Samarium(III)-Catalyzed Hydroboration of Olefins with Catecholborane. A General Approach to the Synthesis of Boronate Esters

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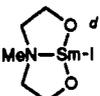*Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138*

Summary: A broad selection of olefins undergo hydroboration with catecholborane in a reaction that is catalyzed by a range of samarium(III) as well as other lanthanide complexes.

The utility of the hydroboration reaction has been significantly extended by the development of transition metal-catalyzed variants.[1,2] As a consequence of the mechanistic differences between the catalyzed and uncatalyzed processes,[3] complementary regio- and diastereoselectivities have been observed. Marks has recently reported a catalyzed hydroboration where the proposed catalytic species is bis(pentamethylcyclopentadienyl)-samarium hydride.[4] The purpose of this paper is to disclose that lanthanide hydroboration catalysis with catecholborane (CB) can be extended beyond lanthanide cyclopentadienyl complexes, to demonstrate that few requirements need be imposed on the catalyst ligand architecture, and to report some of the important mechanistic details of the Sm(III)-catalyzed process.

In the initial set of experiments, various trivalent samarium species were screened as catalysts in the hydroboration of 1-decene with CB to determine whether there are specific ligand requirements for catalyst activity (Table I). Samarium triiodide,[5] (t-BuO)SmI$_2$,[6] and (i-PrO)$_3$Sm[7] were all found to be competent catalysts (entries 1–3) which afforded 1-decanol in good yield after an 18-h reaction period (25 °C, THF) and subsequent peroxide oxidation. On the other hand, SmBr$_3$, SmCl$_3$, and SmF$_3$, as well as Sm(OTf)$_3$,[8] failed to catalyze the reaction. In order to evaluate the possibility that samarium is uniquely required for catalysis, other trivalent lanthanides were screened and found to be efficient catalysts (entries 5–8). Regioselectivity for the hydroboration of 1-decene was found to be dependent on both ligand and metal, with ratios of primary/secondary alcohols ranging from 11–50:1. Although the results in Table I document a range of catalyst options, SmI$_3$ was selected as the focus of further study.

The regioselectivity of the SmI$_3$-catalyzed reaction was discovered to be time-dependent (eq 1). This modulation in regioselectivity during the course of the reaction implies either that formation of the alkylboronate is reversible (*vide infra*) or that the catalyst is being chemically

Table I. Hydroboration of 1-Decene with Trivalent Lanthanides[a]

entry	catalyst	conv,[b] %	ratio,[c] primary:secondary
1	SmI$_3$	98	50:1
2	(t-BuO)SmI$_2$	94	46:1
3	Sm(Oi-Pr)$_3$	98	42:1
4	[d]	78	25:1
5	ScI$_3$	69	43:1
6	PrI$_3$	92	21:1
7	LuI$_3$	84	11:1
8	Eu(tfc)$_3$	92	22:1

[a] All reactions were performed with 10 mol % of catalyst and 1.5 equiv of catecholborane at rt in THF (1 M in olefin) for 18 h. [b] These figures represent the extent of conversion during the 18-h reaction period. [c] Reaction progress and ratios of alcohol products were measured by GLC analysis of the unpurified reaction mixtures. [d] This figure reflects the stoichiometry of lithium alkoxide to SmI$_3$, rather than the actual structure.
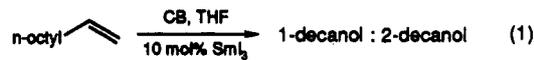
entry	time (h)	conv,%	1°: 2°
1	3	8	3:1
2	7	40	3.5:1
3	18	98	50:1

modified. The increase in rate as the reaction proceeds is also noteworthy. This observation, coupled with the fact that the slightly soluble SmI$_3$ eventually dissolves in the presence of olefin and CB, suggests that SmI$_3$ may not be the actual catalyst.

Scope. The scope of the SmI$_3$-mediated hydroboration was established for a variety of olefins (Table II). In all cases, an 18-h reaction time was employed to obtain a qualitative measure of olefin reactivity. Mono-, di-, and trisubstituted olefins efficiently undergo hydroboration by CB in the presence of 10 mol % SmI$_3$, and the alcohol products were isolated after a conventional oxidative workup.[2] In contrast to the Rh(I)-catalyzed process, the Sm(III)-catalyzed variant preferentially affords the primary alcohol in the hydroboration of styrene (entry 2). The hydroborations of phenylcyclohexene and α-pinene proceed with exclusive cis addition (entries 7 and 8) with the product ratios remaining unchanged even after 48 h. These observations suggest that potential reaction reversibility, if occurring, may be restricted to specific olefin substitution patterns.

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(1) Burgess, K.; Ohlmeyer, M. J. *Chem. Rev.* 1991, *91*, 1179–1191 and references cited therein.

(2) Evans, D. A.; Fu, G. C.; Hoveyda, A. H. *J. Am. Chem. Soc.* 1992, *114*, 6671–6679.

(3) Evans, D. A.; Fu, G. C.; Anderson, B. A. *J. Am. Chem. Soc.* 1992, *114*, 6679–6685.

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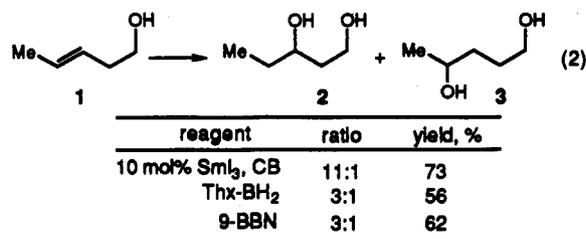(7) Sankhla, S.; Misra, S. N.; Kapoor, R. N. *Chem. Ind. (London)* 1965, 382–383.

(8) Forsberg, J. H.; Spaziano, V. T.; Balasubramanian, T. M.; Liu, G. K.; Kinsley, S. A.; Duckworth, C. A.; Poteruca, J. J.; Brown, P. S.; Miller, J. L. *J. Org. Chem.* 1987, *52*, 1017–1021.

Table II. Catalyzed Hydroboration of Representative Olefins

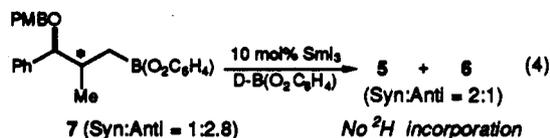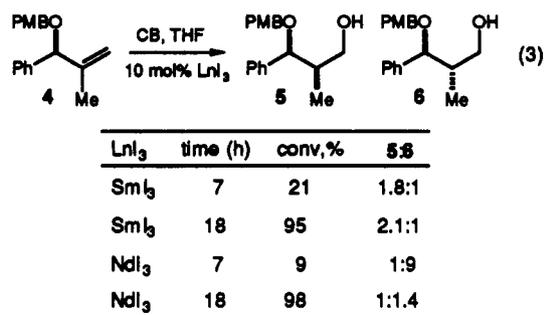| entry	substrate	(conv, %)^a yield, %	ratio
1	n-octyl⌒⌒	(98) 79	50:1^c
2	Ph⌒⌒	(59) 47	5:1^c
3	Ph–C(Me)=CH₂	(91) 81	>99:1^d
4	norbornene	(97) 78	27:1^e
6	Ph⌒⌒Ph	(80) 67	--
7	1-phenylcyclohexene	(85) 64	>99:1^f
8	cyclohexyl–Me	(79) 61^g	cyclohexyl–Me
9	Ph–CH(OH)–CH(Me)	(99) 85	2:1^h

^{a} Conversions after an 18-h reaction time. Ratios were measured by GLC analysis on the unpurified reaction mixtures. ^{b} Values refer to yield of purified product after 18 h. ^{c} Primary:secondary. ^{d} Primary: tertiary. ^{e} Exo:endo. ^{f} Trans:cis. ^{g} Exclusive reaction product. ^{h} Syn: anti diastereomer ratio determined by ¹H NMR spectroscopy.

We have probed the possibilities of directing the course of the reaction through heteroatom coordination.[9] Hydroboration of 3-penten-1-ol with CB (2.5 equiv, THF, 18 h, 25 °C) and SmI₃ (10 mol %) afforded an 11:1 ratio of diols **2** and **3**, respectively, in 73% isolated yield (eq 2).

$$Me\diagdown\diagup\diagdown OH \longrightarrow Me\diagdown\diagup\diagdown_{OH}^{OH} + Me\diagdown\diagup\diagdown_{OH}^{OH} \quad (2)$$

reagent	ratio	yield, %
10 mol% SmI₃, CB	11:1	73
Thx-BH₂	3:1	56
9-BBN	3:1	62

Again, the product ratio in this reaction remained unchanged over the extended reaction time of 30 h. Some type of involvement of the hydroxyl function, possibly as its derived borate, might well be occurring. For example, the analogous hydroboration of **1** with either thexylborane or 9-BBN afforded 3:1 ratios of secondary alcohols. Whether this increase in regioselectivity relative to thexylborane and 9-BBN is due to direct association of substrate oxygen with the catalyst has not yet been established.
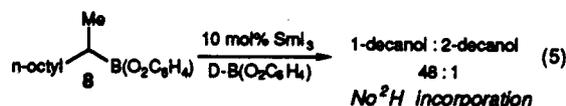
A preliminary assessment of acyclic reaction diastereoselectivity with olefin **4** for two lanthanide catalysts is summarized below (eq 3).[10] The SmI₃-catalyzed process (1.5 equiv of CB, THF, 18 h, 25 °C) afforded, after oxidation, diastereomeric alcohols **5** and **6** in a 2.1:1 ratio (95% conversion).[11] In contrast, the analogous reaction of **4** catalyzed by NdI₃ proceeded in 98% conversion to

$$\underset{\text{4 \ Me}}{\overset{\text{PMBO}}{Ph}}\diagup\diagdown \xrightarrow[\text{10 mol% LnI}_3]{\text{CB, THF}} \underset{\text{5 \ Me}}{\overset{\text{PMBO \ OH}}{Ph}} + \underset{\text{6 \ Me}}{\overset{\text{PMBO \ OH}}{Ph}} \quad (3)$$

LnI₃	time (h)	conv,%	5:6
SmI₃	7	21	1.8:1
SmI₃	18	95	2.1:1
NdI₃	7	9	1:9
NdI₃	18	98	1:1.4

$$\underset{\text{7 (Syn:Anti = 1:2.8)}}{\overset{\text{PMBO}}{Ph}\diagup\overset{*}{\diagdown}_{Me}\diagup B(O_2C_6H_4)} \xrightarrow[\text{D-B(O}_2\text{C}_6\text{H}_4)}{\text{10 mol% SmI}_3} \underset{\text{(Syn:Anti = 2:1)}}{\textbf{5} \ + \ \textbf{6}} \quad (4)$$

No ²H incorporation

give **5** and **6** in a 1:1.4 ratio. A change in diastereoselectivity with reaction time was noted for both the SmI₃- and NdI₃-catalyzed reactions, again demonstrating the time-dependent selectivity observed with some substrates.

To address the issue of reversibility of the Sm(III)-catalyzed process, catecholboronate **7**, as a mixture of diastereomers (syn:anti = 1:2.8),[12] was prepared and submitted to the reaction conditions with 0.5 equiv of deuterated CB. After 18 h, boronate oxidation afforded a 2.1:1 mixture of primary alcohols favoring the syn diastereomer **5**. Analysis of the deuterium content in the product alcohols by high-resolution mass spectrometry established that no deuterium was incorporated during the reaction. Control experiments indicated that SmI₃ alone does not effect isomerization; however, upon addition of 0.5 equiv of CB, isomerization is initiated.

The isomerization of 2-decylboronate **8**[13] was also probed in a similar set of experiments. Under the same conditions (10 mol % of SmI₃, 0.5 equiv of CB or ²H-CB, THF, 18 h, 25 °C), isomerization to the primary boronate ester was also observed (eq 5). Again, this isomerization occurs with

$$\underset{\text{n-octyl}}{\overset{\text{Me}}{}}\overset{*}{\diagdown}\diagup B(O_2C_6H_4) \xrightarrow[\text{D-B(O}_2\text{C}_6\text{H}_4)}{\text{10 mol% SmI}_3} \underset{\text{48 : 1}}{\text{1-decanol : 2-decanol}} \quad (5)$$

No ²H incorporation

no detectable deuterium incorporation as assayed by high-resolution mass spectrometry. We thus conclude that with some olefins (eqs 1 and 3) isomerization of the kinetically formed boronate esters can occur; however, this isomerization must proceed through a presumed nondissociating olefin complex to explain the lack of deuterium incorporation. On the other hand, other olefins such as 1-phenylcyclohexene (Table II, entry 7) do not appear to isomerize, even after an extended time period.

The typical procedure for the Sm(III)-catalyzed hydroboration is as follows: SmI₃ (0.10 mmol) is generated *in situ* from SmI₂ in THF.[5] To this yellow slurry is added 1 mmol of olefin by syringe (or *via* cannula as a solution in 0.5 mL of anhydrous THF), followed by 180 μL (1.5 mmol) of catecholborane. After 12–24 h, the reaction is

(9) For an example of a hydroxyl-directed hydroboration reaction, see: Evans, D. A.; Fu, G. C. *J. Am. Chem. Soc.* **1991**, *113*, 4042–4043. For a recent review on directed reactions see: Hoveyda, A. H.; Evans, D. A.; Fu, G. C. *Chem. Rev.* **1993**, *93*, 1307–1370.

(10) For the analogous Rh(I)-catalyzed hydroboration of the derived silyl ethers of **4** see ref 2.

(11) Stereochemistry of the alcohols was proven by oxidative cyclization to the p-methoxyphenyl acetal (DDQ, 4-Å molecular sieves, CH₂Cl₂, 0 °C, 85%) and analysis of ¹H coupling constants. Oikawa, Y.; Yoshioka, T.; Yonemitsu, O. *Tetrahedron Lett.* **1982**, *23*, 889–892.

(12) Prepared through the Rh(I) hydroboration of **4** (ref 2).

(13) Prepared by the addition of 2-decylmagnesium bromide to B-chlorocatecholborane.

submitted to basic oxidative workup with 30% aqueous hydrogen peroxide.[2] GLC analysis is performed on the unpurified reaction mixture to determine regio- and diastereoselectivity, and purification of compounds is performed by flash column chromatography.

Other Catalysts. Catalysis is by no means limited to lanthanide complexes. For example, our preliminary studies have substantiated that complexes derived from zirconium ($Zr(OEt)_4$, Cp_2ZrCl_2) and titanium ($Ti(O-i-Pr)_4$, Cp_2TiCl_2) also catalyze the CB hydroboration of olefins under conditions identical to those described above.

A Mechanistic Proposal. Although it is reasonable to conclude that catalysis might be proceeding via the intermediacy of the catalyst metal hydride, we would also like to raise the possibility that catecholborane might be activated for hydroboration by Lewis acid (LA) complexation (eq 6). Due to the heightened Lewis acidity of the

(6)

boron center in the CB–LA complex, it is reasonable that its hydroboration capacity might be significantly elevated. This mechanistic proposal will be evaluated in future studies.

The preceding experiments provide preliminary results of a promising variant of the hydroboration reaction. Details of the mechanism, scope, and enantioselective variants of this process are under current investigation.

Supplementary Material Available: Detailed experimental procedure for the samarium triiodide-catalyzed hydroboration, assays for determination of regio- and diastereomeric ratios, and spectroscopic data and stereochemical proofs for compounds 5 and 6 (6 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.