A Cptt-based Trioxo-Rhenium Catalyst for the Deoxydehydration of Diols and Polyols

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Trioxo-rhenium complexes have been known as active catalysts for the deoxydehydration (DODH) of vicinal diols (glycols). In our previous work, the bulky Cp-based trioxo-rhenium complex Cp\textsuperscript{ttt}ReO\textsubscript{3} (Cp\textsuperscript{ttt} = 1,2,4-tri-tert-butylcyclopentadienyl) was reported to be a very active catalyst for the DODH of diols and polyols. The electron-rich Cp\textsuperscript{ttt} ligand of the complex stabilizes the high valence rhenium center, avoiding overreduction, and hampers catalyst dimerization leading to decomposition, to result in a high TON. Interestingly, a slight change of the ligand (removing one tert-butyl) results in a change in the activity of the trioxo-rhenium complex in DODH catalysis. Compared to Cp\textsuperscript{ttt}ReO\textsubscript{3}, the new catalyst Cp\textsuperscript{tt}ReO\textsubscript{3} (Cp\textsuperscript{tt} = 1,3-di-tert-butylcyclopentadienyl) shows a better reactivity when applied to DODH of biomass-derived polyols.

In this review, we report on the DODH of diols and biomass-derived polyols using Cp\textsuperscript{tt}ReO\textsubscript{3} as a new catalyst. The DODH reaction was optimized using 2 mol% of Cp\textsuperscript{tt}ReO\textsubscript{3} and 3-octanol as both reductant and solvent. The Cp\textsuperscript{tt}ReO\textsubscript{3} catalyst exhibits an excellent activity for biomass-derived polyols. Specifically, glycerol is almost quantitatively converted to allyl alcohol and mucic acid gives 75% of muconates at 91% conversion. In addition, the loading of Cp\textsuperscript{tt}ReO\textsubscript{3} can be reduced to 0.1 mol% to achieve a turn-over number as high as 900 per Re when using glycerol as substrate. Examination of DODH reaction profiles by NMR spectroscopy indicates that catalysis is related to Cp-ligand release, which raises questions on the nature of the actual catalyst.

Scheme one. Trioxo Rhenium Catalyzed DODH of Glycerol

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