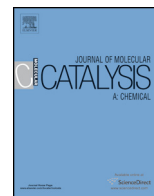




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In situ generation of water-stable and -soluble ruthenium complexes of pyridine-based chelate-ligands and their use for the hydrodeoxygenation of biomass-related substrates in aqueous acidic medium

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ABSTRACT

The complexes $[\text{Ru}(2,2'\text{-dipicolylamine})(\text{OH}_2)_3](\text{OTf})_2$ and $[\text{Ru}(6,6'\text{-bis(aminomethyl)-2,2'\text{-bipyridine})(\text{OH}_2)_2](\text{OTf})_2$ can be prepared by reaction of 2,2'-dipicolylamine or 6,6'-bis(aminomethyl)-2,2'-bipyridine with $[\text{Ru}^{\text{III}}(\text{DMF})_6](\text{OTf})_3$ in aqueous medium. During the reaction an *in situ* reduction from a paramagnetic Ru^{III} to a diamagnetic Ru^{II} -complexes occurs with one equivalent of DMF acting as the reducing agent for two ruthenium centres by its reaction with water and decomposition to dimethylammonium triflate and CO_2 generating an additional equivalent of HOTf in the process. The complex solutions are active as catalysts for the hydrogenation of 2,5-hexanedione and 2,5-dimethylfuran to 2,5-hexanediol and 2,5-dimethyltetrahydrofuran with both complexes realizing very high yields (>95% combined yield of the two products with the selectivity determined as a function of added acid co-catalyst). The 2,2'-dipicolylamine complex is stable to 150 °C, while the 6,6'-bis(aminomethyl)-2,2'-bipyridine complex is stable to 200 °C allowing the *in situ* hydrolysis of 2,5-dimethylfuran to the 2,5-hexanedione and thus direct conversion to the same products in up to 78% combined yield. The effects of co-solvents, acid co-catalysts and temperature on catalyst activity, decomposition and stability are explored.

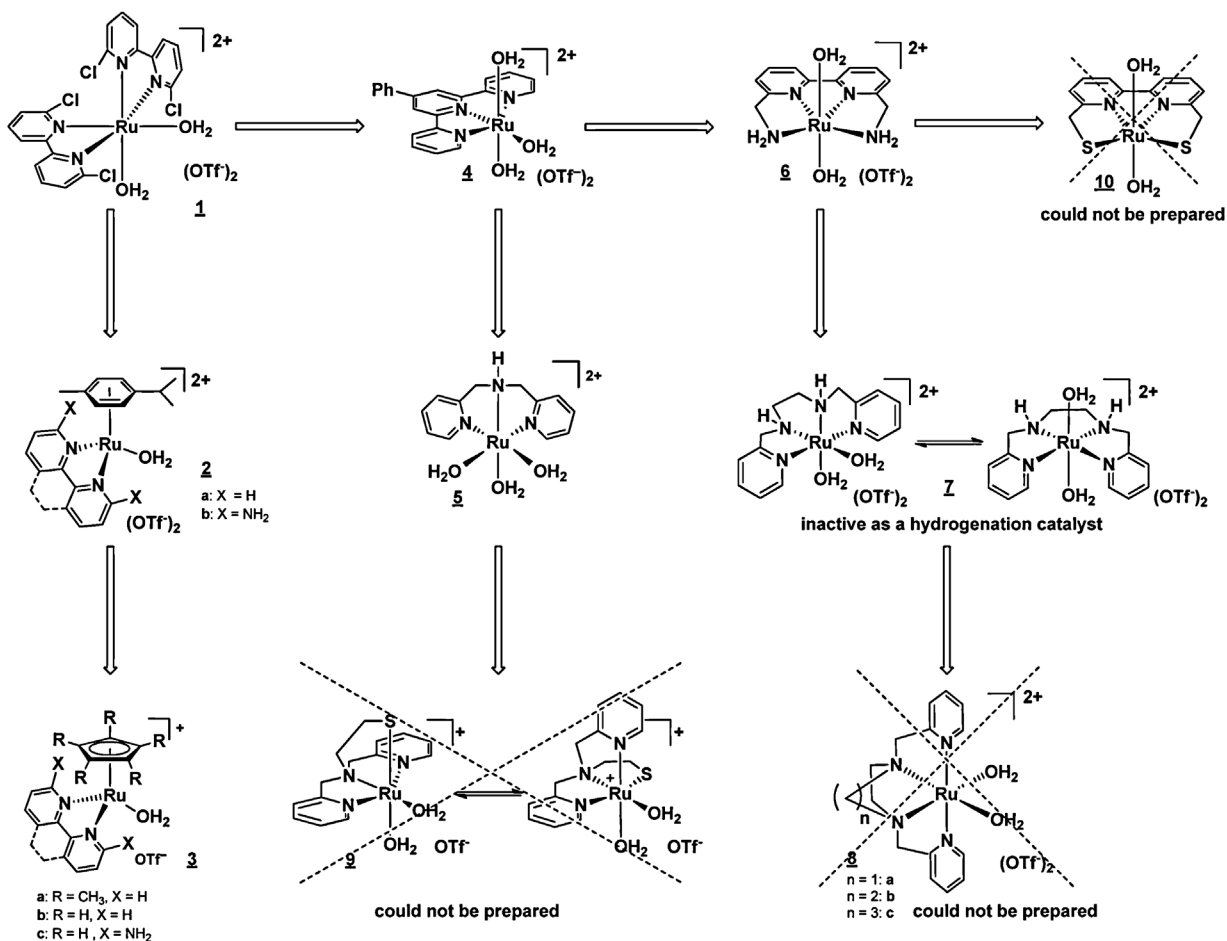
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1. Introduction and motivation

The hydrodeoxygenation of carbohydrate biomass, *i.e.*, sugars and sugar-derived substrates to value-added chemicals can in principle be realized through an iterative reaction cascade composed of Brønstedt or Lewis acid catalyzed dehydrations of the hydroxyl functions abundant in these substrates and metal catalyzed hydrogenations of the resulting C=C and C=O unsaturation, with the net overall reaction being the removal of oxygen. In principle, both hetero- and homogeneous catalysts can be employed, but beginning with the seminal work by Schiavo *et al.* [1], heterogeneous systems have to date dominated the research and development

endeavour [2–9]. Far fewer examples of homogeneous catalysts for the hydrodeoxygenation of polar and water-soluble substrates under acidic conditions have been reported focusing mainly on glycerol and levulinic acid [10–15], with the latter mainly being targeted in ionic liquids or organic solvent medium. Since water is a necessary by-product of the acid catalyzed dehydration steps and the reactions therefore will operate in aqueous medium, such catalysts must – by definition – be water- and acid-stable complexes [16]. In addition, the dehydration of polyalcohol substrates in aqueous conditions empirically requires temperatures in excess of 150 °C. Over the last decade we have engaged in an iterative process of rationally designing, synthesizing, characterizing and testing such catalysts. Scheme 1 shows the structural evolution of the catalyst generations investigated previously (complexes 1–4) [17–22] and the more recent attempts presented and discussed here (complexes 5–10).

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Scheme 1. Structural evolution of water-soluble hydrogenation catalyst investigated and tested.

Acknowledging that an *a priori* and purely theoretically deduced design of catalyst structures and resulting catalytic activity is not possible with present knowledge and therefore has to be based on aspects of both empiricism (*i.e.*, previous knowledge and discovery) and intuition, we targeted the systems shown in **Scheme 1** based on the following principles:

- 1) It is logical to postulate that aquo ligand bearing complexes that can either be isolated or formed *in situ* will be water-stable and – in particular if cationic in nature – also be soluble in water or mixtures of water with other polar solvents.
- 2) The cationic nature of the metal complexes along with the lability of the aquo ligands, whose metal-ligand binding energy has been estimated to be comparable to a (transient) non-classical dihydrogen ligand [23–25], predisposes these systems to act as ionic hydrogenation catalysts [26], in which dihydrogen gas is heterolytically activated into a hydride ligand on the metal centre without inducing a change in the metal's formal oxidation state and a proton taken up by the counter-ion, solvent, substrate or a proton-shuttle incorporated into the ligand framework (*vide infra*). This charge separation process is facilitated by the polar, aqueous reaction medium.
- 3) Based on both entropy and enthalpy effects [27,28], the use of bi-, tri- and ultimately tetra-dentate chelating ligands should result in increased complex formation constants and hence higher temperature stability. In contrast to typical homogeneous hydrogenation catalysts that operate at low temperature and aim to introduce functionality to the substrate while achieving maximal chemo-, regio- or even enantio-selectivity of the

reaction catalyzed, in the hydrodeoxygenation reactions targeted here the goal is to remove functionality from the substrate. The main role of the ligand in these systems is then to prevent reduction and precipitation of bulk metal in oxidation state zero leading to the formation of a heterogeneous catalyst. Our current choice of pyridine and amine rather than phosphine-based ligands is motivated by their anticipated higher long-term stability against air and acidic aqueous media [29–31].

- 4) Dihydrogen must – at least at elevated pressure – be able to effectively compete with all other ligands present in the reaction mixture. Therefore only non-coordinating or only weakly coordinating solvents (ideally water), auxiliary ligands (*e.g.*, CH₃CN), counter-ions and acid co-catalysts can be employed. In addition, the anion must be hydrolysis and redox-stable, limiting the choices to sulfonic acids such as triflate and triflic acid (as shown in **Scheme 1**), the strongest non-oxidizing and hence least coordinating acid known [32], and potentially phosphates and phosphoric acid or sulfates and sulfuric acid with the latter two offering substantial cost advantages. However, regardless of which acid is used, in the – necessarily – aqueous reaction medium solvent levelling of any acid to the pK_a of H₃O⁺ (–1.74, aqueous scale) will occur.
- 5) The incorporation of coordinated or pendant amine or thiolate functions that can act as proton-shuttles within the coordination sphere of the metal may lead to a metal-ligand-bifunctional (MLB) hydrogenation mechanism [33–46], facilitating both the heterolytic activation of dihydrogen and the either step-wise or concerted transfer of a proton and hydride to the unsaturated substrate, potentially resulting in overall higher catalyst activity.

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