Metal-Catalyzed Hydrosilylation

DOI: 10.1002/anie.201008199

1,4-Hydrosilylation of Pyridine by Ruthenium Catalyst: A New Reaction and Mechanism**

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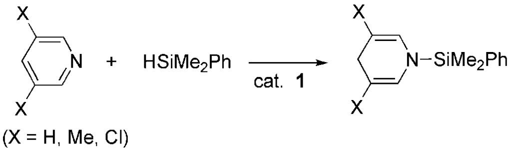
homogeneous catalysis · hydrosilylation · pyridine · ruthenium

The hydrosilylation of unsaturated molecules is recognized as the most common means of introducing a silicon-containing functionality to organic substrates. Complexes of various transition metals are employed as homogeneous catalysts for the hydrosilylation of $C=C$ and $C=O$ bonds.[1] Reports on the hydrosilylation of $C=N$ bonds, however, were even much less common than those on the reaction of $C=O$ bonds until recently. Over the past 15 years, complexes of various metals, including early-, late-, and post-transition metals (including Ti,[2] Re,[3] Ru,[4] Rh,[5] Ir,[6] Cu,[7] and Zn[8]), have been reported to catalyze the addition of Si$-$H groups of primary or secondary organosilanes or of polymethylhydrosiloxanes (PMHS) to imines. Since no hydrogenation of imines, giving the corresponding amines, takes place under mild conditions, the hydrosilylation of prochiral imines and the subsequent hydrogenolysis of the N$-$Si bond formed provide an alternative for the conversion of prochiral imines into optically active amines.

Nikonov et al. of Brock University chose a cationic ruthenium complex, $[Cp(iPr_3P)Ru(NCMe)_2][B(C_6F_5)_4]$ (**1**; Cp = cyclopentadienyl), as the catalyst for the hydrosilylation of ketones and nitriles in their recent studies.[9] This catalyst converts aliphatic and aromatic nitriles into the corresponding *N*-silylimines with high chemoselectivity or into *N*,*N*-disilylamines formed by double hydrosilylation, depending on the reaction conditions. This Highlights describes the latest report from this research group on catalysis by the complex in the hydrosilylation of pyridine.[10]

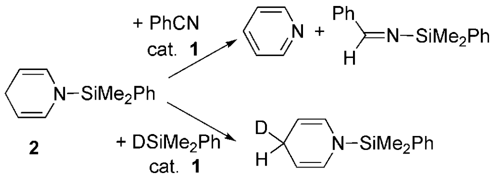
Pyridine and its derivatives having chloro and methyl substituents at 3- and 5-positions undergo hydrosilylation with $HSiMe_2Ph$ in the presence of catalytic amounts of **1** (2–5 mol% of the substrate) to yield the *N*-silyl-4-hydropyridine derivatives, as shown in Equation (1). The reaction is complete within several hours at room temperature.



(1)

$[Cp_2TiMe_2]$ catalyzes the hydrosilylation of pyridine, which is the sole precedent using a homogeneous catalyst.[11] The reaction, however, requires higher amounts of the titanium catalyst (10 mol% of the substrate) and heating the reaction mixture at 80 °C. The 1,2-addition of the Si$-$H group in the hydrosilylation was confirmed by deuterium-labeling experiments. The actual products are tetrahydropyridine derivatives which result from the concurrent hydrogenation of the pyridine ring. Thus, hydrosilylation using the half-sandwich ruthenium complex as the catalyst differs in chemoselectivity from the reaction catalyzed by the titanium complex and proceeds under milder conditions.

The experimental results in this recent article may encourage creative applications by the readers who are interested in the reaction mechanism. Scheme 1 summarizes the reactions of *N*-silyl-4-hydropyridine (**2**) catalyzed by the complex **1**. PhCN reacts with **2** in the presence of the catalyst **1** leading to the formation of *N*-silylphenylimine and the regeneration of pyridine (Scheme 1, top). The formal elimination of $HSiMe_2Ph$ from **2** and its addition to the $C\equiv N$ bond of PhCN would explain formation of the products. The addition of 3,5-lutidine to **2** yields an equilibrated mixture of the 1,4-addition products of pyridine and 3,5-lutidine. These results suggest the reversibility of this hydrosilylation, although mechanistic studies of the hydrosilylation reported thus far did not discuss details of this issue.[12]



Scheme 1. Reactions of the hydrosilylation product **2** in the presence of catalyst **1**.

Hydrosilylation reactions generate two stable chemical bonds, H$-$C and X$-$Si (X = C, O, N), and its reverse process should result in the activation of these bonds in the produced

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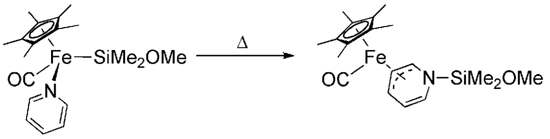
[**] The author is grateful to Dr. Makoto Tanabe for helpful discussions.

molecule. The bond-forming reactions in the Chalk–Harrod mechanism and its modified version for olefin hydrosilylation[13] are the insertion of $C{=}C$ bond into the M−H or M−Si bonds and the reductive elimination of product from alkyl(silyl)– or alkyl(hydride)–metal intermediates. Reverse processes for each of these reactions, β-hydrogen (β-silyl) elimination and cleavage of the Si−C bond through oxidative addition, may occur depending on the metal center and ligand. Organometallic chemists should be interested in the mechanistic issues, such as details of the reverse reaction of the hydrosilylation of pyridine as well as the microscopic reversibility of the total reaction.

The reaction of $DSiMe_2Ph$ with **2** in the presence of the catalyst yields *N*-silyl-4-deuteriopyridine (Scheme 1, bottom). The results imply selective and reversible 1,4-addition in the hydrosilylation. Tobita et al. studied the properties of the complex with another Group 8 transition metal (Fe) and a 14-electron fragment containing Cp and CO ligands.[14] They found that heating the complex with silyl and pyridine ligands produces a complex with *N*-silylpyridine as the π-allylic ligand, as shown in Equation (2).



(2)

A similar type of intermediate may be involved in the 1,4-addition of a H−Si bond of pyridine in the ruthenium-catalyzed reaction. Nikonov and co-workers have already reported coordination of organosilanes to the ruthenium center of complexes composed of the cationic $\{Ru(Cp)(PR_3)\}$ or $\{Ru(Cp^*)(PR_3)\}$ fragment.[15] The real mechanism of the catalytic hydrosilylation will be elucidated through a detailed study of these complexes in the near future.

The Chalk–Harrod-type mechanism has long been dominant in the hydrosilylation of olefins catalyzed by late-transition-metal complexes. In 2003, Tilley and Glaser proposed a novel mechanism involving the insertion of an olefin into the Si−H bond of a silylene-coordinated intermediate complex on the basis of results of a detailed study of the properties and catalytic activity of Ru complexes.[16] A new mechanism of the hydrosilylation or a new mode of catalysis may be revealed from further studies in this field.[17]

Received: December 27, 2010

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