

Silylation of O-H Bonds by Catalytic Dehydrogenative and Decarboxylative Coupling of Alcohols with Silyl Formates

Timothé Godou, Clément Chauvier, Thibault Cantat

► **To cite this version:**

Timothé Godou, Clément Chauvier, Thibault Cantat. Silylation of O-H Bonds by Catalytic Dehydrogenative and Decarboxylative Coupling of Alcohols with Silyl Formates. GECOM CONCOORD 2018, May 2018, Longeville sur mer, France. cea-02340279

HAL Id: cea-02340279

<https://hal-cea.archives-ouvertes.fr/cea-02340279>

Submitted on 30 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.

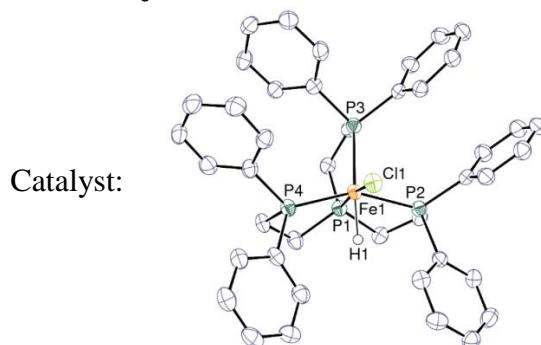
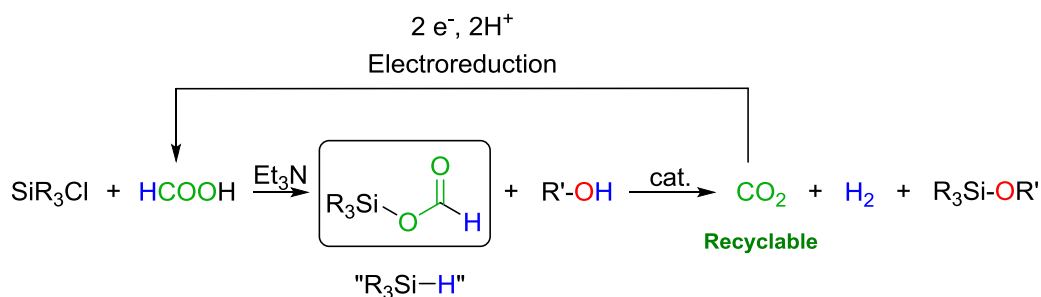
Silylation of O–H Bonds by Catalytic Dehydrogenative and Decarboxylative Coupling of Alcohols with Silyl Formates.

Timothé Godou^a; Clément Chauvier^a; Thibault Cantat*

^a CEA Saclay 91191 Gif sur Yvette CEDEX, France

The replacement of polar O–H bonds in alcohols and phenols with the O–Si linkage is of great importance across the chemical sciences. For example, in synthetic organic chemistry, the silyl ether functionality is frequently installed for the temporary protection of otherwise reactive hydroxyl groups. In this respect, the wide availability of various silyl groups with tunable stereo-electronic properties has considerably facilitated the total synthesis of complex natural products. In addition, silyl ethers generally display increased thermal stability and volatility as well as decreased polarity compared to their parent alcohols and trimethylsilylation of the latter has thus become an invaluable tool for their derivatisation prior to GC analysis.

In this context, we have developed a new method consisting in the utilization of silyl formates ($R_3SiOC(O)H$), as surrogates of hydrosilanes.¹ The key feature of this endeavor relies on the reactivity of silylformates, which undergo decarboxylation and dehydrogenation in the presence of the alcohol reagent and the metal catalyst. The resulting Si–O coupling proceeds with the release of H_2 and CO_2 gases as the sole by-products. Importantly, the renewability of the silyl formate reductant is provided by the possible $2e^-$ electroreduction of CO_2 .^{2,3,4} In this work, a new synthesis pathway of silyl formate prepared from sodium formate and chlorosilanes is exposed as the use of an earth-abundant transition-metal as catalyst for the reaction.⁵



¹ 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. c) C. Chauvier, P. Thuéry, T. Cantat, *Angew. Chem., Int. Ed.* **2016**, 55, 14096–14100

² A. S. Agarwal, Y. Zhai, D. Hill, N. Sridhar, *ChemSusChem*, **2011**, 4, 1301.

³ C. Chauvier, P. Thuéry, T. Cantat, *ACS Catal.* **2017**, 7, 2107–2115

⁴ C. Chauvier, T. Godou, T. Cantat, *Chem. Commun.*, **2018**, 53, 11697–11700, 2017.

⁵ T. Godou, C. Chauvier, T. Cantat, *Synlett*, **2018**, 28, 2473–2477, 2017