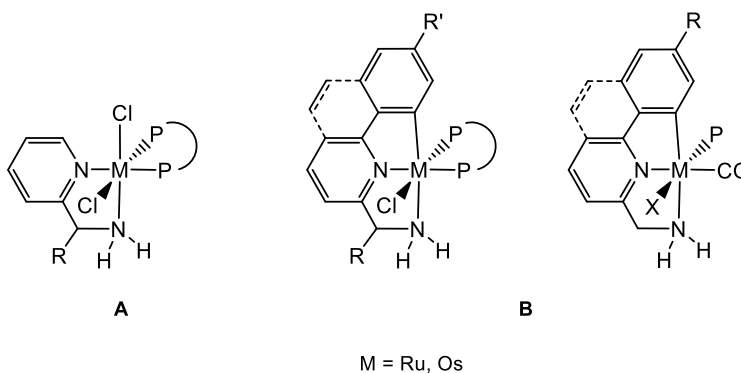


## Highly Efficient Hydrogenation Ruthenium and Osmium Catalysts based on Ampy type Ligands

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Ruthenium phosphine complexes have been widely examined in homogeneous hydrogenation (HY) and transfer hydrogenation reactions (TH), which are cost-effective and environmentally benign ways accepted in the industry for the reduction of carbonyl compounds. On account of the reversibility of the C-H bond activation, ruthenium catalysts have attracted a great deal of interest for a number of organic transformations, including borrowing hydrogen reactions. In this context, the design of efficient chelating and non-innocent ligands is crucial to achieve high activity and retard catalyst deactivation. Highly efficient Ru and Os catalysts for both TH and HY reactions were obtained by our group with ligands based on the 2-(aminomethyl)pyridine motif (**A**).



More productive catalysts were subsequently developed by employment of pincer terdentate CNN ligands showing a metal-carbon  $\sigma$ -bond (**B**).<sup>1</sup> These complexes allow fast reduction of ketones and aldehydes, including some biomass derivatives (5-HMF, ethyl levulinate), with H<sub>2</sub>, 2-propanol or ammonium formate at S/C up to 10<sup>5</sup>. Employment of chiral catalysts in the ketone reduction afforded alcohols with up to 99% *ee*. The Ru and Os derivatives **A** and **B** can also catalyze the acceptorless DHY of alcohols to ketones and other transformations involving alcohol C-H activation, namely alcohol racemization, deuteration and ketone  $\alpha$ -alkylation. Evidence has been provided that the catalytically active Ru hydride species are in rapid equilibrium with metal-amino alkoxides.

(1) (a) S. Giboulot, S. Baldino, M. Ballico, R. Figliolia, A. Pöthig, S. Zhang, D. Zuccaccia, W. Baratta, *Organometallics* **2019**, 38, 1127; (b) G. Chelucci, S. Baldino, W. Baratta, *Coord. Chem. Rev.* **2015**, 300, 29.