Novel C=O Bond Reductions with Renewable Surrogates of Hydrosilanes

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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 CO_2 or biomass derivatives into value-added chemicals and/or fuels.[1] Among the archetypical reductants employed in C=O reduction reactions, main group element-based hydrides (e.g. $NaBH_4$ or Et_3SiH) are particularly attractive in terms of both selectivity and versatility.[2] 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.[3]

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.[4] 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 CO_2 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.[5] 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 CO_2 (Fig. 1, left arrow), will also be discussed as this new reaction well illustrates the potential of silyl formates in sustainable chemistry.

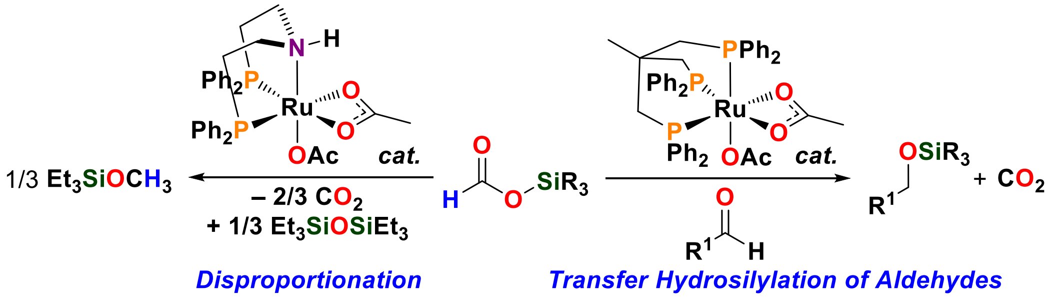

Figure 1: Examples of transfer hydrosilylation protocols

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

[2] J. Fernández-Alvarez, Francisco; M. Aitanib, Abdullah; A. Oro, Luis *Catal. Sci. Technol.*, **2014**, *4*, 611-624.

[3] Chauvier, Clément; Cantat, Thibault *ACS Catal.*, **2017**, *7*, 2107–2115.

[4] For conceptually related works, see: a) Chauvier, Clément; Thuéry, Pierre; Cantat, Thibault *Chem. Sci.*, **2016**, *7*, 5680–5685; b) Oestreich, Martin, *Angew. Chem., Int. Ed.*, **2016**, *55*, 494–499.

[5] Chauvier, Clément; Thuéry, Pierre; Cantat, Thibault *Angew. Chem Int. Ed.*, **2016**, *55*, 14096–14100.