Novel C=O Bond Reductions with Renewable Surrogates of Hydroisilanes

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The reduction of C=O bonds has gathered tremendous momentum in recent years because they are a key part of the strategy to valorize renewable oxidized feedstocks such as CO₂ or biomass derivatives into value-added chemicals and/or fuels. Among the archetypical reductants employed in C=O reduction reactions, main group element-based hydrides (e.g. NaBH₄ or Et₃SiH) are particularly attractive in terms of both selectivity and versatility. Nevertheless, their methods of preparation mainly rely on energy-demanding processes, which in turn limit the recyclability of these reductants and therefore reduce their potential of applications within the framework of sustainable chemistry.

To circumvent these limitations, we have developed a conceptual alternative consisting in the utilization of boryl and silyl formates (E–OC(O)H, E = B or Si) as surrogates of the corresponding E–H reductants. The key features of this endeavor stems not only from the renewability of the formate moiety since formic acid can be obtained by 2e⁻ electroreduction of CO₂ but also from the pre-existence of a E–O bond prior to the C=O reduction.

The viability of the aforementioned concept will be demonstrated with the catalytic transfer hydrosilylation of aldehydes (Fig. 1, right arrow). In the presence of a well-defined ruthenium catalyst, various aldehydes were indeed reduced to the corresponding silyl ethers with high chemoselectivity and efficiency.

Mechanistic insights based on both experimental observations and DFT calculations will be provided to point out the difference between this new protocol and classical hydrosilylation methodologies. A particular case of transfer hydrosilylation, namely the disproportionation of silyl formates into methoxysilanes and CO₂ (Fig. 1, left arrow), will also be discussed as this new reaction well illustrates the potential of silyl formates in sustainable chemistry.

Figure 1: Examples of transfer hydrosilylation protocols

1 Liu, Qiang; Wu, Lipeng; Jackstell, Ralf; Beller, Matthias Nat. Commun., 2015, 6, 5933.