RHENIUM-CATALYSED DEOXYGENATION AND REDUCTIVE COUPLING OF BIOMASS-DERIVED ALCOHOLS

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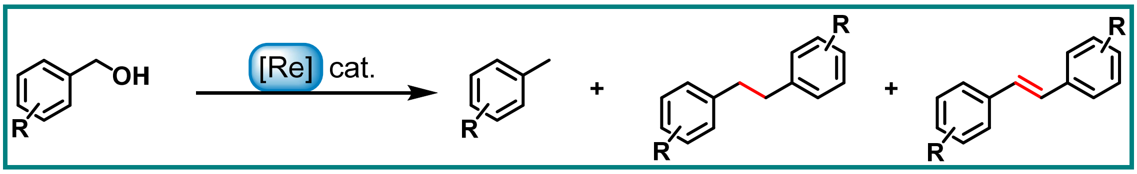
Chemical industry relies heavily on the use of fossil fuels, not only for energy production, but also as feedstocks in production processes, thus exerting a significant burden on the environment in form of greenhouse gas emission.[1] Growing interest in alternatives to fossil fuels has instigated research into novel methods to utilise biomass-derived feedstocks. The main objective of biomass conversion is the reduction of its oxygen content, resulting in an increase in its energy content.[2]

The challenging task of developing methods for biomass conversion for the production of other valuable chemicals has led to the emergence of approaches such as deoxygenative coupling. This results in a new carbon–carbon bond formation, thus opening possibilities to access and assemble more complex molecular scaffolds.[3]



Building upon previous accounts with catalytic systems based on rhenium(V)[3], molybdenum(VI)[4] and vanadium(V)[5] metal centres, herein we report rhenium-catalysed deoxygenative coupling of biomass-derived benzylic alcohols.

A series of d^2 and d^4 rhenium complexes bearing phosphine ligands in the coordination sphere of the metal centre, as well as the commercially available catalyst methyl trioxorhenium (MTO) were tested in deoxygenation and reductive coupling of benzylic alcohols. Upon screening and optimisation of the catalyst system, excellent activity was observed for all the catalysts tested, resulting in full deoxygenation of substrates with a concurrent formation of the deoxygenation product, as well as derivatives of stilbene and bibenzyl as coupling products. The d^4 rhenium systems and methyl trioxorhenium strongly favoured the formation of the saturated over the unsaturated coupling product over an extended substrate scope. In addition, in this study, we provide the first insights into the mechanism of the catalytic reaction.

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[1] Levi, P. G.; Cullen, J. M. *Environ. Sci. Technol.* **2018**, 52, 1725–1734.

[2] Selective Catalysis for Renewable Feedstocks and Chemicals; Nicholas, K. M., Ed.; *Top. Curr. Chem.*; Springer International Publishing: Cham, 2014; Vol. 353.

[3] Kasner, G. R.; Boucher-Jacobs, C.; Michael McClain, J.; Nicholas, K. M. *Chem. Commun.* **2016**, 52, 7257–7260.

[4] Jiang, H.; Lu, R.; Luo, X.; Si, X.; Xu, J.; Lu, F. *Chem. Eur. J.* **2021**, 27, 1292–1296.

[5] a) Steffensmeier, E.; Nicholas, K. M. *Chem. Commun.* **2018**, 54, 790–793. b) Griffin, S. E.; Schafer, L. L. *Inorg. Chem.* **2020**, 59, 5256–526.