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Uranyl triflate as selective catalyst in the hydrosilylation of aldehydes

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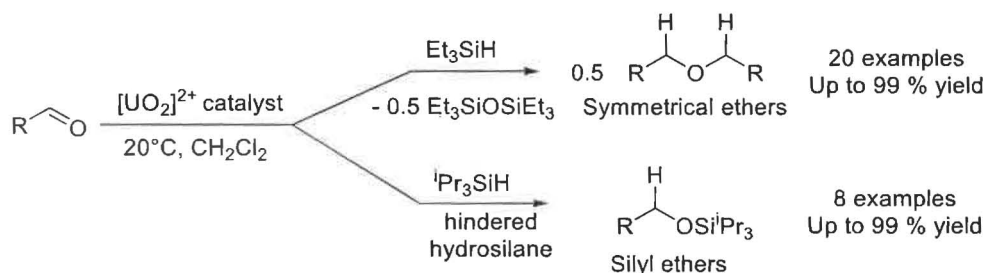
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The chemistry of uranium has attracted considerable attention in industrial and environmental fields and fundamental researches have revealed unique chemical features of this element. For years, transformation of oxygenated compounds with actinide catalysts was not considered due to the strength of the actinide-oxygen bond that should preclude efficient catalytic turnover. However, this idea vanished in 2008 when the group of Eisen unveiled the ability of actinide(IV) complexes (U and Th) to promote the catalytic dimerization of aldehydes.¹ A few reports now describe activation of oxygen substrates with U^{4+} , Th^{4+} and $[UO_2]^{2+}$ complexes.²

While the reduction of oxygenated substrates, involving the cleavage of C–O and/or C=O bonds, is of fundamental importance, the utilization of actinide catalysts in this area is extremely rare. In particular, hydrosilanes (R_3SiH) have never been combined with the 5f elements for the reduction of carbonyl groups although the slight polarization of the Si–H bond displays advantages for the development of selective reduction processes in organic chemistry, the valorization of biomass,³ and the recycling of plastics.⁴

Here, we report the first use of an actinide complex to carry out catalytic hydrosilylation of

C=O bonds.⁵ The



Scheme 1 : hydrosilylation of aldehydes catalyzed by $[UO_2(OTf)_2]$

uranyl cation $[UO_2]^{2+}$, which is the most oxidized uranium fragment ubiquitous in the environment and in the nuclear industry, proved, as the uranyl triflate species, an efficient catalyst in the reductive hydrosilylation of aldehydes into symmetric ethers and silylated alcohols depending on the nature of the hydrosilane (Scheme 1). The reactions also show that, although the uranyl ion contains oxidizing U=O bonds, reduction of the C=O group and C–O bond cleavage are possible without loss of integrity of the uranyl moiety.

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