



Acceptorless dehydrogenative coupling of alcohols catalysed by ruthenium PNP complexes: Influence of catalyst structure and of hydrogen mass transfer



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ABSTRACT

Base-free catalytic acceptorless dehydrogenative homo-coupling of alcohols to esters under neat conditions was investigated using a combined organometallic synthesis and kinetic modelling approach. The considered bifunctional ruthenium aliphatic PNP complexes are very active, affording TONs up to 15,000. Notably, gas mass transfer issues were identified, which allowed us to rationalize previous observations. Indeed, the reaction kinetics are limited by the rate of transfer from the liquid phase to the gas phase of the hydrogen co-produced in the reaction. Mechanistically speaking, this relates to the interconverting couple amido monohydride/amino bishydride. Overcoming this by switching into the chemical regime leads to an initial turnover frequency increase from about 2000 up to 6100 h⁻¹. This has a significant impact when considering assessment of novel or reported catalytic systems in this type of reaction, as overlooking of these engineering aspects can be misleading.

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1. Introduction

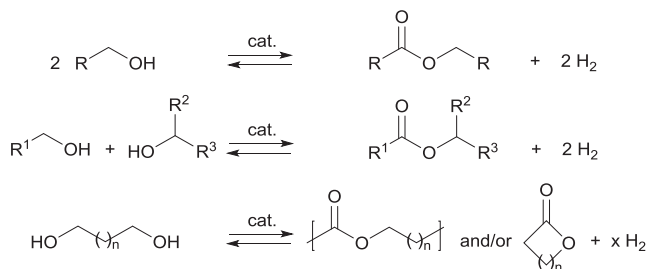
The majority of chemicals arising from raw biomass transformations are (poly)oxygenated compounds such as alcohols, polyols, sugars and carboxylic acids [1]. The overwhelming abundance of hydroxyl group in the bio-based chemicals designates the alcohol function as a key in the production of higher-value chemicals from bio-based feedstock. Bio-based primary alcohols are actually used as biofuels as well as platform molecules in the production of higher-added value chemicals. For example, 1-butanol is considered as an advanced biofuel and bioethanol, for which worldwide production has reached 93 billion litres in 2014, currently accounts almost 90% of the global biofuel production [2,3]. These alcohols have been identified as platform molecules to give industrial access to hydrogen, hydrocarbons, heavier alcohols and oxygenated derivatives [4].

In this context, a reaction such as primary alcohol acceptorless dehydrogenative coupling (ADC) has gained interest as an environ-

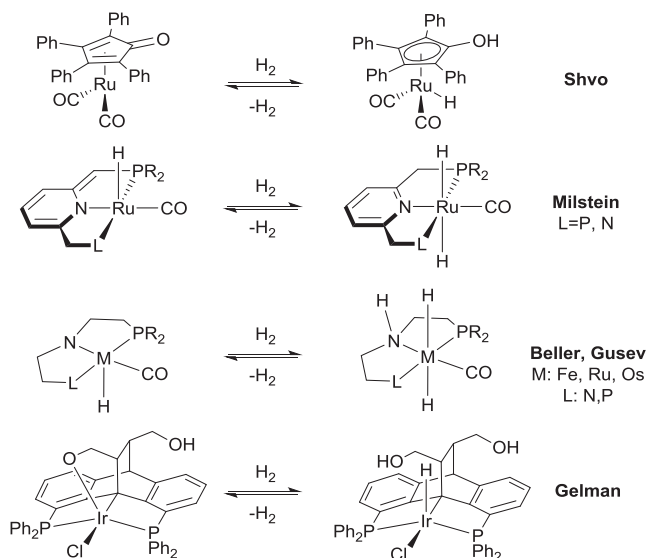
mentally friendly, atom-efficient catalytic process producing simultaneously esters and hydrogen [5]. Depending on the reaction conditions and the substrates nature, this reaction's scope is not limited to the production of symmetric esters from primary alcohols homocoupling: it can be extended to mixed primary-secondary esters, lactones and polyesters, for instance (Scheme 1) [6–8].

Catalytic systems involving conventional (“innocent”) ligands, i.e., ligands that are not involved in the alcohol activation, typically require high reaction temperatures (about 180 °C) and few examples were reported [9]. On the other hand, Shvo's pioneering work demonstrated that cyclopentadienone-based ruthenium complexes are capable of catalysing the ADC of benzyl alcohol to the corresponding ester in the presence of 2 mol% ruthenium catalyst loading and at comparatively milder temperature (145 °C). This is enabled by the use of ligand-metal bifunctional catalyst, wherein the redox activity is combined between the metal center and a cyclopentadienone ligand (Scheme 2) [10]. Further on, building on this metal-ligand cooperativity (MLC) concept, Milstein et al. achieved multiple, major breakthroughs using specific metal/non-innocent ligand combinations that involve the nowadays

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Scheme 1. Alcohols acceptorless dehydrogenative coupling reactions variations and corresponding reverse hydrogenation reactions.



Scheme 2. Selected MLC systems used for ADC of alcohols.

well-established aromatization/dearomatization process of pyridine-based pincer complexes (Scheme 2), which is applied to promote the ADC of alcohols, among other transformations [11]. Remarkably, such systems yield high selectivity under mild conditions (0.1 [Ru] mol% loading, 115 °C).

Following Milstein's initial reports [12], several other related complexes were further developed and have found numerous applications [13]. Iron, ruthenium and osmium complexes supported by pincer ligands bearing a central secondary amino function (PNP [14], PNN [15] or SNS [16]) have been introduced, mostly by Beller and Gusev. These rely on the MLC concept involving an amido-amino couple (Scheme 2) [17]. Similarly, cooperative catalytic systems involving alkoxy-alcohol pairs developed by Gelman (Scheme 2) were also studied. They however require longer reaction times (36 h) to reach satisfactory yields [18]. Among these examples, the PNP systems have attracted a specific interest. The remarkable catalytic performances and fair ease of access to such catalysts has blossomed into their application in organic synthesis [19–23] and potentially in industrial processes [19b]. Several examples of such complexes and corresponding ligands are commercially available from major suppliers. Most frequently, the hydrido chloride precursors, more stable than the catalytically-involved dihydride counterparts, are employed in combination with a large excess of base as a catalyst activator [14a,15,16]. One of the main drawbacks of the use of such additives is the generation of additional base-induced side-products, which implies the need for further additional purification efforts prior to isolation of the targeted product. Thus, development of efficient and robust base-free catalytic

systems is a matter of concern when considering future developments in the use of such catalytic systems at larger scales.

To date, only a few examples describing the base-free ADC reaction were reported (Fig. 1). Milstein complexes and related PNN systems are active using typically catalyst loadings ranging from 0.1 to 1 mol% [12,24]. Examples of the use of osmium and ruthenium hydrides catalysts supported by a aliphatic PNP pincer ligand to prepare the esters are scarce, and mixed results regarding yields were obtained [14b–d]. Iron hydrido-borohydride PNP analogues exhibit good catalytic activity but suffer from fast deactivation and thus require higher catalyst loadings to reach comparable performances [25]. Benefiting from PNN pincer-type ligand design, Gusev osmium complexes achieved this transformation in moderate to high yield [15a,15c]. In almost all the cases, the addition of a base, typically an alkali metal alkoxide in large excess, was still necessary to enable reaching higher catalytic activity [14a,15c].

In the present study, we focused on ruthenium complexes featuring archetypal aliphatic PNP ligands based on the amino-bis(2-phosphinoethyl) framework, with variation of phosphine substituents. We applied the as-designed catalytic systems in the ADC reactions under base-free conditions. We further addressed mechanistic and kinetic modelling aspects, which allowed us to rationalize previous experimental observations from the literature. We could thus highlight previously underestimated engineering aspects that are definitely key to achieve a larger process efficiency for this reaction.

2. Results and discussion

2.1. Synthesis and characterisation of (pre)catalysts

The complexes used in the present study are displayed on Fig. 2. **1a–c**, **2c**, **3a**, **3c**, **4** and **5** have been reported in the literature [14c,21a,26,27]. Several of them (**1c**, **2c** and **5**) are now commercially available. We describe here the synthesis and characterisation of the missing elements of the series (**2a**, **2b**, **3b**). The main spectroscopic features of the complexes are given in Table 1 for comparison. This combines both new and previously reported data for enabling a complete overview of the

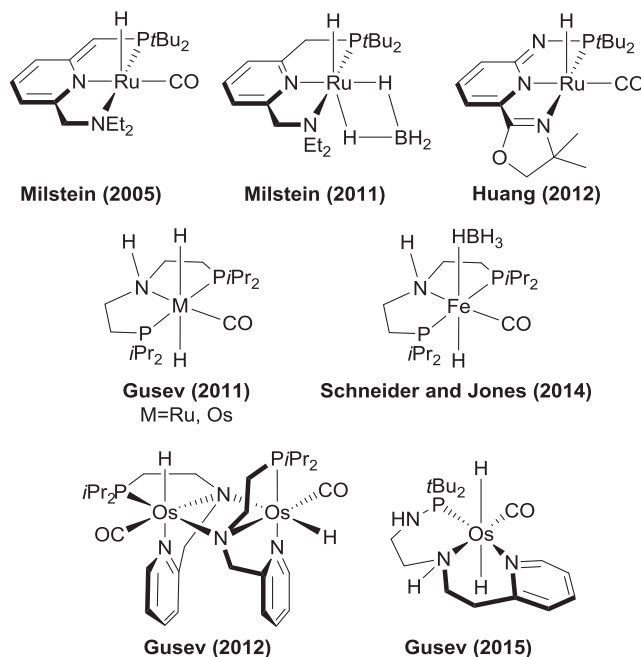


Fig. 1. Main examples of complexes used in the base-free ADC reaction.

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