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Ruthenium(II) carbonyl complexes containing bidentate 2-oxo-1,2-dihydroquinoline-3-carbaldehyde hydrazone ligands as efficient catalysts for catalytic amidation reaction

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ABSTRACT

The coordination behavior of 2-oxo-1,2-dihydroquinoline-3-carbaldehyde hydrazone ligands in ruthenium(II) and the catalytic activity of newly synthesized complexes have been studied. The complexes $[RuCl(CO)(PPh_3)_2(L_1)]$ (**1**), $[RuCl(CO)(AsPh_3)_2(L_1)]$ (**2**), $[RuCl(CO)(PPh_3)_2(L_2)]$ (**3**) and $[RuCl(CO)(AsPh_3)_2(L_2)]$ (**4**) were synthesized by reactions of $[RuHCl(CO)(EPh_3)_3]$ (E = P or As) precursors with hydrazone ligands and characterized by analytical and spectroscopic methods. The molecular structure of complex **2** was identified by means of single-crystal X-ray diffraction analysis. The structural analysis revealed that all the complexes possess a distorted octahedral geometry with the ligand coordinating in a uni-negative bidentate NO fashion. Further, the catalytic efficiency of the complexes have been investigated in the case of direct amidation of alcohols with amines. The influence of base, reaction temperature and catalyst loading in the amidation reaction was also evaluated. Notably, complex **3** was found to be very efficient catalyst towards amidation of alcohols with amine. A variety of aromatic (hetero) amines and alcohols with various functional groups have also been successfully used for amidations.

1. Introduction

The amide bond is the key backbone in organic chemistry and constitutes the key functional group in peptides, polymers, and many natural products and pharmaceuticals [1]. Not less than 25% of the drug molecules prepared by leading pharmaceutical companies contain an amide unit, indicating its importance and prevalence in synthetic organic chemistry. Some examples of pharmaceutical molecules containing amide unit have been shown in the Fig. 1. Amides are usually prepared by coupling of carboxylic acids and amines by the use of either an alkylating reagent [2] or by prior conversion of the carboxylic acid into a derivative [3]. Alkylating agents used for amide synthesis are typically genotoxic and thus pose toxicity problems for large-scale commercial syntheses [4]. The presence of trace amounts of genotoxic impurities in the final pharmaceutical product creates huge problem in the pharmaceutical industries and the regulatory agencies are more focused on the genotoxic impurities.

Moreover, alkylating agents for amide synthesis from a carboxylic acid and an amine generate waste; for example, dicyclohexylcarbodiimide (DCC) gives the corresponding urea, a material that is hard to recycle. A more environmental friendly protocol for oxidative amide synthesis is the direct amidation of alcohols and amines by liberating hydrogen gas as the byproduct have been extensively studied and it can offer efficient catalytic protocols and minimum amounts of waste are considered important for chemical processes [5,6]. In recent years, green routes have been developed for amide synthesis that do not involve traditional alkylating or coupling agents but instead involve the transition metal-catalyzed coupling of primary amines and alcohols [7]. Several groups [8] have reported catalytic amide formation from alcohols, using transition metal catalysts to oxidize the alcohol to aldehyde *in situ* and then further oxidize the hemiaminal to the desired amide via the loss of two molecules of dihydrogen. Some reports utilized different

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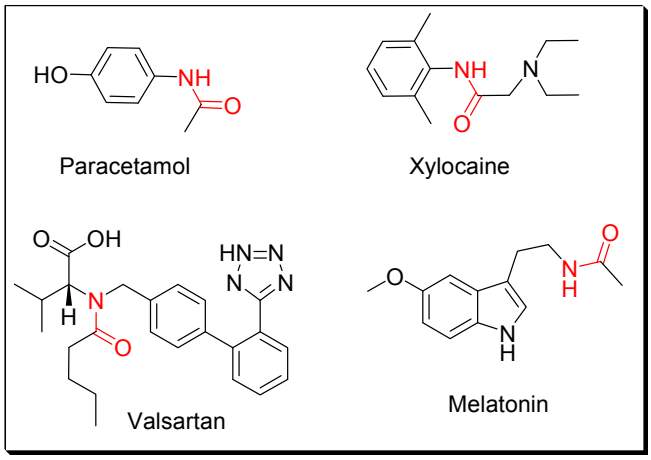

Fig. 1. Representative examples of drug molecules containing amide bond.

reagents, particularly sodium hydride [9] in argon atmosphere while applying metal catalyst for amidation of alcohol with amine. The hydride donor enhances the insertion of alkoxy moiety into the metal catalyst thereby the activity of catalysts enhances with NaH with the consequent higher yields. Among the transition metal catalysts, ruthenium complexes have been extensively studied due to their catalytic significances in variety of organic transformations, such as the hydrogenation of esters to alcohols [10], direct synthesis of imines from alcohols and amines [11], synthesis of amides from esters and amines [12], and direct synthesis of polyamides from diols and diamines [13]. Hence in this work ruthenium catalyst bearing different catalytically active ligands in presence of hydride donor is used for the amidation reactions.

Hydrazones are versatile ligands and adopt various binding modes with transition-metal and main-group-metal ions [14]. A number of reasons have been offered as responsible for their versatility in coordination, such as intramolecular hydrogen bonding, bulkier coligands and steric crowding on the azomethine carbon atom [15]. Hydrazones functionalized with an additional donor group have become important ligands due to the potential hemilability of the new donor group, which can play a dual role in a catalyst since they can easily enable coordination sites and, at the same time, protect the coordination sites by a dynamic "on and off" chelating effect [16]. Several donor groups such as N, O, S, C and P have been reported to functionalize hydrazones, their complexes exhibit high activity when used as catalysts in the Pd-catalyzed Suzuki–Miyaura cross coupling reaction [17], Ni(II) catalyzed olefin oligomerization [18] and Mn(II), V(V) and Fe(III) mediated oxidation of hydrocarbons [19–22]. More recently ruthenium mediated transfer hydrogenation of ketones [23] and aldehyde to amide conversion [24] have also appeared in the literature.

In continuation of our research on the synthesis, characterization and catalytic applications of ruthenium complexes [25,26] and in view of the interesting coordination modes of aroylhydrazone ligands, we herein describe new Ru(II) carbonyl complexes incorporating 2-oxo-1,2-dihydroquinoline-3-carbaldehyde hydrazone ligands and triphenylphosphine/triphenylarsine as ancillary ligands. The applicability of these complexes as homogeneous catalysts for the synthesis of amide with alcohols was also investigated.

2. Experimental section

2.1. General procedures

All the chemicals used for reactions were pure and AR grade. The starting complexes [RuHCl(CO)(PPh_3)$_3$], and [RuHCl(CO)($AsPh_3$)$_3$] were prepared according to literature procedures [27,28]. Thin-layer chromatography (Merck 1.05554 aluminum sheets pre-coated with silica gel 60 F254) was used for the reaction monitoring and the spots were visualized with UV light at 254 nm or under iodine. Column chromatography purifications were performed by neutral alumina. The C, H and N analyses were carried out with a Vario EL III Elemental analyzer. Mass spectra were measured on a LC–MS Q–ToF Micro Analyzer (Shimadzu), using electrospray ionization (ESI) mode. The ^{1}H, ^{13}C and ^{31}P NMR spectra were measured by Bruker AV400 instrument. Infrared spectra of the ligands and the metal complexes were recorded as KBr discs in the range of 4000–400 cm^{-1} using a Nicolet Avatar model FT-IR spectrophotometer. The electronic spectra of the complexes were performed on a Shimadzu UV–1650 PC spectrophotometer using dichloromethane as the solvent. The melting points were checked with a Lab India melting point apparatus.

2.2. Preparation of the ligands

2-oxo-1,2-dihydroquinoline-3-carbaldehyde was prepared according to literature procedure [29]. The ligand was obtained by the addition of benzhydrazide (0.681 g, 5 mmol)/Isoniazid (0.686 g, 5 mmol) in warm methanol (20 mL) to a methanol solution (20 mL) containing 2-oxo-1, 2-dihydroquinoline-3-carbaldehyde (0.865 g, 5 mmol). The mixture was refluxed for an hour during which period yellow precipitate was formed. The solid compound was filtered and washed with methanol for further purification.

2.2.1. 2-oxo-1, 2-dihydroquinoline-3-carbaldehyde benzhydrazide (L_1)

Yield: 0.2621 g (90%). Mp: 312 °C. Anal. Calcd for $C_{17}H_{13}N_3O_2$: C, 70.09; H, 4.50; N, 14.42%. Found: C, 70.27; H, 4.88; N, 14.20%. IR (KBr discs, cm^{-1}): 3231 (s, $\nu_{N\text{-}H}$); 3063 (m, $\nu_{N\text{-}H}$); 1654 (s, $\nu_{C=O}$), 1620 (m, $\nu_{C=O}$); 1556 (s, $\nu_{C=N}$); UV–Vis (CH_2Cl_2), λ_{max} (nm): 240, 309, 336, 375. ^{1}H NMR (DMSO-d_6, 400 MHz, ppm): 12.01 (s, 1H, $NH_{Quinoline}$); 11.75 (s, 1H, $NH_{Hydrazinic}$); 8.71 (s, 1H, HC=N); 8.53 (s, 1H, Ring CH); 7.94–7.59 (m, 4H, Ar H); 7.35–7.26 (m, 5H, Ar H).

2.2.2. 2-oxo-1, 2-dihydroquinoline-3-carbaldehyde isoniazid (L_2)

Yield: 0.2543 g (87%). Mp: 303 °C. Anal. Calcd for $C_{16}H_{12}N_4O_2$: C, 65.75; H, 4.14; N, 19.17%. Found: C, 65.89; H, 4.37; N, 19.46%. IR (KBr discs, cm^{-1}): 3235 (s, $\nu_{N\text{-}H}$); 3043 (m, $\nu_{N\text{-}H}$); 1655 (s, $\nu_{C=O}$), 1618 (m, $\nu_{C=O}$); 1557 (s, $\nu_{C=N}$). UV–Vis (CH_2Cl_2), λ_{max} (nm): 258, 328, 386. ^{1}H NMR (DMSO-d_6, 400 MHz, ppm): 11.98 (s, 1H, $NH_{Quinoline}$); 11.72 (s, 1H, $NH_{Hydrazinic}$); 8.70 (s, 1H, HC=N); 8.58 (s, 1H, Ring CH); 7.97–7.52 (m, 4H, Ar H); 7.35–7.21 (m, 4H, Ar H).

2.3. Synthesis of new ruthenium complexes

To a suspension of hydrazone ligand in warm ethanol (15 mL), an equimolar ethanolic solution (15 mL) of ruthenium precursor complex was added. The resulting mixture was refluxed for 8 h and the progress of the reactions was monitored by TLC. The orange powder was obtained on slow evaporation and it was purified by column chromatography (neutral alumina) using petroleum ether: ethylacetate mixture in the ratio of 60:40 as a mobile phase. The single crystals were obtained from the purified complex solution by slow evaporation.

2.3.1. [RuCl(CO)(PPh_3)$_2$(L_1)] (1)

2-oxo-1,2-dihydroquinoline-3-carbaldehyde benzhydrazide (L_1) (0.291 g, 1 mmol) was reacted with [RuHCl(CO)(PPh_3)$_3$] (0.952 g, 1 mmol) to form complex **1**. Yield = 0.7835 g (80%). Mp: 280 °C. Anal. Calcd for $C_{54}H_{42}N_3O_3P_2RuCl$: C, 66.22; H, 4.32; N, 4.29%. Found: C, 66.58; H, 4.10; N, 4.40%. IR (KBr discs, cm^{-1}): 3055 (ms,