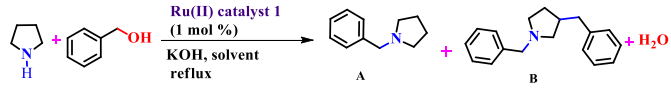
Table 3
Screening of bases for N-alkylation and N,C_3-dialkylation of pyrrolidine with benzyl alcohol.[a].



Entry	Base	Amount of base (mol%)	A (%)[b]	B(%)[b]
1	Na_2CO_3	50	–	–
2	K_2CO_3	50	–	–
3	Cs_2CO_3	50	21	–
4	KOH	20	‘10	41
5	KOH	30	22	70
6	**KOH**	**40**	**24**	**76**
7[c]	KOH	40	–	–
8	NaOH	50	18	44
9	NaO*t*Bu	20	20	38
10	NaO*t*Bu	50	22	52

[a] Reagents and conditions: Pyrrolidine (1 mmol), alcohol (2.5 mmol), base (20–50 mol %), catalyst **1** (1 mol %), toluene (2 mL), reflux at 110 °C for 12 h.
[b] The yields of A and B were determined by GC using dodecane as an internal standard.
[c] Room temperature.

Table 4
Screening of solvents for N-alkylation and N,C_3-dialkylation of pyrrolidine with benzyl alcohol.[a].



Entry	Solvent	T °C	Time	A (%)[b]	B (%)[b]
1	CH_3CN	80	12	18	45
2	DMF	150	12	16	42
3	DMSO	152	12	15	39
4	DMA	162	12	13	32
5	1, 4 dioxane	100	12	14	38
6	THF	65	12	17	43
7	Benzene	81	12	20	65
8	**Toluene**	**110**	**12**	**24**	**76**

[a] Reagents and conditions: Pyrrolidine (1 mmol), alcohol (2.5 mmol), KOH (40 mol %), catalyst **1** (1 mol %), solvent (2 mL), reflux for 12 h.
[b] The yields of A and B were determined by GC using dodecane as an internal standard.

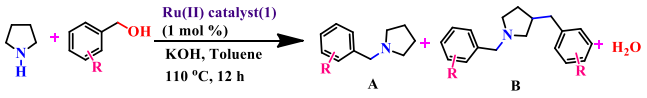
Table 5
Catalyst screening for N-alkylation and N,C_3-dialkylation of pyrrolidine with benzyl alcohol.[a]

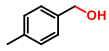
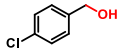
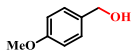
Entry	Catalyst	Amount of catalyst (mol %)	A (%)[b]	B (%)[b]
1	1	**0.15/0.25/0.5/1**	**8/11/18/24**	**0/15/33/76**
2	2	0.15/0.25/0.5/1	10/14/21/28	0/12/18/72
3	3	0.15/0.25/0.5/1	0/15/21/27	0/8/14/73
4	4	0.15/0.25/0.5/1	0/15/19/29	0/8/14/71
5	5	0.15/0.25/0.5/1	0/15/20/26	0/8/14/74
6	6	0.15/0.25/0.5/1	0/15/21/25	0/8/14/75

[a] Reagents and conditions: Pyrrolidine (1 mmol), alcohol (2.5 mmol), KOH (40 mol %), catalyst (mol %), toluene (2 mL), reflux at 110 °C for 12 h.
[b] The yields of A and B were determined by GC using dodecane as an internal standard.

reaction in different solvents used such as CH_3CN, DMF, DMSO, THF, 1,4 dioxane, toluene, benzene and DMA (Table 4). Aromatic solvents such as benzene and toluene (Table 4, entries 7 and 8) were found to be good reaction media than polar aprotic solvents (Table 4, entries 1–4). Ether like solvents 1,4 dioxane and THF lead the N-alkylation and N,C_3-dialkylation reactions moderately (Table 4, entries 5 and 6). The results reveal that toluene was the solvent of choice for the N-alkylation and N,C_3-dialkylation reactions.

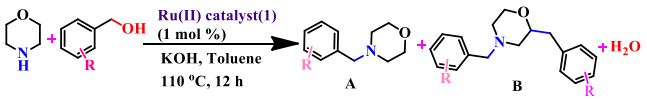
Table 6
Catalytic N-alkylation and N,C_3-dialkylation of pyrrolidine with benzyl alcohol derivatives.[a].

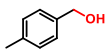
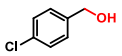
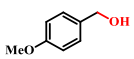


Entry	Alcohol	A (%)[b]	B (%)[b]
1		24	76
2		36	64
3		74	26
4		42	58

[a] Reagents and conditions: Pyrrolidine (1 mmol), alcohol (2.5 mmol), KOH (40 mol %), catalyst **1** (1 mol %), toluene (2 mL), reflux at 110 °C for 12 h.
[b] The yields of A and B were determined by GC using dodecane as an internal standard.

Table 7
N-alkylation and N,C_3-dialkylation of morpholine with benzyl alcohol derivatives.[a].

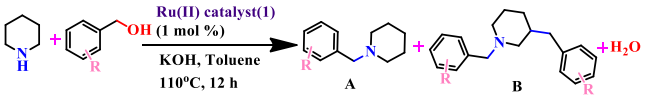


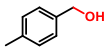
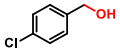
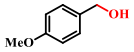
Entry	Primary alcohol	A (%)[b]	B (%)[b]
1		93	7
2		91	9
3		89	11
4		95	5

[a] Reagents and conditions: Morpholine (1 mmol), alcohol (2.5 mmol), KOH (40 mol %), catalyst **1** (1 mol %), toluene (2 mL), reflux at 110 °C for 12 h.
[b] The yields of A and B were determined by GC using dodecane as an internal standard.

After finding out need for a strong base and suitable solvent for the reaction, we took up the investigation on finding the influence of the catalyst loading on the catalytic activity. The results indicate that lower catalyst loadings lead to moderate yields, higher catalyst loadings lead to higher yields and higher amine content in the product distribution (Table 5). It is clear from the results that the complex containing thiophene as terminal substituent in the hydrazone ligand and triphenylphosphine as coligand (Table 5, entry 1) lead to higher yields than those containing phenyl or pyridine as terminal substituent and triphenyl arsine as coligand (Table 5, entries 2–6). Hence, complex **1** is selected for further studies.

Table 8
N-alkylation and N, C_3-dialkylation of piperidine with benzylalcohol derivatives.[a].



Entry	Primary alcohol	A (%)[b]	B (%)[b]
1		91	9
2		88	12
3		85	15
4		93	7

[a] Reagents and conditions: Piperidine (1 mmol), alcohol (2.5 mmol), KOH (40 mol %), catalyst **1** (1 mol %), toluene (2 mL), reflux at 110 °C for 12 h.
[b] The yields of A and B were determined by GC using dodecane as an internal standard.

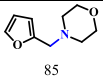
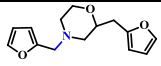
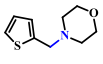
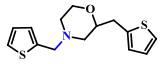
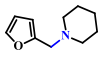
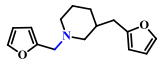
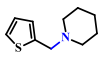
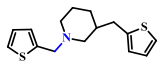
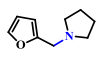
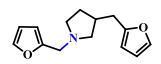
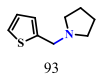
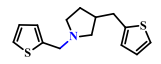
To expand the scope of the present homogeneous catalyst system, the N-alkylation and N, C_3-dialkylation reaction have been carried out with a number of benzyl alcohol consisting of different substituents. Table 6 summarizes the results obtained on the catalytic activity of **1** for the reaction of pyrrolidine with various benzyl alcohols in toluene/KOH. The unsubstituted alcohol gives N,C_3-dialkylation product as major product with 76% yield (Table 6, entry 1). When compared to unsubstituted benzyl alcohol, the yield of N,C_3-dialkylation product is decreased (64%) whereas N-alkylation product is increased (36%) for methyl substituted benzyl alcohol (Table 6, entry 2). The electron with drawing groups in substituted benzyl alcohols such as *p*-chloro, the N-alkylation product is predominant over N,C_3-dialkylation product (Table 6, entry 3).

Taking complex **1** as the catalyst, we wanted to see whether there is any change in yields in the reaction if it is carried out with morpholine as the amine since morpholine moiety has played a significant role in pharmaceutical molecules besides being an active intermediate in many chemical reactions. Hence, the N-alkylation and N,C_3-dialkylation reactions have been carried out with a number of benzyl alcohol consisting of different substituents. Table 7 summarizes the results obtained on the catalytic activity of **1** with toluene/KOH for this C–N coupling reaction. It is to be noted that the there is only a very low yield of the dialkyl product in all the cases indicating that there is no effect of the change of amine in these reactions.

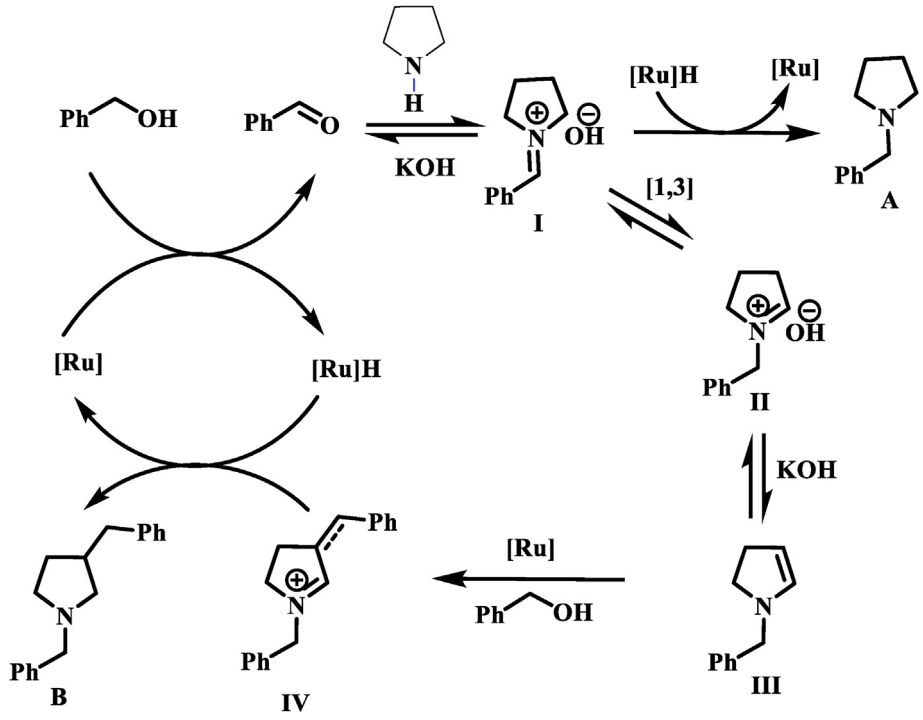
Having checked the dialkylation with pyrrolidine and morpholine with substituted alcohols, we thought of looking at the yield of the product if we use piperidine as the amine and the results obtained are shown in Table 8. It is seen that the N,C_3-dialkylation products were observed only as a minor product in all of the reactions were carried out using substituted benzyl alcohol and piperidine.

Finally, we carried out similar catalytic reactions using various secondary amines with different types of heteroaromatic alcohols and the results obtained are given in Table 9. It has been observed that only the mono alkylated product formed in high yields and dialkylated product formed in very low yields. Hence, it is to be pointed out from our studies that best result for the synthesis of N-alkylation and N, C3-dialkylated product could be obtained using complex **1** as the catalyst taking pyrrolidine and benzyl alcohol. When compared to previously reported catalysts for N alkylation reactions [33–35], the present catalyst required lower temperature and shorter time for effective formation of alkylated products. Moreover, the catalyst can be applied to a wide range of substrates including heterocyclic secondary amines and primary alcohols that were scarcely addressed by previously reported catalysts for N alkylation reactions.

Table 9
N-alkylation and N, C_3-dialkylation of secondary amines with heteroaromatic alcohol.[a].

Entry	2 °Aryl amine	Primary alcohol	Alkylated products Yield (%)[b]	
			A	B
1			 85	 15
2			 89	 11
3			 79	 21
4			 82	 18
5			 91	 9
6			 93	 7

[b] The yields of A and B were determined by GC using dodecane as an internal standard.
[a] Reagents and conditions: Secondary amines (1 mmol), primary alcohol (2.5 mmol), KOH (40%), catalyst **1** (1 mol %), toluene (2 mL), reflux at 110 °C for 12 h.



Scheme 3. Plausible reaction mechanism for the catalytic alkylation reactions.

A plausible mechanism for alkylation reactions based on an autotandem catalytic cycle [36] is depicted in Scheme 3. Benzyl alcohol is converted into benzaldehyde along with the generation of the ruthenium hydride species mechanism according to previous literature [37]. The in situ generated benzaldehyde reacts with the secondary amine to form the iminium ion **I** which, in the absence of base undergoes reduction and gives 1-benzylpyrrolidine (A). The iminium ion **I** might move into the iminium ion **II** via a [1,3] hydride shift. Deprotonation of II might lead to the formation of enamine **III** as key intermediate. Finally, enamine **III**, would lead via nucleophilic substitution of benzyl alcohol or aldol-type reaction on benzaldehyde [38] to the iminium species **IV** which, in turn, would afford the expected dialkylated amine 1,3-dibenzylpyrrolidine (B) after reduction in the presence of the ruthenium hydride species.

4. Conclusions

A simple route to the synthesis of novel ruthenium(II) complexes with 8-hydroxyquinoline-2-carboxyaldehyde hydrazones has been described. The characterizations of the complexes (**1**–**6**) were carried out by analytical and spectral methods (IR, ^{1}H, ^{13}C & ^{31}P NMR, and ESI-Mass). The solid state structures of the complexes (**1** and **4**) were established by single crystal X-ray diffraction study. The structure determination indicates the formation of distorted octahedral complexes with the coordination of O atom of the phenolic group and N atom of the quinoline. The other four coordination sites have been filled by one terminal carbonyl, one hydride and two phosphines/arsines. A detailed study using the new Ru(II) complexes as homogeneous catalysts towards N-alkylation and N,C_3-dialkylation reactions with various amines and alcohols was carried out. From the results obtained from our investigations, it is concluded that complex **1** was found to be very efficient catalysts toward N-alkylated and N,C_3-dialkylated products of a wide range of heterocyclic secondary amines with aromatic primary alcohols. Hence, this method can be successfully used for the synthesis of various N-alkylated and N,C_3-dialkylated products from the desired amines and alcohols.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors thank CIMF, Periyar University, Salem for the help to record single crystal X-ray studies.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jorganchem.2020.121411.

References

[1] (a) Amines: Synthesis, Properties and Applications by S. A. Lawrence, Cambridge University Press, Cambridge, 2006;
(b) A.R. Cartolano, G.A. Vedage, Kirk-Othmer Encyclopedia of Chemical Technology, vol. 2, Wiley, New York, 2004;
(c) S. Gomez, J.A. Peters, T. Maschmeyer, Adv. Synth. Catal. 344 (2002) 1037–1057;
(d) R.N. Salvatore, C.H. Yoon, K.W. Jung, Tetrahedron 57 (2001) 7785–7811.
[2] Top 200 World's Best Selling Medicines, Med Ad News, 2004.
[3] J.S. Carey, D. Laffan, C. Thomson, M.T. Williams, Org. Biomol. Chem. 4 (2006) 2337–2347.
[4] (a) J.M.J. Williams, OH activation for nucleophilic substitution, in: P.J. Dunn, K.K. Hii, M.J. Krische, M.T. Williams (Eds.), Sustainable Catalysis: Challenges And Practices For the Pharmaceutical And Fine Chemical Industries, Wiley, Hoboken, New Jersey, 2013;
(b) S. Bahn, S. Imm, L. Neubert, M. Zhang, H. Neumann, M. Beller, ChemCatChem 3 (2011) 1853–1864;
(c) G.E. Dobereiner, R.H. Crabtree, Chem. Rev. 110 (2010) 681–703;
(d) G. Guillena, D.J. Ram, M. Yus, Chem. Rev. 110 (2010) 1611–1641;
(e) A.J.A. Watson, J.M.J. Williams, Science 329 (2010) 635–636.
[5] K. Amreen K. Bains, A. Kundu, S. Yadav, D. Adhikar, ACS Catal. 9 (2019) 9051–9059.
[6] M. Subaramanian, Siba P. Midya, Palmurukan M. Ramar, E. Balaraman, Org. Lett. 21 (2019) 8899–8903.
[7] (a) D. Weickmann, W. Frey, B. Plietker, Chem. Eur J. 19 (2013) 2741–2748;
(b) S. Agrawal, M. Lenormand, B. Martin-Matute, Org. Lett. 14 (2012)

1456–1459;
(c) A.J.A. Watson, A.C. Maxwell, J.M.J. Williams, Org. Biomol. Chem. 10 (2012) 240–243;
(d) W. Li, X. Zheng, Z. Li, Adv. Synth. Catal. 355 (2013) 181–190;
(e) P. Yang, C. Zhang, Y. Ma, C. Zhang, A. Li, B. Tang, J.S. Zhou, Angew. Chem. Int. Ed. 56 (2017) 14702–14706;
(f) O.S. Nayal, M.S. Thakur, M. Kumar, N. Kumar, S.K. Maurya, Adv. Synth. Catal. 360 (2018) 730–737;
(g) B. Emayavaramban, P. Chakraborty, E. Manoury, R. Poli, B. Sundararaju, Org. Chem. Front. 6 (2019) 852–857;
(h) T.J. Brown, M. Cumbes, L.J. Diorazio, G.J. Clarkson, M.J. Wills, Org. Chem. 82 (2017) 10489–10503;
(i) L. Homberg, A. Roller, K.C. Hultzsch, Org. Lett. 21 (2019) 3142–3147;
(j) T. Yan, B.L. Feringa, K. Barta, Nat. Commun. 5 (2014) 5602–5608;
(k) A.J. Rawlings, L.J. Diorazio, M. Wills, Org. Lett. 17 (2015) 1086–1089;
(l) A.K. Bains, A. Kundu, S. Yadav, D. Adhikari, ACS Catal. 9 (2019) 9051–9059.

[8] (a) A. Wetzel, S. Wçckel, M. Schelwies, M.K. Brinks, F. Rominger, P. Hofmann, M. Limbach, Org. Lett. 15 (2013) 266–269;
(b) Y.H. Chang, Y. Nakajima, F. Ozawa, Organometallics 32 (2013) 2210–2215;
(c) A. Bartoszewicz, R. Marcos, S. Sahoo, A.K. Inge, X. Zou, B. Martin-Matute, Chem. Eur J. 18 (2012) 14510–14519;
(d) J. Norinder, A. Boerner, ChemCatChem 3 (2011) 1407–1409;
(e) M.A. Berliner, S.P.A. Dubant, T. Makowski, K. Ng, B. Sitter, C. Wager, Y. Zhang, *Org. Process Res. Dev*. 15 (2011) 1052–1060;
(f) R. Kawahara, K. Fujita, R. Yamaguchi, Adv. Synth. Catal. 353 (2011) 1161–1168;
(g) S. Michlik, R. Kempe, Chem. Eur J. 16 (2010) 13193–13198;
(h) O. Saidi, A.J. Blacker, M.M. Farah, S.P. Marsden, J.M.J. Williams, Chem. Commun. 46 (2010) 1541–1543.

[9] M. Mastalir, M. Glatz, N. Gorgas, B. Stçger, E. Pittenauer, G. Allmaier, L.F. Veiros, K. Kirchner, Chem. Eur J. 22 (2016) 12316–12320.

[10] M. Mastalir, M. Glatz, E. Pittenauer, G. Allmaier, K. Kirchner, J. Am. Chem. Soc. 138 (2016) 15543–15546.

[11] Z. Yin, H. Zeng, J. Wu, S. Zheng, G. Zhang, ACS Catal. 6 (2016) 6546–6550.

[12] P. Satyanarayana, G.M. Reddy, H. Maheswaran, M.L. Kantam, Adv. Synth. Catal. 355 (2013) 1859–1867.

[13] (a) G. Prakash, P. Viswanathamurthi, Spectrochim. Acta, Part A 129 (2014) 352;
(b) G. Prakash, R. Ramachandran, M. Nirmala, P. Viswanathamurthi, W. Linert, Monatsh. Chem. 145 (2014) 1903–1912.

[14] A. Corma, J. Navas, M.J. Sabater, Chem. Rev. 118 (2018) 1410–1459.

[15] R. Grigg, T.R.B. Mitchell, S. Sutthivaiyakit N. Tongpenyai, J. Chem. Soc., Chem. Commun. 12 (1981) 611–612.

[16] (a) Y. Tsuji, H.-T. Huh, Y. Ohsugi, Y. Watanabe, J. Org. Chem. 50 (1985) 1365–1370;
(b) Y. Watanabe, Y. Tsuji, Y. Ohsugi T. Ohta, J. Org. Chem. 49 (1984) 3359–3363;
(c) Y. Watanabe, Y. Tsuji Y. Ohsugi, Tetrahedron Lett. 22 (1981) 2667–2670.

[17] (a) T. Yan, B.L. Feringa, K. Barta, Nat. Commun. 5 (2014) 5602;
(b) H.J. Pan, T.W. Ng, Y. Zhao, Chem. Commun. 51 (2015) 11907–11910;
(c) A.J. Rawlings, L.J. Diorazio, M. Wills, Org. Lett. 17 (2015) 1086–1089;
(d) M. Mastalir, B. Stoger, E. Pittenauer, M. Puchberger, G. Allmaier, K. Kirchner, Adv. Synth. Catal. 358 (2016) 3824–3831;
(e) T.J. Brown, M. Cumbes, L.J. Diorazio, G.J. Clarkson, M. Wills, J. Org. Chem. 82 (2017) 10489–10503.

[18] M. Bertoli, A. Choualeb, A.J. Lough, B. Moore, D. Spasyuk, D.G. Gusev, Organometallics 30 (2011) 3479–3482.

[19] (a) L.M. Wang, Y. Morioka, K. Jenkinson, Andrew E.H. Wheatley, S. Saito, H. Nak, Sci. Rep. 8 (2018) 6931;
(b) H.G. Aslan, S. Ozcan, N. Karacan, Inorg. Chem. Commun. 14 (2011) 1550–1553;
(c) Z. Xu, X. Zhang, W. Zhang, Y. Gao, Z. Zeng, Inorg. Chem. Commun. 14 (2011) 1569–1573.

[20] (a) J. Hou, W.H. Sun, D. Zhang, L. Chen, W. Li, D. Zhao, H. Songc, J. Mol. Catal. Chem. 231 (2005) 221–233;
(b) O. Pouralimardan, A.C. Chamayou, C. Janiak, H. Hosseini-Monfared, Inorg. Chim. Acta. 360 (2007) 1599–1608;
(c) H.H. Monfared, R. Bikas, P. Mayer, Inorg. Chim. Acta. 363 (2010) 2574–2583;
(d) H.H. Monfared, S. Sadighiana, M.A. Kamyabia, P. Mayer, J. Mol.Chem. 304 (2009) 139–146;
(e) D. Pandiarajan, R. Ramesh, J. Organomet. Chem. 708 (2012) 18;
(f) R.N. Prabhu, R. Ramesh, RSC Adv. 2 (2012) 4515–4524.

[21] (a) J. Deng, P. Yu, Z. Zhang, J. Zhang, S. Zhewen, M. Cai, H. Yuan, H. Liang, F. Yang, Metall 11 (2019) 1847–1863;
(b) R. Fekri, M. Salehi, A. Asadi, M. Kubicki, Inorg. Chim. Acta. 484 (2019) 245–254;
(c) R. Manikandan, P. Viswanathamurthi, M. Muthukumar, Spectrochim. Acta, Part A 83 (2011) 297–303.

[22] W. Cao, Y. Liu, T. Zhang, J. Jia, Polyhedron 147 (2018) 62–68.

[23] M. Mohanraj, G. Ayyannan, G. Raja, C. Jayabalakrishnan, Appl. Organomet. Chem. 30 (2016) 550–560.

[24] (a) P. Nithya, J. Simpson, S. Govindarajan, Inorg. Chim. Acta. 467 (2017) 180–193;
(b) Shubha S. Kumar, S. Biju, V. Sadasivan, J. Mol. Struct. 1156 (2018) 201–209;
(c) E. Jayanthi, S. Kalaiselvi, V. Vijaya Padma, Nattamai S.P. Bhuvanesh, N. Dharmaraj, Dalton Trans. 45 (2016) 1693–1707.

[25] (a) C.P. Lau, S.M. Ng, G. Jia, Z. Lin, Coord. Chem. Rev. 251 (2007) 2223–2237;
(b) R. Ramachandran, G. Prakash, P. Viswanathamurthi, J.G. Malecki, T. Ramkumar, Dalton Trans. 43 (2014) 7889–7902;
(c) R. Ramachandran, G. Prakash, S. Selvamurugan, P. Viswanathamurthi, RSC Adv. 5 (2015) 11405–11422;
(d) G. Prakash, R. Ramachandran, M. Nirmala, P. Viswanathamurthi, Inorg. Chim. Acta. 427 (2014) 203–210;
(e) R. Ramachandran, G. Prakash, P. Viswanathamurthi, J.G. Malecki, Inorg. Chim. Acta. 477 (2018) 122–129.

[26] A.I. Vogel, Textbook of Practical Organic Chemistry, fifth ed., Longman, London, 1989.

[27] N. Ahmed, J.J. Levison, S.D. Robinson, M.F. Uttley, Inorg. Synth. 15 (1974) 45–60.

[28] R.A. Sanchez-Delgado, W.Y. Lee, S.R. Choi, Y. Cho, M.J. Jun, Trans. Met. Chem. 16 (1991) 241–244.

[29] M. Hassani, W. Cai, D.C. Holley, J.P. Lineswala, B.R. Maharjan, G.R. Ebrahimian, H. Seradj, M.G. Stocksdale, F. Mohammadi, C.C. Marvin, J.M. Gerdes, H.D. Beall, M. Behforouz, J. Med. Chem. 48 (2005) 7733–7749.

[30] G.M. Sheldrick, Acta Crystallogr. A 64 (2008) 112–122.

[31] T. Sathiya Kamatchi, N. Chitrapriya, H. Lee, C.F. Fronczek, F.R. Fronczek, K. Natarajan, Dalton Trans. 41 (2012) 2066–2077.

[32] R. Ramachandran, G. Prakash, M. Nirmala P. Viswanathamurthi, J.G. Malecki, *J. Organomet. Chem*. 791 (2015) 130–140.

[33] Z. Sahin, N. Gurbuz, I. Ozdemir, O. Sahin, O. Buyukgungor, M. Achard, C. Bruneau, Organometallics 34 (2015) 2296–2304.

[34] S. Shan, T.T. Dang, A.M. Seayad, B. Ramalingam, ChemCatChem 6 (2014) 808–814.

[35] O.D. Ulu, N. Gurbuz, I. Ozdemir, Tetrahedron 74 (2018) 645–651.

[36] (a) D.E. Fogg, E.N. dos Santos, Coord. Chem. Rev. 248 (2004) 2365;
(b) B. Sundararaju, Z. Tang, M. Achard, G.V.M. Sharma, L. Toupet, C. Bruneau, Adv. Synth. Catal. 352 (2010) 3141–3146.

[37] (a) M.H.S.A. Hamid, P.A. Slatford, J.M.J. Williams, Adv. Synth. Catal. 349 (2007) 1555;
(b) G.W. Lamb, J.M.J. Williams, Chim. Oggi 26 (2008) 17;
(c) T.D. Dixon, M.K. Whittlesey, J.M.J. Williams, Dalton Trans. 7 (2009) 53;
(d) G.E. Dobereiner, R.H. Crabtree, Chem. Rev. 110 (110) (2010) 681;
(e) G. Guillena, D.J. Ramon, M. Yus, Chem. Rev. 110 (2010) 1611;
(f) R. Yamaguchi, K.I. Fujita, M. Zhu, Heterocycles 81 (2010) 1093.

[38] (a) B. Blank, R. Kempe, J. Am. Chem. Soc. 132 (2010) 924;
(b) G. Guillena, D.J. Ramon, M. Yus, Angew. Chem. 119 (2007) 2410–2416.