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HIGHLY CHEMOSELECTIVE CATALYTIC TRANSFER HYDROSILYLATION OF ALDEHYDES

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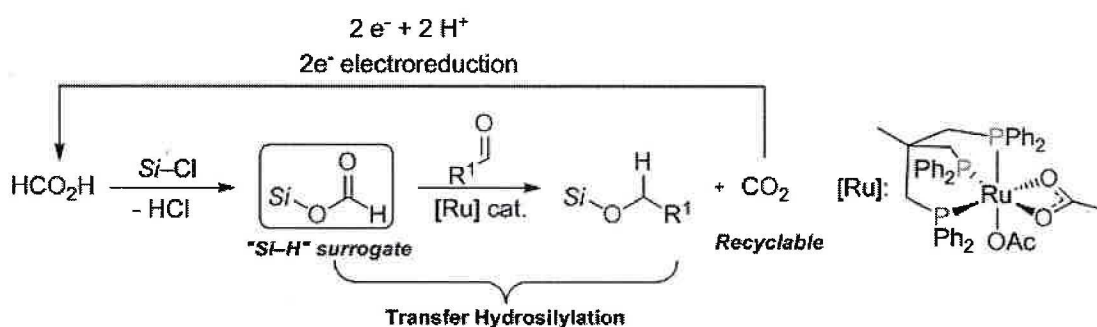
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Catalytic hydrosilylation has found widespread applications in the silicon industry and in synthetic organic chemistry owing to its ability to induce both reduction (*hydro*) and functionalization (*silylation*) of unsaturated bonds such as C=C or C=O bonds in an atom-economical manner.¹ Nevertheless, the preparation of hydrosilanes (R₃SiH) relies on energy-intensive processes based either on costly redox-manipulation of Si or on the reduction of chlorosilanes with highly reactive metal hydrides such as LiAlH₄.

To circumvent these limitations, we have developed a conceptual alternative consisting in the utilization of silyl formates (R₃SiOC(O)H), readily prepared from formic acid and chlorosilanes, as surrogates of hydrosilanes in hydrosilylation reactions.² The key feature of this endeavor stems from the renewability of the hydridic counterpart in the silyl formates since formic acid can be obtained by 2e⁻ electroreduction of CO₂.³

The viability of the aforementioned concept has been demonstrated with the catalytic transfer hydrosilylation of aldehydes. In the presence of a well-defined ruthenium catalyst, various aldehydes are efficiently and chemoselectively reduced to silyl ethers with the concomitant release of CO₂. Mechanistic insights were gained by both experimental observations and DFT calculations and they highlight the pivotal role of a transmetallation step to rationalize the outstanding chemoselectivity of the process.⁴



1 B. Marciniak, H. Maciejewski, C. Pietraszuk, P. Pawluc, Hydrosilylation: A Comprehensive Review on Recent Advances, Vol. 1 (Ed.: B. Marciniak), Springer, Berlin, 2009.

2 For conceptually related works, see: a) C. Chauvier, P. Thuéry, T. Cantat, *Chem. Sci.* **2016**, 7, 5680; b) M. Oestreich, *Angew. Chem., Int. Ed.* **2016**, 55, 494.

3 A. S. Agarwal, Y. Zhai, D. Hill, N. Sridhar, *ChemSusChem*, **2011**, 4, 1301.

4 C. Chauvier, P. Thuéry, T. Cantat, *Angew. Chem Int. Ed.* **2016**, 55, 14096.