

Base-metal and Metal-free Hydride Donor Reagents – From Fundamentals to Applications in Electrocatalysis

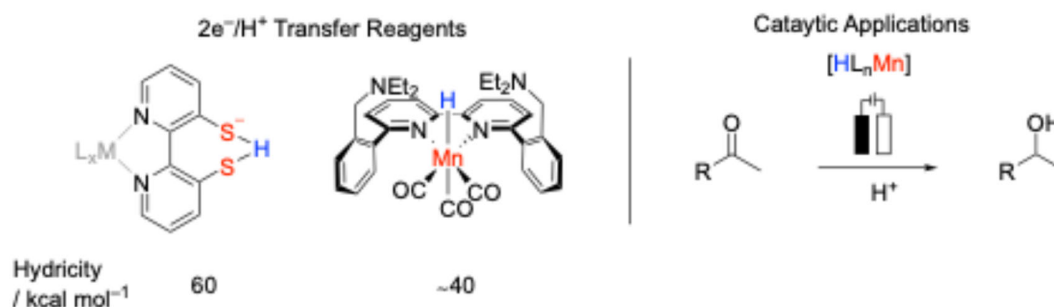
Inke Siewert

Georg-August-Universität Göttingen, Germany

Hydride transfer reactions are fundamental for functional group transformations in chemical synthesis, especially for the conversion of carbonyl compounds. Hydride transfer reactions proceed in a concerted two-electron, proton-coupled fashion thereby circumventing the formation of high energy intermediates. Noble metal hydride complexes, particularly Rh, Pd and Pt species, are generally excellent hydride donors and can be used in catalytic amounts in thermal hydrogenation reactions. However, due to the low abundance of noble metal-based hydrides, recent scientific efforts have shifted to base-metal and metal-free hydride donor reagents and their utilization in (electro)catalytic reduction processes.

In an electrocatalytic application, the conjugated reagent must be (re)generated by consecutive single electron transfer and protonation steps, which is usually challenging. Electrochemical $1e^-$ -reduction often produces highly reactive radical species as intermediates, which have a strong tendency to e.g. dimerize instead of undergoing the desired $1H^+/1e^-$ follow-up reactivity. I will present the electrochemical formation of base-metal and metal-free hydride donor reagents for storing multiple electrons and protons focusing of the distinct differences and similarities in their formation and reactivity.^[1,2]

Furthermore, I will show the application of such hydride transfer reagents in the electrochemical hydrogenation of C=O bonds in ketones and aldehydes using electrons and protons.^[2] A large variety of substrates is accessible by this method and in-depth mechanistic studies gave valuable insights for catalyst improvement.



References:

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