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Ruthenium(II) NNO pincer type catalyst for the conversion of aldehydes to amides

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ABSTRACT

The reaction of $[RuHCl(CO)(PPh_3)_3]$ and 2-(2-thiazolylazo) cresol ligand (TAC) in benzene under reflux afforded a new pincer type ruthenium(II) carbonyl complex containing thiazolylazo cresol of general formula $[RuCl(CO)(PPh_3)(TAC)]$ (TAC = mono anionic NNO donor). The complex has been characterized by elemental analyses, FT-IR, UV–Vis, and ^1H NMR spectral methods. The crystal structure of the complex $[RuCl(CO)(PPh_3)(TAC)]$ has been determined by single crystal X-ray diffraction which reveals the presence of a distorted octahedral geometry in the complex. The complex has been shown as an efficient catalyst for the conversion of aldehydes to amides in a one-pot process in the presence of $NH_2OH \cdot HCl/NaHCO_3$.

The chemistry of ruthenium by different types of ligands is of significant importance [1,2] because of the fascinating reactivities exhibited by the resultant complexes and the nature of the ligand that dictates the property of those complexes. Particularly, *N*-heterocyclic *o*-hydroxy substituted ligands represent an interesting class of highly sensitive complexing reagents. A novel property of this azomethine $(-N{=}C-N{=}N-)$ nitrogen donor ligands is its ability to stabilize low oxidation state metal centers through its strong π-acidity and weak δ donor character [3,4]. Because hetero atoms, ring size and the presence of substituents in the heterocyclic ring significantly change the π-acidity of the ligands and influence the physical and chemical properties of the metal complexes. For example, thiazolylazo reagents are popular as metal complexing ligands in spectrophotometry, high performance ligands chromatography [5,6] and capillary electrophoresis [7] due to the advantages that they can form highly sensitive metal complexes.

Amides are an important class of chemicals that have been widely used as chemical intermediates in organic synthesis, raw materials for engineering plastics, detergents, and lubricants. The conversion of carbonyl compounds, such as aldehydes, ketones, and oximes, is a good candidate for the synthesis of amides [8–10]. Beckmann rearrangement is commonly used to transform oximes into the corresponding amides [11]. This rearrangement is commonly used to transform ketoximes into the corresponding N-substituted amides requiring the use of strong acids [12]. Further, the synthesis of primary amides from aldoximes is very difficult and reactive reagents have to be used in stoichiometric amounts for the transformation to occur. In addition, the selectivities for the desired amides are often very low with reactive stoichiometric reagents because undesired nitriles, carboxylic acids, and aldehydes are formed in some cases. While the migrating group can be alkyl or aryl, it is rarely hydrogen that migrates, and so the Beckmann rearrangement is not a general process for the conversion of aldoximes into primary amides [13–15].

The rearrangement of aldoximes into amides has been reported using transition metal catalysts containing nickel [16], copper [17], palladium [18], iridium [19,20], rhodium [21] and zinc [22]. In a recent advance, Williams and coworkers reported a ruthenium catalyst for this reaction with high selectivity, excellent yield and low catalyst loading with *p*-toluenesulfonic acid as an additive [23]. Further, Crabtree et al. reported ruthenium terpyridine complexes as an efficient catalyst to achieve high yields without any additive [24]. In addition, $[RuCl_2(DMSO)_4]$ complex was used as a catalyst for the aldehydes to primary amide reactions [25]. In contrast to the considerable growth of literature on the chemistry of azo complexes, to the best of our knowledge there are no reports available for catalytic transformation of aldehydes to amides by ruthenium(II) carbonyl complex containing 2-(2-thiazolylazo) cresol incorporating triphenyl phosphine.

The ligand was prepared by modification of the reported procedure [26]. The general procedure for the synthesis of ruthenium(II) NNO pincer type complex is as follows. To a benzene solution of $[RuHCl(CO)(PPh_3)_3]$ [27] (100 mg, 0.105 mmol) was added to the 2-(2-thiazolylazo) cresol ligand (23.02 mg, 0.105 mmol) and the mixture was refluxed for 6 h (Scheme 1). The solvent was then removed under high vacuum at low temperature followed by dichloromethane and petroleum ether workup gave blue colored solids. The complex is recrystallized from CH_2Cl_2/pet. ether and dried under vacuum. Yield is 70%.

The complex is found to be air stable and soluble in common organic solvents, such as $CHCl_3$, CH_2Cl_2, CH_3CN, etc. The elemental analyses are in good agreement with the molecular formula proposed for the complex. The IR spectrum of the complex confirmed the coordination of the azo group ($\nu_{(N{=}N)}$ 1391 cm^{-1}) and phenolic oxygen

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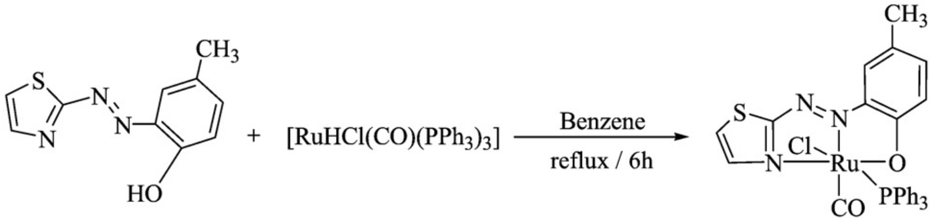


Scheme 1. Synthesis of pincer type complex [RuCl(CO)(PPh_3)(TAC)].

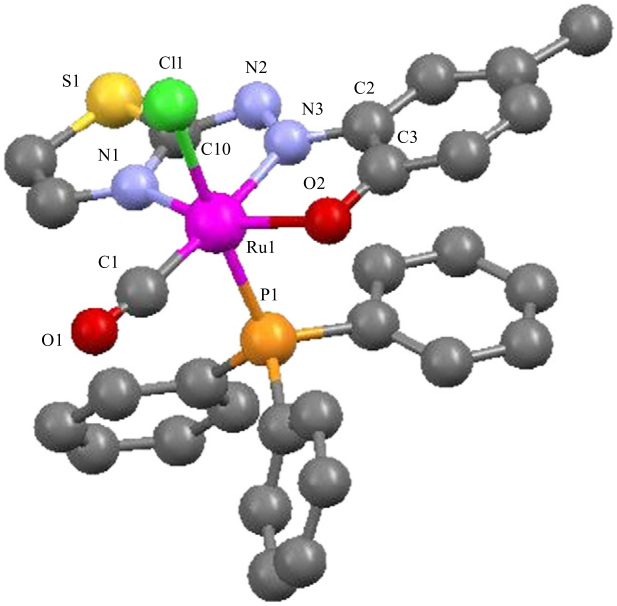


Fig. 1. The X-ray crystal structure of the complex [RuCl(CO)(PPh_3)(TAC)].

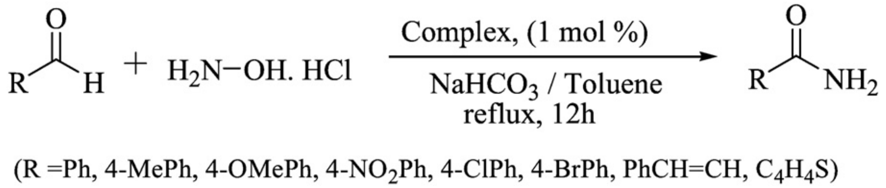
($\nu_{(C-O)}$ 1289 cm^{-1}) to the metal atoms. The spectrum of complex shows a strong band in the region 1978 cm^{-1} due to the coordinated $\nu_{C\equiv O}$ group [28]. In addition, this complex showed new bands near 530, 695, 740 and 1557 cm^{-1} due to the triphenyl phosphine ligands. The electronic spectrum of the complex has been recorded in chloroform solution. The spectrum of the complex shows a visible region with an intense absorption at 446 nm (ε = 1020–2051 dm^3/mol/cm) region due to MLCT in addition to the π–π* and n–π* ligand centered transitions (263–242 nm) [29]. In ^1H NMR spectrum of the complex, the aromatic protons appeared as a multiplet in the region of 6.6–7.3 ppm. The absence of broad singlet at δ 10.4–11.5 ppm indicates the coordination of phenolic oxygen to ruthenium. A singlet appeared at 1.8 ppm is due to the presence of methyl proton in the complex [30].

To understand the coordination mode of the 2-(2-thiazolylazo) cresol ligand and the geometry of the ruthenium(II) complex, the X-ray crystal structure of the complex [RuCl(CO)(PPh_3)(TAC)] was determined and is shown in Fig. 1. The ligand coordinates to the ruthenium(II) ion with the O, N, N donor atom forming two five membered chelate rings as in the case of typical pincer complex within the bite angles of N(3)–Ru(1)–N(1) = 76.58(8) and N(1)–Ru(1)–O(2) = 79.53(7). The bond length of Ru(1)–N(1) = 2.066(2) (A°), Ru(1)–N(3) = 2.020(2) (A°), Ru(1)–C(1) = 1.881(2) (A°) and Ru(1)–O(2) = 2.1040(2) (A°). Similarly, the bond distances of the Ru(1)–P(1) and Ru(1)–Cl(1) are 2.3151(6) (A°) and 2.4282(7) (A°) respectively. It has been observed that the PPh_3 is mutually trans to chlorine atom. The Ru − C bond length 1.8807 (A°) in Ru(1)–C(1), fragment is quite normal like that in the structurally characterized carbonyl complexes of ruthenium [31]. The overall C1N2O1P1Cl1 coordination sphere around the ruthenium is distorted octahedral in nature, which is reflected in all the bond parameters around ruthenium.

Further, the catalytic organic transformation of aldehydes to amides by the synthesized ruthenium(II) thiazolylazo cresol complex has been studied in toluene in the presence of $NH_2OH\cdot HCl/NaHCO_3$ (Scheme 2) and the products were passed through the celites and silica gel to get pure compounds [32]. The catalytic reaction was carried out under a set of conditions and a series of blank or control experiments suggests that none of ruthenium(II) precursors or 2-(2-thiazolylazo) cresol alone or as a mixture causes these transformations under identical reaction conditions. Complex [RuCl(CO)(PPh_3)(TAC)] efficiently catalyzes the rearrangement of aldehydes into amides with high yields, according to the proposed mechanism [25].

In order to optimize the reaction conditions, different catalyst: substrate ratios were tested and the results are summarized in Table 1. For these initial experiments benzaldehyde was selected as a test-substrate and allowed it to react in toluene with catalytic quantities of complex [RuCl(CO)(PPh_3)(TAC)] in the presence of $NaHCO_3$ as an additive. In the reaction optimization, we started the C/S ratios of 1:100, 1:200 and 1:500, the reaction proceeds with excellent conversions. When increasing the C:S ratio from 1:500 and 1:1000 in toluene, the reaction still proceeds by a drop in yield of amide. When decreasing the C:S ratio to 1:200, the reaction proceeds by a moderate yield. Thus, it was concluded that catalyst:substrate ratio of 1:100 is the best compromise between optimal reaction rates in toluene and we obtained 95% yield of amide (entry 4).

To study the effects of different solvents in our catalytic system, we have chosen the reaction between benzaldehyde with NH_2-$OH\cdot HCl$ and $NaHCO_3$ in the presence of various solvents (Table 2). Benzene, toluene, xylene, acetonitrile, dichloromethane and chloroform are taken for our solvent variation study. Toluene gives an excellent yield of 95% (entry 2) and acetonitrile yields 82% (entry 4).



Scheme 2. Catalytic organic transformation of aldehydes to amides.

Table 1
Effect of catalyst/substrate ratio for benzaldehyde to benzamide using complex [RuCl(CO)(PPh$_3$)(TAC)].[a]

Entry	Ratio	Time	Yield[b] (%)
1	1:1000	12	<25
2	1:500	12	25
3	1:200	12	56
4	1:100	12	95

[a] Conditions: reactions were carried out. Substrate (1–10 mmol), $NH_2OH\cdot HCl$ (1–10 mmol), catalyst (1 mol%) and 2 ml of toluene were refluxed for 12 h.
[b] Isolated yield after column chromatography.

Table 2
Effect of solvents for benzaldehyde to benzamide using complex [RuCl(CO)(PPh$_3$)(TAC)].[a]

Entry	Solvents	Time	Yield[b] (%)
1	Benzene	24	32
2	Toluene	12	95
3	Xylene	24	37
4	Acetonitrile	12	82
5	Dichloromethane	24	30
6	Chloroform	24	24

[a] Aldehydes (1 mmol), $NH_2OH\cdot HCl$ (1 mmol), $NaHCO_3$ (1 mmol), catalyst (1 mol%) and 2 ml solvent.
[b] Isolated yield after column chromatography.

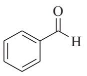
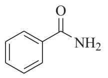
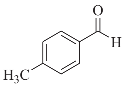
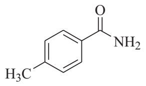
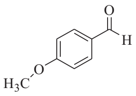
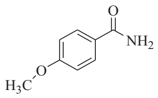
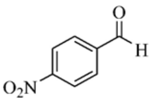
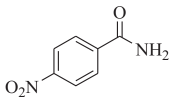
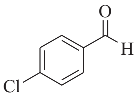
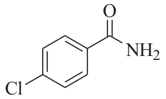
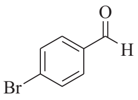
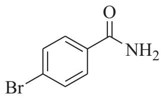
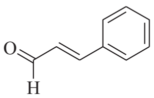
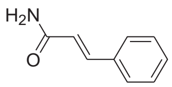
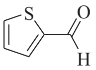
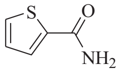
Further benzene and xylene gave yields such as 32% and 37% respectively. Lowest yield was obtained with dichloromethane and chloroform (entries 5 and 6) 30% and 24% respectively.

The scope of our catalytic system is applicable to a wide range of aromatic, substituted, conjugated and heterocyclic aromatic aldehydes. These aldehydes were converted to their corresponding amides in one pot process using $NaHCO_3$ and the results are summarized in Table 3 (entries 1–9).

Using [RuCl(CO)(PPh$_3$)(TAC)], an excellent yield was obtained for benzaldehyde to benzamide (entry 1) in 95%. Benzaldehydes with its derivatives were all smoothly converted to the corresponding amides in good yields. The presence of electron donating groups like $-CH_3$ and $-OCH_3$ (entries 2 and 3) in the substrates alters the reactions and the corresponding amides were obtained in good yields 80% and 75% respectively. On the other hand, electron withdrawing groups, such as the $-NO_2$, $-Cl$ and $-Br$ substituents (entries 4, 5 and 6) offering better yields (88%, 90% and 91%) when compared to substrate containing electron donating group. Recently, a similar observation has been made on [RuCl$_2$(DMSO)$_4$] complex as catalyst in toluene medium [25]. The present catalyst shows good catalytic activity for the conjugated aldehyde such as, cinnamaldehyde which was converted to the conjugated amides (entry 7) in 90% yield. Further, the complex efficiently catalyzes the thiophenealdehyde to thiophenecarboxamide (entry 8) with yields up to 91%.

In conclusion, new air stable ruthenium(II) carbonyl complex containing pincer type NNO donor of general formula [RuCl(CO)(PPh$_3$)(TAC)] has been synthesized and characterized. X-ray diffraction study of the complex confirms the N, N and O coordination of the ligand and reveals the presence of a distorted octahedral geometry. The catalytic ability of the present complex for the conversion of aldehydes to amides has been studied and the conversions are found to be excellent.

Table 3
One pot conversion of aldehydes to amides by complex [RuCl(CO)(PPh$_3$)(TAC)].[a]

S. no	Aldehydes	Amides	Yield[b] (%)
1			95
2			80
3			75
4			88
5			90
6			91
7			90
8			91

[a] Aldehydes (1 mmol), $NH_2OH\cdot HCl$ (1 mmol), $NaHCO_3$ (1 mmol), catalyst (1 mol%) and toluene (2 ml) were refluxed for 12 h.
[b] Isolated yield after column chromatography.

Acknowledgments

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Appendix A. Supplementary data

Crystallographic data for the structural analysis have been deposited with Cambridge crystallographic center, CCDC No. 825814. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union roads, Cambridge.CB2 1EZ, UK (email: deposit@ccdc.cam.ac.uk). Complete sets of refined positional coordinates as well as anisotropic thermal parameters and complete tabulations of bond lengths and bond angles.

Supplementary data to this article can be found online at doi:10.1016/j.inoche.2012.01.035.

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[32] Typical procedures for the conversion of aldehydes to amides: The reaction vessel was charged with aldehyde (1 mmol), $NH_2OH \cdot HCl$ (1 mmol), $NaHCO_3$ (69.5 mg, 1 mmol), and ruthenium catalyst (6.5 mg, 0.01 mmol) and the mixture was placed under an atmosphere of N_2. About 2 ml of dry and degassed toluene was added and the mixture was stirred for 15 min at room temperature and followed by the reflux for 12 h. On completion of the reaction, 2–3 ml MeOH was added to the mixture followed by filtration through celite to remove catalyst and $NaHCO_3$. The crude product was then purified using column chromatography ($MeOH/CH_2Cl_2$) and the pure amide was obtained in good yield.