

Metal-free Hydrogenolysis of Halogenosilanes to Hydrosilanes Catalyzed by Frustrated Lewis Pairs

Gabriel Durin, Jean-Claude Berthet, Emmanuel Nicolas, Thibault Cantat

Université Paris-Saclay, CEA, CNRS, NIMBE, 91191 Gif-sur-Yvette Cedex, France gabriel.durin@cea.fr



Base = piperidine, guanidine, phosphazene

Hydrosilanes are convenient reductants for a large variety of organic oxygenated substrates and they have been successfully applied in the conversion of bio-based materials¹ and CO_2 .² Hydrosilanes are however produced *via* energy intensive processes³ and they generate, after use, silicon oxides wastes such as siloxanes, which are difficult to recycle. These limitations call for the development of catalytic processes able to transform Si–O bonds in siloxanes into Si–H hydrides. Previous reports⁴ have shown that halogenosilanes can be prepared from siloxanes through dehydration by acidic treatment. Catalytic methods that would convert Si–X (X = OTf, I, Br, CI) linkages into Si–H hydrides are thus particularly attractive. The works of Shimada and Schneider have highlighted the use of noble metal catalyst to perform the hydrogenolysis of halogenosilanes into hydrosilanes.⁵ But, no catalysis involving non noble metal complexes or metal-free species has been reported so far.

We report here an efficient hydrogenolysis of halogenosilanes, using frustrated Lewis pairs as catalyst, in mild conditions with selective formation of hydrosilanes in high yields (up to 95 %). These results have been rationalized based on NMR investigations, kinetic studies and DFT calculations.

¹ L. Monsigny, E. Feghali, J.-C. Berthet and T. Cantat, *Green Chem.*, **2018**, *20*, 1981.

² S.N. Riduan, , Y. Zhang and J.Y. Ying, *Angew. Chem. Int. Ed.*, **2009**, *48*, 3322.

³ W. Kalchauer, B. Pachaly, In *Handbook of Heterogeneous Catalysis*.Wiley, **2008**, 2635-2647.

⁴ P. A. Di Giorgio, W. A. Strong, L. H. Sommer and F. C. Whitmore *J. Am. Chem. Soc.*, **1946**, *68*, 7, 1380.
⁵ D. Tsushima, M. Igarashi, K. Sato and S. Shimada, *Chem. Lett.*, **2017**, *46*, 1532–1534 ;T. Beppu, K. Sakamoto, Y. Nakajima, K. Matsumoto, K. Sato and S. Shimada, *J. Org. Chem.*, **2018**, *869*, 75-80 ; A. Glüer, J. I. Schweizer, U. S. Karaca, C. Würtele, M. Diefenbach, M. C. Holthausen and S. Schneider, *Inorg. Chem.*, **2018**, *57*, 13822-13828.