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Nickel(II) NHC-pycolyl complexes as catalysts for the hydrosilylation of carbonyl compounds: evidence for NHC-nickel nanoparticles under harsh reaction conditions

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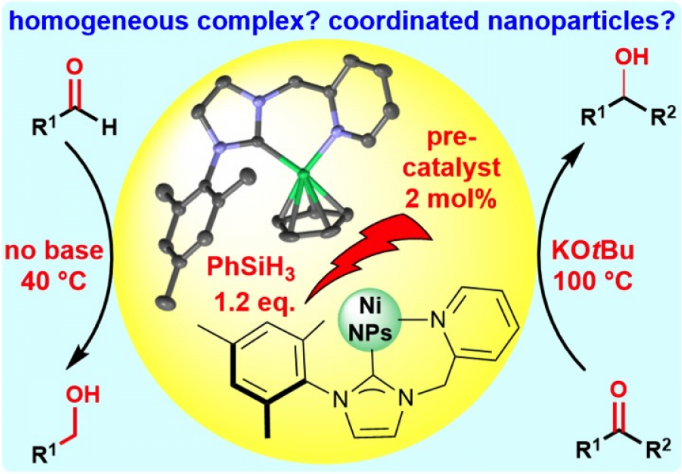
PURPOSE OF THE ABSTRACT

Hydrosilylation is a reaction of interest for the selective reduction of carbonyl compounds under mild conditions using transition-metal-based catalysts [1,2]. Indeed, the use of hydrosilanes as reductants, which proceeds without the need of high-pressures or elevated temperatures, is an advantageous surrogate to hydrogenation procedures. As the reactivity of hydrosilanes is modular and depends on their substitution patterns, the hydrosilylation may behave as a highly chemo- and regioselective reduction process that tolerates other reducible functionalities [2].
Beside catalysts based on noble metals, attention has recently turned to catalysts based on earth-abundant 3d metals, due to sustainability concerns [3]. Among these developed catalysts, half-sandwich [Ni(h5-C5R5)L(NHC)](+) complexes have shown interesting activities for the hydrosilylation of carbonyl derivatives. In 2012, some of us reported that [NiCpCl(IMes)] (Cp = h5-C5H5, IMes = 1,3-dimesitylimidazol-2-ylidene) effectively catalysed the hydrosilylation of a broad range of aldehydes and ketones at 25 °C in the presence of NaHBEt3 as a co-catalyst with a turnover frequency (TOF) that reached values up to 390 h-1 for the hydrosilylation of benzaldehyde [4a]. At the same time, Royo et al. described the synthesis of a related half-sandwich nickel(II) complex bearing a bidentate tetramethylcyclopentadienyl-functionalised carbene ligand, [Ni(Cp*-NHC-Me)(OtBu)], that catalysed the reduction of carbonyl derivatives at temperatures ranging from 25 °C (aldehydes) to 100 °C (ketones) with a TOF up to 2 300 h-1 for the hydrosilylation of 4-trifluoromethylbenzaldehyde [4b]. In 2016, Albrecht et al. reported a potentially hemilabile pyridyl-triazolylidene NiCp precatalyst for the hydrosilylation of aldehydes with a TOF as high as 13 350 h-1 observed with 4-methoxybenzaldehyde at 60 °C [4c].
The high TOF observed with the latter complex was tentatively rationalized as the result a well-balanced hemilabile ligand, with a C,N-chelate that can both stabilize the catalyst by a strong bidentate chelation in the resting state and enable an effective reactivity at the nickel centre by ring opening on the substrate's approach [4c]. The hemilabile balance of chelates may indeed be of utmost importance to develop efficient catalysts. This is especially true for [Ni(h5-C5R5)(NHC-Y)](+) complexes, which do not have potentially available coordination site aside from those resulting from decoordination of the Lewis basic Y atom and/or Cp ring slippage from h5- to h3- or even h1- or decoordination [5]. Following a recent work in our group on nickel complexes bearing hemilabile k2-C,S-thioether-functionalised NHCs [6], we wondered whether a NHC-picolyl ligand could afford a suitable balance in such type of complexes for nickel-catalysed hydrosilylation reactions.

In this communication, we will show that a readily accessible cationic half-sandwich Ni(II)-NHC-picolyl complex bearing a bromide counter-ion effectively catalyzes the hydrosilylation of a broad range of aldehydes without additive at 40 °C, and of ketones in the presence of KOtBu at 100 °C. In addition, we will present (i) single-crystal X-ray diffraction and VT 1H NMR studies that tend to show the absence of hemilability of the picolyl-functionalized carbene ligand (Figure 1), and (ii) studies by DLS, STEM, XPS, ICP-AES and CHN elemental analyses that show evidence for the involvement of NHC-stabilized picolyl Ni particles when KOtBu is used as an additive in the catalytic reactions (Figure 2).

FIGURES



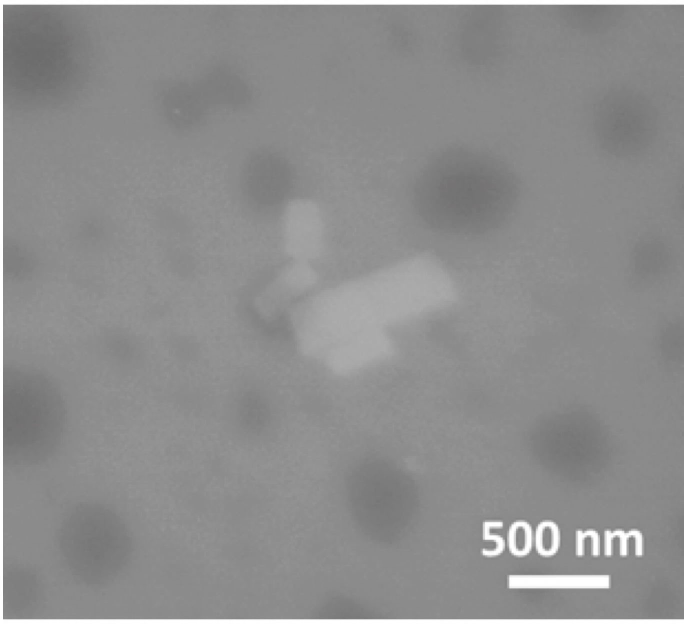


FIGURE 1

Figure 1

A Ni-NHC-picolyl complex effectively catalyzes the hydrosilylation of carbonyls. Studies by DLS, STEM and XPS show evidence for the involvement of NHC-stabilized nickel NPs when KOtBu is used as an activator

FIGURE 2

Figure 2

STEM image of Ni NHC-picolyl nanoparticles

KEYWORDS

Nickel | Hydrosilylation | N-Heterocyclic Carbene | Nanoparticles

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