

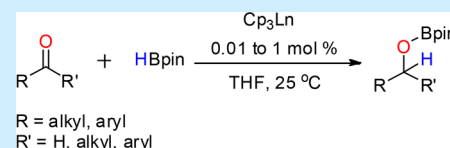
Tris(cyclopentadienyl)lanthanide Complexes as Catalysts for Hydroboration Reaction toward Aldehydes and Ketones

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Supporting Information

ABSTRACT: It was found that homoleptic cyclopentadienyl lanthanide complexes Cp_3Ln ($Ln = Y$ (1), Yb (2), Sm (3), Nd (4), La (5), $Cp =$ cyclopentadienyl) can be employed as excellent catalysts for the hydroboration of various aldehydes and ketones toward pinacolborane. These robust lanthanide catalysts exhibited high reactivity with low catalyst loadings (0.01–1 mol %) under mild conditions and good functional group tolerability. These complexes also demonstrated uniquely carbonyl-selective hydroboration in the presence of alkenes and alkynes.



Organoborane compounds as a class of vital organic intermediates have demonstrated miscellaneous conversions in organic synthesis.¹ Hydroboration is a powerful reaction that is mostly utilized for the conversion of carbonyl compounds into alcohols with good chemical and regional selectivity.² In the past decades, much attention has been paid to the hydroboration of unsaturated C–C bonds.³ In contrast to the hydroboration of unsaturated C–C bonds, investigations of C–X ($X = N, O$ heteroatoms) have been relatively sluggish.⁴ In recent years, the arena for the hydroboration of C–N, C–O unsaturated bonds has gained continuous momentum and developed rapidly. A variety of transition and main group metal complexes have proven efficient catalysts for the hydroboration reaction toward unsaturated compounds.^{1f,2a–c,3d,5} To our surprise, rare earth metal complexes as one of important branch of organometallic chemistry are rarely reported for hydroboration of carbonyl compounds. Only two examples concerning hydroboration have been investigated, by Marks et al., until now. In 2014, Marks' team reported that lanthanide hydride complexes could act as excellent catalysts for dearomatization of pyridine and its derivatives.⁶ Very recently, Marks et al. have proven that $La[N(TMS)_2]_3$ can serve as a catalyst for the hydroboration.⁷ During the same period, our group also found that a series of lanthanide complexes, $La[N(TMS)_2]_3$,^{8a} $[2,6\text{-}iPr_2\text{-}C_6H_3\text{-}NC(Me)CHC(Me)N\text{-}C_6H_3\text{-}2,6\text{-}iPr_2]LnBH_4\cdot 2THF$ ($Ln = Sm, Yb$)^{8b} and $[2\text{-}Me\text{-}C_6H_4\text{-}NC(Me)CHC(Me)N\text{-}C_6H_4\text{-}2\text{-}Me]_2Ln\text{-}N(SiMe_3)_2$ ($Ln = Nd, Pr$),^{8c} could serve as very efficient catalysts for this transformation. Therefore, further exploration of suitable lanthanide complexes to realize this highly valuable hydroboration transformation is of significant importance.⁹

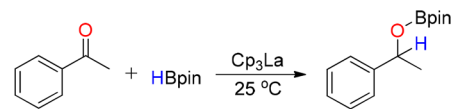
Organolanthanide complexes stabilized by Cp and modified Cp ligands have played a vital role in organolanthanide chemistry and witnessed the prosperity of organolanthanide chemistry during the past 60 years.¹⁰ Over the past decades, a vast number of lanthanide complexes supported by Cp or Cp-functionalized ligands have been synthesized and proven to have versatile reactivity.¹⁰ Moreover, many Cp lanthanide

complexes act as excellent catalyst precursors in organic reactions and polymer science.¹¹ In contrast to their counterparts, mono- and bis-cyclopentadienyl complexes, the application of readily attainable homoleptic Cp_3Ln complexes is rather limited, which may be attributed to its three less reactive spectator Cp ligands around the center Ln atom.¹² The exploration of the catalytic behavior of homoleptic Cp_3Ln complexes is limited to polymerization by far.¹³ There is only one report on stoichiometric Cp_3Ln with small molecules, i.e., benzophenone, reported by Zhou et al.¹⁴ It is thus rewarding to expand the application of Cp_3Ln complexes in catalytic chemistry.

In this paper, we found that the very simple and readily attainable Cp_3Ln complexes could serve as extremely efficient catalysts for the hydroboration toward aldehydes and ketones for the first time. The Cp_3Ln complexes also exhibited good chemical selectivity toward unsaturated carbonyl compounds.

The homoleptic lanthanide complexes Cp_3Ln ($Ln = Y$ (1), Yb (2), Sm (3), Nd (4), and La (5)) were prepared on the basis of the well-documented files.⁹ The modeling trial was performed by means of diamagnetic complex Cp_3Y to explore the possibility of hydroboration of acetophenone with pinacolborane (HBpin) at ambient atmosphere (25 °C). We were pleased to observe that with 1 mol % catalyst loading and within 10 min, in various organic solvents including Tol, THF, $CHCl_3$, DME, CH_2Cl_2 , and 1,4-dioxane, this hydroboration transformation can be realized with an excellent conversion rate (higher than 95%) (Table 1, entries 2–7). Noticeably, without solvent, the conversion is only 63% (Table 1, entry 1), which may be attributed to the poor solubility of the catalyst in the reaction mixture. The blank experiment indicated that the hydroboration reaction can hardly proceed without catalyst, which is consistent with the literature report.⁷ Herein, THF was chosen to be the reaction solvent for the definition of the

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Table 1. Optimization of the Reaction Conditions^a


entry	cat. (mol %)	solvent	time (min)	substrate ratio ^b	conv ^c (%)
1	1 (1)	neat	10	1:1	63
2	1 (1)	THF	10	1:1	>99
3	1 (1)	Tol	10	1:1	99
4	1 (1)	CHCl ₃	10	1:1	98
5	1 (1)	DME	10	1:1	98
6	1 (1)	CH ₂ Cl ₂	10	1:1	95
7	1 (1)	1,4-dioxane	10	1:1	99
8	1 (0.01)	THF	60	1:1	88
9	1 (0.01)	THF	10	1:1	22
10	2 (0.01)	THF	10	1:1	12
11	3 (0.01)	THF	10	1:1	51
12	4 (0.01)	THF	10	1:1	77
13	5 (0.01)	THF	10	1:1	88
14	1 (0.01)	THF	60	1:1.2	99
15	2 (0.01)	THF	60	1:1.2	97
16	3 (0.01)	THF	60	1:1.2	99
17	4 (0.01)	THF	60	1:1.2	>99
18	5 (0.01)	THF	60	1:1.2	>99

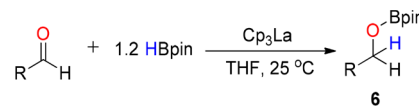
^aAcetophenone, HBpin, and Cp₃Ln at ambient atmosphere (25 °C).

^bAcetophenone, HBpin. ^cConversion was determined by ¹H NMR spectroscopy.

optimal reaction conditions. Further, the amount of catalyst loading was investigated. We found that even when the loading is lowered to 0.01 mol %, 88% conversion is achieved within 60 min (Table 1, entry 8). With the optimized reaction conditions mentioned above, reaction activity trials of different central Ln metals were also conducted (Table 1, entries 9–13). It was found that the La complex showed paramount catalytic efficiency in the Cp₃Ln system. By slightly increasing the molar amount of HBpin to 1.2 equiv (excess HBpin may stabilize the resting state of the catalyst and thus preserve it),⁵ⁿ both larger radius metal Nd and La complexes obtain full conversions within 1 h, which show superior performances than those of the smaller Y, Yb, and Sm complexes (Table 1, entries 14–18). It should be noted that the reactivity of Cp₃La toward acetophenone is higher than that of the recorded La[N(TMS)₂]₃ complex as the catalytic amount is 10-fold of our system.⁷

Enlightened by the aforementioned modeling reaction, the substrate scope was broadened. The representative hydroboration outcomes are listed in Tables 2 and 3, respectively.

Table 2 delineates the scope of aldehydes investigated in this manuscript. The preliminary results evidently display that the Cp₃La complex is an excellent catalyst toward a variety of aldehyde compounds with good compatibility of various substituted functional groups. It can be seen that with 0.01 mol % catalyst loading in 60 min benzaldehyde skeleton substrates with both electron-donating groups and electron-withdrawing groups could deliver excellent conversion rates for the target hydroboration products (Table 2, entries 2–4 and 6–8). The catalytic activity is proven to be higher than that of the La[N(TMS)₂]₃ system as 0.1 mol % loading was required.⁷ Note that for the monohalogen-substituted benzaldehyde substrates, the group position (*o*, *p*, *m*) on the benzene ring

Table 2. Hydroboration of Aldehydes Catalyzed by 5^a


entry	aldehydes	cat. (mol %)	time (min)	product	conv ^b (%)	TOF (h ⁻¹)
1		0.01	60	6a	>99	9900
2		0.01	60	6b	>99	9900
3		0.01	60	6c	>99	9900
4		0.01	60	6d	>99	9900
5		0.01	60	6e	96 (87) ^c	9600
6		0.01	60	6f	>99 (93) ^c	9900
7		0.01	60	6g	96 (86) ^c	9600
8		0.01	60	6h	>99	9900
9		0.1	10	6i	>99	9900
10		0.1	10	6j	>99	9900
11		0.01	60	6k	98	9800
12		0.01	60	6l	>99	9900
13		0.1	120	6m	>99	9900

^aAldehyde (1 mmol) was added to the HBpin solution (1.2 mmol) and Cp₃La added from a stock solution of appropriate concentration.

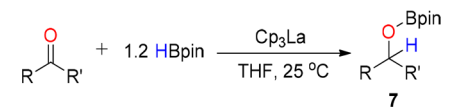
^bConversions of aldehydes are based on ¹H NMR analysis of the reaction mixture. ^cIsolated alcohol yields.

have no significant impact on the reactivity within 60 min (Table 2, entries 6, 7, and 8). The highly efficient catalytic activity is demonstrated with the multisubstituted 2,4,6-trimethylbenzaldehyde (Table 2, entry 5). Aliphatic substrate (Table 2, entry 11) and heterocyclic substrate nicotinaldehyde (Table 2, entry 12) also gave excellent conversions with 0.01 mol % catalyst loading within 60 min.

The typical hydroboration outcomes toward ketone compounds are shown in Table 3. Generally, like aldehydes, Cp₃La could serve as a very robust catalyst to reduce pertinent carbonyl groups. However, the reactivity toward aldehydes is higher than that of ketones (Table 3, entry 2, and Table 2, entry 2), which may be due to less electrophilic and sterically more hindered carbonyl centers in the latter. This trend is consistent with the previously reported transition and main group metal complexes^{5g-i} but opposite to that reported by Marks et al.⁷

Quantitative conversions of most aldehydes and ketones (TON > 9900) were observed within 1 h.^{5g} Turnover frequency (TOF) up to 33200 h⁻¹ was observed (Table 3, entry 1), which is a very high value albeit lower than that of Okuda's report (60000 h⁻¹).^{1f}

Steric hindrance shows a more conspicuous influence on the reactivity toward ketone than aldehyde. The representative examples are listed in Table 3, entry 9, and Table 2, entry 5, respectively. With 0.01 mol % catalyst loading, only 91% conversion of 2,4,6-trimethylacetophenone can be achieved

Table 3. Hydroboration of Ketones Catalyzed by 5^a


entry	ketones	cat. (mol %)	time (min)	prod uct	conv (%) ^b	TOF (h ⁻¹)
1		0.01	15	7a	83	33200
		0.01	60	7a	99 (92) ^c	9900
2		0.01	60	7b	89 (69) ^c	8900
3		0.01	60	7c	97 (87) ^c	9700
4		0.01	60	7d	96 (85) ^c	9600
5		0.01	60	7e	99 (90) ^c	9900
6		0.01	60	7f	99 (91) ^c	9900
7		0.01	60	7g	98 (89) ^c	9800
8		0.01	120	7h	98 (87) ^c	4900
9		0.01	30 h	7i	91(79) ^c	303
		1	1.25 h	7i	87	69.6
10		0.01	60	7j	92 (83) ^c	9200
11		0.01	60	7k	>99 (95) ^c	9900
12		0.01	60	7l	88 (72) ^c	8800
13		1	60	7m	>99	99
14		1	60	7n	>99	99
15		0.1	60	7o	>99	990
16		0.1	10	7p	>99	5940

^aKetone (1 mmol) was added to the HBpin solution (1.2 mmol) and Cp₃La added from a stock solution of appropriate concentration.

^bConversions of ketones are based on ¹H NMR analysis of the reaction mixture. ^cIsolated alcohol yields.

even when the reaction time is extended to 30 h (Table 3, entry 9), and when the catalyst loading was increased to 1 mol %, 87% conversion was achieved within 1.25 h (Table 3, entry 9), which is comparable with the reported result (91%).⁵ⁿ

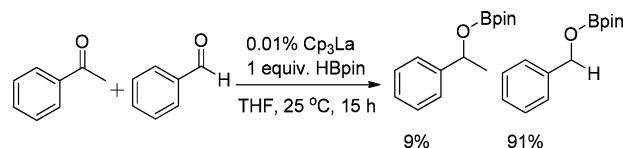
Pursuing the chemoselectivity for the reduction of specific unsaturated function group is one of the most important topics in organic and pharmaceutical synthesis.¹⁵ Intramolecular function selectivity is demonstrated by using various bifunctional group substrates (Table 2, entries 9, 10, and 13, and Table 3, entry 16). Carbonyl groups are demonstrated to be a unique group being reduced with satisfactory conversion by elevating the catalyst amount to 0.1 mol %, while other unsaturated groups, such as C=C and CN, are intact.

It is worth noting that within 2 h the diketone substrate was successfully converted into the target bis(borate ester) product (8) (see the Supporting Information). This provides a very easy approach to give bis(borate ester) with a high conversion rate.⁵ⁿ

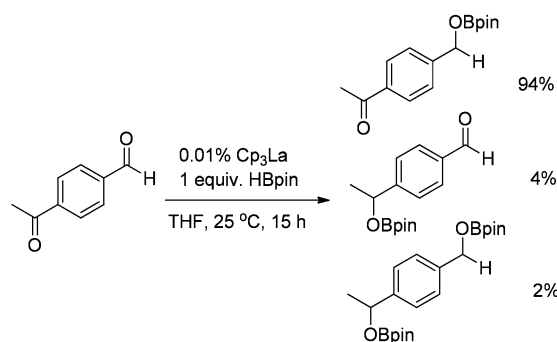
Both intermolecular and intramolecular selectivities toward aldehyde and ketone were investigated. The results indicated that aldehyde is preferentially reduced in both cases, reaching 91% conversion of benzaldehyde for intermolecular selective hydroboration (Scheme 1A) and 94% conversion of aldehyde

Scheme 1. Competitive Aldehyde/Ketone Hydroboration Selectivity Study

A. Intermolecular Chemoselective Reaction



B. Intramolecular Chemoselective Reaction



only in 4-acetylbenzaldehyde for intramolecular selective hydroboration (Scheme 1B), respectively. This chemical selectivity is in line with the results of the La[N(TMS)₂]₃ complex.⁷

Kinetic studies to determine the reaction order were carried out via ¹H NMR monitoring (eq 1 and 2) (see the Supporting Information for details). The relatively retarded ketone 2-methylacetophenone (Table 3, entry 2) and the structurally similar counterpart 2-methylbenzaldehyde (Table 2, entry 2) were utilized to fulfill this purpose.

Under the present reaction conditions, the rates in both reactions were proven to be first order in [ketone]/[aldehyde], [HBpin], and [Cp₃La].

$$\text{rate} = k[\text{Cp}_3\text{La}]^1[\text{HBpin}]^1[\text{ketone}]^1 \quad (1)$$

$$\text{rate} = k[\text{Cp}_3\text{La}]^1[\text{HBpin}]^1[\text{aldehyde}]^1 \quad (2)$$

In summary, we have demonstrated that Cp₃Ln can act as an excellent catalyst for the hydroboration of aldehydes and ketones under mild conditions with low catalyst loadings for a broad range of aromatic and aliphatic substrates. Investigation of the detailed mechanism of the catalytic cycle is ongoing in our laboratory. Meanwhile, our attention is drawn to more interesting findings of the catalytic behavior of homoleptic lanthanide complexes supported by substituted Cp ligands.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b01335.

Experimental procedures and characterization data (PDF)

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Notes

The authors declare no competing financial interest.

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