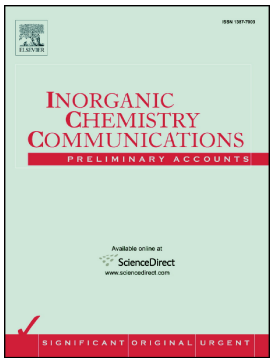

Ru(II) mediated C-H activation of 1-(biphenylazo)naphthol: Synthesis and catalytic evaluation for transfer hydrogenation of ketones

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Ru(II) mediated C–H activation of 1-(biphenylazo)naphthol: Synthesis and catalytic evaluation for transfer hydrogenation of ketones

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Abstract

New cyclometalated ruthenium(II) complexes of the type $[Ru(L)(CO)(EPh_3)_2]$ (L = di-anionic CNO- donor of 1-(biphenylazo)naphthol; E = P, As) have been synthesized by the reaction using $[RuHCl(CO)(EPh_3)_3]$ (E = P, As) with 1-(biphenylazo)naphthol ligand (H_2L). The 1-(biphenylazo)naphthol ligand and ruthenium complexes are characterized by analytical, spectral (FT–IR, UV–Vis, ^1H NMR and ^{31}P NMR) methods. The molecular structure of ruthenium complex **1** was further confirmed by single crystal X–ray diffraction method. The catalytic efficiency of ruthenium complex **1** was evaluated for the transfer hydrogenation of various ketones to alcohols with excellent conversion up to 99% in the presence of *i*-PrOH/KOH at 82 ^oC.

Keywords: C−H activation; Ruthenium(II) complexes; Crystal structure; Transfer hydrogenation

Cyclometalation has become an important part of organometallic chemistry and the application of organometallic compounds to organic transformation has considerable interest [1–4]. Over the past few years, cyclometalated ruthenium complexes have opened up enormous possibilities for variety of organic processes [5] due to great advances in the design and synthesis of new and efficient catalysts. The responsible for these progresses are mainly by introduced ligands, particularly with O- and N- donors. Some ligands induce unprecedented catalyst tolerance towards organic functional groups, air and moisture, thus expanding the scope of utilization of corresponding metal complexes. It is reported that the O- and N- donors of the azo ligands play an important role in the catalytic reactions particularly with transfer hydrogenation reactions [6]. Further, substituents on the nitrogen atom of the azo moiety also play an important role in tuning steric and electronic properties of the molecule [7].

The transfer hydrogenation of carbonyl compounds using 2-propanol as a hydrogen source to alcohols is one of the most applied processes in organic chemistry. Ruthenium-based catalytic systems are found to be effective in the transfer hydrogenation of ketones [8] and imines [9,10]. Verpoort and co-workers reported that ruthenium azonaphthol complexes were used as efficient catalysts for olefin isomerization reactions [11**]**. Furthermore, ruthenium complexes containing CNN- donor ligands (**A** & **B**) have been used as catalysts for the transfer hydrogenation of ketones [12] (Fig. 1). When compared to catalyst **A**, catalyst **B** shows poor catalytic activity and it is due to less labile nature of ligand in the catalyst. The interest behind the choice of present 1-(biphenylazo)naphthol ligand in the cyclometalated ruthenium(II) complexes is that it can also act as di-anionic tridentate CNO- donor which generates a five-membered metallacycles. The bulky biphenyl and naphthol moiety provides greater steric crowding compared to the phenyl ring in these complexes.

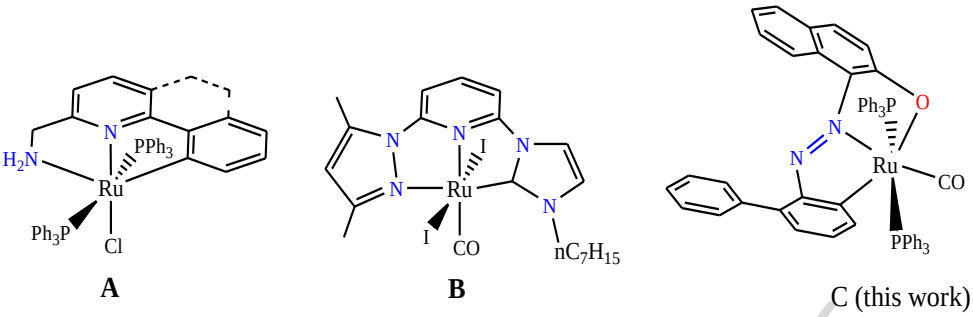
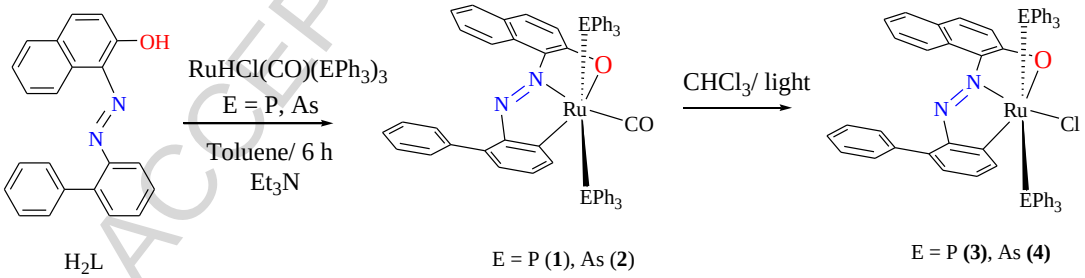


Fig. 1. Models of Ru-complexes.

Herein, we describe the synthesis of new air stable ruthenium(II) 1-(biphenylazo)naphtholate complexes incorporated with carbonyl and triphenylphosphine/triphenylarsine as ancillary ligands. The characterization of the complexes was investigated by spectral (FT-IR, UV–Vis, ^{1}H NMR and ^{31}P NMR) and single crystal X–ray diffraction method. Further, the catalytic efficiency of complex **1** was examined for the transfer hydrogenation of various ketones. To the best of our knowledge, there are no reports available for catalytic transfer hydrogenation of ketones by this type ruthenium(II) 1-(biphenylazo)naphthol complexes so far.



Scheme 1. Synthesis of cyclometalated ruthenium(II) 1-(biphenylazo)naphtholate complexes.

New 1-(biphenylazo)naphthol ligand (H_2L) was prepared by coupling diazotized 2-aminobiphenyl with *β*-naphthol (see Supplementary material). The reaction of

[RuHCl(CO)(EPh_3)$_3$] (E = P, As) [13,14] with 1-(biphenylazo)naphthol ligand (H_2L) in 1:1 molar ratio refluxing in toluene for 6 h in the presence of Et_3N afforded a green colored cycometalated complexes of the composition [Ru(L)(CO)(EPh_3)$_2$] (E = P, As) (L = di-anionic tridentate CNO- ligand (Scheme 1). The oxidation state of ruthenium remains unchanged during the formation of cyclometalated species. The exclusive formation cyclometalated complexes are due to steric hindrance of bulkier ligand which did not allow another (H_2L) within the coordination sphere. The successful ruthenium(II) mediated C–H activation of the biphenyl moiety in the 1-(biphenylazo)phenol ligand (H_2L) and trapping of the resulting CNO- ligated ruthenium(L) fragment by triphenylphosphines/triphenylarsine prompted us to check the feasibility of donor atoms. These complexes are readily soluble in common organic solvents like $CHCl_3$, CH_2Cl_2, CH_3CN and C_6H_6 etc., Preliminary characterization by microanalysis of the isolated complexes supports the expected composition.

The IR spectra of the complexes display a band of azo group ν(N=N) around 1399 cm^{-1} which is slightly lower frequency than that of free 1-(biphenylazo)naphthol ligand (H_2L) 1447 cm^{-1} indicating coordination of azo nitrogen to ruthenium(II) metal ion. The band corresponding to naphtholic ν(C–O) stretching frequency 1275 cm^{-1} in (H_2L) is shifted to higher frequency in the region 1298 cm^{-1} in these complexes is further conforming the coordination of oxygen atom to ruthenium(II) ion. In addition, a strong sharp signal observed at 1903 cm^{-1} has been assigned to carbonyl group ν(C≡O) in these complexes [15]. The IR spectra of the ligand (H_2L) and complexes are given in Figs. S1–S3 (see supplementary material). The UV–Vis spectra of the complexes **1** and **2** in $CHCl_3$ solution exhibited well characteristic absorptions near 450 nm and 700 nm regions. The absorption appears at 450 nm is probably due to MLCT transitions and the intense absorptions in the visible region of 700 nm are attributed to d–d

transitions. Representative UV–Vis spectrum of the complexes **1** and **2** are given in Figs. S4–S5 (see supplementary material**)**.

The ^{1}H NMR spectra of the complexes were recorded in $CDCl_3$. The aromatic protons of the complexes appeared in the range δ = 7.4–6.9 ppm. A sharp singlet appeared for OH proton of 1-(biphenylazo)naphthol ligand in the region δ = 11.9 ppm is absent in these complexes indicating the coordination of oxygen atom. Further, ^{31}P NMR spectrum of complex **1** was recorded to confirm the presence of PPh_3 groups which was observed as a sharp singlet at 29.13 ppm. Therefore, the ^{1}H NMR spectral data of the complexes confirms the coordination of tridentate CNO- donor mode of the 1-(biphenylazo)naphthol ligand to ruthenium(II) ion. Relevant ^{1}H NMR & ^{31}P NMR spectra are given in Figs. S6–S9 (see supplementary material).

Attempts made to obtain a single crystals of complex **1** suitable for X–ray structure determination by recrystallization using chloroform as solvent over a long period of time and in the presence of light resulted in oxidation Ru(II) to Ru(III) (**3)** and the replacement of CO group by Cl ligand (Scheme 1). The molecular structure of **3** is depicted (Fig. 2). Crystal data and structure refinement for molecule **3** is shown (Table S10 see supplementary material). Molecule **3** is a monomer. The ruthenium center in **3** is in distorted octahedral geometry. The coordination environment of ruthenium is satisfied by two PPh_3, one Cl^-, and $\mathbf{L}^{2-}$ ligands. The two PPh_3 groups are in *trans* positions. As shown (Fig. 2) the $\mathbf{L}^{2-}$ ligand is coordinated to the ruthenium metal *via* O, N and C- donors as tridentate fashion. The bond angles for ruthenium metal center at two five membered chelate rings with bite angles of 77.8(4)^{o} for N(1)–Ru(1)–O(1) and 88.15(19)^{o} for Cl(1)–Ru(1)–P(2). The Ru–C(11) bond length is 2.112(13) Å. The Ru–O(1) bond distance is 2.140(8) Å. The Ru–N(1) bond distance is 2.049(9) Å. The Ru–P bond distances are nearly comparable (Ru(1)–P(1), 2.370(3) Å and Ru(1)–P(2), 2.376(3) Å.

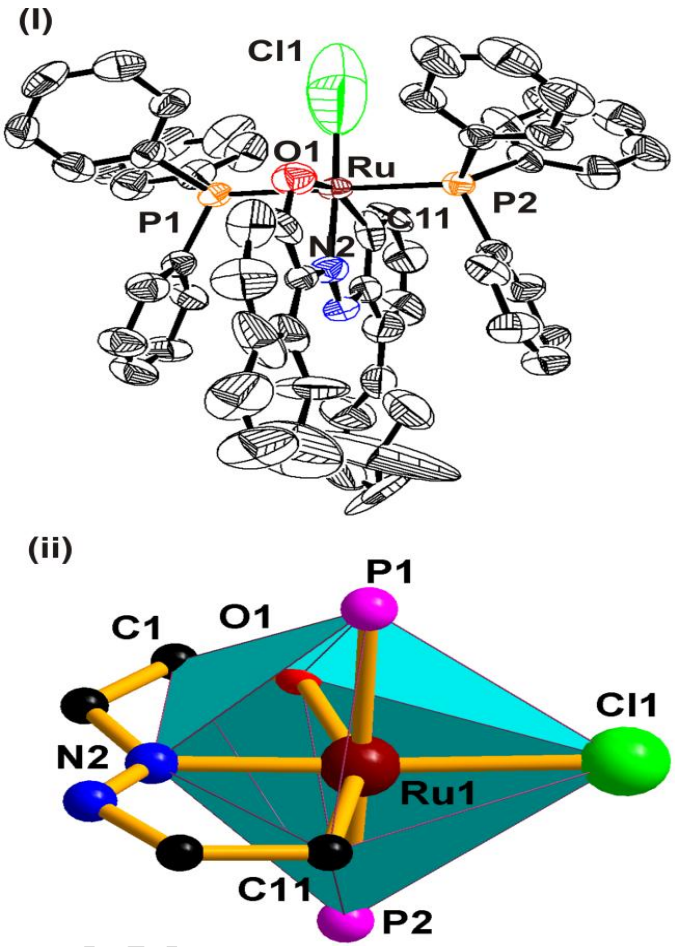
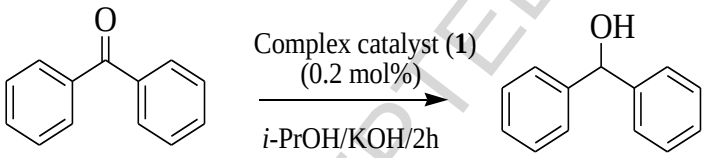


Fig. 2. (I) The molecular structure of **3**. The hydrogen atoms have been omitted for clarity. (II) The core structure of **3**. The non-coordinating atoms were omitted for clarity.

The catalytic transfer hydrogenation of ketones to alcohols using complex **1** was performed in the presence of *i*-PrOH/KOH. In order to prove the optimized reaction conditions, different catalyst: substrate ratios were tested and the results summarized in Table 1. Benzophenone was chosen as a test-substrate to explore the catalytic activity of complex **1**. It was observed that C/S ratio of 1:500 is best compromise for good conversion (99%) under mild optimal reaction conditions. A blank experiment was carried out either in the absence of catalyst

or base gave hydrogenation of benzophenone. According to optimization results, the catalytic transfer hydrogenation involving a variety of aliphatic and aromatic ketones was carried out under inert atmosphere by a mixture containing the ketone (1 mmol), complex catalyst (0.2 mol%) and base (0.005 mmol), heated to reflux for 2 h in 5 mL of *i*-PrOH at 82 ^{o}C. The catalyst was removed from the reaction mixture by the addition of light petroleum followed by filtration and subsequent neutralization with 1M HCl. The ether layer was filtered through a short path of silica gel and condensed under reduced pressure in vacuum to afford corresponding alcohols, conversion of the product was determined by comparison with GC analysis of authentic samples. The conversion of benzophenone to benzhydrol catalyzed by complex **1** versus reaction time was plotted in Fig. 3. The yield of benzhydrol gradually increased to 42% in 0.5 h and reached 99% conversion within 2 h.

Table 1. Effect of catalyst/substrate/base ratio[a]



Entry	Substrate/ catalyst/ base ratios			Time (h)	Conv. (%)	TON[b]
1	1500	1	2.5	12	32	160
2	1000	1	2.5	12	67	335
3	500	1	2.5	2	99	495
4	500	–	2.5	2	–	–
5	500	1	–	2	–	–

[a] Conditions: reactions were carried out at 82 ^{o}C using different catalyst/substrate ratio in 5 mL of isopropanol and KOH.

[b] GC analysis with authentic samples.

[c] TON = ratio of moles of product formed to moles of catalyst used.

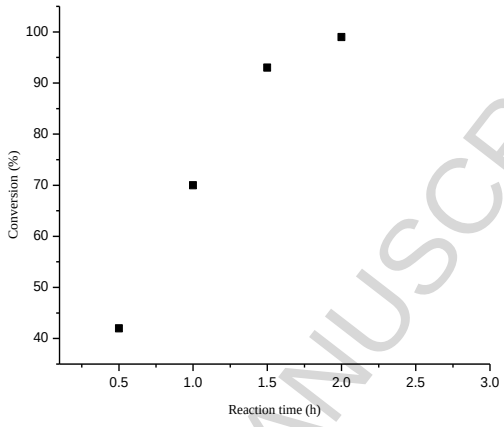
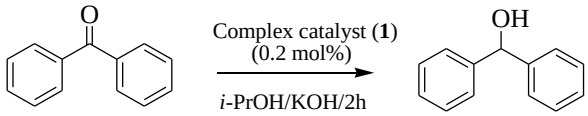


Figure 3. Influence of reaction time on the formation of benzhydrol.

The choice of solvent influences was chosen for the optimization reaction condition. The rates of reaction were strongly dependent on the solvent as it is employed as hydrogen donor. The influence of solvents was investigated by use of methanol, ethanol and isopropanol. As seen (Table 2) the use of isopropanol is found to be efficient one to obtain the maximum conversion of benzhydrol from benzophenone.

Table 2. Effect of solvents[a]



Entry	Solvents	Conv. (%) [b]	TON[c]
1	Methanol	18	90
2	Ethanol	24	120
3	Isopropanol	99	495

[a] Conditions: reactions were carried out at 82 ^{o}C using substrate (1mmol), catalyst (0.2 mol%) in 5 mL of solvents and base (0.005 mmol).

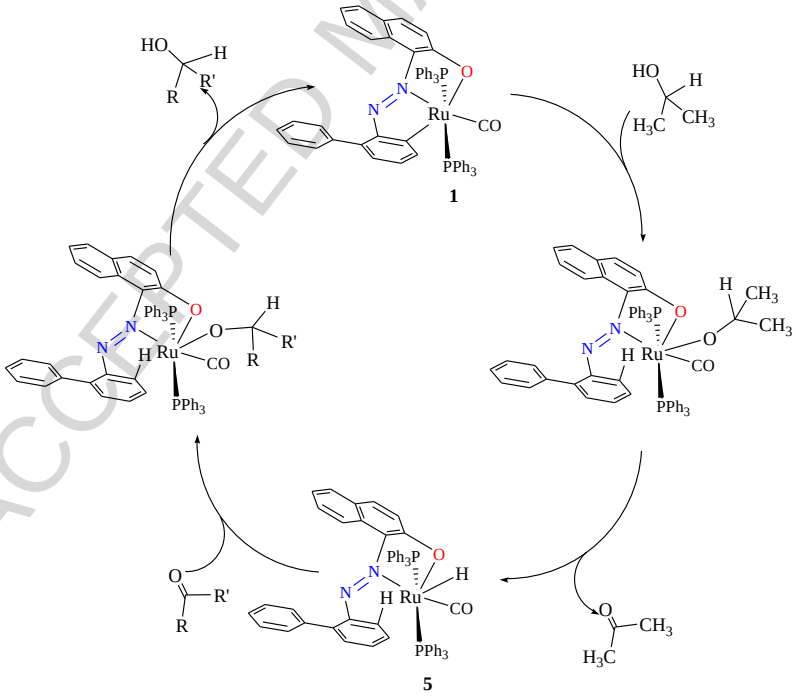
[b] GC analysis with authentic samples.

[c] TON = ratio of moles of product formed to moles of catalyst used.

A plausible mechanism is proposed (Scheme 2) to demonstrate Ru–hydride is the catalytic active species. To support the mechanistic proposal, the complex **1** was refluxed for 2 h with KOH in *i*-PrOH to yield the complex **5**. The ^{1}H NMR spectrum of this complex shows a triplet at δ = -8.5 ppm, indicating the presence of Ru–H bond in the complex **5** (Fig. S11 see supplementary material). The results of the catalytic activity are shown (Table 3). The complex **1** catalyze the ketones to corresponding alcohols with good to excellent conversion (>90%) in most cases within 2 h with TON/TOF value up to 495/247 h^{-1} (entry 2). Electron withdrawing group present in the aryl ring of acetophenone increases the rate of the reaction (entry 5–7) whereas donating group (entry 3 and 4) decrease it reasonably. Further, benzophenone is reduced into corresponding alcohol up to 99% conversion. In addition, the complex efficiently catalyzes the

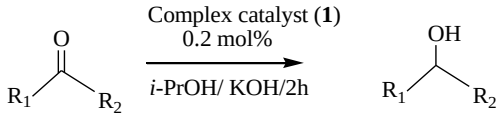
reduction of five, six-membered cyclic and aliphatic ketones into the corresponding alcohols up to 98% conversion.

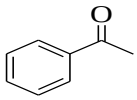
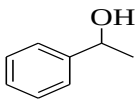
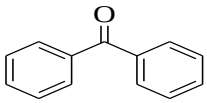
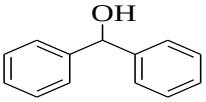
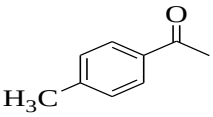
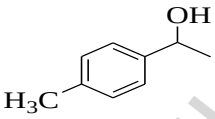
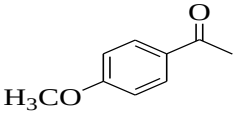
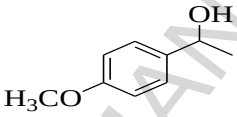
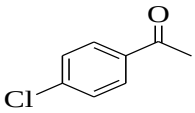
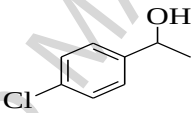
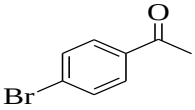
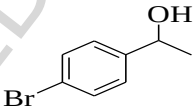
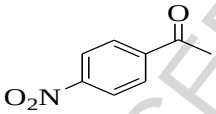
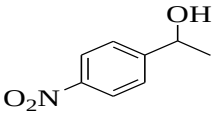
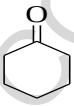
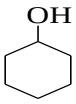
The work up process is very simple for this catalytic system as the catalyst is stable in all organic solvents and it can be recovered. L. T. Ghoochany *et al.*[16] reported that ruthenium complex containing symmetrical NNN– donors and CO ligand shows no catalytic activity for transfer hydrogenation reaction and it is due to unavailability of labile PPh_3 ligands. Further, the present catalytic system exhibited remarkably high catalytic activity when compared to the catalytic activity of the catalyst **B** (Fig. 1) containing CNN– donor ligand and other ruthenium complexes [17] under similar conditions. The enhancement of the catalytic activity of the present complex **1** is may be due to the unsymmetrical environment around the metal center by the tridentate CNO- donor ligand in addition to labile PPh_3 ligands.



Scheme 2. Probable mechanism for the observed transfer hydrogenation by the complex $[Ru(L)(CO)(PPh_3)_2]$ (**1**).

Table 3. Transfer hydrogenation of ketones using [Ru(L)(CO)(PPh_3)$_2$] (**1**)[a].



Entry	Substrates	Products	Conv. (%)	TON[b]	TOF[c]
1			96	480	240
2			99	495	247
3			78	390	195
4			76	380	190
5			91	485	242
6			89	445	222
7			90	450	225
8			92	460	230
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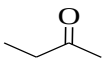
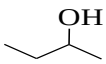
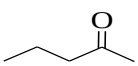
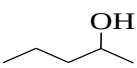
10			92	460	230
11			98	490	245

[a] Conditions: reactions were carried out at 82 ^{o}C using 1 mmol of ketone, 0.2 mol% catalyst in 5 mL *i*-PrOH.

Catalyst/substrate/KOH ratio is 1:500:2.5.

Conversion was determined by GC analysis with an authentic samples.

[b] TON = ratio of moles of product formed to moles of catalyst used.

[c] TOF = TON/h.

In conclusion, the ruthenium precursor [RuHCl(CO)(PPh_3)$_3$] and [RuHCl(CO)($AsPh_3$)$_3$] are effectively mediates C–H activation of 1-(biphenylazo)naphthol and two new cyclometalated ruthenium(II) complexes have been obtained. The characterization of the complexes was accomplished by analytical, spectral (FT–IR, UV–Vis, ^{1}H NMR and ^{31}P NMR) and single crystal XRD analysis. Ruthenium complex **1** was investigated as catalyst and turned out to be efficient catalyst for the transfer hydrogenation of various ketones.

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Supplementary data

The experimental section, single crystal X-ray study, crystal data and structure refinement parameters for the molecule **3**, FT-IR, UV-Vis, ^{1}H NMR and ^{31}P NMR spectra of the ligand and complexes are associated with this article. CCDC 1530992 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

Graphical Abstract

Ru(II) mediated C–H activation of 1-(biphenylazo)naphthol: Synthesis and catalytic evaluation for transfer hydrogenation of ketones

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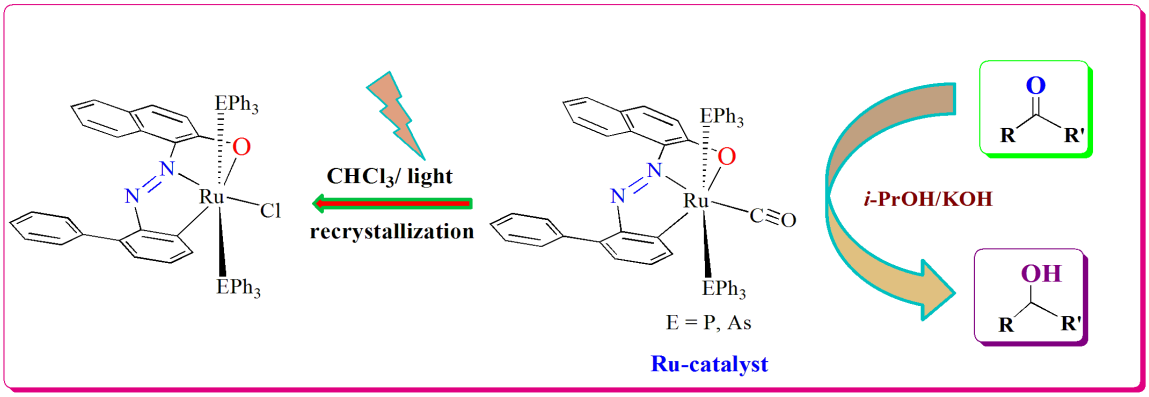

Highlights

- New air stable of Ru(II) 1-(biphenylazo)naphtholate complexes has been reported.
- Carbonyl group replaced by using $CHCl_3$/light, recrystallization method.
- Structure of the complex was confirmed by single crystal XRD.
- Synthesized complex as efficient catalyst (0.2 mol%) for transfer hydrogenation.