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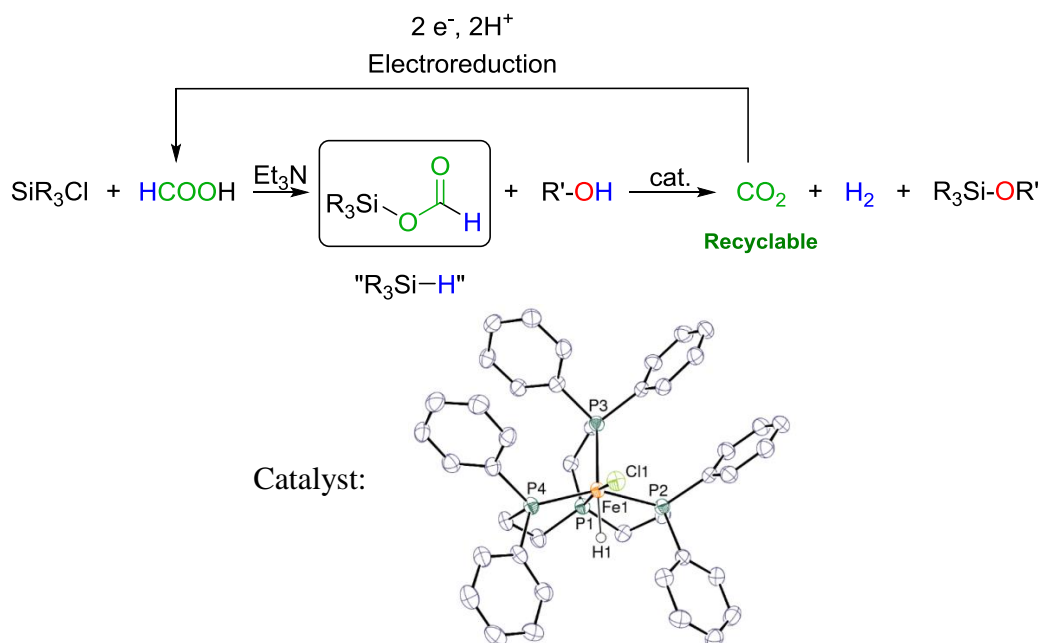
Silylation of O–H Bonds by Catalytic Dehydrogenative and Decarboxylative Coupling of Alcohols with Silyl Formates.

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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