

## A Surface Organometallic Chemistry Platform for Efficient Deoxygenation of Small Molecule Oxygenates

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Current chemicals and fuels are mostly derived from fossil fuels and are thus not sustainable due to the limited resources and the emissions of CO<sub>2</sub> associated with their production and use. Moving to biomass-derived feedstocks would offer several advantages: they are renewable, (more) carbon neutral, already available as a waste byproduct of various industries.<sup>1</sup> However, biomass intrinsically contains a large variety and number of oxygen-containing functional groups, that need to be converted to bridge the gap with most value-added chemical products, hence the need for synthetic methodologies for selective and efficient deoxygenation while leaving the carbon skeleton intact.<sup>2</sup> Ideally, this transformation can be achieved using only (green) dihydrogen as a reactant, rendering it both atom economical and forming only water as benign byproduct. In this context, bimetallic catalysts are privileged materials by displaying bifunctional properties, enabling dihydrogen activation and acid-catalyzed reactions from the co-existence of metallic nanoparticles and metal oxide — e.g., the combination of group XI-X metals and a group VI-VII metal oxide such as MoO<sub>3</sub>.<sup>3,4</sup> However, the mechanism and exact role and synergies between the two metals and the support is poorly understood. In order to be able to study these materials and establish meaningful structure activity correlations, well-defined model catalysts are required. We have thus developed a platform of organometallic precursors based on diisopropylamidinate ligands for the metals Rh, Ir, Ni, Pd, and Pt, that can be employed to generate size-homogeneous supported nanoparticles on oxide-based supports, via surface organometallic chemistry.<sup>5,6</sup> We have examined bimetallic materials synthesized from a Mo-doped SiO<sub>2</sub> support to evaluate their activity in deoxygenation. During this study, we have identified catalyst materials active in the deoxygenation of primary, secondary, and tertiary alcohols, various ketones, and  $\alpha$ -ketoesters. Almost quantitative yields can be achieved for some substrates, and functional group tolerance towards both electrophilic and nucleophilic functional groups was observed, allowing for a synthetic handle for further diverse functionalization of the products.

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