



Short communication

Lanthanide aryloxides catalyzed hydroboration of aldehydes and ketones

Zhangye Zhu, Ping Dai, Zhenjie Wu, Mingqiang Xue*, Yingming Yao, Qi Shen, Xiaoguang Bao*

Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Dushu Lake Campus, Soochow University, Suzhou 215123, China

ARTICLE INFO

Keywords:

Lanthanide aryloxide
Hydroboration
Carbonyl compound
Chemoselectivity
DFT calculation

ABSTRACT

The lanthanide aryloxides $\text{Ln}(\text{OAr})_3(\text{THF})_2$ ($\text{Ar} = \text{Ar}^1 = 2,6\text{-}^t\text{Bu}_2\text{-4-MeC}_6\text{H}_2$, $\text{Ln} = \text{Yb}$ (1), Y (2); $\text{Ar} = \text{Ar}^2 = 2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$, $\text{Ln} = \text{Y}$ (3); $\text{Ar} = \text{Ar}^3 = 2,6\text{-Me}_2\text{C}_6\text{H}_3$, $\text{Ln} = \text{Y}$ (4); $\text{Ar} = \text{Ar}^1$, $\text{Ln} = \text{Sm}$ (5), Nd (6)) could be served as highly efficient catalysts for the hydroboration of aldehydes and ketones with good functional group tolerance and excellent chemoselectivity. Computational studies were carried out to probe a feasible mechanism of the Ln-aryloxides catalyzed hydroboration of aldehydes/ketones.

1. Introduction

The catalytic hydroboration of unsaturated C-X bond ($X = \text{C}, \text{N}$ or O atoms) is a straightforward and atom-economical method for the construction of a variety of boronic esters. Boronic esters are ubiquitous in organic syntheses and capable of being transformed into various important functional groups [1–3]. Among these transformations, the selective hydroboration/reduction of carbonyl compounds represents a powerful tool for the synthesis of alcohols which are present in numerous targets of synthetic interest [4–6].

To date, various organometallic complexes including main group [7–17] and transition [18–23] metal complexes have been extensively studied and described to be efficient for carrying out the hydroboration of carbonyl compounds. However, the use of lanthanide (Ln) complexes for this transformation is limited in spite of their excellent catalytic performance [24–26]. In particular, the Ln-O complexes, as one of the most important class of Ln complexes, have still remain unexplored in driving the hydroboration reaction. This is probably due to the strong affinity of the Ln-O bond of complexes, thus suppressing their activity [27]. The unique advantages of Ln-O complexes such as relative stability in air, easy accessibility and their catalytic activities in organic and polymer science have spurred our interest in exploring their utility in hydroboration reactions.

Herein, we report a highly efficient hydroboration of aldehydes and ketones catalyzed by homoleptic Ln-OAr complexes, which exhibit excellent chemoselectivity and broad functional group compatibility.

2. Results and discussion

2.1. Catalytic hydroborations

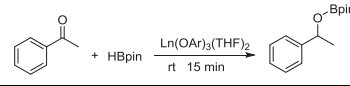
The catalysts $\text{Ln}(\text{OAr})_3(\text{THF})_2$ ($\text{Ar} = \text{Ar}^1 = 2,6\text{-}^t\text{Bu}_2\text{-4-MeC}_6\text{H}_2$, $\text{Ln} = \text{Yb}$ (1), Y (2); $\text{Ar} = \text{Ar}^2 = 2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$, $\text{Ln} = \text{Y}$ (3); $\text{Ar} = \text{Ar}^3 = 2,6\text{-Me}_2\text{C}_6\text{H}_3$, $\text{Ln} = \text{Y}$ (4); $\text{Ar} = \text{Ar}^1$, $\text{Ln} = \text{Sm}$ (5), Nd (6)) were synthesized according to previously described methods [28–30]. A preliminary study was carried out using 1 of 0.01 mol% together with a 1:1 M ratio of acetophenone and pinacolborane (HBpin) under ambient temperature (25 °C). Pleasingly, the hydroboration can occur within 15 min as evidenced by NMR analysis (Table 1, entries 1–4), while there is no reaction in the absence of a catalyst which is consistent with previous studies [24,31]. Furthermore, the screening of solvents indicates THF to be superior to toluene and hexane. It should be noted that the reaction can also take place under neat condition and give the product with similar yield as in THF (Table 1, entries 3 and 4). In addition, the steric effect of the OAr ligand on the catalytic activity was evaluated (Table 1, entries 5–7). The catalytic performance could be significantly improved by using bulkier ligands, which is consistent with results from analogous Ln-OAr catalysts in driving the reaction of amines with carbodiimides [32]. The screening of the central Ln metals demonstrates that the order of catalytic activity follows $\text{Y} > \text{Yb} < \text{Sm} < \text{Nd}$ (Table 1, entries 4–5 and 8–9). The same trend has also been found in the hydroborations with Ln-Cp complexes [25]. Full conversion could be achieved by increasing the catalyst loading to 0.05 mol% and adding a slight excess of HBpin (1.1 eq) (entry 13).

With the optimized reaction conditions in hand, the scope of hydroboration with respect to a wide range of carbonyl compounds was explored. In the case of aldehydes, most of the aromatic substrates

* Corresponding authors.

E-mail addresses: xuemingqiang@suda.edu.cn (M. Xue), xgbao@suda.edu.cn (X. Bao).

Table 1
Optimization of the reaction conditions.^a



Entry	Cat. (mol%)	Sol	Substrate ratio ^b	Conv ^c (%)
1	1 (0.01%)	Hex	1:1	34
2	1 (0.01%)	Tol	1:1	54
3	1 (0.01%)	–	1:1	78
4	1 (0.01%)	THF	1:1	79
5	2 (0.01%)	THF	1:1	77
6	3 (0.01%)	THF	1:1	64
7	4 (0.01%)	THF	1:1	58
8	5 (0.01%)	THF	1:1	88
9	6 (0.01%)	THF	1:1	91
10	6 (0.05%)	THF	1:1	97
11	6 (0.01%)	THF	1:1.1	93
12	6 (0.03%)	THF	1:1.1	97
13	6 (0.05%)	THF	1:1.1	> 99

^a Acetophenone, HBpin, and Ln(OAr)₃(THF)₂ at ambient temperature (25 °C).

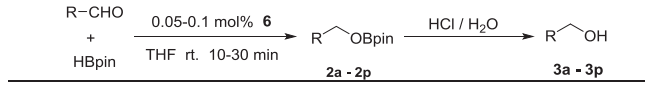
^b Acetophenone, HBpin.

^c Conversion was determined by ¹H NMR spectroscopy.

required only 0.05 mol% of catalyst loading for complete conversion into the corresponding boronate esters within a short period. For example, benzaldehyde can be converted to the target product in just 10 min, which corresponds to a TOF > 11,800 h⁻¹, demonstrating the most active catalytic system among the lanthanide complexes reported [24–26]. No steric inhibitory effect is observed with either ortho- or para- methylbenzaldehyde (Table 2, entries 2 and 3). For a more sterically hindered substrate such as 2,4,6-trimethylbenzaldehyde, a slightly longer reaction time is required for full conversion (Table 2, entry 4). The reaction shows good tolerance toward various functional groups (Table 2, entries 5–10). For instance, the fluoro-containing substrate can be completely converted to the desired product after 20 min (Table 2, entry 5). The reaction of α , β -unsaturated cinnamaldehyde affords the single carbonyl reduction product which is in line with recently reported hydroboration protocols (Table 2, entry 10) [7,25,26,31]. Furthermore, no dearomatization of the hetero ring is observed with either 2-pyridinecarboxaldehyde or thiophene-2-carbaldehyde, demonstrating the exclusive chemoselectivity towards C=O bond (Table 2, entries 11 and 12). The hydroboration reaction is also applicable to 2-naphthaldehyde and anthracene-9-carbaldehyde (Table 2, entries 13 and 14). In addition, the aliphatic substrate heptanal is successfully converted into the target product (Table 2, entry 15). In general, the lanthanide aryloxides catalyzed hydroboration of aldehydes can produce the boronate esters with excellent yields. Subsequently, the generated boronate esters can be efficiently hydrolyzed into the corresponding alcohol products.

The lanthanide aryloxides catalyzed hydroboration protocol was extended to ketones and a range of substrates were examined. All the reactions can undergo smoothly and give the complete conversions of various substrates to the corresponding products in high yields using **6** as a catalyst. In general, the reactivity of ketones is lower compared with aldehydes. For instance, the complete conversion of acetophenone requires 15 min, while only 10 min is required for benzaldehyde (Table 2, entry 1 vs Table 3, entry 1). A similar trend is observed with *p*-tolualdehyde/*o*-tolualdehyde and *p*-acetyltoylene/*o*-acetyltoylene (Table 2, entries 2 and 3 vs Table 3, entries 2 and 3). This is supported by DFT calculations which show that the energy barriers are substantially higher for ketones than for aldehydes [31]. This observation is also in line with known catalysts [4,7,21,25,26,33], although in contrast with La[N(SiMe₃)₂]₃ [24]. In the cases of isobutyrophenone and benzophenone, a higher catalyst loading (0.1 mol%) is required for full conversion because of the steric hindrance in these substrates (Table 3, entries 8 and 9). A slightly longer time as well as higher

Table 2
Hydroboration of aldehydes catalyzed by **6**.^a



Entry	Aldehydes	Cat. (mol%)	Time (min)	Conv ^b (%)	Alcohols	Yields ^c (%)
1		0.05	10	>99		95
2		0.05	10	>99		96
3		0.05	10	>99		93
4		0.05	15 (10)	>99 (95)		93
5		0.05	20	99		91
6		0.05	15	>99		89
7		0.05	10	>99		87
8		0.05	15	>99		94
9		0.05	15	>99		93
10		0.1	15	97		91
11		0.1	30	>99		88
12		0.1	15	>99		94
13		0.05	15	>99		92
14		0.1	30	>99		90
15		0.05	15	>99		92
16		0.05	30	>99		90

^a Aldehydes (1 mmol), pinacolborane (1.1 mmol) and **6** (0.05 mol%) at rt., THF (0.2 mL) for solid substrate.

^b Conversion of aldehydes based on ¹H NMR analysis.

^c Isolated yield of 1° alcohol by column chromatography.

catalyst loading is necessary for the quantitative conversion of 2-acetylthiophene (Table 3, entry 11). Finally, the aliphatic substrate 3-methyl-2-butanone (Table 3, entry 12) exhibits comparable reactivity with the aliphatic aldehyde (Table 2, entry 15). It is worth noting that complex **6** shows unique compatibility toward OH and NH₂ substituted substrates. Both aldehyde and ketone can undergo full conversion as well as satisfactory isolation yields of carbonyl groups with NH₂ and OH groups intact (Table 2, entry 16 and Table 3, entry 13), exhibiting the unique chemoselectivity of complex **6**, as those groups are readily reliable to B–N, B–O coupling [34]. Moreover, the very low catalyst loading and short reaction period exhibit dominant advantages over the previously reported cases [7,26].

To further evaluate the selectivity of hydroboration of aldehydes versus ketones, a competitive intermolecular reaction involving a mixture of benzaldehyde and acetophenone was carried out in the presence of **6**, which results in the preferential reduction of the aldehyde rather than ketone (Scheme 1). Meanwhile, separate experiments involving 4-fluorobenzaldehyde, 4-methylbenzaldehyde and heptanal firmly establish the selectivity of aldehydes over ketones. Notably, near

Download English Version:

<https://daneshyari.com/en/article/6502939>

Download Persian Version:

<https://daneshyari.com/article/6502939>

[Daneshyari.com](https://daneshyari.com)