

Catalysed hydrosilylations: from precious metals to abundant metals and organocatalysts

Dr. Christophe Michon
University of Strasbourg - CNRS
LIMA UMR7042 - ECPM 25 Rue Becquerel
FR-67087 Strasbourg
cmichon@unistra.fr

Hydrosilylation is a reaction of growing interest for the mild and selective reduction of organic compounds like alkenes, alkynes, carbonyls and imines using mainly transition-metal catalysts.[1,2] Indeed, the use of hydrosilanes as reductants, which proceeds without any high-pressure equipment or high temperatures, is an interesting alternative to hydrogenation. Because the reactivity of such reagents and related reaction intermediates is modular and depends on the substituents on the silicon atoms, the hydrosilylation reaction can become a highly chemo- and regioselective reduction method that tolerates various other reducible functional groups.[2] The known silane activation modes operate through oxidative addition,[3] metal-ligand cooperation,[4] metal-substrate double activation,[5] heterolytic polar electrophilic activation with organometallics[6] or through the use of frustrated Lewis pairs.[7] Beside catalysts based on late-transition metals, attention is gradually turned on catalysts based on abundant and non-precious metals, i.e. first row transition metals, as well as frustrated Lewis pairs due to economic, environmental and societal reasons.[8]

At first, we have shown iridium(III) metallocycles[9a] can catalyze the hydrosilylation of alkynes,[9b] imines,[9c] and various carbonyl and carboxylic acid derivatives.[9d-g] We have specifically highlighted in details the selective hydrosilylation of esters to aldehydes[9d], the efficient hydrosilylation of amides into amines[9f] and the controlled hydrosilylation of ene-amides into amides or amines through a tandem process.[9g] These reactions are fast, selective and performed with low catalyst loadings using mild conditions. The reaction mechanisms were detailed through studies based on NMR, HRMS, DFT calculations and on the isolation of key intermediates.

Afterwards, we have shown cobalt(II) salts combined with NaBHET₃ and eventually a base catalyze efficiently and selectively the reduction of esters to aldehydes or alcohols through hydrosilylation by using phenylsilane. Catalyst characterisations by XRD, XPS, TEM and STEM analyses indicate the materials were partially crystalline with the presence of cobalt nanoparticles. Control experiments suggested low valent Co(0) was the active catalytic species involved. Interestingly, one catalyst was successfully reused up to 4 cycles without significant loss of selectivity.[10] Moreover, we have shown a half-sandwich nickel NHC-picolyl complex effectively catalyzed the hydrosilylation of aldehydes and ketones. Studies by DLS, STEM, XPS, ICP-AES and elemental analyses showed evidence for the involvement of NHC-stabilized Ni(0) nanoparticles when potassium t-butoxide is used as an activator.[11]

Finally, we have reported a catalytic and transition metal-free reductive deoxygenation of esters to ethers through the use of a hydrosilane and a fluorinated borate BArF salt as catalyst. Experimental and theoretical studies support the role of noncovalent interactions between the fluorinated catalyst, the hydrosilane and the ester substrate in the activation of silane and therefore in the reaction mechanism.[12]

References

- [1] P. A. Dub, T. Ikariya, *ACS Catal.* **2012**, *2*, 1718.
- [2] a) M. Oestreich, *Angew. Chem. Int. Ed.* **2016**, *55*, 494; b) T. D. Tilley, *Angew. Chem. Int. Ed.* **2017**, *56*, 2260.
- [3] P. B. Glaser, T. Don Tilley, *J. Am. Chem. Soc.* **2003**, *125*, 13640.
- [4] T. T. Metsänen, P. Hrobárik, H. F. T. Klare, M. Kaupp, M. Oestreich, *J. Am. Chem. Soc.* **2014**, *136*, 6912.
- [5] a) K. A. Nolin, J. R. Krumper, M. D. Pluth, R. G. Bergman, F. D. Toste, *J. Am. Chem. Soc.* **2007**, *129*, 14684; b) M. A. Rankin, G. Schatte, R. McDonald, M. Stradiotto, *J. Am. Chem. Soc.* **2007**, *129*, 6390.
- [6] a) M. Hamdaoui, C. Desrousseaux, H. Habbita, J.-P. Djukic, *Organometallics* **2017**, *36*, 4864; b) P. W. Smith, T. Don Tilley, *J. Am. Chem. Soc.* **2018**, *140*, 3880.
- [7] J. Lam, K. M. Szkop, E. Mosafari, D. W. Stephan, *Chem. Soc. Rev.* **2019**, *48*, 3592.
- [8] J. R. Ludwig, C. S. Schindler, *Chem* **2017**, *2*, 313.
- [9] a) C. Michon, F. Agbossou-Niedercorn et al., *ChemCatChem* **2016**, *8*, 1755; b) C. Michon et al., *J. Mol. Cat. A Chem.* **2016**, *423*, 256; c) C. Michon et al., *Catal. Sci. Technol.* **2015**, *5*, 1452; d) C. Michon et al., *Chem. Eur. J.* **2016**, *22*, 14036; e) C. Michon et al., *Eur. J. Org. Chem.* **2017**, 4820; f) C. Michon et al., *ChemCatChem* **2017**, *9*, 2009; g) C. Michon et al., *Eur. J. Org. Chem.* **2020**, 6212.
- [10] C. Michon, F. Agbossou-Niedercorn et al., *Catal. Sci. Technol.* **2018**, *8*, 3504.
- [11] C. Michon, V. Ritleng et al., *Eur. J. Inorg. Chem.* **2021**, 3074
- [12] C. Michon, K. Vanka et al., *Catal. Sci. Tech.* **2020**, *10*, 4586.