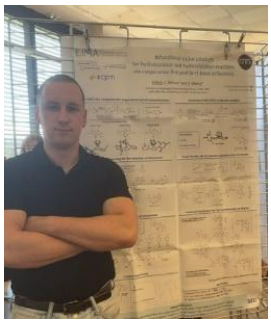

Bifunctional Nickel Catalysts for Hydroboration and Hydrosilylation Reactions via Cooperative B–H and Si–H Bond Activations

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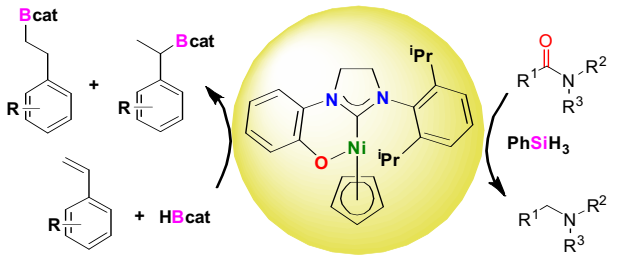
The transition-metal-catalyzed hydroboration1,2 and hydrosilylation1,3 are powerful synthetic methodologies because they provide valuable organoboron and organosilicon compounds by straightforward and atom economic synthetic routes. Organoboronate derivatives are widely employed for the construction of C–C, C−N, C−O, and C−S bonds and, as such, are significant feedstocks for the synthesis of pharmaceuticals, agrochemicals, liquid crystals, and organic light-emitting diodes.1,2 By comparison, organosilicon derivatives are less involved in organic transformations though significant progresses have been made.[4] Such organic compounds are mainly applied in the industrial production of commodity silicones or as pharmaceuticals.[1,3] In addition to these applications, the use of hydrosilanes and hydroboranes is an interesting alternative to hydrogenation, their use as reductants allowing reactions to proceed without any high-pressure equipment or high temperatures. Furthermore, as the reactivity of such boron and silicon reagents and related reaction intermediates is modular and depends on their substituents, hydroboration and hydrosilylation reactions can become highly chemo- and regioselective reduction methods that tolerate various other reducible functional groups.[1,3] The main drawback, however, of the synthetic methodologies involving hydroboration or hydrosilylation is that they are principally developed with noble metal-based catalysts. In addition, whether various organic insaturations can be reduced through the sole use of a hydrosilane activated by a catalyst, their hydroboration using boranes like catechol or pinacol borane most often requires the combination of a catalyst and a basic activator.

In this context, based on preliminary results,[5] our research project aims at developing bifunctional activator-free catalysts based on nickel, an abundant first-row transition metal. In particular, we target Ni(II)-NHC (NHC = N-heterocyclic carbene) catalysts able to assist hydroboration and hydrosilylation reactions by cooperative E–H (E = B, Si) bond activation and therefore result in effective catalytic processes. A first generation of nickel catalysts has been developed based on a NHC ligand substituted by a phenolate moiety. These cooperative catalysts are effective without any additive for the chemoselective hydroboration of various styrenes derivatives and the straightforward reduction of amides toward the corresponding amines through hydrosilylation (Scheme 1).



Scheme 1. Catalytic hydroboration and hydrosilylation using a Ni(II)-NHC-phenolate complex.

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