

Highly chemoselective catalytic transfer hydrosilylation of aldehydes

Clément Chauvier, Thibault Cantat

► **To cite this version:**

Clément Chauvier, Thibault Cantat. Highly chemoselective catalytic transfer hydrosilylation of aldehydes. 3rd International Green Catalysis Symposium, Mar 2017, Rennes, France. cea-02341556

HAL Id: cea-02341556

<https://hal-cea.archives-ouvertes.fr/cea-02341556>

Submitted on 31 Oct 2019

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

HIGHLY CHEMOSELECTIVE CATALYTIC TRANSFER HYDROSILYLATION OF ALDEHYDES

Clément Chauvier,^a Thibault Cantat*

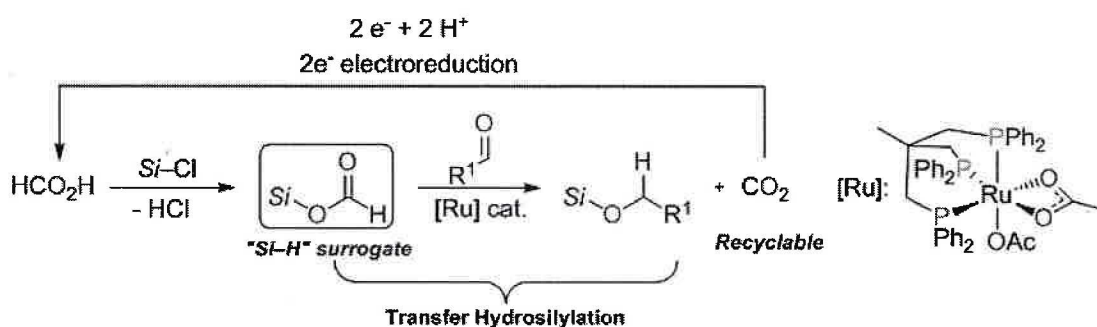
¹NIMBE, CEA, CNRS, Université Paris-Saclay, Gif-sur-Yvette, France

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.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.