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ARTICLE

Highly Efficient Hydroboration of Carbonyl Compounds Catalyzed by Tris(methylcyclopentadienyl)lanthanide Complexes

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Homoleptic lanthanide complexes coordinated by Me-substituted Cp ligand [(MeCp)$_3$Ln] demonstrate unprecedently high efficiency in catalyzing the hydroboration of aldehydes and ketones with pinacolborane. This protocol is also applicable for the hydroboration of aryl-substituted imines. In addtion, broad functional group compatibility and excellent chemoselectivity is also achived. DFT calculations are employed to shed light on the reaction mechanism.

Introduction

Organolanthanide chemistry has played an important role in organometallic chemistry and is gaining continuous momentum on account of its rich chemical reactivities and wide applications in various disciplines, such as polymer science, pharmaceuticals, material science as well as organic synthesis.[1] A vast number of lanthanide (Ln) complexes have been proven to be efficient in catalyzing organic transformation.[2] It is of significant importance to further explore and broaden the catalytic scope of Ln complexes. The area of using catalysts for carrying out the hydroboration of aldehydes, ketones and imines is of considerable interest and rapidly expanding. Although main group[3] and transition[4] metal complexes catalyzed hydroborations have been well reported, Ln complexes catalyzed hydroboration remains relatively unexplored. Marks' group first report that La[N(SiMe$_3$)$_2$]$_3$ can be served as a catalyst for the hydroboration of carbonyl-containing compounds.[5] Analogously, we documented that Ln complexes with Ln-N[6a,b] and Ln-B[6c] bonds could be efficient to drive this hydroboration transformation. The latest work published by our team unfolded that the very simple and readily available Cp$_3$Ln (Cp = cyclopentadienyl) complexes were excellent catalysts for hydroboration of a variety of aldehydes and ketones with low catalyst loading.[7] In addition, good substrates tolerability as well as chemical selectivity was also achieved. Nevertheless, it is worthy to exploit more highly efficient catalysts which are essential for the mitigation of environmental concern over the use of metal catalysts and developing potential capability for industrial scale up.

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Electronic Supplementary Information (ESI) available: Characterization data, copies of ^{1}H, ^{13}C NMR spectra, kinetic analysis details and DFT calculations See DOI: 10.1039/x0xx00000x

Results and discussion

Modification of ligands of Ln complexes by adjusting the steric hindrance has been proven to be a powerful approach to improve catalytic behaviors.[8] Hence, we commenced our study by examining (MeCp)$_3$Ln complexes as catalysts for the hydroboration of aldehydes/ketones with pinacolborane (HBpin).

Homoleptic (MeCp)$_3$Ln complexes were prepared according to the literature reported[9] and the screening data are listed in the supporting information (see the ESI, Table S1). Subsequently, the substrate scope was investigated by adopting the same reaction conditions in Cp$_3$La system.[7]

The catalytic performance of the (MeCp)$_3$La complex was tested for the hydroboration of aldehydes and the representative results are listed in Table 1. Generally, the addition of HBpin to various aldehydes, including aromatic, hetero ring (2-pyridinecarboxaldehyde) as well as aliphatic substrates, in the presence of 0.001-1 mol% of catalyst loading can afford corresponding boronic esters in high yields (84 to 99%). Remarkably, with 0.001 mol% catalyst loading, benzaldehyde achieved quantitative conversion within 60 min, which marks the unprecedented reactivity in comparison with the published literatures.[7,10] The corresponding TOF of 97 000 hr^{-1} also represents the most rapid HBpin-based reduction to date.[5,7,10-12] Analogous to the catalytic performance of Cp$_3$La, (MeCp)$_3$La shows good compatibility with different function groups. Substrates bearing electron donating groups (Table 1, entries 2-4) or electron withdrawing groups (Table 1, entries 5-7) also gave the corresponding reduction products in high yields. For halogen substituted benzaldehyde, F- and Cl-substrates show comparable catalytic reactivity with 0.01 mol% catalyst loading, while Br- substrate presents slightly higher activity as only 0.005 mol% loading is required. Interestingly, in contrast to Cp$_3$La, no evident steric hindrance

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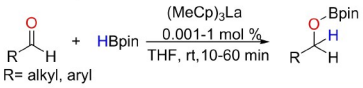
Table 1 Substrate scope for aldehydes[a]



Entry	R	Cat (mol%)	Time (min)	NMR yield (%)	Isolated yield (%)
1	Ph	0.001	60	97	90
2	2-MeC_6H_4	0.005	60	99	95
3	2,4,6-$Me_3C_6H_2$	0.005	60	98	89
4	2-OMeC_6H_4	0.01	10	99	92
5	4-FC_6H_4	0.01	10	99	90
6	4-ClC_6H_4	0.01	10	99	87
7	4-BrC_6H_4	0.005	60	91	81
8	4-CNC_6H_4	0.01	60	99	85
9	2-C≡CHC_6H_4	0.01	60	99	90
10	C_6H_5CH=CH	0.1	20	92	80
11	3-cyclohexene	0.01	10	99	84
12	4-N$Me_2C_6H_4$	1	60	99	—
13	2-pyridine	0.01	10	99	85
14	4-OHC_6H_4	0.1	40	84	73

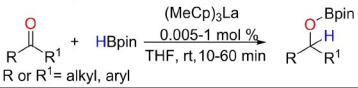
[a] Reaction conditions: aldehydes (1 mmol), HBpin (1.2 mmol) and $(MeCp)_3La$ solution of the appropriate concentration, N_2, room temperature.

effect is observed under defined reaction conditions (Table 1, entries 2 and 3). It can be seen that even 2,4,6-trimethylbenzaldehyde could be completely converted to target product. Intramolecular chemoselective hydroboration is also achievable: dedicated reduction towards C=O bond and keep CN, -yne as well as C=C bonds intact (Table 1, entries 8-11). With respect to the hetero cyclic substrate (2-pyridinecarboxaldehyde), although catalyst loading of 0.01 mol% is equivalent as that of Cp_3La,[7] the reaction time is significantly shortened from 60 min to 10 min (Table 1, entry 13). It is worth noting that the catalyst also shows tolerability with –OH (Table 1, entry 14), demonstrating the unique chemoselectivity of $(MeCp)_3La$ complex, as the alcohol group is readily reliable to B-O coupling with HBpin.[13]

Furthermore, a range of ketone substrates were subjected to hydroboration with HBpin using $(MeCp)_3La$. Similar to the cases reported previously, the catalytic hydroboration of ketones is relatively sluggish thus a longer reaction time or higher catalyst loading is needed.[12] Nevertheless, the $(MeCp)_3La$ shows superior reactivity over the Cp_3La complex. For instance, 0.005 mol% catalyst loading can lead to 97% hydroboration transformation of acetophenone within 60 min, and quantitative product is obtained in 10 min upon slightly increasing the loading to 0.01 mol%, showing apparently higher reactivity than that of Cp_3La.[7] This corresponds to a TOF > 59 000 h^{-1}, which is comparable with the highest TOF > 60 000 h^{-1} for the hydroboration of acetophenone.[14] With 1 mol% catalyst loading, cyclododecanone could be fully converted to the desired product within 10 min, and the shortened reaction time implies, again, the superior reactivity of $(MeCp)_3La$ than that of Cp_3La (Table 2, entry 8).[7]

Additional investigation to probe both intra- and inter-molecular chemoselectivities was carried out with $(MeCp)_3La$

Table 2 Substrate scope for ketones[a]



Entry	R	R^1	Cat (mol%)	Time (min)	NMR yield (%)	Isolated yield (%)
1	Ph	Me	0.01 0.005	10 60	99 97	94 —
2	2-Me-C_6H_4	Me	0.01	10	99	85
3	4-OMe-C_6H_4	Me	0.01	10	99	81
4	4-NO_2-C_6H_4	Me	0.01	60	96	87
5	3-FC_6H_4	Me	0.01	10	94	89
6	2-ClC_6H_4	Me	0.01	10	99	92
7	Ph	Ph	0.1	10	99	83
8	cyclododecanone		1	10	99	89
9	$PhCH_2$	$PhCH_2$	1	10	99	93
10	C_4H_3S	Me	0.01	10	97	80

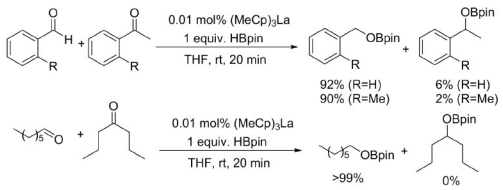
[a] Reaction conditions: ketones (1 mmol), HBpin (1.2 mmol) and $(MeCp)_3La$ solution of the appropriate concentration, N_2, room temperature.

(Scheme 1). The results showed evidently hydroboration preference of aldehydes over ketones. The selectivity of benzaldehyde and substituted benzaldehyde presented comparable outcomes in $La[N(SiMe_3)_2]_3$[5] and Cp_3La.[7] In particular, nearly quantitative conversion of heptaldehyde was accomplished in the presence of 4-heptanone.

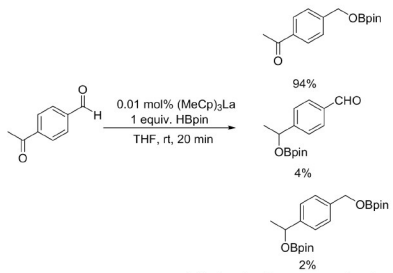
The kinetics of the reaction was studied via ^1H NMR monitoring, indicating the first order in [ketone]/[aldehyde], [HBpin] and [$(MeCp)_3La$], respectively (see the Supporting Information for details).

To further broaden the application scope of catalytic hydroboration with other function group substrates. A catalytic amount of $(MeCp)_3La$ was used to test the adaptability with aryl-substituted imines. A preliminary screening was performed and the representative outcomes

A. Intermolecular chemoselective reaction



B. Intramolecular chemoselective reaction



Scheme 1 Competitive aldehyde/ketone hydroboration selectivity study.

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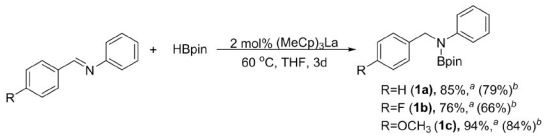

Scheme 2 Hydroboration of imine using $(MeCp)_3La$ as a catalyst. [a] Yields were determined by ^1H NMR analysis of the reaction mixture. [b] Yields are isolated yields of secondary amines.

were displayed in Scheme 2. We were delighted that with 2 mol% catalyst loading under 60 °C, all selected substrates including electron withdrawing (N-(4-fluorobenzylidene)aniline) and electron donating (N-(4-methoxybenzylidene)aniline) delivered medium to good yields of target products. In comparison with the single component catalyst serve this transformation reported by Sen's group, not only a lower catalyst loading but also a significant improvement in conversion was achieved.[15]

DFT calculations were carried out to investigate the mechanism of the hydroboration of aldehydes catalyzed by the complex Cp_3La. The ΔH for the isodestmic reaction (1) is exothermic by 6.7 kcal/mol, indicating that the binding energy of Cp_3La with PhCHO is 6.7 kcal/mol higher than with HBpin. Therefore, the coordination of PhCHO with the catalyst via O…La interaction is more likely to occur, forming the initial complex **INT1**. Subsequently, the other substrate, HBpin, might undergo a metathesis reaction with PhCHO to afford the desired product in a concerted manner. The corresponding transition state (TS) was located as **TS1**, in which the O…B and C…H distances are shortened to 1.87 and 1.62 Å, respectively, while the B…H and C…O distances are lengthened to 1.26 and 1.29 Å, respectively. The predicted energy barrier is 39.2 kcal/mol. Alternatively, the substrate HBpin could undergo electrophilic attack to the Cp ligand, generating the addition intermediate **INT3**. Next, the formed pin(Cp)BH- group in **INT3** is ready to undergo the hydride transfer step to the positively charged carbon site of the aldehyde group to produce **INT4**. Afterwards, the generated alkyloxide group in **INT4** is very ready to undergo the migratory insertion to the electron deficient B site of pinBCp to afford **INT5**. Then, the desired product could be released from the Cp ligand via the cleavage of the B-C bond and the Cp_3La catalyst is regenerated. The predicted energy barrier of the rate determining step for the stepwise pathway is 36.0 kcal/mol, which is ca. 3 kcal/mol lower in energy than that of the former concerted route. Therefore, the above mentioned stepwise mechanism is more feasible for the hydroboration of aldehydes catalyzed by Cp_3La.[16] Overall, computational studies reveal that the high efficiency for this catalytic reaction could be attributed to the critical role of the Cp_3La catalyst in trapping both substrates effectively, metal center for PhCHO and Cp ligand for HBpin, respectively. Then, the hydride transfer and the alkyloxide migration steps are followed to produce the final product.

The organolanthanide catalyst with MeCp ligand shows superior catalytic performance than the Cp ligand. Based on the stepwise mechanism revealed previously, computational results suggest that HBpin favors to attack C2 position of the methyl substituted cyclopentadienyl group.[17] The predicted

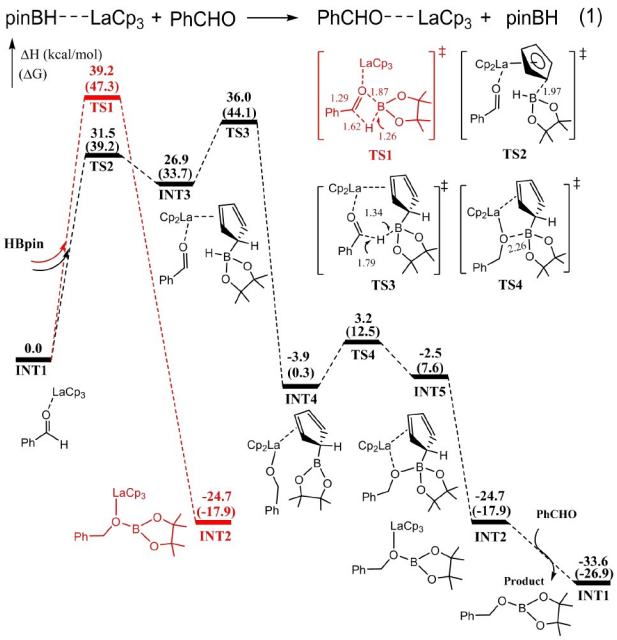

Figure. 1 Energy profile (in kcal/mol) for the Cp_3La catalyzed of hydroboration benzaldehyde with pinacolborane. Bond lengths are shown in Å.

energy barrier of the rate limiting step of the $(MeCp)_3La$ catalyzed hydroboration is 32.8 kcal/mol, which is ca. 3 kcal/mol lower in energy than the employment of Cp_3La catalyst (Figure S61). Computational studies suggest that $(MeCp)_3La$ could be a better catalyst than Cp_3La, which is consistent with experimental results. The slightly enhanced nucleophilicity of the carbon adjacent to the methyl group substituted carbon in the Me-Cp ligand, could account for, at least partially, the superior catalytic performance of the $(MeCp)_3La$ catalyst. In addition, the methyl group of MeCp ligand could form a C-H…O weak H-bond with O atom of the pinBH substrate in TS2', providing slightly more stabilizing effect (Figure S61).

Conclusions

In conclusion, we have described $(MeCp)_3Ln$ could be employed as excellent catalysts for hydroboration of carbonyl compounds with low catalyst loading under mild conditions. The catalyst $(MeCp)_3La$ demonstrates even higher activity in comparison with Cp_3La. One possible mechanism is presented on the basis of DFT study. Moreover, the $(MeCp)_3La$ complex also shows potent capability to catalyze imine hydroboration.

Experimental

General information

All catalytic reactions were carried out under nitrogen atmosphere using glovebox and Schlenk techniques. All solvents were distilled from Na prior to use. All liquid substrates were dried over CaH_2, freshly distilled, and degassed prior to use. All solid substrates were treated with anhydrous anaerobic treatment. $CDCl_3$ was purchased from TCI

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chemicals and stored over activated 4 Å molecular sieves prior to use. Pinacolborane (HBpin) was purchased from Sigma-AldrichCo. ^{1}H and ^{13}C NMR spectra were recorded using Bruker Avance 400-MHz NMR spectrometer, with chemical shifts (δ) referenced to the residual solvent signal. High resolution mass spectra (HRMS) were obtained using a Bruker MicroTOF-Q III instrument with an ESI source. Carbon, hydrogen and nitrogen analyses were performed by direct combustion using a CarloErba EA-1110 instrument.

General Procedure for Catalytic Hydroboration of Aldehydes. In the glovebox, aldehyde (1 mmol) and pinacolborane (1.2 mmol) were charged in the vial with a stir bar, and a stock solution containing an appropriate loading of $(MeCp)_3La$ (0.001 mol% ~ 1 mol%) was added. The reaction mixture was allowed to run at room temperature. The progress of the reaction was monitored by ^{1}H NMR, which indicated the completion of the reaction by the disappearance of the aldehyde proton and appearance of a new CH_2 peak. The product boryl ester was hydrolyzed by refluxing with silica gel and H_2O overnight. The resulting alcohol was extracted with $CHCl_3$. The product was isolated by flash column chromatography with SiO_2 using ethyl acetate/hexane (1:5 or 1:10) mixtureas eluent. The solvent of organic phase was removed by rotary evaporation and the alcohol product was characterized by ^{1}H and ^{13}C NMR.

General Procedure for Catalytic Hydroboration of Ketones. In the glovebox, ketone (1 mmol) and pinacolborane (1.2 mmol) were charged in the vial with a stir bar, and a stock solution containing an appropriate loading of $(MeCp)_3La$ (0.005 mol% ~ 1 mol%) was added. The reaction mixture was allowed to run at room temperature. The progress of the reaction was monitored by ^{1}H NMR, which indicated the completion of the reaction by the appearance of a new CH peak. The product boryl ester was hydrolyzed by refluxing with silicagel and H_2O overnight. The resulting alcohol was extracted with $CHCl_3$. The product was isolated by flash column chromatography with SiO_2 using ethyl acetate/hexane (1:5 or 1:10) mix ture as eluent. The solvent of organic phase was removed by rotary evaporation and the alcohol product was characterized by ^{1}H and ^{13}C NMR.

Competing Experiment for Intermolecular Hydroboration of Aldehyde vs Ketone. In the glovebox, aldehyde (1 mmol), pinacolborane (1 mmol) and ketone (1 mmol) were charged in the vial and a stock solution containing an appropriate loading of $(MeCp)_3La$ (0.01 mol%) was added. The reaction mixture was stirred at room temperature for 20 min. Reaction progress was monitored by ^{1}H NMR (final spectra are provided).

Competing Experiment for Entramolecular Hydroboration of Aldehyde vs Ketone. In the glovebox, 4-acetylbenzaldehyde (1 mmol) and pinacolborane (1 mmol) were charged in the vial and a stock solution containing an appropriate loading of $(MeCp)_3La$ (0.01 mol%) was added. The reaction mixture was stirred at room temperature for 20 min. Reaction progress was monitored by ^{1}H NMR (final spectra are provided).

General Procedure for Catalytic Hydroboration of Imines. Aryl-substituted imine (1 mmol), pinacolborane (1.2 mmol) and $(MeCp)_3La$ (2 mol%) were charged in Schlenk tube inside glove box. The reaction mixture was allowed to run at 60 °C. The progress of the reaction was monitored by ^{1}H NMR. Upon completion of the reaction, resulted boronate ester residues were hydrolysed with silica gel and methanol at 65 °C for 4-6 h. The completion of hydrolysis was checked by TLC. The reaction mixture was filtered and washed three times with dichloromethane. The combined organic layers were dried, evaporated and the residue was purified by column chromatography over silica gel (100–200 mesh) with pet ether/ethyl acetate (1:5) mixture as eluent, which provided the pure secondary amines.

Acknowledgements

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16 Although the formation of the Cp_3La…HBpin complex is less favourable than the formation of **INT1**, one may propose that HBpin might undergo σ-metathesis reaction with the Cp_3La catalyst to afford the $(CpBpin)LaHCp_2$ intermediate. Computational results show that the ΔH for formation of the $(CpBpin)LaHCp_2$ intermediate is endothermic by 36.4 kcal/mol relative to **INT1**. Although the TS of this σ-metathesis pathway was not located, the overall barrier much be higher than the proposed pathway.
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18 The energy barrier of electrophilic attack of HBpin to C3 position of the MeCp ligand is ca. 1 kcal/mol higher than that of attack C2 position (Figure S60, SI).

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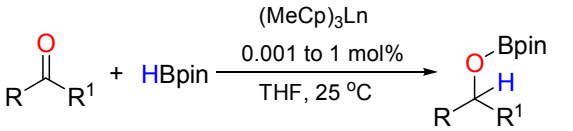
TOC



R = alkyl, aryl

R^1 = H, alkyl, aryl

TOF up to 97000 h^{-1}

$(MeCp)_3Ln$ complexes are reported as highly efficient catalysts in promoting hydroboration and a plausible stepwise mechanism is proposed.