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Ruthenium complexes bearing amino-bis(phosphinite) or amino-bis(aminophosphine) ligands: Application in catalytic ester hydrogenation

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ABSTRACT

Mononuclear hydrido and dinuclear chloro ruthenium(II) complexes derived from readily available amino-bis(phosphinite) and amino(bisaminophosphine) tridentate ligands were applied in the catalytic hydrogenation of ester derivatives. Notably, the cationic ruthenium dimer **2c** proved to be an efficient pre-catalyst when used in combination with KO^tBu in THF at 120 °C and 50 bar H₂ with aromatic and aliphatic esters.

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Introduction

Reduction of esters into alcohols is an important chemical transformation that is typically performed with high quantities of inorganic hydrides [1]. However, these reactions imply a highly exothermic hydrolysis step along with the formation of significant amounts of wastes, which raises major safety and cost issues. In contrast, catalytic reduction of esters with H₂ is considered as one of the most attractive and suitable method to produce the corresponding alcohols [2–6]. Since the pioneering work of Teunissen and Elsevier in the late 90's [7,8], lots of efforts have been successfully put by both academia and industry in designing efficient homogeneous catalysts, mainly pincer-type complexes based on Ru [9–41], and, to a lesser extent, on Os [20,42,43], Ir [38,44,45], Fe [46–49], Co [50,51], and Mn [52,53] (Scheme 1). This has enabled, for instance, much promising development for the direct conversion of CO₂ captured from air into CH₃OH using a homogeneous Ru-MACHO-polyamine catalytic system [54].

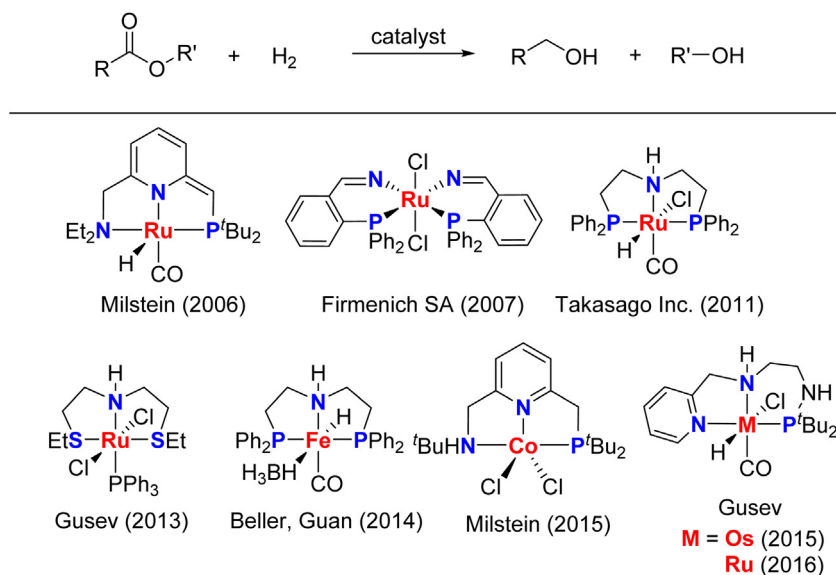
Most of these catalyst systems proceed *via* so-called “metal-ligand cooperation”, which results in efficient heterolytic cleavage

of H₂ [57,58], thereby allowing hydrogenation to be performed under rather mild reaction conditions. However, a main limitation in the use of most of these pincer complexes is their high cost, which is often a consequence of the presence of ligands that require several costly synthetic steps. Hence, there is still a high interest in the design of efficient hydrogenation catalysts that comprise less expensive ligands. In that sense, we became interested in the use of amino-bis(phosphinite) (**1**) [59] and amino-bis(aminophosphine) (**2**) [60] ligands, which are obtained in a straightforward one-step synthesis starting from relatively cheap commercial reagents (Scheme 2).

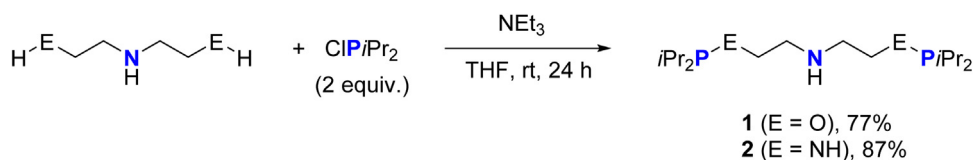
The group of Stephan has studied the coordination chemistry of Ru complexes derived from ligand **1** which were shown to catalyze the dehydrogenation of HMe₂NBH₃ [59]. On the other hand, ligand **2** was used to synthesize a series of Ni(II), Pd(II) and Pt(II) complexes which metal-hydride, –alkyl and –aryl derivatives can be obtained *via* an elegant oxidative addition strategy [61]. We thus became interested in using Ru-{amino-bis(phosphinite)} complexes described by Stephan, as well as in the synthesis and catalytic application of Ru-{amino-bis(aminophosphine)} derivatives in the hydrogenation of esters. To our knowledge, we are aware of only three examples using metal complexes based on aminophosphine-derived pincer ligands for the hydrogenation of esters (Fig. 1) [32,40,42].

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Scheme 1. Ester hydrogenation with representative examples of efficient metal-based homogeneous catalysts [9,24,25,40,42,47,50,55,56].



Scheme 2. Synthesis of amino-bis(phosphinite) (**1**) [59] and amino-bis(aminophosphine) (**2**) [60] ligands.

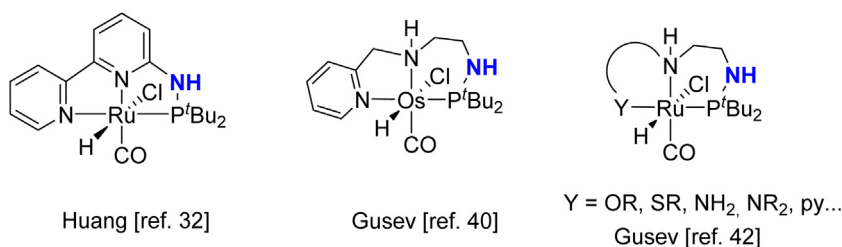


Fig. 1. Reported examples of ester hydrogenation catalysts comprising an aminophosphine moiety.

Notably, an unsymmetrical PNN {bispyridine-aminophosphine}-Ru complex allowed to perform efficiently, under mild conditions (120 °C, 27 atm), the hydrogenation of simple aromatic and aliphatic esters in non-distilled solvents [32]. Also, Gusev has developed recently an Os-based pre-catalyst with another unsymmetrical PNN pyridine-amino-aminophosphine ligand that allows unprecedented chemoselectivities in the hydrogenation of unsaturated esters, where the C=C bond remained unchanged in most cases [42]. Finally, and during the course of our study, the same author reported a series of analogous Ru-PNN complexes that were applied in the hydrogenation of methyl 10-undecenoate [40]. Despite the fact that these complexes all proved to be less efficient than the Os-PNN analogue, some of them clearly outperformed Ru-MACHO [62] and Ru(H)Cl(CO)[(PyrNHCH₂CH₂PPh₂)] [20] catalysts, which are known to be among the most efficient homogeneous hydrogenation catalysts, in terms of activity and selectivity [40].

Based on these promising observations, we interrogated ourselves if Ru complexes derived from readily available amino-bis(aminophosphine) **2** could also provide high catalytic activity and selectivity in the hydrogenation of esters. Herein, we report the synthesis and characterization of new ruthenium complexes derived from tridentate ligand **2**. The catalytic performance of the

resulting complexes and of Stephan's Ru-{amino-bis(phosphinite)} complexes derived from **1** in the hydrogenation of a range of representative esters have been investigated and compared with those of a benchmark catalyst [25].

Results and discussion

Synthesis of Ru complexes

Ligand **1** was used to synthesize the known Ru complexes **1a-c** via slightly modified procedures (Scheme 3) [59]. Following the same complexation conditions (1:1 Ru-to-ligand ratio, toluene, 110 °C, 3 h), the new complexes **2a-c** were obtained in good yields as well starting from ligand **2**.

Thus, reaction of **2** with Ru(H)Cl(CO)(PPh₃)₃ yielded a light yellow solution from which complex **2a** was isolated in 92% yield as a white solid upon addition of hexanes. The two main resonances observed at δ 89.8 (**2a**) and -5.55 (free PPh₃) ppm in the ³¹P{¹H} spectrum of the crude reaction mixture were indicative of complete conversion of the precursors. NMR studies conducted on the isolated complex revealed the presence of a triplet resonance at δ -15.06 ppm (*J*_{HP} = 21.8 Hz) in the ¹H spectrum, and a singlet reso-

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