Silylative Reduction of Various Functional Groups *via* Boron Catalysis: Mechanism and Selectivity

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The catalytic addition process of a Si–H bond of hydrosilanes across unsaturated functionalities such as alkenes and imines, referred to as *hydrosilylation* is one of the most extensively studied and widely utilized synthetic methods in both academia and industry. The most distinguished feature of this method from hydrogenation would be *convenience* to perform reactions and *easy-tuning* catalytic reactivity with various silanes. Although transition metal-catalyzed hydrosilylation is still taking superior position in this context, the majority of these catalysts are based on precious metals of Pt, Rh, and Ru, which can be the practical obstacle in developing an efficient hydrosilylation process. From such point of view, one might interest in employing *transition metal-free catalysts*.

Recently, tris(pentafluorophenyl)borane $B(C_6F_5)_3$ and its related e^--deficient analogues have drawn significant attention as a metal-free catalyst for hydrosilylation of a range of unsaturated functionalities, probably due to its environmental friendliness, excellent stability, and activity. Among various substrates within the $B(C_6F_5)_3$/silane catalyst system, we are particularly interested in dearomative hydrosilylation of *N*-heteroarenes such as pyridines since the reduced products (hydropyridines or piperidines) are important building blocks as well as versatile intermediates in the synthesis of alkaloids, pharmaceuticals, and agrochemicals.[1]

In the first part of this talk, we present the $B(C_6F_5)_3$-catalyzed silylative reduction of quinolines, pyridines, and additional types of N-heteroaromatics[2-4] with strong emphasis on reaction mechanism and selectivity. Moreover, we demonstrate that conjugated nitriles and conjugated imines undergo hydrosilylation cascade in the presence of $B(C_6F_5)_3$ catalyst, leading to β-silylated primary and secondary amines, respectively.[5] *In the second part*, we introduce our recently developed new borane catalysts, which show unique reactivity with substrates to enable selective hydrosilylation of sugars and natural products.[6,7] *In the last part*, we show preliminary mechanistic studies of the $B(C_6F_5)_3$-catalyzed intramolecular carbocyclization of arylalkenes with exclusive chemo- and stereoselectivity.

References

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