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Ruthenium(II) carbonyl complexes bearing quinoline-based NNO tridentate ligands as catalyst for one-pot conversion of aldehydes to amides and *o*-allylation of phenols

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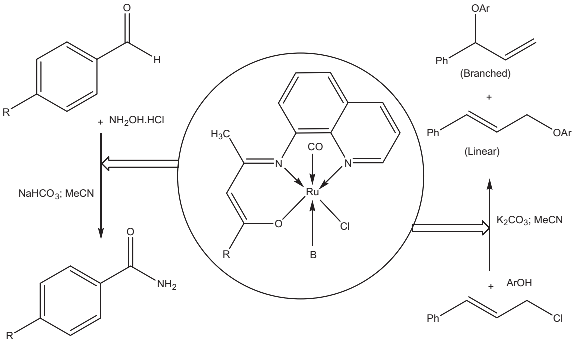
HIGHLIGHTS

- Six new Ru(II) carbonyl complexes with quinoline based ligands were synthesized.
- Spectral and elemental data have used to prove the binding modes in complexes.
- Catalytic efficiency of the complexes in aldehyde to amide reaction was evaluated.
- The complexes have used as catalyst for the synthesis of allyl aryl ethers.

GRAPHICAL ABSTRACT

Ruthenium(II) carbonyl complexes containing quinoline based NNO tridentate ligands were synthesized and characterized. They have been assigned an octahedral structure. The new complexes were found to be efficient catalyst for aldehydes to amides and *o*-allylation of phenols.



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ABSTRACT

Six new octahedral ruthenium(II) carbonyl complexes having the general molecular formula [RuCl(CO)(B)L^{1-2}] (B = PPh_3, $AsPh_3$ or py; L^{1-2} = quinoline based NNO ligand) were synthesized. The quinoline based ligands behave as monoanionic tridentate donor and coordinated to ruthenium via ketoenolate oxygen, azomethine nitrogen and quinoline nitrogen. The composition of the complexes has been established by elemental analysis and spectral methods (FT-IR, electronic, ^1H NMR, ^{13}C NMR, ^{31}P NMR and ESI-Mass). The complexes were used as efficient catalysts for one-pot conversion of various aldehydes to their corresponding primary amides in presence of $NH_2OH{\cdot}HCl$ and $NaHCO_3$. The effect of catalyst loading and reaction temperature on catalytic activity of the ruthenium(II) carbonyl complexes were also investigated. The synthesized complexes also possess good catalytic activity for the *o*-allylation of phenols in the presence of K_2CO_3 under mild conditions. The complexes afforded branched allyl aryl ethers according to a regioselective reaction.

Introduction

A large number of transition metal complexes with a variety of acyclic [1–3] and macrocyclic [4–6] Schiff bases have been prepared and studied extensively. The central metal in these complexes act as active sites and thereby successfully catalyze chemical reactions [7,8]. The Schiff base transition metal complexes are a family of attractive oxidation catalysts for a variety of organic substrates because of their cost effective synthesis, chemical and thermal stability. They are also used to catalyze transformation of simple organic substrates to functionalised

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derivatives of commercial and synthetic interest [9–12]. Among the transition metal complexes, the synthesis of ruthenium(II) complexes containing oxygen and nitrogen donor Schiff base is of significant importance due to their multi-electron transfer properties, ability to have a wide range of oxidation states and potential catalytic activity [13–15]. In particular, triphenylphosphine and triphenylarsine ligands are known to stabilize the lower oxidation states of ruthenium in their carbonyl complexes [16].

Amides are one of the most important and prolific functional groups, with a great importance in both research and industrial chemistry due to their prevalence in detergents, lubricants, biologically active compounds and pharmaceuticals [17]. Although, there are many strategies to prepare them, enormous amount of wastes generated by the standard protocols forces the industry to look forward for better strategies [18]. The Beckmann type rearrangement [19] is a very efficient approach for the preparation of amides. In fact, about 3.8 million tons per year of ε-caprolactam is produced through this process, starting from the corresponding ketoximine [20]. The similar reaction with aldoximes is, however, more challenging [21], with the dehydration reaction to give nitriles being the main process.

Besides all aforementioned drawbacks, Raney's nickel transformation of aldoximes to amides was introduced as early as 1937 [22]. The other organometallics being recently tested in a similar protocol, including those derived from boron [23], nickel [24], copper [24,25], ruthenium [26], rhodium [27], palladium [28] and bimetallic species containing cobalt–zinc [29] and silver–gold [30] combinations. However, the preparation of starting aldoxime usually needed stoichiometric amounts of acids, as catalyst, and use of hydroxylamine reagent in large excess, therefore, this approach had still possibilities to be improved [31]. In fact, the direct one-pot protocol, starting from nearly equimolecular amounts of aldehydes and hydroxylammonium derivatives, has been recently introduced, using catalysts derived from copper [32], zinc, indium [33], ruthenium [34], rhodium [35] and palladium [36].

Aryl ethers are common subunits of biologically active molecules. A part from their use as precursors for the Claisen rearrangement [37,38], aryl allyl ethers have not been used extensively as building blocks for natural product synthesis because methods for their enantioselective construction are limited. Two reports of stereospecific allylic etherification of branched carbonates catalyzed by Ru [39] and Rh [40,41] were reported, and a few enantioselective palladium-catalyzed examples have also been reported [42,43]. Elegant applications of the palladium-catalyzed chemistry for the synthesis of natural products demonstrate the potential of asymmetric allylic etherification in organic synthesis [44]. Thus, new, more general, regioselective methods for the construction of allylic ethers would be synthetically valuable.

In contrast to the considerable growth of literature on the chemistry of quinoline based Schiff base complexes, to the best of our knowledge there are no reports available for catalytic transformation of aldehydes to amides and *o*-allylation of phenols by ruthenium(II) carbonyl complex containing quinoline based Schiff base ligand. Hence in continuation of our research on the synthesis and catalytic applications of ruthenium(II) and ruthenium(III) complexes [45,46] and in view of interesting coordination modes of quinoline-based NNO ligands with ruthenium metal complexes, we herein describe new ruthenium(II) carbonyl complexes with substituted 8-aminoquinoline diketone ligands incorporated with chloride and PPh_3/$AsPh_3$/pyridine as ancillary ligands. All the complexes have been characterized by analytical and spectral methods. The applications of these complexes as homogeneous catalyst for the one pot conversion of aldehydes to corresponding primary amides using $NH_2OH{\cdot}HCl$ and *o*-allylation of phenols were also investigated.

Experimental

Materials and methods

All the reagents used were chemically pure and AR grade. The solvents were purified and dried according to standard procedures [47]. $RuCl_3{\cdot}3H_2O$ was purchased from Loba Chemie Pvt Ltd., India. The starting complexes $[RuHCl(CO)(PPh_3)_3]$, $[RuHCl(CO)(PPh_3)_2(Py)]$ and $[RuHCl(CO)(AsPh_3)_3]$ were prepared according to the literature methods [48–50]. Microanalyses of carbon, hydrogen and nitrogen were carried out using Vario EL III Elemental analyzer at SAIF – Cochin India. The IR spectra of the ligands and their complexes were recorded as KBr pellets on a Nicolet Avatar model spectrophotometer in 4000–400 cm^{-1} range. Electronic spectra of the ligands and their complexes have been recorded in dichloromethane using a Shimadzu UV-1650 PC spectrophotometer in 800–200 nm range. ^1H, ^{13}C and ^{31}P NMR spectra were recorded in Jeol GSX-400 instrument using DMSO-d_6 as the solvent. ^1H NMR and ^{13}C NMR spectra were obtained at room temperature using TMS as the internal standard. ^{31}P NMR spectra of the complexes were obtained at room temperature using *o*-phosphoric acid as a reference. The ESI-MS spectra were recorded by LC-MS Q-ToF Micro Analyzer (Shimadzu) in the SAIF, Panjab University, Chandigarh. Melting points were recorded on a Technico micro-heating table and are uncorrected. The catalytic yields were determined using ACME 6000 series GC-FID with DP-5 column of 30 m length, 0.53 mm diameter and 5.00 μm film thickness.

General procedure for the preparation of quinoline based ligands (HL^{1-2})

8-Aminoquinoline (0.4 g, 2.8 mmol), pentane-2, 4-dione (0.56 mL, 5.6 mmol) or 1-phenyl-1, 3-butanedione (0.45 g, 2.8 mmol), activated molecular sieves (0.5 g), toluene (20 mL) and 7 drops of formic acid were added to a flask equipped with magnetic stirring bar. The mixture was refluxed under stirring for 40 h and then cooled to room temperature. The molecular sieves were filtered off and washed with toluene (3 × 10 mL). The combined organic solution was washed with saturated brine and water successively and then dried over $NaSO_4$. The $NaSO_4$ was removed by filtration and volatiles were removed from the filtrate by rotary evaporation to give yellow powder. Recrystallisation of the solid from mixture of dichloromethane and n-hexane generated pale yellow crystals [51].

Compound HL^1

Yield: 0.50 g (79%), yellow, m.p. 80 °C. Anal. Calcd for $C_{14}H_{14}N_2O$:C 74.31; H 6.23; N 12.38%. Found:C 74.82; H 6.26; N 12.90%. IR (KBr, cm^{-1}):1692 (C=O), 1662 (C=N), 1596 (ring C=N). UV (λmax, CH_2Cl_2):390, 310, 250. ^1H NMR (400 MHz, DMSO-d_6, δ, ppm):13.24 (s, 1H, OH), 8.94–8.93 (d, *J* = 4.8 Hz, 1H, Ar), 8.41–8.38 (d, *J* = 8.4 Hz, 1H, Ar), 7.71–7.54 (m, 4H, Ar), 5.37 (s, 1H, CH), 2.27 (s, 3H, CH_3), 2.05 (s, 3H, CH_3).

Compound HL^2

Yield: 0.61 g (76%), yellow, m.p. 120 °C. Anal. Calcd for $C_{19}H_{16}N_2O$:C 79.14; H 5.59; N 9.71%. Found:C 78.78; H 5.62; N 9.73%. IR (KBr, cm^{-1}): 1694 (C=O), 1663 (C=N), 1595 (ring C=N) UV (λmax, CH_2Cl_2):384, 305, 253. ^1H NMR (400 MHz, DMSO-d_6, δ, ppm):10.78 (s, 1H, OH), 8.94–8.92 (d, *J* = 9.2 Hz, 1H, Ar), 8.67–8.65 (d, *J* = 7.2 Hz, 1H, Ar), 8.59–7.52 (m, 9H, Ar), 6.57 (s, 1H, CH), 2.19 (s, 3H, CH_3).

General procedure for synthesis of new ruthenium(II) carbonyl complexes

All new metal complexes were synthesized according to following general procedure. To a solution of $[RuHX(CO)(EPh_3)_2(B)]$ (X = H or Cl; E = P or As; B = PPh_3, $AsPh_3$ or Py) (0.0769 g–0.1084 g; 0.1 mmol) in benzene (20 mL), the appropriate ligand (0.0226 g–0.0288 g; 0.1 mmol) was added in 1:1 M ratio. The mixture was heated under reflux for 7 h on water bath. Then the resulting solution was concentrated to 3 mL and the product precipitated by the addition of small amount of petroleum ether (60–80 °C). The resulting complexes were recrystallized from CH_2Cl_2/petroleum ether and dried under vacuum.

$[RuCl(CO)(PPh_3)(L^1)]$ **1**

Yield: 0.52 g (79%), Green, m.p. 270 °C. Anal. Calcd for $C_{33}H_{28}ClN_2O_2PRu$:C 60.78; H 4.33; N 4.30%. Found:C 60.82; H 4.53; N 4.80%. IR (KBr, cm^{-1}):1963 ($C{\equiv}O$), 1620 ($C{=}N$), 1570 (ring $C{=}N$), 1373 ($C{-}O$). UV (λmax, CH_2Cl_2):423, 352, 255, 232. ^1H NMR (400 MHz, DMSO-d_6, δ, ppm):8.92–8.91 (d, J = 4.4 Hz, 1H, Ar), 8.62–8.60 (d, J = 8.0 Hz, 1H, Ar), 8.39–7.16 (m, 19H, Ar), 5.52 (s, 1H, CH), 1.38 (s, 3H, CH_3), 1.23 (s, 3H, CH_3). ^{13}C NMR (400 MHz,DMSO-d_6, δ, ppm):204.84 ($C{\equiv}O$), 198.78 ($C{-}O$), 175.75 ($C{=}N$), 136.59–122.21 (m, ArC), 102.87 (CH), 28.54 (CH_3), 22.48 (CH_3). ^{31}P NMR (400 MHz, $CDCl_3$, δ, ppm):22.35. MS (ESI), m/z = 652.9 [M^+].

*$[RuCl(CO)(PPh_3)(L^2)]$***2**

Yield: 0.53 g (75%), Green, m.p. 246 °C. Anal. Calcd for $C_{38}H_{30}ClN_2O_2PRu$:C 63.91; H 4.23; N 3.93%. Found:C 63.42; H 4.16; N 3.92%. IR (KBr, cm^{-1}):1960 ($C{\equiv}O$), 1620 ($C{=}N$), 1569 (ring $C{=}N$), 1373 ($C{-}O$). UV (λmax, CH_2Cl_2):426, 309, 262, 231. ^1H NMR (400 MHz, DMSO-d_6, δ, ppm):8.62–8.61 (d, J = 4.2 Hz, 1H, Ar), 8.0–7.98 (d, J = 8.0 Hz, 1H, Ar), 7.85–6.82 (m, 24H, Ar), 6.21 (s, 1H, CH), 2.16 (s, 3H, CH_3). ^{13}C NMR (400 MHz, DMSO-d_6, δ, ppm):208.12 ($C{\equiv}O$), 196.36 ($C{-}O$), 168.25 ($C{=}N$), 138.52–125.62 (m, ArC), 102.22 (CH), 28.34 (CH_3). ^{31}P NMR (400 MHz, $CDCl_3$, δ, ppm): 22.73. MS (ESI), m/z = 714.9 [M^+].

*$[RuCl(CO)(Py)(L^1)]$***3**

Yield: 0.32 g (70%), Green, m.p. 166 °C. Anal. Calcd for $C_{20}H_{18}ClN_3O_2Ru$:C 51.23; H 3.87; N 8.96%. Found:C 51.73; H 3.76; N 8.91%. IR (KBr, cm^{-1}):1944 ($C{\equiv}O$), 1615 ($C{=}N$), 1560 (ring $C{=}N$), 1373 ($C{-}O$). UV (λmax, CH_2Cl_2):415, 380, 262, 231. ^1H NMR (400 MHz, DMSO-d_6, δ, ppm):8.96–8.95 (d, J = 6.8 Hz, 1H, Ar), 8.58–8.57 (d, J = 3.2 Hz, 1H, Ar), 8.23–6.98 (m, 9H, Ar), 5.91 (s, 1H, CH), 1.38 (s, 3H, CH_3), 1.28 (s, 3H, CH_3). ^{13}C NMR (400 MHz,DMSO-d_6, δ, ppm): 206.43 ($C{\equiv}O$), 191.87 ($C{-}O$), 178.25 ($C{=}N$), 137.29–121.82 (m, ArC), 102.78 (CH), 27.92 (CH_3), 25.23 (CH_3). MS (ESI), m/z = 468.1 [M^+].

*$[RuCl(CO)(Py)(L^2)]$***4**

Yield: 0.37 g (71%), Green, m.p. 154 °C. Anal. Calcd for $C_{25}H_{20}ClN_3O_2Ru$: C 56.55; H 3.80; N 7.91%. Found: C 56.70; H 3.40; N 7.42%. IR (KBr, cm^{-1}): 1943 ($C{\equiv}O$), 1604 ($C{=}N$), 1580 (ring $C{=}N$), 1373 ($C{-}O$). UV (λmax, CH_2Cl_2): 400, 316, 257, 229. ^1H NMR (400 MHz, DMSO-d_6, δ, ppm): 8.56–8.55 (d, J = 6.4 Hz, 1H, Ar), 8.34–8.33 (d, J = 4.8 Hz, 1H, Ar), 8.60–6.83 (m, 24H, Ar), 5.82 (s, 1H, CH), 1.28 (s, 3H, CH_3). ^{13}C NMR (400 MHz, DMSO-d_6, δ, ppm):206.52 ($C{\equiv}O$), 183.65 ($C{-}O$), 174.39 ($C{=}N$), 133.56–127.69 (m, ArC), 104.23 (CH), 26.67 (CH_3). MS (ESI), m/z = 530.1 [M^+].

$[RuCl(CO)(AsPh_3)(L^1)]$ **5**

Yield: 0.50 g (73%), Green, m.p. 280 °C. Anal. Calcd for $C_{33}H_{28}ClN_2O_2AsRu$:C 56.95; H 4.05; N 4.03%. Found:C 56.56; H 4.23; N 4.52%. IR (KBr, cm^{-1}):1963 ($C{\equiv}O$), 1618 ($C{=}N$), 1571 (ring $C{=}N$), 1374 ($C{-}O$). UV (λmax, CH_2Cl_2):436, 348, 256, 231. ^1H NMR (400 MHz, DMSO-d_6, δ, ppm): 8.94–8.93 (d, J = 4.2 Hz, 1H, Ar), 8.68–8.65 (d, J = 8.8 Hz, 1H, Ar), 8.59–6.98 (m, 19H, Ar), 5.75 (s, 1H, CH), 2.01 (s, 3H, CH_3), 1.38 (s, 3H, CH_3). ^{13}C NMR (400 MHz,DMSO-d_6, δ, ppm):205.23 ($C{\equiv}O$), 193.57 ($C{-}O$), 172.24 ($C{=}N$), 138.95–128.31 (m, ArC), 101.02 (CH), 30.96 (CH_3), 22.07 (CH_3). MS (ESI), m/z = 698.1 [M^+].

*$[RuCl(CO)(AsPh_3)(L^2)]$***6**

Yield: 0.56 g (75%), Green, m.p. 176 °C. Anal. Calcd for $C_{38}H_{30}ClN_2O_2AsRu$:C 60.20; H 3.99; N 3.70%. Found:C 60.22; H 3.72; N 3.58%. IR (KBr, cm^{-1}):1955 ($C{\equiv}O$), 1621 ($C{=}N$), 1571 (ring $C{=}N$), 1373 ($C{-}O$). UV (λmax, CH_2Cl_2):465, 390, 254, 231. ^1H NMR (400 MHz, DMSO-d_6, δ, ppm):8.66–8.65 (d, J = 4.4 Hz, 1H, Ar), 8.16–8.13 (d, J = 8.4 Hz, 1H, Ar), 8.0–6.96 (m, 24H, Ar), 6.02 (s, 1H, CH), 2.19 (s, 3H, CH_3). ^{13}C NMR (400 MHz, DMSO-d_6, δ,ppm):204.75 ($C{\equiv}O$), 189.75 ($C{-}O$), 168.37 ($C{=}N$), 138.72–124.33 (m, ArC), 103.50 (CH), 28.56 (CH_3). MS (ESI), m/z = 758.0 [M^+].

Catalytic conversion of aldehydes to amides

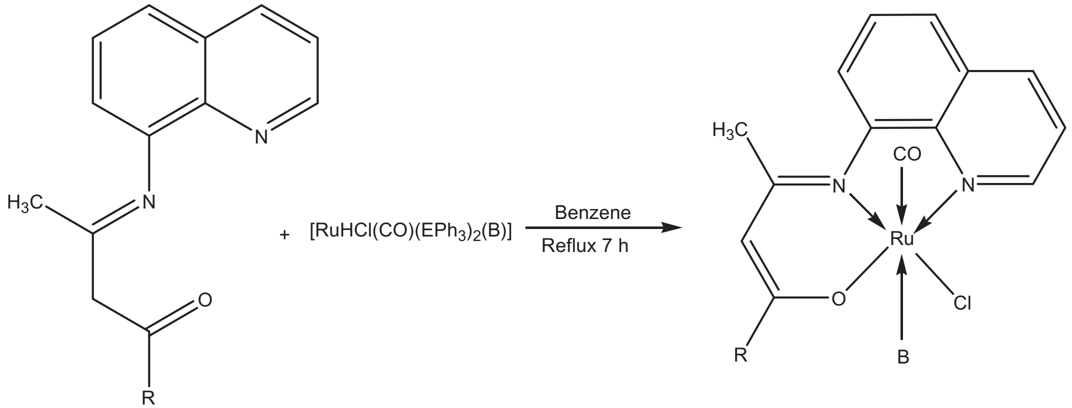
Catalytic conversion of aldehydes into their corresponding amides was carried out by ruthenium(II) carbonyl complexes as catalyst in the following general procedure. The reaction vessel was charged with aldehyde (2 mmol), $NH_2OH{\cdot}HCl$ (2 mmol), $NaHCO_3$ (2 mmol) and ruthenium catalyst (0.01 mmol) and the mixture was placed under an atmosphere of nitrogen. About 4 mL of dry and degassed toluene was added and the mixture was stirred for 15 min at room temperature followed by reflux for 10 h. On completion of the reaction, 2–3 mL methanol was added to the mixture followed by filtration through Celite to remove catalyst and $NaHCO_3$. The filtrate was subjected to GC analysis and the product was identified and determined with authentic samples.

o-Allylation of phenols

A 0.3 mL (2 mmol) of cinnamyl chloride was added to a mixture consisting of 0.42 g (3 mmol, 1.5 equivs.) of K_2CO_3, 0.023–0.038 g (0.05 mmol) of ruthenium(II) carbonyl complex, and acetonitrile (12 mL). Then, phenol (3 mmol, 1.5 equivs.) was added and the mixture was stirred at room temperature for 40 h. The resulting slurry was evaporated under vacuum and the residue was extracted with dichloromethane (20 mL). The collected solution was filtered. Small amount of NaH was added to the filtrate (to trap residual phenol) until evolution of gas ceased and the solution was filtered again. The filtrate was evaporated under vacuum to leave pale brown oil consisting mixture of expected branched 1-phenyl-1-phenoxy-2-propene and linear aryl ethers, as determined by ^1H NMR spectroscopy [52].

Results and discussion

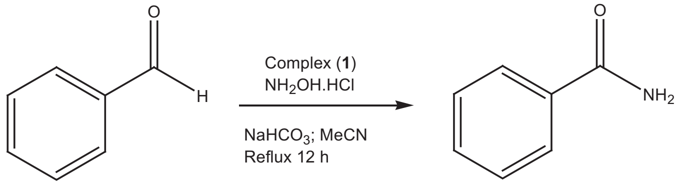
Diamagnetic, hexa-coordinated low spin ruthenium(II) carbonyl complexes of general formula $[RuCl(CO)(B)(L^{1-2})]$ (B = PPh_3, $AsPh_3$ or Py; L^{1-2} = quinoline based NNO ligand) were synthesized in quantitative yield from the reaction of $[RuHCl(CO)(EPh_3)_2(B)]$ (E = P or As; B = PPh_3, $AsPh_3$ or Py) with quinoline ligands in dry benzene in 1:1 M ratio (Fig. 1). In all these reactions, it was observed that the quinoline based NNO ligands behaved as mononegative tridentate ligands by replacing two molecules of triphenylphosphine or triphenylarsine and one molecule of hydride from the starting complexes. All the complexes are green in color, air stable in both solid and liquid states at room temperature and are nonhygroscopic. The synthesized ruthenium(II) complexes are highly soluble in commonly used solvents such as benzene,



R = CH_3 (L^1) or C_6H_5 (L^2); E = P or As; B = PPh_3, $AsPh_3$ or py

Fig. 1. Schematic representation of synthesis of complexes.

Table 1
Effect of catalyst loading in the one-pot conversion of benzaldehyde to benzamide using complex (**1**).[a]



Entry	Amount of complex (**1**) (mmol)	Yield (%)[b]
1	Absence of catalyst	2
2	0.005	24
3	0.0075	52
4	0.01	89
5	0.02	91
6	0.03	93

[a] Reaction conditions: complex (**1**), benzaldehyde (2 mmol), $NH_2OH.HCl$ (2 mmol) and $NaHCO_3$ (2 mmol) in MeCN (4 mL) refluxed for 12 h under an N_2 atmosphere.
[b] The conversion is determined by GC.

toluene, chloroform, dichloromethane, acetonitrile, dimethyl formamide, and dimethyl sulfoxide, producing intense colored solutions. The analytical data of all the ruthenium(II) carbonyl complexes are in good agreement with the molecular structure as proposed.

Infrared spectroscopic analysis

The FT-IR spectra of the ligands, showed no significant peak in the region of 3100–3250 cm^{-1} corresponds to free -NH_2 group of quinoline indicated that the formation of Schiff base ligands by the condensation of amine with diketones [53]. The formation of Schiff base ligands is also be confirmed by the presence of a peak in the region 1662–1663 cm^{-1} due to azomethine (>C=N) group. This band has been shifted to lower frequencies (1604–1621 cm^{-1}) in metal complexes showed that the coordination of the ligand to ruthenium through the azomethine nitrogen atom. The band due to C=O appeared around 1692–1694 cm^{-1} in the free ligands have disappeared and new band appeared around 1373–1374 cm^{-1} (C—O) on complexation. These observation attributed to ketoenolization of the —CH_2—C=O group and subsequent coordination through the deprotonated oxygen. The band appeared around 1595–1596 cm^{-1} in ligands are assigned to C=N group of quinoline. This band has been shifted to lower frequencies around 1560–1580 cm^{-1} in metal complexes indicated that the third coordination is through quinoline nitrogen. Hence, from the infrared spectroscopic data, it was inferred that azomethine, enolic oxygen and quinoline nitrogen atoms are involved in the coordination of the tridentate Schiff bases to ruthenium ion in all the complexes. Further the strong absorption around the 1943–1963 cm^{-1} has been assigned to the terminally coordinated carbonyl group in the new ruthenium complexes [54]. In the case of complexes containing coordinated heterocyclic nitrogen bases [55], a medium intensity band was observed in the region 1028–1029 cm^{-1}.

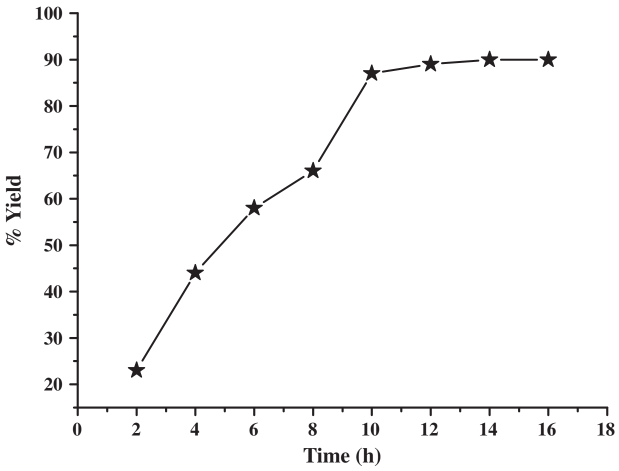
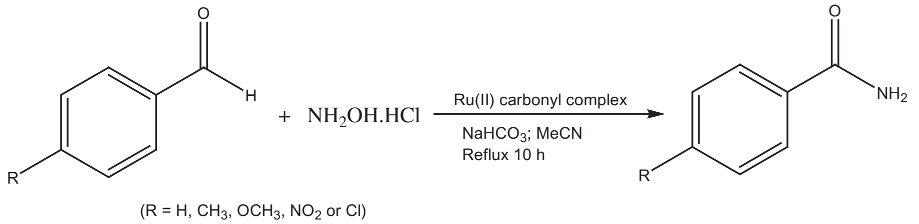


Fig. 2. Effect of reaction time on the yield of benzaldehyde to benzamide. Reaction conditions: benzaldehyde (2 mmol), $NH_2OH{\cdot}HCl$, $NaHCO_3$ (2 mmol), complex **1** (0.01 mmol) and solvent (4 mL) were refluxed under an N_2 atmosphere.

Table 2
One-pot conversion of aldehydes to amides using various ruthenium(II) complexes as catalyst.



Complex	Aldehydes	Amides	Yield (%)[a]
1	Benzaldehyde	Benzamide	87
	4-Methylbenzaldehyde	4-Methylbenzamide	80
	4-Methoxybenzaldehyde	4-Methoxybenzamide	78
	4-Nitrobenzaldehyde	4-Nitobenzamide	91
	4-Chlorobenzaldehyde	4-Chlorobenzamide	89
2	Benzaldehyde	Benzamide	84
	4-Methylbenzaldehyde	4-Methylbenzamide	78
	4-Methoxybenzaldehyde	4-Methoxybenzamide	74
	4-Nitrobenzaldehyde	4-Nitobenzamide	90
	4-Chlorobenzaldehyde	4-Chlorobenzamide	86
3	Benzaldehyde	Benzamide	73
	4-Methylbenzaldehyde	4-Methylbenzamide	69
	4-Methoxybenzaldehyde	4-Methoxybenzamide	63
	4-Nitrobenzaldehyde	4-Nitobenzamide	82
	4-Chlorobenzaldehyde	4-Chlorobenzamide	77
4	Benzaldehyde	Benzamide	72
	4-Methylbenzaldehyde	4-Methylbenzamide	66
	4-methoxybenzaldehyde	4-methoxybenzamide	60
	4-Nitrobenzaldehyde	4-Nitobenzamide	80
	4-Chlorobenzaldehyde	4-Chlorobenzamide	75
5	Benzaldehyde	Benzamide	81
	4-Methylbenzaldehyde	4-Methylbenzamide	76
	4-methoxybenzaldehyde	4-methoxybenzamide	71
	4-Nitrobenzaldehyde	4-Nitobenzamide	88
	4-Chlorobenzaldehyde	4-Chlorobenzamide	84
6	Benzaldehyde	Benzamide	79
	4-methylbenzaldehyde	4-methylbenzamide	73
	4-methoxybenzaldehyde	4-methoxybenzamide	68
	4-Nitrobenzaldehyde	4-Nitobenzamide	85
	4-Chlorobenzaldehyde	4-Chlorobenzamide	80

[a] GC yield based on the amount of amides.

Electronic spectroscopic analysis

The absorption spectra of all the complexes in dichloromethane at room temperature showed three to four bands in the region 229–465 nm. The high intensity bands in the region 229–390 nm were assignable to ligand-centred (LC) transitions and have been designated as π–π^* (phenyl ring) and n–π^* (azomethine (C=N)) transitions. In all the complexes the lowest energy bands observed in the region 400–465 nm were attributed to the Ru(dπ) → L(π^*) metal to ligand charge transfer (MLCT) transitions [54]. The fact that there is essentially no variation in the energy of the MLCT band suggested that the energy gap between the metal-dπ and the ligand-π^* levels remains constant despite the variation of the substituent in the complexes. The pattern of the electronic spectra of all the complexes indicated the presence of an octahedral environment around the ruthenium(II) ion, similar to that of other octahedral ruthenium(II) complexes [56].

^{1}H NMR spectroscopic analysis

^{1}H NMR spectra of the ligands and their complexes were recorded to confirm the coordinating modes of the ligands. The spectra of free ligands have shown signal at δ 10.28–13.24 which is characteristic signal of —OH proton, which is absent in the complexes suggesting the coordination through deprotonated oxygen. The multiplets at δ 6.02–8.94 for all the complexes and ligands are assigned to aromatic protons. The peak appeared commonly at δ 5.37–6.57 in both the ligands and complexes have been assigned to (—CH=C—) group. In addition, methyl protons appeared in the region δ 1.23–2.27. The new complexes did not show any signals in the upfield region at δ −5 to −12, confirmed the removal of hydride from the starting complexes. The above observations made it clear that the quinoline based NNO donor Schiff base ligands coordinated with ruthenium ion in all the complexes.

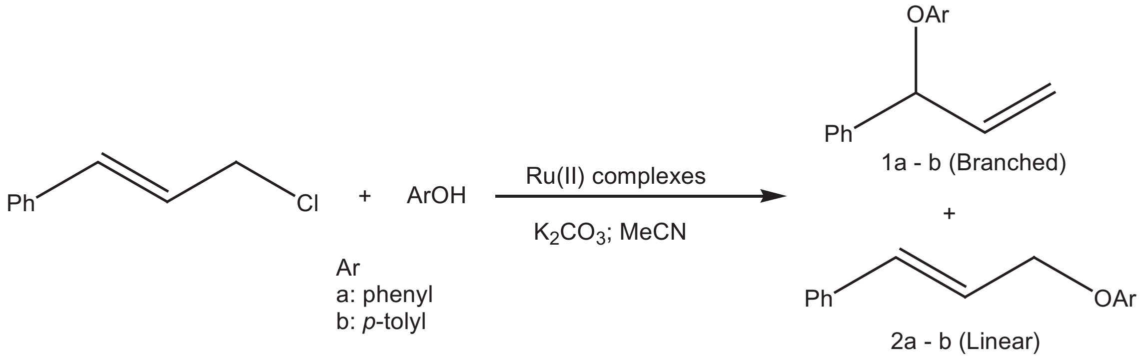
^{13}C NMR spectroscopic analysis

The appearance of peak at 204.75–208.12 ppm region is due to carbonyl carbon (—C≡O). The azomethine carbon (—CH=N—) has shown their signal around 168.25–178.25 ppm region. The peak at 183.65–198.78 ppm has been assigned to (=C—O—) carbon. The multiplets at 121.82–138.95 ppm region were assigned to aromatic carbons. The singlet around 101.02–104.23 ppm region which can be assigned to (—CH=C) carbon. The methyl carbon appeared in the region 22.07–30.96 ppm.

^{31}P NMR spectroscopic analysis

^{31}P NMR spectra of some of the complexes were recorded to confirm the presence of triphenylphosphine group in the complexes. A sharp singlet was observed around 22.35–22.73 ppm due to presence of triphenylphosphine ligand in the complexes.

Table 3
o-Allylation of phenols from cinnamyl chloride using various ruhenium(II) carbonyl complexes as catalyst.



Complex	Allylic chloride	ArOH	Products	Yield (%)[a,b]	B/L[b]
1	Cinnamyl chloride	Phenol	1a, 2a	72	98/2
	Cinnamyl chloride	*p*-Cresol	1b, 2b	75	89/11
2	Cinnamyl chloride	Phenol	1a, 2a	64	90/10
	Cinnamyl chloride	*p*-Cresol	1b, 2b	67	84/16
3	Cinnamyl chloride	Phenol	1a, 2a	54	87/13
	Cinnamyl chloride	*p*-Cresol	1b, 2b	55	90/10
4	Cinnamyl chloride	Phenol	1a, 2a	48	88/12
	Cinnamyl chloride	*p*-Cresol	1b, 2b	45	77/23
5	Cinnamyl chloride	Phenol	1a, 2a	61	96/4
	Cinnamyl chloride	*p*-Cresol	1b, 2b	63	88/12
6	Cinnamyl chloride	Phenol	1a, 2a	55	89/11
	Cinnamyl chloride	*p*-Cresol	1b, 2b	58	86/14

[a] Isolated yields of the combined regioisomers.
[b] As determined by ^{1}H NMR.

Mass spectroscopic analysis

ESI-Mass spectral analyses of the new complexes were studied in order to confirm molecular mass of the complexes. The *m*/*z* values of molecular ion peaks for the complexes $[RuCl(CO)(PPh_3)(L^1)]$ **1**, $[RuCl(CO)(PPh_3)(L^2)]$ **2,** $[RuCl(CO)(Py)(L^1)]$ **3,** $[RuCl(CO)(Py)(L^2)]$ **4,** $[RuCl(CO)(AsPh_3)(L^1)]$ **5** and $[RuCl(CO)(AsPh_3)(L^2)]$ **6** were obtained at 652.9, 714.9, 468.1, 530.1, 698.1 and 758.0 respectively. The calculated molecular weights corresponds to these complexes are 652.09, 714.17, 468.90, 530.97, 698.04 and 758.11. This showed that the obtained molecular masses are in good agreement with that of the calculated molecular weights.

On the basis of analytical and spectral data, the following octahedral structure has been tentatively proposed for all the new ruthenium(II) carbonyl quinoline based NNO-tridentate Schiff base complexes (Fig. 1).

Catalytic activity towards aldehydes to amides conversion

The catalytic study towards the one-pot conversion of various aldehydes to the corresponding amides in presence of $NH_2OH{\cdot}HCl$ using ruthenium(II) carbonyl complexes as catalysts was investigated. In order to systematically investigate the influence of time and effect of catalyst loading, a proper model had to be established.

To study the effect of catalyst concentration on the reaction, substrate to catalyst ratio was varied from total catalyst amount 0.005 mmol to 0.03 mmol (Table 1). A moderate yield was observed even at very low catalyst loading of 0.0075 mmol (entry 3). The yield improved with increase in catalyst loading and reached to the highest value of 91% with 0.03 mmol of catalyst (entry 6). The reaction proceeded with good yield (89%) when the catalyst loading was 0.01 mmol (entry 4). Therefore the catalyst loading 0.01 mmol was the best suitable for the catalytic conversion of aldehydes to amides. The dependence of the product yield on reaction time was also studied by analyzing the reaction mixture at regular intervals of time under similar reaction conditions. The results (Fig. 2) indicated that the formation of benzamide increased initially with the progress of the reaction time, reached a maximum and then remained unchanged. A reasonable yield for the formation of benzamide was observed at the optimum reaction time of 10 h (87%), whereas over a period of 16 h the maximum yield (90%) was achieved.

Further, the efficiency of all the six ruthenium(II) carbonyl complexes towards the one-pot conversion of aldehydes to amides was also investigated by optimized reaction conditions (Table 2). The order of catalytic activity based on yield was **1** > **2** > **5** > **6** > **3** > **4**. In terms of substituent present in the Schiff base moiety and co-ligands, the order of activity is $CH_3 > C_6H_5$ and $PPh_3 > AsPh_3 > Py$. Hence, it was inferred that the electron donating/withdrawing substituent plays a major role in deciding the catalytic activity of their corresponding complexes. The presence of electron donating/withdrawing group in the substrate benzaldehyde derivatives also alters yield of the products. Electron donating groups like $-CH_3$ and $-OCH_3$ in the substrate have shown 80–66% and 78–60% yields respectively which is slightly lesser than that of unsubstituted benzaldehyde (87–72%). On the other hand, substitution of electron withdrawing groups like $-NO_2$ and $-Cl$ in benzaldehyde exhibited higher yield (91–80% and 89–75%) than above aldehydes.

Ruthenium(II) catalyzed o-allyl phenols formation

The reaction of allylic chloride with phenols in presence of K_2CO_3 requires thermal activation. After prolonged heating, cinnamyl chloride is selectively converted to its linear ether $PhCH=CHCH_2OPh$ [57,58]. Whereas, opposite regioselectivity was observed at room temperature with high yields when ruthenium(II) complexes used as catalyst [52]. The present catalytic systems were evaluated for regioselective allylation, using cinnamyl chloride as linear substrate in the presence of phenols acting as nucleophile and K_2CO_3 as mineral base at room temperature in a low catalyst loading with good yields. The results are reported in

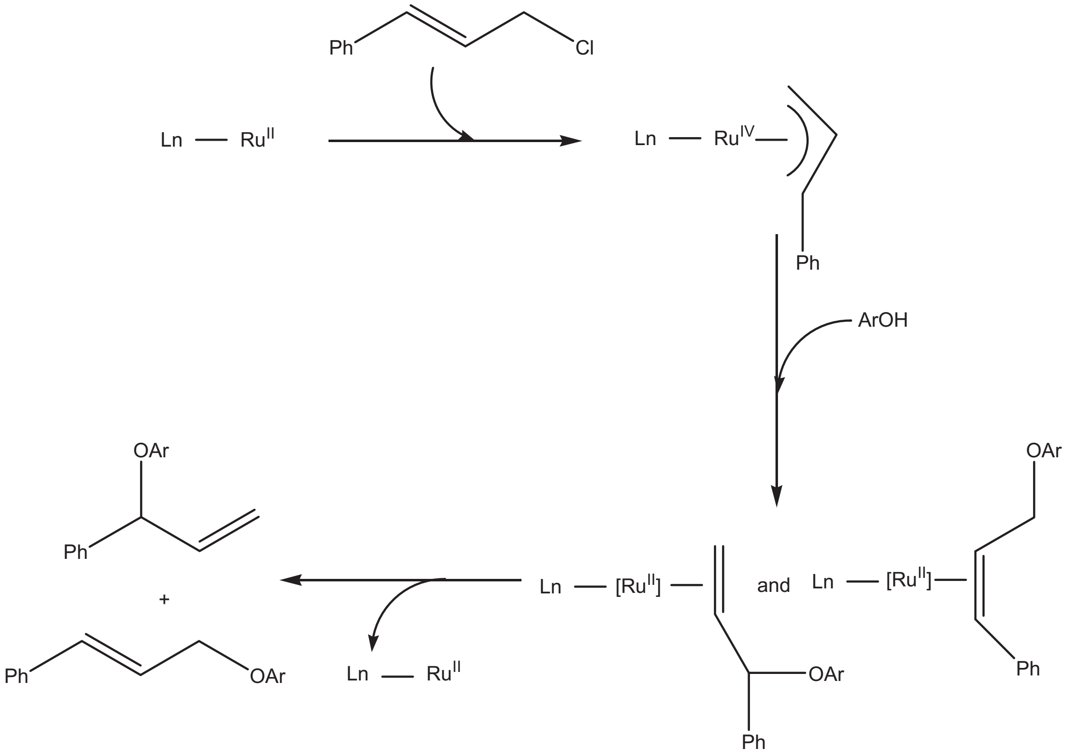


Fig. 3. A plausible mechanism for the ruthenium(II) carbonyl complex catalyzed formation of *o*-allylation of phenols.

Table 3. The branched isomer cinnamyl phenyl ether was obtained with very good regioselectivity up to 98/2. These values are very close to the highest reported for the classic catalytic test of allylic etherification with PhOH/K_2CO_3 [50]. From mechanistic point of view (Fig. 3), a ruthenium(IV) allylic intermediate was formed due to the oxidative addition of cinnamyl chloride with ruthenium(II) catalysts. This is followed by a reductive addition of phenol, results in the formation of a labile olefinic ruthenium(II) intermediate. Elimination of allyl–aryl ethers from the intermediate regenerates the ruthenium(II) center [52].

Conclusion

A simple and convenient route for the formation of ruthenium(II) carbonyl complexes of general formula [RuCl(CO)(B)(L^{1-2})] (B = PPh_3, $Asph_3$ or Py; L^{1-2} = Quinoline based ligands) has been established. The catalytic ability of the complexes for the conversion of aldehydes to amides has been studied and the conversions were found to be good. The presence of electron donating groups like —CH_3 in catalysts have shown enhanced catalytic activity. The complexes were also active catalysts for the synthesis of allyl aryl ethers starting from cinnamyl chloride and phenols using K_2CO_3 as base. This catalytic system favoured the formation of branched allyl aryl ethers under mild conditions at room temperature.

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References

[1] L.S. Chen, S.C. Cummings, Inorg. Chem. 17 (1978) 2358–2361.
[2] G.S. Devi, P. Indrasenan, Inorg. Chim. Acta 133 (1987) 157–160.
[3] P.A. Vigato, S. Tamburini, Coord. Chem. Rev. 252 (2008) 1871–1995.
[4] C.J. Van, J.V. Erden, F.C.J.M. Van Veggel, S. Harkema, D.N. Reinkeadt, J. Am. Chem. Soc. 110 (1988) 4994–5008.
[5] S. Brooker, Coord. Chem. Rev. 222 (2001) 33–56.
[6] R. Paryzek, V. Patroniak, J. Lisowski, Coord. Chem. Rev. 249 (2005) 2156–2175.
[7] R.A. Sheldon, J.K. Kochi, in: Metal Catalysed Oxidations of Organic Compounds, Academic Press, New York, 1981.
[8] L. Canali, D.C. Sherington, Chem. Soc. Rev. 28 (1999) 85–93.
[9] R.A. Sheldon, Chem. Technol. 21 (1991) 566–571.
[10] R.A. Sheldon, I.W.C.E. Arends, H.E.B. Lempers, Catal. Today 41 (1998) 387–407.
[11] R.K. Grasselli, Catal. Today 49 (1999) 141–153.
[12] K.C. Gupta, A. Kumar Sutar, Coord. Chem. Rev. 252 (2008) 1420–1450.
[13] T.S. Lobana, R. Sharma, G. Bawa, S. Khanna, Coord. Chem. Rev. 253 (2009) 977–1055.
[14] I.D. Kostas, F.J. Andreadaki, D. Kovala-Demertzi, C. Prentjas, M.A. Demertzis, Tetrahedron Lett. 46 (2005) 1967–1970.
[15] M. Pagliaro, S. Campestrini, R. Ciriminna, Chem. Soc. Rev. 34 (2005) 837–845.
[16] O.C.P. Beers, M.M. Bouman, C.J. Elsevier, W.J.J. Smeets, A.L. Spek, Inorg. Chem. 32 (1993) 3015–3021.
[17] M.G. Loudon, Organic Chemistry, Oxford University Press, New York, NY, 2002, pp. 982–983.
[18] D.J.C. Constable, P.J. Dunn, J.D. Hayler, G.R. Humphrey, J.L. Leazer, R.J. Linderman, K. Lorenz, J. Manley, B.A. Pearlman, A. Wells, A. Zaks, T.Y. Zhang, Green Chem. 9 (2007) 411–420.
[19] E. Beckmann, Ber. Dtsch. Chem. Ges. 19 (1886) 988–993.
[20] Y. Izumi, H. Ichihashi, Y. Shimazu, M. Kitamura, H. Sato, Bull. Chem. Soc. Jpn. 80 (2007) 1280–1287.
[21] M.B. Smith, J. March, Advanced Organic Chemistry, fifth ed., Wiley, New York, 2001, pp. 1415–1416.
[22] R. Paul, Compt. Rend. 204 (1937) 363–365.
[23] D.S. Hoffenberg, C.R. Hauser, J. Org. Chem. 20 (1995) 1496–1500.
[24] L. Field, P.B. Hughmark, S.H. Shumaker, W.S. Marshall, J. Am. Chem. Soc. 83 (1961) 1983–1986.
[25] G. Saidulu, N. Anand, K.S. Rama Rao, A. Burri, S.E. Park, D.R. Burri, Catal. Lett. 141 (2011) 1865–1871.
[26] N.A. Owston, A.J. Parker, J.M. Williams, J. Org. Lett. 9 (2007) 3599–3601.
[27] M. Kim, J. Lee, H.Y. Lee, S. Chang, Adv. Synth. Catal. 351 (2009) 1807–1812.
[28] A.J. Leusink, T.G. Meerbeek, J.G. Noltes, Recl. Trav. Chim. Pay-B 95 (1976) 123–125.
[29] A. Mishra, A. Ali, S. Upreti, R. Gupta, Inorg. Chem. 47 (2008) 154–161.
[30] R.S. Ramon, J. Bosson, S.D. Gonzalez, N. Marion, S.P. Nolan, J. Org. Chem. 75 (2010) 1197–1202.
[31] C.L. Allen, R. Lawerence, L. Emmett, J.M.J. Williams, Adv. Synth. Catal 353 (2011) 3262–3268.
[32] N.C. Ganguly, S. Roy, P. Mondal, Tetrahedron Lett. 53 (2012) 1413–1416.
[33] C.L. Allen, C. Burel, J.M.J. Williams, Tetrahedron Lett. 51 (2010) 2724–2726.
[34] R. Narayana Prabhu, R. Ramesh, RSC Adv. 2 (2012) 4515–4524.

[35] H. Fujiwara, Y. Ogasawara, K. Yamaguchi, N. Mizuno, Angew. Chem. Int. Ed. 46 (2007) 5202–5205.

[36] M.A. Ali, T. Punniyamurthy, Adv. Synth. Catal. 352 (2010) 288–292.

[37] P. Wipf, B.M. Trost, I. Fleming, L.A. Paquette, Comprehensive Organic Synthesis, vol. 5, Pergamon Press, Oxford, 1991, pp. 827–874.

[38] R.C. Larock, in: Comprehensive Organic Transformations: A Guide to Functional Group Preparations, VCH Publishers, New York, 1989.

[39] B.M. Trost, P.L. Fraisse, Z.T. Ball, Angew. Chem. Int. Ed. 41 (2002) 1059–1061.

[40] P.A. Evans, D.K. Leahy, J. Am. Chem. Soc. 122 (2000) 5012–5013.

[41] P.A. Evans, D.K. Leahy, J. Am. Chem. Soc. 124 (2002) 7882–7883.

[42] B.M. Trost, F.D. Toste, J. Am. Chem. Soc. 121 (1999) 4545–4554.

[43] B.M. Trost, H.C. Tsui, F.D. Toste, J. Am. Chem. Soc. 122 (2000) 3534–3535.

[44] B.M. Trost, W. Tang, J. Am. Chem. Soc. 124 (2002) 14542–14543.

[45] R. Manikandan, P. Viswanathamurthi, M. Muthukumar, Spectrochim. Acta A 83 (2011) 297–303.

[46] R. Manikandan, P. Viswanathamurthi, Spectrochim. Acta A 97 (2011) 864–870.

[47] A.I. Vogal, in: Textbook of Practical Organic Chemistry, fifth ed., ELBS, London, 1989, p. 395.

[48] N. Ahmed, J.J. Levison, S.D. Robinson, M.F. Uttley, Inorg. Synth. 15 (1974) 45–64.

[49] S. Gopinathan, I.R. Unny, S.S. Deshpande, C. Gopinathan, Ind. J. Chem. A 25 (1986) 1015–1017.

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

[51] W.A. Ma, Z.X. Wang, Dalton Trans. 40 (2011) 1778–1786.

[52] M.D. Mbaye, B. Demerseman, J.L. Renaud, L. Toupet, C. Bruneau, Adv. Synth. Catal. 346 (2004) 835–841.

[53] B. Sarkar, G. Bocelli, A. Cantoni, A. Ghosh, Polyhedron 27 (2008) 693–700.

[54] K. Nareshkumar, R. Ramesh, Polyhedron 24 (2005) 1885–1892.

[55] K. Nareshkumar, R. Ramesh, Spectrochim. Acta A 60 (2004) 2913–2918.

[56] S. Kannan, M. Sivagamasundari, R. Ramesh, Y. Liu, J. Organomet. Chem. 693 (2008) 2251–2257.

[57] L. Claisen, F. Kremers, F. Roth, E. Tietze, Liebigs. Ann. Chem. 442 (1925) 210–245.

[58] L. Claisen, E. Tietze, Ber. Dtsch. Chem. Ges. 59B (1926) 2344–2351.