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Review

Metal-catalyzed nitrile hydration reactions: The specific contribution of ruthenium

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ABSTRACT

The hydration of nitriles is an atom economical route to generate primary amides of great academic and industrial significance. From an academic perspective, considerable progress has been made toward the development of transition metal catalysts able to promote this hydration process under mild conditions. In this context, with regard to activity, selectivity, functional group compatibility and modes of reactivity, the most versatile nitrile hydration catalysts discovered to date are based on ruthenium complexes. Herein, a comprehensive account of the different homogeneous ruthenium catalysts described in the literature is presented. Heterogeneous ruthenium-based systems are also discussed.

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Contents

Introduction

The amide functionality is one of the most relevant in organic and biological chemistry. Amides are present in multitude of natural products, pharmaceuticals and drug candidates, and have found applications as starting materials in the preparation of various industrial products including detergents, lubricants and polymers [1]. Amides are commonly prepared by the reaction of activated carboxylic acid derivatives (acid chlorides, anhydrides and esters) with amines including ammonia [2], or by direct union of the acids with the amines assisted by coupling reagents, such as carbodiimides or 1*H*-benzotriazole derivatives [3]. However, despite being of great applicability, these methods suffer from a low atom economy and are associated to the generation of large quantities of waste products, making their environmental profile unfavorable. For this reasons, increasing attention is being devoted to the development of more efficient and sustainable synthetic routes that allow access to this important class of compounds [4].

The hydration of nitriles is probably the simplest method for preparing primary amides in an atom-economical manner (Scheme 1). However, conventional protocols for hydrating nitriles involve the use of highly acidic/basic media and harsh reaction conditions, methods that are frequently unable to control hydrolysis to the corresponding carboxylic acids (Scheme 1) and are not compatible

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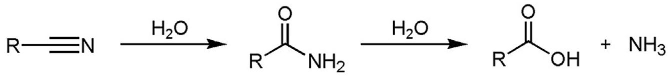


Scheme 1. The nitrile hydration and amide hydrolysis reactions.

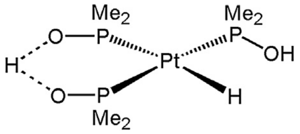


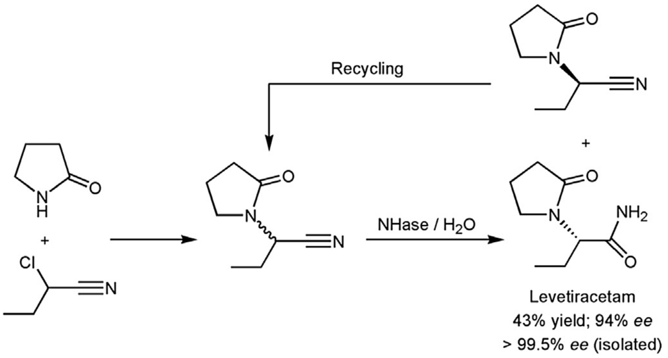
Fig. 1. Structure of the Parkins catalyst.

with many sensitive functional groups [2]. The formation of a large amount of salts after neutralization is another problem associated with these classical methodologies.

To overcome these drawbacks, considerable efforts have been expended in the search for alternative methods for the nitrile hydration process. In this context, nitrile hydratases (NHases), a family of enzymes containing non-heme low spin Fe(III) or non-corrinoid low-spin Co(III) active centers, have demonstrated great potential to promote the selective transformation of nitriles into amides under mild conditions [5]. In fact, this type of biocatalysts have found application in the commercial production of some relevant amides, such as acrylamide, nicotinamide, 5-cyanovaleramide and levetiracetam, an antiepileptic drug marketed under the trade name Keppra® (Scheme 2) [5,6]. However, the necessity of special procedures to handle microorganisms, their high cost and narrow substrate specificity restrict severely the use of NHases.

Metal ions are able to favor nitrile hydration by activating the nitrile substrate, the water nucleophile, or both upon coordination. Accordingly, a variety of homogeneous [7] and heterogeneous [8] metal-based catalysts, showing a high selectivity to the amide under milder conditions to those employed with strong acids or bases, have been described in the literature during the last two decades. For synthetic purposes, given their greater substrate scope and easier handling, these methods based on metal catalysts are much appealing than the enzymatic ones. This fact is endorsed, for example, by the extraordinary success achieved by the hydrido-platinum(II) complex $[PtH\{(PMe_2O)_2H\}(PMe_2OH)]$ developed by Parkins and co-workers (Fig. 1) [9]. This Pt system is able to catalyze the selective hydration of a wide range of nitriles, including very bulky nitriles, unsaturated nitriles (such as acrylonitrile) and nitriles containing acid and base-sensitive functional groups, under relatively mild (70–100 °C) and neutral reaction conditions. All these properties, along with its exquisite functional group tolerance, has allowed the implementation of $[PtH\{(PMe_2O)_2H\}(PMe_2OH)]$ in the synthesis of a large number of complex organic molecules and natural products [10].

Ruthenium compounds constitute a versatile class of catalysts for synthetic organic chemistry and feature a large panel of applications [11]. There are several aspects that make ruthenium interesting for homogeneous catalysis, such as its rich coordination chemistry, the wide range of oxidation states that it can adopt (from −2 to +8) or its ability to accommodate a large variety of ligands in various coordination geometries. No less important is the fact that ruthenium is much less expensive than other platinum-group metals such as palladium, platinum, rhodium and iridium. Ruthenium complexes have therefore a great potential for the development of new nitrile hydration catalysts. Indeed, the most recent breakthroughs in the field have been reached using this metal. Herein, a comprehensive account of the different ruthenium-based catalysts for nitrile hydration described in the literature is presented. Both homogeneous and heterogeneous systems will be discussed.

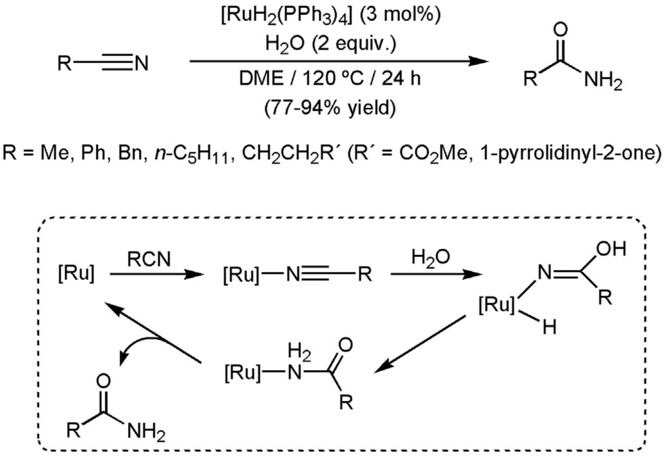


Scheme 2. Synthetic route of levetiracetam employing a nitrile hydratase.

Homogeneous ruthenium-based catalysts

The application of a ruthenium complex to promote the selective hydration of nitriles to primary amides was described for the first time by Taube and co-workers in the 1970's [12]. Thus, using a stoichiometric amount of $[RuCl(NH_3)_5][Cl]_2$ in combination with Ag_2O, trifluoroacetic acid and zinc amalgam, they were able to transform in high yields (64–95%) several aromatic, aliphatic and α,β-unsaturated organonitriles into the corresponding amides after 6–8 h of heating at 40–50 °C in wet dichloromethane. However, despite this early discovery, it was not until 1992 that the first truly catalytic system could be developed by Murahashi and co-workers employing the ruthenium-dihydride complex $[RuH_2(PPh_3)_4]$ as catalyst [13,14]. In the presence of 3 mol% of this complex and 2 molar equivalents of water, several organonitriles were successfully hydrated in 1,2-dimethoxyethane (DME) under neutral conditions, giving the desired amides in excellent yields (77–94%) after 24 h of heating at 120 °C (TOF ≤ 2 h^{-1}; Scheme 3) [13]. A reaction pathway involving the intermolecular nucleophilic addition of water to the coordinated nitrile, to give an iminolate complex, was proposed. Reductive elimination, isomerization of the iminol to the amide, and subsequent dissociation regenerates the catalytically active ruthenium species [13c].

Under the same reaction conditions, complex $[RuH_2(PPh_3)_4]$ was also able to transform a large variety of δ-ketonitriles into ene-lactams through a *tandem* process involving the initial hydration of the C≡N unit, followed by intramolecular condensation of the



Scheme 3. Catalytic hydration of nitriles by means of complex $[RuH_2(PPh_3)_4]$.

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