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## HIGHLY CHEMOSELECTIVE CATALYTIC TRANSFER HYDROSILYLATION OF ALDEHYDES

Clément Chauvier,<sup>a</sup> Thibault Cantat\*

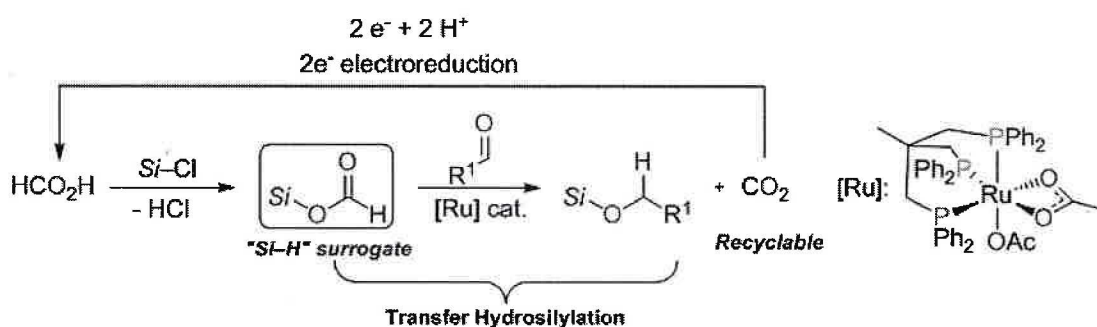
<sup>1</sup>NIMBE, CEA, CNRS, Université Paris-Saclay, Gif-sur-Yvette, France

[clement.chauvier@cea.fr](mailto:clement.chauvier@cea.fr)

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.<sup>1</sup> Nevertheless, the preparation of hydrosilanes (R<sub>3</sub>SiH) 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 LiAlH<sub>4</sub>.

To circumvent these limitations, we have developed a conceptual alternative consisting in the utilization of silyl formates (R<sub>3</sub>SiOC(O)H), readily prepared from formic acid and chlorosilanes, as surrogates of hydrosilanes in hydrosilylation reactions.<sup>2</sup> 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<sup>-</sup> electroreduction of CO<sub>2</sub>.<sup>3</sup>

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 CO<sub>2</sub>. Mechanistic insights were gained by both experimental observations and DFT calculations and they highlight the pivotal role of a transmetalation step to rationalize the outstanding chemoselectivity of the process.<sup>4</sup>



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.