

N°53 / OC

TOPIC(s) : Homogenous, heterogenous and biocatalysis

Reduction of esters and alpha, beta-unsaturated carbonyl compounds to alcohols using Fe or Ru MACHO-BH catalysts and ethanol as a source of hydrogen

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## PURPOSE OF THE ABSTRACT

The production of butadiene from ethanol via the Lebedev & Ostromislensky reaction[1] is an important industrial process, however, the overall yield is only about 60%. One of the key transformations is believed to be the reduction of crotonaldehyde to crotyl alcohol.[2] In order to improve the efficiency of the process we decided to look at it in a step-by-step manner; therefore we performed a search for a new catalyst for the reduction of alpha, beta-unsaturated carbonyl compounds to alcohols. Ru-MACHO-BH is a commercially available complex which was reported to catalyze various hydrogenation reactions[3], including the dehydrogenation of alcohols.[4] Motivated by these reports, we studied its performance in the transfer hydrogenation of  $\alpha,\beta$ -unsaturated carbonyl compounds.

We will demonstrate here for a large range of substrates that the reaction can work with low catalyst loadings (down to 0.1 mol%) and high selectivity (Scheme 1a)[5]. While isopropanol is commonly used for transfer hydrogenation of this type of substrates, we found that in this case ethanol can work equally well.

After the results obtained with the Ru catalyst, we decided to explore MACHO-BH complexes of the cheaper and more abundant 1st row transition metals. While Fe-MACHO-BH was able to perform the transfer hydrogenation of  $\alpha,\beta$ -unsaturated carbonyl compounds (although with much lower activity and selectivity than the Ru catalyst), we found that it catalyzed the transfer hydrogenation of esters (Scheme 1b) [6]. To the best of our knowledge, this is the first reported transfer hydrogenation of esters using iron catalysts. In fact, only ruthenium was reported to perform the reaction in the past[7]. We will show a range of substrates which were reduced by ethanol in the presence of Fe-MACHO-BH with isolated yields of up to 99%. In addition to using ethanol as a sustainable source of hydrogen, this catalyst was also able to convert polyesters into diols, which could be applied in plastic recycling.

## FIGURES

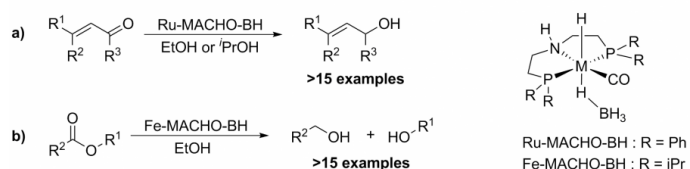


FIGURE 1

Scheme 1.

FIGURE 2

## KEYWORDS

transfer hydrogenation

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