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Interconverting Lanthanum Hydride and Borohydride Catalysts for C=O Reduction and C–O Bond Cleavage

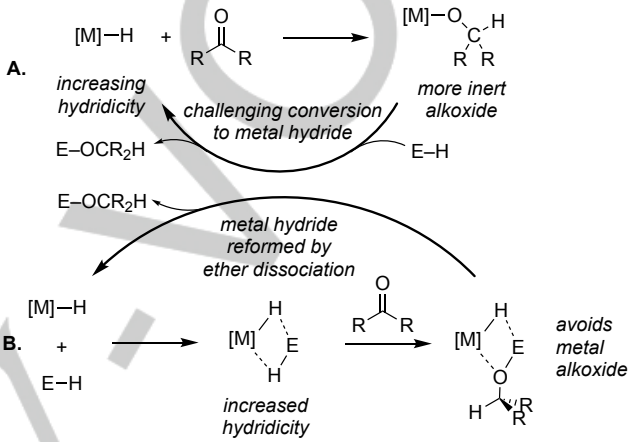
Smita Patnaik, and Aaron D. Sadow*[a]

Abstract: The high catalytic reactivity of homoleptic tris(alkyl) lanthanum La{C(SiHMe$_2$)$_3$}$_3$ is highlighted by C–O bond cleavage in the hydroboration of esters and epoxides at room temperature. The catalytic hydroboration tolerates functionality typically susceptible to insertion, reduction, or cleavage reactions. Turnover numbers (TON) up to 10 000 are observed for aliphatic esters. Lanthanum hydrides, generated by reactions with pinacolborane, are competent for reduction of ketones but are inert toward esters. Instead, catalytic reduction of esters requires activation of the lanthanum hydride by pinacolborane.

Strategies that rely on highly nucleophilic metal hydrides to affect catalytic reduction and C–O bond cleavage of unsaturated oxygenates are limited by the stability of the corresponding metal alkoxide intermediates, which impedes regeneration of the metal hydride (Scheme 1A).[1] More reactive catalysts are needed for conversions of inert substrates, such as esters and ethers, and new mechanisms are needed to ameliorate the thermodynamic barriers associated with breaking strong M–O bonds. One approach that could avoid M–O bond formation involves an activating interaction of the hydride source with the electrophilic catalytic center (Scheme 1B).

Pinacolborane (HBpin) is promising in this regard because it generates metal hydrides upon reaction with organometallic compounds, and it also forms adducts with nucleophilic metal hydrides.[1-2] For example, hydride species Cp*$_2$LaH and {HC(CMeNDipp)$_2$}MgH (Dipp = 2,6-C$_6$H$_3$*i*Pr$_2$) are proposed catalytic intermediates in ketone, aldehyde, imine, carbodiimide, nitrile, and pyridine hydroborations.[2f, 3] Alternatively, isolable pinacolborohydrides To^{M}Mg{HXBpin} (To^M = tris(4,4-dimethyl-2-oxazolinyl)phenylborate; X = H, alkoxide) are proposed in hydroboration of esters, and the postulated mechanism avoids M–O intermediates.[4] In contrast, pinacolborohydride compounds are also proposed as off-cycle states or as precursors to catalyst deactivation.[2f, 2h, 3c]

Early trivalent lanthanide hydrides often provide high catalytic activity.[5] For example, La{N(SiMe$_3$)$_2$}$_3$ and LaCp$_3$, which may provide entry to lanthanum hydrides upon reaction with HBpin, afford highly active catalysts for hydroboration of ketones and aldehydes.[6] While hydroboration of aldehydes and ketones is



Scheme 1. Conceptual approach for kinetically-enhanced catalytic reduction of oxygenates.

catalyzed by a large number of metal complexes,[7] fewer catalysts, mainly magnesium[2f, 4, 8] and molybdenum compounds,[9] mediate hydroboration of esters. Moreover, hydroboration of epoxides is uncommon, with reports of only a nickel catalyst (involving C–O oxidative addition)[10] and an iron catalyst limited to aryl-substituted substrates.[11]

In the present contribution, we demonstrate that the easily synthesized tris(alkyl)lanthanum compound La{C(SiHMe$_2$)$_3$}$_3$ (**1**)[12] catalyzes the hydroboration of esters and epoxides. With 5 mol % **1** at room temperature, alkyl esters, alkyl benzoates, and aryl benzoates are reduced to boryl esters. Hydrolysis gives the corresponding alcohol in high isolated yield (Table 1). Halogen-, nitro-, alkoxy-, and trifluoromethyl-substituted benzoate esters are reduced without affecting the functional group. Olefins are untouched, whereas La{N(SiMe$_3$)$_2$}$_3$ is reported to catalyze addition of alkenes and HBpin.[13] Electron-poor esters react more rapidly than electron-rich ones.

While the reduction of ethyl acetate is complete within 5 min. using 5 mol % **1**, catalyst loadings down to 0.01 mol % are also effective. For example, hydroboration using **1** gives 3560 turnovers (TON) within 30 min providing an initial turnover frequency (TOF) of 7120 h^{-1}, (35% conversion within 1 h), and quantitative conversion after 2 h (TON = 10,000); ([**1**]$_{ini}$ = 0.183 × 10^{-4} M, [EtOAc]$_{ini}$ = 0.188 M, [HBpin]$_{ini}$ 0.662 M). Aryl esters react more slowly. For example, hydroboration of benzyl benzoate using 1 mol % **1** gives full conversion over 24 h, whereas methyl p-iodobenzoate is reduced by 0.1 mol % **1** in the same time.

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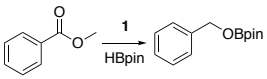
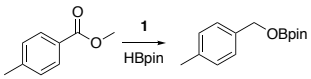
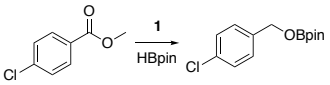
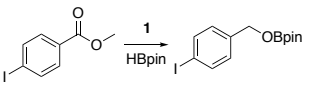
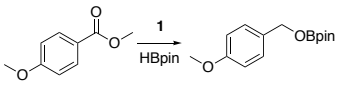
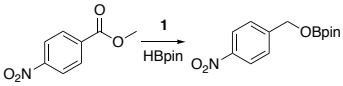
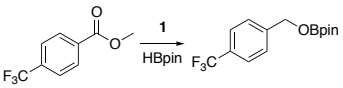
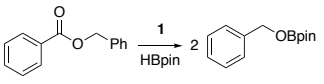
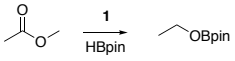
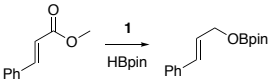
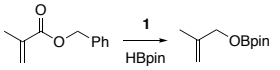
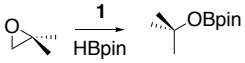
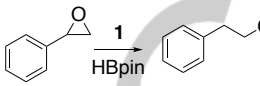
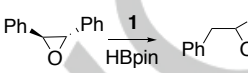
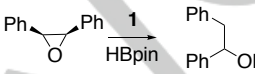
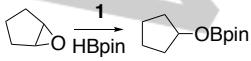
Table 1. La{C(SiHMe$_2$)$_3$}$_3$ (**1**) catalyzed hydroboration of esters.

Reaction[a]	Time (h)	Yield[f]	k_{obs}/[**1**]
	0.5	100 (98)	1.352
	2	100 (92)	0.954
	0.5	100 (98)	1.589
	0.5 6[b] 24[c]	100 (98) 100 100	2.096
	1	92 (90)	0.658
	1	100 (95)	—
	0.5	98 (95)	2.219
	0.5 24[b]	100 (92) 100	4.738
	0.16 2[d]	100 (85) 100	—
	0.5	100 (96)	—
	1[e]	90 (72)	—

[a] Reaction conditions: 5 mol % catalyst in C_6D_6, 2.5 equiv. of HBpin, 25 °C. MeOBpin is the by-product. [b] 1 mol % catalyst. [c] 0.1 mol % catalyst. [d] 0.01 mol % catalyst. [e] $PhCH_2OBpin$ is the byproduct. [f] NMR yield was determined with respect to Si(SiMe$_3$)$_4$ as an internal standard, and isolated yield is given in parenthesis. k_{obs}/[**1**] is the ternary rate constant ($M^{-2}s^{-1}$) obtained from kinetic experiments with 3.5 equiv. of HBpin at a known [**1**].

On the basis of the high catalytic reactivity of **1** towards esters, we investigated ring-opening of epoxides to boryl esters, which would also involve a C–O bond cleavage step. In fact, **1** is an active catalyst for this process, giving high yields within 1 d at room temperature (Table 2). The reaction is effective for 2,2-disubstituted epoxides, 2,3-disubstituted epoxides, styrenic derivatives, and cycloalkane oxides. Interestingly, trans-2,3-stilbene oxide gives a single product at room temperature, whereas the cis isomer gives a mixture of 1,2- and 2,2-diphenyl ethanol after hydrolytic workup. The latter product results from a 1,2-aryl shift, which occurs both at room temperature and 60 °C.

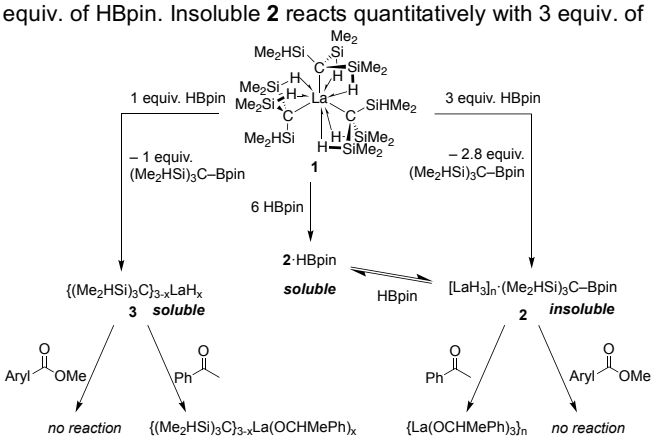
Table 2. Catalytic hydroboration of epoxides.

Reaction[a]	Yield[b]
	100 (92)
	98 (85)
	98 (95)
	100 (98)
	31:100[c]
	98 (78)

[a] Reaction conditions: 5 mol % catalyst, C_6D_6, 1.3 equiv. of HBpin, 25 °C, 24 h. [b] NMR yield was determined with respect to Si(SiMe$_3$)$_4$ as an internal standard, and isolated yield is given in parenthesis. [c] 60 °C, 5 mol % **1** or 25 °C, 10 mol % **1**.

The catalysis is initiated by reaction of **1** and HBpin, which instantaneously produces (Me$_2$HSi)$_3$CBpin (^{11}B NMR: 33 ppm). In contrast, mixtures of **1** and methyl anisate or 2,2-dimethyloxirane, as representative substrates, contain only starting materials after 1 h at room temperature. Characterization of the lanthanum-containing product(s) formed in reactions of **1** and HBpin requires additional analysis. First, quantitative conversion of **1** and 3 equiv. of HBpin gives 2.8 equiv. of (Me$_2$HSi)$_3$CBpin, and the precipitate **2** (Scheme 2) forms over 7 h. That solid is insoluble in hydrocarbon solvents (e.g., benzene, pentane) and reacts with methylene chloride or THF.

Crude **2** contains small quantities of (Me$_2$HSi)$_3$CBpin (ca. 0.2 equiv. with respect to initial **1**), and ^{1}H NMR spectra of ketone-quenched materials revealed unidentified aliphatic signals. The latter problem is avoided by in situ precipitation of **2** from **1** and 3 equiv. of HBpin. Insoluble **2** reacts quantitatively with 3 equiv. of



Scheme 2. Reactivity of **1** and HBpin to give lanthanum hydride species, which are reactive toward ketones but not esters.

acetophenone to afford soluble species. The ^{1}H NMR spectrum of this mixture revealed three doublets at 1.47, 1.42, 1.30 ppm and a multiplet signal at 5.47 ppm, together assigned to OCHMePh groups bonded to lanthanum. Signals associated with PhMeHCOBpin could not be detected in the ^{11}B NMR spectrum of this mixture, and HBpin was not detected in the in situ generated samples of **2**, ruling out consumption of acetophenone by hydroboration in these experiments. The product of **2** and acetophenone was assigned as $\{La(OCHMePh)_3\}_n$ on the basis of hydrolysis which gives HOCHMePh. Compound **2** is tentatively assigned as containing LaH_3 on the basis of the stoichiometry of its formation and reaction with ketones.[14] This approach was previously used to assign reactive magnesium hydride.[3a] The tris(alkoxide)lanthanum species, **1**, and **2** are all competent precatalysts for acetophenone and benzaldehyde hydroboration in the presence of HBpin. Remarkably, in situ generated **2** and esters, such as methyl anisate and methyl para-chlorobenzoate, do not react under these conditions (Scheme 1, right) and **2** does not dissolve upon addition of esters in the absence of HBpin.

Reaction of **1** and 6 equiv. of HBpin provides a mixture of $(Me_2HSi)_3CBpin$ and HBpin (1:0.9 ratio) as determined by ^{11}B NMR spectroscopy. Compound **2** does not precipitate under these conditions. Evaporation of the volatile components, including HBpin, provides a material that is insoluble in benzene and appears equivalent to **2**. Apparently, the presence of HBpin solubilizes **2** in benzene (Scheme 1, center).

In addition, reaction of **1** and 1 equiv. of HBpin produces 1 equiv. of $(Me_2HSi)_3CBpin$ (based on ^{1}H and ^{11}B NMR spectroscopy) and soluble La-containing species **3**; however, the ^{1}H NMR signals from -C(SiHMe$_2$)$_3$ groups on **1** and in this mixture appear with equivalent chemical shifts. The product(s) **3** could be a mixture of $\{(Me_2HSi)_3C\}_2LaH$, $\{(Me_2HSi)_3C\}LaH_2$, and **1** in stoichiometry-required ratios, or a combination of 1/3 equiv. of **1** and 2/3 equiv. of **2**. The possibility that **3** is actually a mixture of **1** and **2** is ruled out by its reaction with acetophenone, which gives –OCHMePh signals in the ^{1}H NMR spectrum distinct from those obtained in the reaction of **2**. It is further noteworthy that **3** and methyl anisate also do not react under these conditions (Scheme 1, left). Thus, the lanthanum hydride species of **2** and **3** are reactive toward the C=O bond of ketones but not competent for reaction with esters. As is the case for many catalytic species, isolation of **2** and **3** in pure form was not possible, and the related YH_3 species has been assigned on the basis of mass balance in reactions trimethylyttrium and H_2AlMes.[15]

Further mechanistic insight was sought from in situ-monitored catalytic experiments. Second-order plots indicate that reaction rate is directly proportional to the concentration of HBpin and ester. The pseudo-second-order rate constants (k_{obs}) plotted vs [**1**] reveal a linear relationship consistent with first-order dependence on catalyst concentration, giving the ternary-order rate constant k'_{obs} = 1.95 ± 0.86 M^{-2}s^{-1} for the experimental rate law in eq. 1.

$$-\frac{d[\text{ester}]}{dt} = k'_{obs}[\mathbf{1}]^1[\text{ester}]^1[\text{HBpin}]^1 \qquad (1)$$

The rate law is further complicated by inverse dependence on [HBpin]. The ternary rate constants k'_{obs} decrease as [HBpin]$_{ini}$ increases over a series of experiments in which [**1**] and [ester]$_{ini}$ are held constant (Figure 1). Likewise, a plot of the initial rate (d[product]/dt) vs [HBpin]$_{ini}$ shows saturation at high concentrations of pinacolborane (Figure S43). Similar experiments, in which [**1**]$_{total}$ and [HBpin]$_{ini}$ are held constant and [ester]$_{ini}$ is varied, also show saturation behavior.

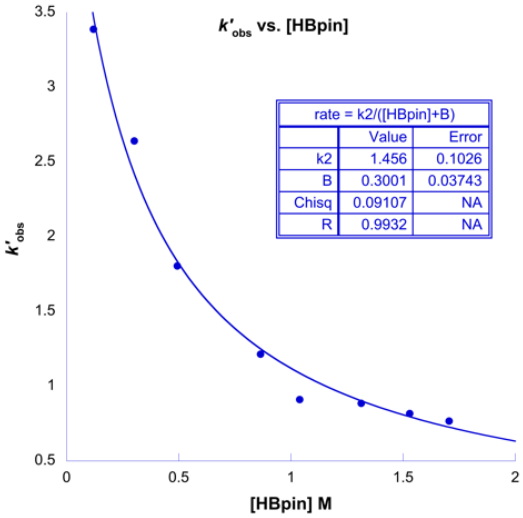


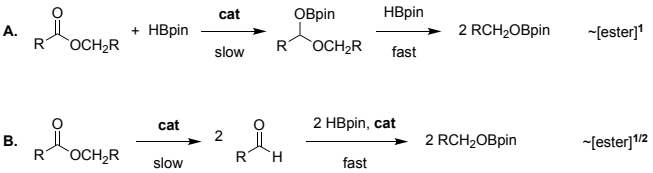
Figure 1. Plot of k'_{obs} vs [HBpin], fit to the equation: $k'_{obs} = k_2/\{[\text{HBpin}] + B\}$ where the constant $B = k_{-1}/k_1 + k_2[\text{ester}]/k_1$.

Saturation in both [HBpin] and [ester] is consistent with a two-step mechanism, in which one reactant reversibly binds to the catalyst, followed by the adduct's bimolecular combination with the second reactant in the turnover-limiting step. This mechanism is described by the rate law of eq. 2, where k'_{obs} of eq. 1 equals $k_1k_2/\{k_1[\text{HBpin}]+k_{-1}+k_2[\text{ester}]\}$.

$$-\frac{d[\text{ester}]}{dt} = \frac{k_1k_2[\mathbf{1}][\text{ester}][\text{HBpin}]}{k_1[\text{HBpin}]+k_{-1}+k_2[\text{ester}]} \qquad (2)$$

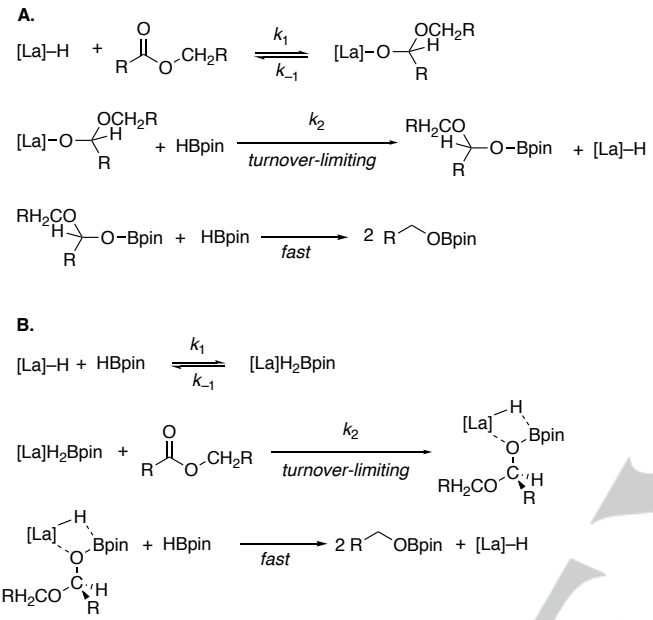
A value of k_2 = 1.5 ± 1 M^{-1}·s^{-1} is determined from a nonlinear least-squares regression analysis of the data in Figure 1.

These kinetic data provide significant mechanistic insight. First-order dependence on the [ester] indicates that its cleavage occurs after the turnover-limiting step (Scheme 3A).[4] In contrast, the To^{M}Mg-catalyzed hydroboration of esters follows a rate law exhibiting half-order ester dependence (Scheme 3B).[4]



Scheme 3. (A) First-order dependence on [ester] indicates C–O bond cleavage occurs after the turnover-limiting step, whereas (B) half-order dependence on ester indicates C–O bond cleavage happens prior to or during the turnover limiting step.

Two mechanisms are consistent with the experimental rate law. In the "ester-first" mechanism of Scheme 4A, [La]–H and ester interact reversibly, likely via insertion/β-H elimination steps, followed by irreversible reaction of the [La]–OCHR(OR) intermediate and HBpin. Alternatively, an "HBpin-first" mechanism involves [La]–H and HBpin reversibly binding to give a lanthanum hydridoborate [La]{H_2Bpin}, followed by irreversible interaction with ester (Scheme 4B). In both cases, the combination of ester and HBpin is slower than the second addition of HBpin and C–O cleavage, as required by the rate law.



Scheme 4. Mechanisms for **1**-catalyzed hydroboration of esters. Mechanisms **A** and **B** are both consistent with kinetic experiments, but **A** is less likely based on reactivity of in situ generate hydridolanthanum species.

Several points favor the mechanism of Scheme 4B (See SI). Esters are not reactive toward hydridolanthanum compounds **2** and **3**, whereas ketones react readily. The catalytic activity for ester hydroboration is engendered in **2** and **3** by HBpin. Moreover, **2** is solubilized by HBpin, although a direct interaction between these species is not detected. In contrast, esters do not solubilize compound **2**, suggesting that these compounds do not interact.

Although the slower nature of epoxide hydroboration has limited extensive kinetic studies, and the mechanism of this reaction is distinct from that of ester hydroboration, linear second-order plots of ln{[HBpin]/[styrene oxide]} vs time suggest a similar rate law. In this context, reversible cleavage of a C–O bond in the epoxide by the hydridolanthanum catalyst, in analogy to the first step of Scheme 4A (see Figure S45A), appears unlikely. Thus, the mechanisms of Schemes 4B and S45B are favored by analogous rate laws.

The experimental rate law of eq. 1 is valid for the hydroboration of all the aryl esters in this study, indicating one general mechanism is operative. The kinetic studies, however, show that comparisons of ternary experimental rate constants only partially capture the relevant terms that describe relative catalytic reactivity. Activity depends on rate constants and concentrations of [HBpin] and [ester]. Moreover, the data and the interpretation of rate law of eq. 2 show that experimental rate laws change drastically with variations in reactant concentration, with orders in [HBpin] and [ester] varying from zero to one. In addition, the apparent inhibition by HBpin is a natural consequence of reversible formation of [La]{H_2Bpin} adducts.

In conclusion, while lanthanum hydride is chemically competent for hydroboration of ketones, likely via carbonyl insertion and alkoxide transfer to boron, [La]{H_2Bpin} is required for the more challenging reductions of esters and epoxides.

Acknowledgements

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Keywords: hydroboration • C–O bond cleavage • lanthanum hydride • homogeneous catalysis • saturation kinetics

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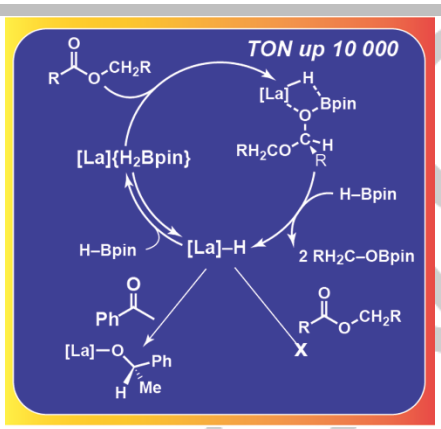
Entry for the Table of Contents

COMMUNICATION

Lanthanum hydride, generated by reaction of lanthanum alkyl and pinacolborane, is a catalyst for ester and epoxide hydroboration. Yet, lanthanum hydride reacts with ketones by insertion, whereas pinacolborane is required for ester conversion.



*Smita Patnaik, Aaron D. Sadow**

Page No. – Page No.

Interconverting Lanthanum Hydride and Borohydride Catalysts for C=O Reduction and C–O Bond Cleavage