Polynuclear lanthanide-diketonato clusters: Catalytic hydroboration of carboxamides and esters

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Abstract

In this presentation, we will discuss an operationally facile and efficient hydroboration of unsaturated species such as amides and esters to afford the corresponding amines and alcohols using lanthanum catalysts in the presence of HBpin. Lanthanide polyoxometalates (POMs) are generated upon heating commercial sources of Ln(acac)$_3$ (La, Y, Gd, Eu, and Er) salts. The POMs contain a polynuclear tetrahedral Ln$_n$(µ-O)$_2$ core, as confirmed by X-ray crystallography and elemental analysis. We applied these POMs as catalysts in the hydroboration of amides and esters. The results of our catalytic (and preliminary) mechanistic studies will be presented.

Introduction

Reactivity of amides

Scheme 1. Scope of tertiary amides

Scheme 2. Scope of secondary amides

Scheme 3. Scope of primary amides

Selected examples for hydroboration of 1°, 2°, 3° carboxamides

Selected examples for hydroboration of esters

Kinetics data

Figure 1. Plot of [La]$_n$ vs. reaction rate (K$_{cat}$), the reaction follows 1° order till 3 mol % catalyst loading.

Figure 2. Plot of [Substrate] vs. reaction rate (K$_{cat}$), the reaction follows 0° order dependence on the substrate.

Figure 3. Plot of [HBpin] vs. reaction rate (K$_{cat}$), the reaction follows 1° order dependence on HBpin till 3 equiv. [HBpin], and then 0° order at higher concentration.

Synthesis of lanthanide polyoxometalates

Reference/ Funding